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# Mechanical Behavior of Molecular Crystals Induced by Combination of Photochromic Reaction and Reversible Single-Crystal-to-Single-Crystal Phase Transition

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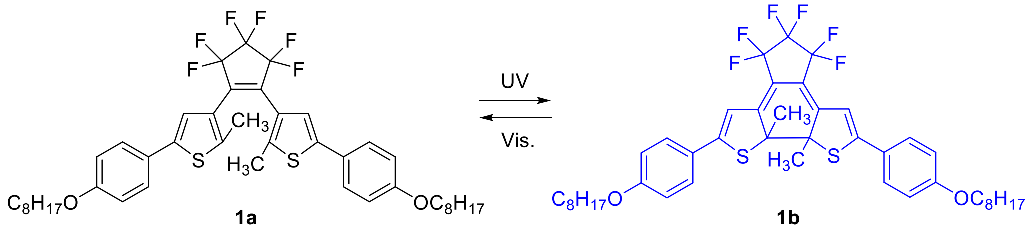
**ABSTRACT:** We herein report a unique mechanical behavior of a molecular crystal induced by combination of a photochromic reaction and a reversible single-crystal-to-single-crystal (SCSC) phase transition. A crystal of a diarylethene having octyl group at both sides (**1a**) was found to undergo a reversible thermodynamic SCSC phase transition accompanying a change in crystal length, which was clarified by DSC measurement, X-ray crystallographic analysis, and direct microscopic observation of the crystal length. Furthermore, upon irradiation with ultraviolet light, the diarylethene crystal exhibited an unusual photomechanical behavior. The mechanism of the behavior was proposed based on photoisomerization of the diarylethene from the open-ring isomer to the closed-ring isomer and a reversible thermodynamic SCSC phase transition, which was well supported by thermal bending behavior of a photoirradiated crystal.

## Introduction

Mechanically responsive molecular crystals that exhibit contraction, expansion, jumping, explosion, bending, twisting, curling, and splitting by external stimuli such as light, heat, and mechanical force have been widely investigated for application to molecular machines, molecular rotors, molecular robots, and artificial muscles.[1–7] Such mechanical responses are generally induced by changes in molecular geometry and/or intermolecular interaction in the crystalline phase. Recently, some interesting examples of mechanically responsive molecular crystals have been reported. For example, Bardeen *et al.* reported a ratchet-like rotational motion of branched molecular crystals.[8] They revealed that slow pH-driven reprecipitation of 4-fluoroanthracenecarboxylic acid from aqueous solution results in the growth of branched microcrystals and a ratchet-like rotation of the overall crystal can be induced by the twisting of the branches upon photoirradiation. Reddy *et al.* successfully demonstrated a crystal engineering strategy to achieve plastically flexible organic single crystals by introducing a low frictional plane with weak interactions in structure, which allowed molding the crystals into any shape.[9] Moreover, Naumov *et al.* reported a self-healing molecular crystal.[10] The separated crystals of dipyrazolethiuram disulfide were healed by only mechanical compression due to the disulfide bonding shuffling. Thus, these molecular crystals provide not only unexplored aspects of the crystal chemistry of molecular solid but also a new possibility for molecular crystals as functional materials.

Among various external stimuli to induce mechanical responses, light is very useful tool because it can remotely induce mechanical motions. From this point, a lot of photomechanical molecular crystals have been reported such as diarylethenes,[11–21] furylfulgide,[22] azobenzene,[23–25] anthracene carboxylates,[26–33] salicylideneaniline,[34,35] 4-chlorocinnamic acid,[30] 1,2-bis(4-pyridyl)ethylene salt,[36] benzylidenedimethylimidazolinone,[7] and others.[37–39] Almost all of photomechanical responses are caused by photoreactions of molecules in the crystalline phase such as 6$\pi$-electrocyclization, dimerization, and *cis*-*trans* isomerization accompanying changes in molecular geometry and/or intermolecular interaction. In these systems, photomechanical responses depend on the conversion ratio of photoreactions. The photoreaction in a whole crystal is required to achieve large, powerful, and/or new photomechanical motions. However, in many cases, the photoreaction does not occur in a whole crystal owing to high absorbance of molecules in the crystal and/or side reactions. If a photoreaction in a low conversion ratio can cause a change in molecular arrangement in the whole crystal, the nonlinear mechanical response relative to the conversion ratio of photoreactions could be accomplished. To realize the nonlinear mechanical response relative to the conversion ratio of photoreactions, we have focused on a reversible thermodynamic single-crystal-to-single-crystal (SCSC) phase transition of molecular crystals. Although SCSC phase transition is rare, it has been attracting much attention because of the possibility to provide unexplored new functions.[40–46] SCSC phase transition can un-

**Scheme 1.** Molecular structure of diarylethene used in this work



dergo in a whole crystal accompanying changes in molecular geometry and/or intermolecular interaction with no cracks and breaks in the crystal. If a crystal can exhibit both photoreaction and SCSC transition, it provides not only new photomechanical phenomena but also strategy for design of materials showing nonlinear mechanical response relative to the conversion ratio of photoreactions.

In the course of study on photochromic diarylethene crystals, we found that a diarylethene, 1,2-bis(2-methyl-5-(4-octyloxyphenyl)-3-thienyl)perfluorocyclopentene (**1a**), exhibits a reversible SCSC phase transition in addition to the photochromic reaction. Herein, we report a unique photomechanical behavior of a photochromic diarylethene crystal induced by combination of a photochromic reaction and a reversible SCSC phase transition. The SCSC phase transition of crystal **1a** was fully investigated by DSC measurement, X-ray crystallographic analysis, and direct observation of crystal length. Furthermore, the mechanism of the unusual photomechanical behavior is discussed based on both the photochromic reaction and the SCSC phase transition.

## Experimental section

**General.** Solvents used were spectroscopic grade and purified by distillation before use. $^1H$ NMR spectra were recorded on a Bruker AV-300N spectrometer at 300 MHz. Deuterated chloroform ($CDCl_3$) was used as the solvent and tetramethylsilane (TMS) as an internal standard, respectively. High resolution mass spectra (HR-MS) were obtained using a Bruker FT-ICR/solariX mass spectrometer. Matrix-assisted laser desorption/ionization (MALDI) was used for ionization. High-performance liquid chromatography (HPLC) was carried out using a Hitachi L-7150/L-2400 HPLC system equipped with a Kanto Chemical Mightysil Si60 column. Recycling preparative HPLC was conducted using a JASCO UV-4075/PU-4086 HPLC system equipped with two columns (JAI JAIGEL-2HR) using chloroform as the eluent. Absorption spectra in *n*-hexane were measured using a JASCO V-560 absorption spectrophotometer. Single crystal X-ray crystallographic analysis was carried out using a Rigaku AFC/Mercury CCD diffractometer with Mo$K_\alpha$ radiation ($\lambda$ = 0.71073 Å) monochromated by graphite. The crystal structures were solved by a direct method using SIR92 and refined by the full-matrix least-squares method on $F^2$ with anisotropic displacement parameters for non-hydrogen atoms using SHELXL-97. The polarized absorption spectra in the single-crystalline phase were measured using a Nikon ECLIPSE E600POL polarizing optical microscope attached a Hamamatsu PMA-11 photonic multi-channel analyzer as the photodetector and a super high pressure mercury lamp (100 W; UV-1A filter (365-nm light). Visible light irradiation was carried out using a halogen lamp (100 W). The bending behavior of crystals was observed using a Keyence VHX-500 digital microscope, equipped with a Mettler-Toledo FP82HT hot stage and FP90 central processor or a Tokai Hit MATS-2002S thermoplate. Differential scanning calorimetry (DSC) was performed using a Hitachi DSC7000X instruments. Photomechanical behavior of crystals was also observed using a Keyence VHX-500 digital microscope. UV irradiation was carried out using a Keyence UV-LED UV-400/UV-50H (365-nm light).

**Photochemical reaction in solution.** Photocyclization and cycloreversion quantum yields were determined in *n*-hexane as relative quantum yields using diarylethene whose quantum yields have already been determined.[47] Photoirradiation was conducted using a 200 W mercury–xenon lamp (MORITEX MUV-202) or a 300 W xenon lamp (Asahi Spectra MAX-301) as a light source. Monochromatic light was obtained by passing the light through a monochromator (Jobin-Yvon H10-UV). Photocyclization conversion ratio of a diarylethene derivative was determined by absorption spectroscopic analysis.

**Materials.** Diarylethene **1a** was synthesized as follows. **1,2-Bis(2-methyl-5-(4-octyloxyphenyl)-3-thienyl)perfluorocyclopentene (1a):** To 80 mL of dry THF solution containing 3-bromo-2-methyl-5-(4-octyloxyphenyl)thiophene (1.0 g, 2.6 mmol) was added 1.6 mL of 1.6 M *n*-BuLi hexane solution (2.6 mmol) at −78 °C under argon atmosphere, and the solution was stirred for 1.5 h at −40 °C. Octafluorocyclopentene (0.2 mL, 1.5 mmol, Nippon Zeon) was slowly added to the reaction mixture at −78 °C, and the mixture was stirred for 3 h at that temperature. The reaction was stopped by the addition of water. The product was extracted with ether. The organic layer was dried over $MgSO_4$, filtrated, and concentrated. The residue was purified by column chromatography on silica gel using *n*-hexane/ethyl acetate (95:5), recycling preparative HPLC on polystyrene gel using chloroform as the eluent, and HPLC on silica gel using *n*-hexane/ethyl acetate (98:2) as the eluent to give 400 mg of **1a** in 40% yield: $^1H$ NMR (300 MHz, $CDCl_3$): δ 0.89 (t, *J* = 6.8 Hz, 6H), 1.3–1.5 (m, 20H), 1.7–1.9 (m, 4H), 1.94 (s, 6H), 3.97 (t, *J* = 6.6 Hz, 4H), 6.9 (d, *J* = 8.7 Hz, 4H), 7.15 (s, 2H), 7.45 (d, *J* = 8.7 Hz, 4H). HR-MS (MALDI) *m*/*z* = 776.3150 ($M^+$, 100%). Calcd. for $C_{43}H_{50}F_6O_2S_2^+$ = 776.3151

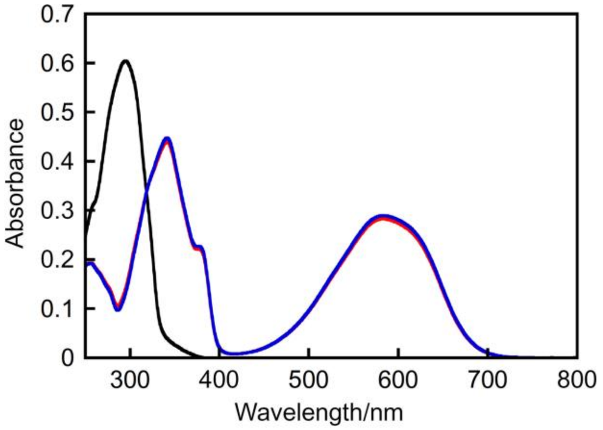


**Figure 1.** Absorption spectra of **1a** (black line), **1b** (blue line), and the solution in the photostationary state upon irradiation at 313 nm (red line) in *n*-hexane: [**1**] = 1.24 × $10^{-5}$ M.

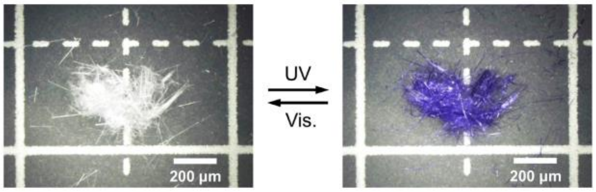


**Figure 2.** Photochromism of crystal **1a** upon alternating irradiation with UV and visible light. See also Video S1.

## Results and discussion

**Photochromism in solution.** Diarylethene **1a** shows reversible photochromic reactions upon alternating irradiation with UV and visible light. **Figure 1** shows the absorption spectral change of diarylethene **1a** in *n*-hexane upon UV light. Diarylethene **1a** has an absorption maximum at 295 nm. Upon irradiation with 313-nm light, the colorless solution of **1a** turned blue, in which a visible light absorption maximum appeared at 585 nm. The absorption spectral change is ascribed to the photoisomerization from the colorless open-ring isomer to the colored closed-ring isomer. The blue color disappeared by irradiation with visible light (>500 nm), and the absorption spectrum returned to that of **1a**. The closed-ring isomer **1b** was isolated by HPLC. The $\varepsilon$ values are 48700 M$^{-1}$ cm$^{-1}$ at 295 nm for **1a** and 23300 M$^{-1}$ cm$^{-1}$ at 585 nm for **1b** in *n*-hexane. The photoisomerization conversion ratio from **1a** to **1b** was determined to be 98% in *n*-hexane upon irradiation with 313-nm light. The open-ring isomer **1a** and the closed-ring isomer **1b** were stable at room temperature. The photocyclization and cycloreversion quantum yields were determined to be 0.54 (upon irradiation at 313 nm) and 0.0082 (upon irradiation at 585 nm). These values are similar to those of 1,2-bis(2-methyl-5-(4-methoxyphenyl)-3-thienyl)perfluorocyclopentene.[48]

**Photochromism in crystal.** When diarylethene **1a** was recrystallized from *n*-hexane, a rod-like crystal was obtained as shown in **Figure 2**. The crystallographic data of crystal **1a** were summarized in **Table S1**. From X-ray crystallographic analysis, it was revealed that the crystal system and space group is triclinic $P\bar{1}$. **Figure 3** shows the crystal shape and molecular packing diagrams. The face indices are determined as shown in **Figure 3**. The long edge of the crystal is parallel to *a*-axis. There are two molecules in the unit cell and one molecule in the asymmetric unit. The octyl groups of diarylethene **1a** exist in all-*trans* conformation. In

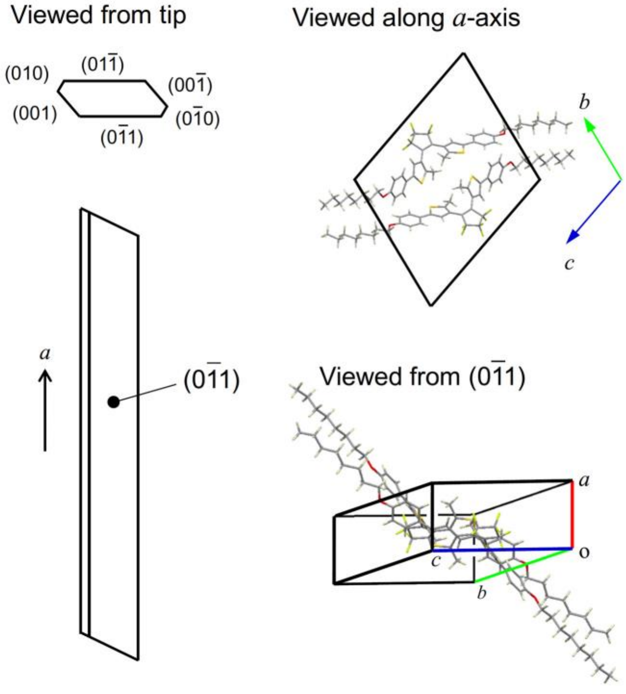


**Figure 3.** Crystal shape and molecular packing of diarylethene **1a**.

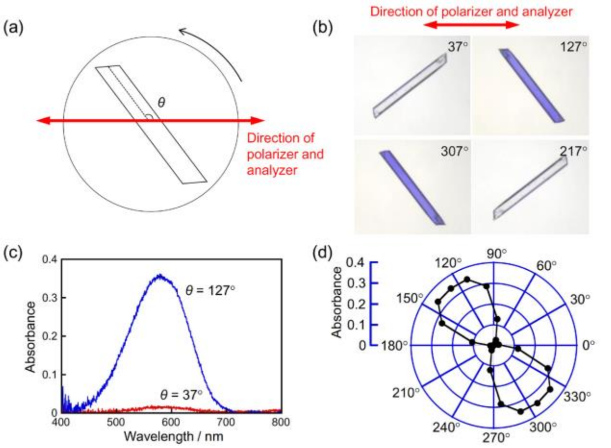


**Figure 4.** Polarized absorption spectra of the closed-ring isomer in the crystal on the $(0\bar{1}1)$ face: (a) crystal shape and direction, (b) photographs of the photoirradiated colored crystal observed under polarized light, (c) polarized absorption spectrum, and (d) polar plots of absorbance at 580 nm.

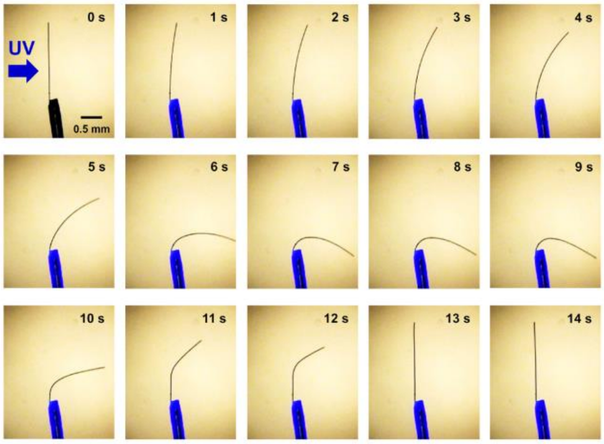


**Figure 5.** Photomechanical behavior of diarylethene **1a**. UV irradiation was conducted from left side.

the crystal, all **1a** molecules exist in photoreactive antiparallel conformations and the distance between reactive carbon atoms is 3.588(5) Å, which is sufficiently short for photocyclization to take place in the crystalline phase.[49] Upon UV light irradiation, the colorless single crystals of **1a** turned blue (**Figure 2** and **Video S1**). The colored crystals of **1a** had absorption maxima at 580 nm. The blue-colored crystals returned to the colorless crystals upon irradiation with visible light. The absorption anisotropy of the blue color at 580 nm viewed on the $(0\bar{1}1)$ face is shown in **Figure 4**. Upon irradiation with UV light, the crystal turned blue at a certain angle (θ = 127°). When the crystal was rotated as much as 90°, the color disappeared (θ = 37°). This clear dichroism indicates that the photochromic reaction took place in the crystalline phase.

**Photomechanical behavior.** The photomechanical behavior of crystal **1a** was investigated. **Figure 5** and **Video S2** show a photoinduced bending motion of diarylethene **1a**. UV irradiation was conducted to the $(0\bar{1}1)$ face. Crystal **1a** exhibited an unusual bending behavior compared with previously reported diarylethenes. In the case of previously reported diarylethene crystals,[17,18,20] upon irradiation with UV light, the crystal bends toward or away from the incident light and gradually tends not to bend because the photoisomerization of the open-ring isomer to the closed-ring isomer takes place in the crystal surface and the conversion ratio in the crystal surface increases up to the photostationary state as shown in **Figure S1**. This is a common bending motion in photomechanical compounds. The mathematical

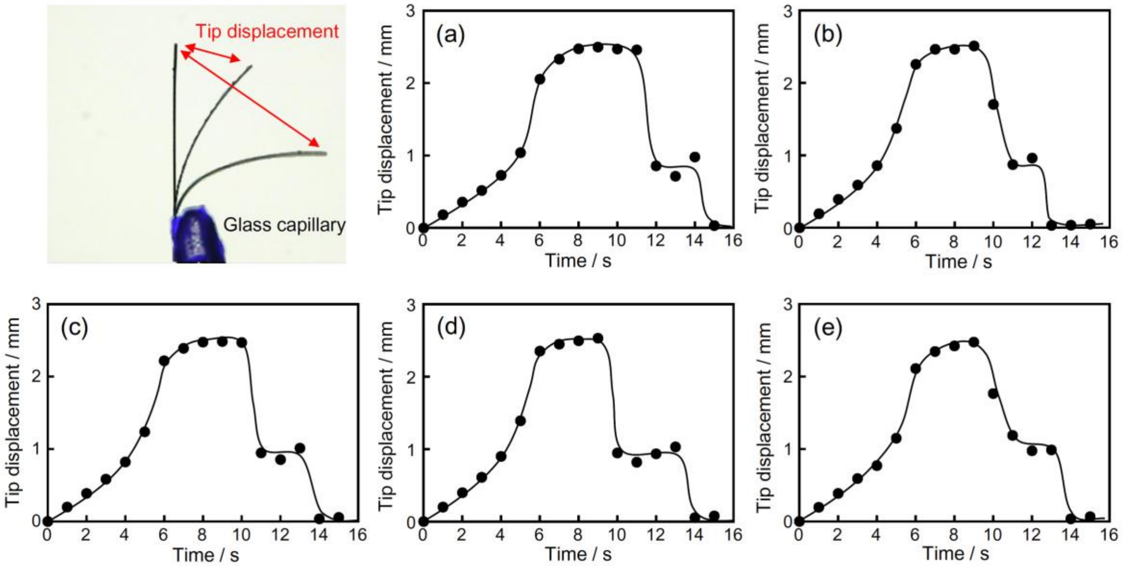


**Figure 6.** Repeatability of the unusual bending behavior of crystal **1a** upon irradiation with UV light: (a) 1st, (b) 2nd, (c) 5th, (d) 10th, (e) 19th cycles. Visible light irradiation to UV-irradiated crystal was carried out in the interval of cycles.

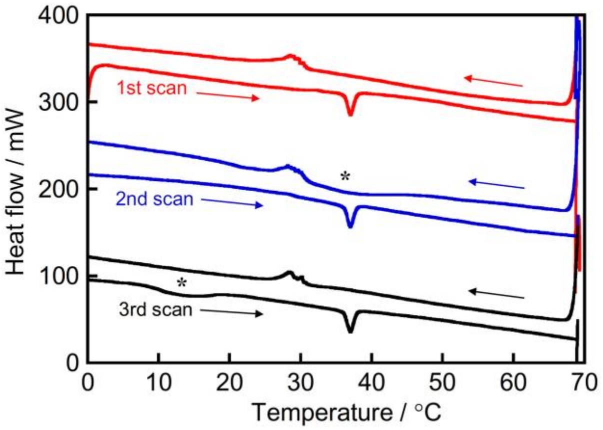


**Figure 7.** DSC traces of diarylethene **1a** in heating and cooling processes at a rate of 1 °C min$^{-1}$. The broad peaks indicated by an asterisk are artifacts.

model has been proposed by Naumov *et al.*[50] On the other hand, in the case of diarylethene **1a**, when UV irradiation was carried out to (0$\bar{1}$1) face of crystal **1a** from left side, the crystal slowly bent away from the incident light at first and the bending speed was increased on the way. After continuous irradiation with UV light, the crystal suddenly returned to a straight shape as shown in **Figure 5**. Upon irradiation with visible light, the crystal largely bent toward right side. Upon continuous irradiation with visible light, the crystal returned to a slightly bent shape. After further irradiation with visible light, the crystal returned to the initial straight shape as shown in **Figure S2**. This unusual photomechanical behavior suggests that there is another factor except photochromic reaction for the bending motion.

To comprehend the bending motion of **1a** in detail, the reversibility of the unusual bending behavior was investigated as shown in **Figure S3** and **Figure 6**. The tip displacement of crystal **1a** was plotted against UV irradiation time. Although the crystal bent with slight twisting, it does not affect to measure the tip displacement. The first slow bending away from the incident light could be repeated more than 20 cycles upon alternating irradiation with UV and visible light without any damage as shown in **Figure S3**. When further UV light irradiation was carried out until the crystal returned to a straight shape, the trajectory of the tip displacement in the 1st cycle was almost the same even after 19th cycles as shown in **Figure 6**. This result indicates that another factor except photochromic reaction for the unusual bending behavior has a good reversibility.

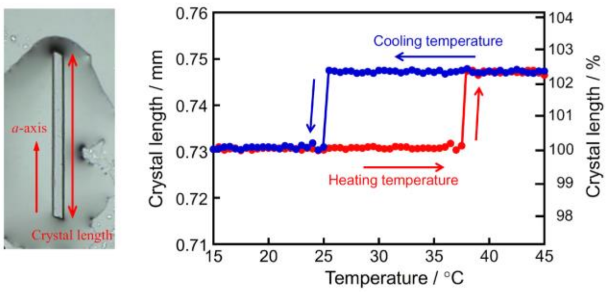


**Figure 8.** Change in crystal length against temperature. Red and blue dots mean heating and cooling processes, respectively.

**Single-crystal-to-single-crystal phase transition.** In the course of measuring the melting point of crystal **1a**, the crystal was found to take place the thermomechanical effect. When the crystal was heated up from 25 °C at a rate of 2 °C min$^{-1}$, the crystal suddenly jumped at 36.5 °C as shown in **Figure S4** and **Video S3**. The speed of jumping was estimated to be more than 35 mm s$^{-1}$. Such thermal jumping phenomena of crystals are known as a thermosalient effect. In general, the thermosalient effect of crystals takes place due to thermodynamic phase transition of crystals.[6,51] To know whether crystal **1a** undergoes thermodynamic phase transition, the differential scanning calorimetry (DSC) measurement was performed. The melting point of crystal **1a** was observed at 96 °C. **Figure 7** shows the DSC traces of diarylethene **1a** in the range of 0−70 °C at a rate of 1 °C min$^{-1}$ in both heating and cooling processes. In the heating process, a small endothermic peak appeared at 36−38 °C. On the other hand, in the cooling process, a small broad exothermic peak appeared at 26−31 °C. The enthalpy change ($\Delta H$) was estimated to be 2.47 kJ mol$^{-1}$. According to the heat of transition rule,[52,53] if endothermic process is involved, the phase transition is reversible, which is called as enantiotropic phase transition. In fact, these endothermic and exothermic behaviors can be repeated more than 3 cycles. This result indicates that the crystal occurred a reversible thermodynamic first-order phase transition with a hysteresis between the heating process and the cooling process.

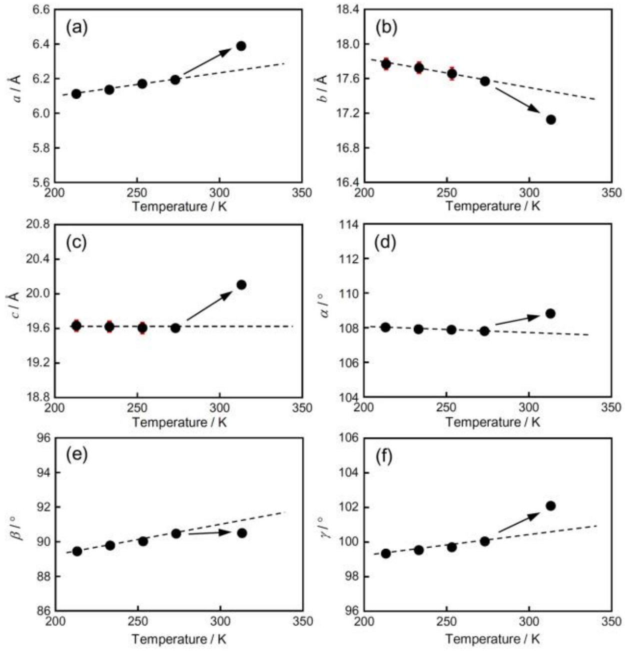


**Figure 9.** Unit cell dimensions of crystal **1a** at various temperatures determined by X-ray crystallographic analysis: (a) *a*-, (b) *b*-, (c) *c*-axes, (d) $\alpha$, (e) $\beta$, (f) $\gamma$. The error bar indicates the standard deviation.

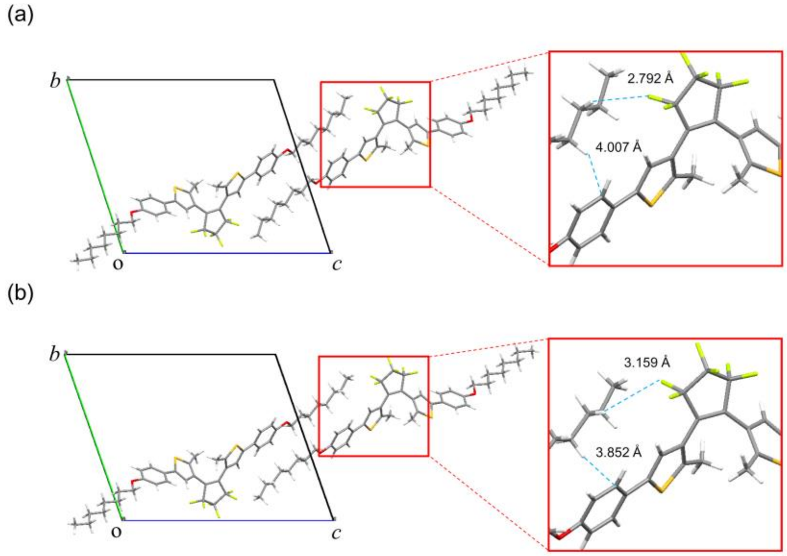


**Figure 10.** Molecular packing diagrams viewed from (100) face at (a) 0 °C and (b) 40 °C.

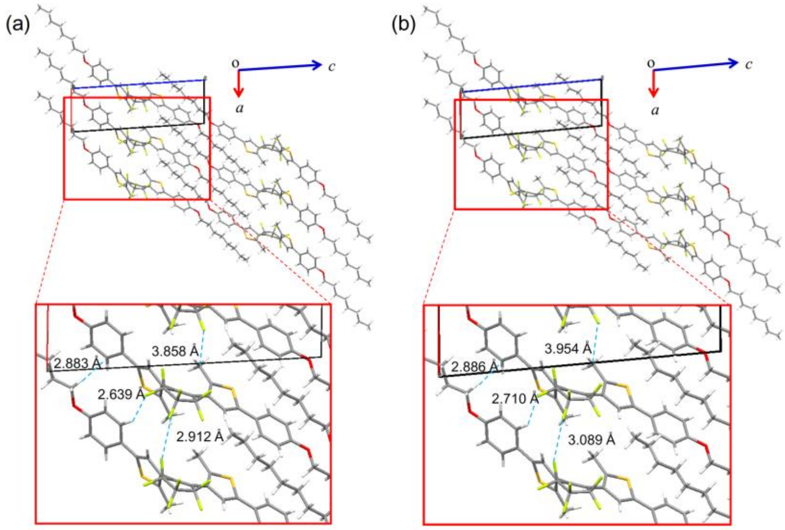


**Figure 11.** Molecular packing diagrams viewed along *b*-axis at (a) 0 °C and (b) 40 °C.

**Figure 8** shows the direct observation of change in crystal length before and after phase transition. The crystal was put in a paraffin oil to avoid jumping. When the crystal **1a** was heated up from 15 °C to 45 °C at a rate of 2 °C min$^{-1}$, the crystal suddenly expanded between 37.9 and 38.0 °C as shown in **Video S4**. On the other hand, the crystal suddenly contracted between 25.4 and 25.3 °C when the crystal **1a** was cooled down from 45 °C to 15 °C at a rate of 2 °C min$^{-1}$ as shown in **Video S5**. This result clearly indicates that **1a** occurs a reversible single-crystal-to-single-crystal (SCSC) phase transition and there is a hysteresis between the heating process and the cooling process. The difference in crystal length of the long axis before and after the phase transition was estimated to be 2.2%. The SCSC phase transition quickly finished within 0.03 s.

To investigate the difference in the crystal structure before and after the phase transition (Form I and Form II, respectively), X-ray crystallographic analysis was performed using the same single crystal at various temperatures. The crystallographic data were summarized in **Table S1**. The crystal system and space group did not change (triclinic $P\bar{1}$). However, the change in the cell dimensions was observed. **Figure 9** shows the plots of cell dimensions against temperatures. The *a*- and *c*-axes largely expanded at 40 °C. On the other hand, the *b*-axis largely contracted at 40 °C. This is ascribed to the thermodynamic phase transition from Form I to Form II. The difference in *a*-axis length before and after the phase transition is estimated to be 2.2%, which is consistent with the result of the direct observation of the change in crystal length. **Figures 10** and **11** show the molecular packing diagrams viewed from (100) face and *b*-axis

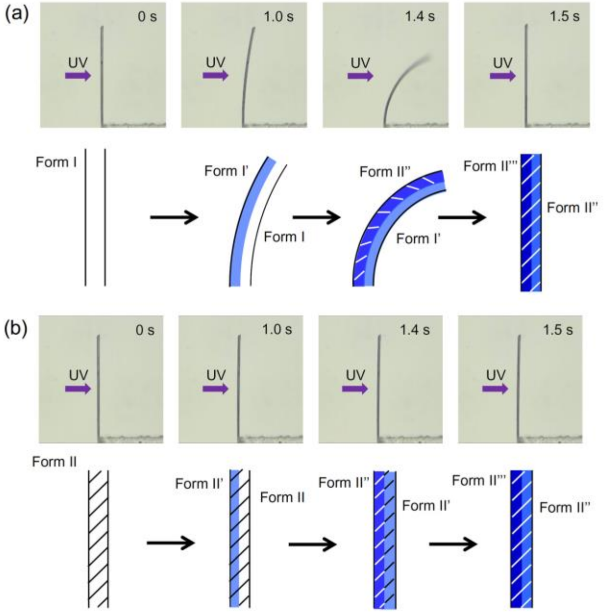


**Figure 12.** Photomechanical behavior of crystal **1a** and proposed mechanism based on photochromic reaction and thermodynamic phase transition at (a) 25 and (b) 66 °C. UV irradiation was conducted from left side.

at 0 °C and 40 °C. Before and after the phase transition, the molecular packing slightly changed. When viewed from (100) face, the distance of C–H⋯F and C–H⋯C changed from 2.792 and 4.007 Å to 3.159 and 3.852 Å, respectively, as depicted in inset of **Figure 10**. These changes are consistent with the expansion of *c*-axis and the contraction of *b*-axis. Moreover, when viewed from *b*-axis, the distance between diarylethene molecules apparently expanded along to *a*-axis. The distance of C–H⋯F (3.858 Å), F⋯F (2.912 Å), F⋯H–C (2.639 Å), and C⋯H–C (2.883 Å) changed to 3.954, 3.089, 2.710, and 2.886 Å, respectively, as depicted in inset of **Figure 11**. This is consistent with the expansion of *a*-axis. These small but apparent changes in molecular packing results in a reversible SCSC phase transition.

**Mechanism of the unusual bending based on photochromic reaction and thermodynamic phase transition.** As another factor for the unusual bending behavior, we considered that the thermodynamic phase transition described above affects the bending behavior. Here, we investigated the thermal effect on the bending behavior and propose the mechanism of the unusual bending behavior based on the combination of the photochromic reaction and the thermodynamic phase transition.

**Figure 12** shows the photomechanical behavior of diarylethene **1a** at 25 °C (before phase transition, Form I, **Video S6**) and 66 °C (after phase transition, Form II, **Video S7**), respectively. When the crystal **1a** was irradiated with UV light at 25 °C, the crystal exhibited the unusual bending behavior described above, as shown in **Figure 12a**. This phenomenon can be explained as follows. First, crystal **1a** is in Form I. Upon irradiation with UV light from left side, the crystal bends away from the incident light due to the expansion in the crystal surface caused by photochromic reaction of diarylethene molecules from the open-ring isomer to the closed-ring isomer. The photoreacted surface layer was depicted as Form I'. The number of prime indicates the conversion ratio of photoisomerization from the open-ring isomer to the closed-ring isomer. After continuous irradiation with UV light, the crystal suddenly bends largely away from the incident light as the photoreacted crystal surface layer undergoes thermodynamic phase transition from Form I'' to Form II''. This is due to a decrease in the phase transition temperature caused by the photoisomerization of diarylethene molecules.[54-57] Upon further irradiation with UV light, the conversion ratio of photoisomerization of diarylethene molecules in right side of crystal also increases and the thermodynamic phase transition from Form I'' to Form II'' also occurs in right side of crystal. As a result, the crystal suddenly returns to the straight shape. If further irradiation is not conducted, such behavior cannot be observed. The behavior of the photoirradiated crystal by visible light irradiation can be explained by following the opposite process. On the other hand, upon irradiation with UV light at 66 °C, the crystal hardly exhibited a bending motion as shown in **Figure 12b**. At 66 °C, the crystal was already

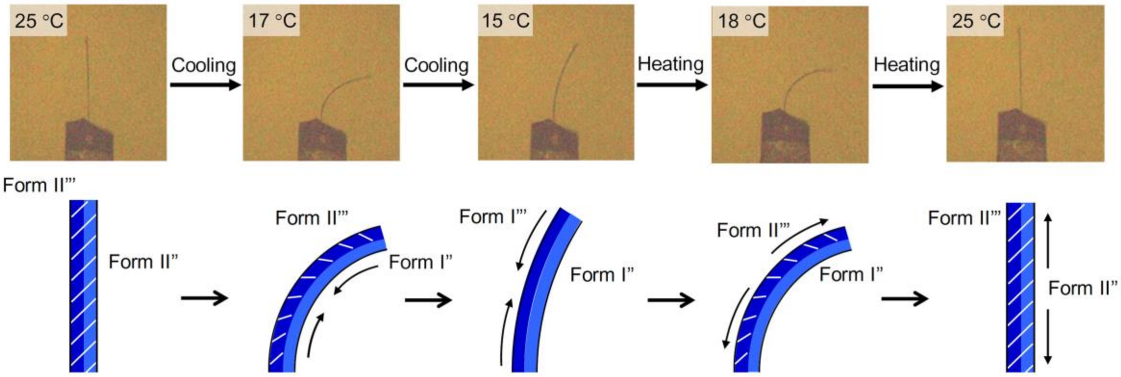


**Figure 13.** Bending behavior of the photoirradiated crystal **1a** by changing temperature. The initial crystal was prepared by irradiation with UV light from left side.

converted from Form I to Form II. In this case, the unusual bending behavior cannot be observed. In addition, the bending speed became quite slower because the intermolecular distance in crystal became longer along with the thermodynamic phase transition. This result clearly suggests that the unusual bending behavior is ascribed to not only the photochromic reaction but also the thermodynamic phase transition from Form I to Form II.

To investigate the mechanism of the unusual bending motion in more detail, the thermal effect to the photoirradiated crystal was also examined as shown in **Figure 13**. The photoirradiated crystal means the crystal after continuous UV irradiation at 25 °C. When the photoirradiated crystal was cooled down from 25 °C, the crystal largely bent toward right side at 17 °C. Upon continuous cooling of the crystal, the crystal returned to the slightly bent shape at 15 °C. When the slightly bent shape crystal was heated up, the crystal largely bent toward right side again. Upon continuous heating of the crystal, the crystal returned to the initial straight shape at 25 °C. The thermal effect to the photoirradiated crystal was also well explained by the thermodynamic phase transition as depicted in **Figure 13**. When the photoirradiated crystal was cooled down, at first, the thermodynamic phase transition from Form II'' to Form I'' in right side of crystal takes place, which results in the large bending toward right side. Upon continuous cooling, the thermodynamic phase transition from Form II''' to Form I''' in left side of crystal also undergoes, which results in the return to the slightly bent crystal shape. Bending behavior by heating can be explained by the reverse process. These results also indicate that the thermodynamic phase transition plays an important role for the unusual photomechanical behavior. Thus, the unusual bending behavior can be well explained by the combination of the photochromic reaction and the thermodynamic phase transition. Such "light-preparative" thermoresponsive mechanical materials could be used for thermosensors capable to make detectable a temperature change at an arbitrary temperature.

### Conclusions

We have synthesized a diarylethene, 1,2-bis(2-methyl-5-(4-octyloxyphenyl)-3-thienyl)perfluorocyclopentene (**1a**), and investigated photochromic reactivity of **1a** in solution and crystalline phase. In the course of study, a thermosalient effect of crystal induced by a reversible thermodynamic phase transition **1a** was found. Moreover, an unusual photomechanical bending behavior with a good repeatability was found. When UV irradiation was carried out to crystal **1a**, the crystal slowly bent away from the incident light at first and quickly bent away from the light source on the way. After continuous irradiation with UV light, the crystal suddenly returned to the initial straight shape. We proposed a mechanism of the unusual bending behavior considering both the photochromic reaction of diarylethene molecules and the thermodynamic phase transition. The proposed mechanism was well supported by the experimental results of the thermal effect to bending behavior. The results in this work provide not only new photomechanical phenomena but also strategy for design of materials showing nonlinear mechanical response to the conversion ratio of photoreactions.

## ASSOCIATED CONTENT

**Supporting Information**. Crystallographic data of **1a** in CIF format, movies of thermosalient effect, single-crystal-to-single-crystal phase transition, photomechanical effect of crystal **1a**, and additional results. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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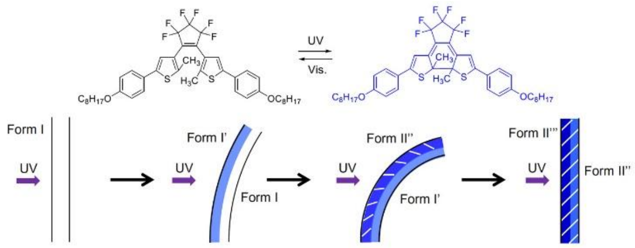

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