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Photomechanical Behavior of Photochromic Diarylethene Crystals

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1.1 Introduction

Photochromism is defined as a reversible transformation reaction between two isomers having different absorption spectra, which is induced in one or both directions by photoirradiation [1]. Among many photochromic compounds, diarylethenes with heteroaryl groups including thiophene, furan, thiazole, and oxazole rings have excellent properties, such as thermal stability of both isomers, fatigue resistance, high coloration quantum yield, rapid response, and high reactivity even in the crystalline phase [2]. Such diarylethenes have potential applications in ultraviolet (UV) sensors, photoswitches, displays, optical waveguides, optical memories, holographic recording media, nonlinear optics, and actuators. Upon UV light irradiation, diarylethenes exhibit color changes because of a molecular structure change from the open-ring isomer form to the closed-ring isomer form. The colors remain stable in the dark at room temperature. The colored isomers revert to their original colorless isomer forms by irradiation with visible light. The reversible color changes can be repeated many times.

Photochromic compounds that undergo a photochromic reaction in the crystalline phase are known for paracyclophanes, triarylimidazole dimer, diphenylmaleronitrile, aziridines, 2-(2,4-dinitrobenzyl)pyridine, *N*-salicylideneanilines, triazenes, and diarylethenes. The large change in geometrical structures prohibits photochromic reactions in the crystalline phase. Even in the crystalline phase, diarylethenes can undergo thermally irreversible and fatigue-resistant photochromic reactions when diarylethene molecules are fixed in the antiparallel conformation and the distance between the reactive carbons is less than 4.2 Å [3]. The photocyclization reaction results in a color change in the crystals from colorless to yellow, red, blue, or green, as shown in Figure 1.1. The color of the crystals can be maintained if they are stored in the dark. The colored crystals return to the initial colorless ones by irradiation with visible light. In the crystalline phase, the photocyclization quantum yield is close to unity and the coloration/decoloration cycles can be repeated more than 10^4

Mechanically Responsive Materials for Soft Robotics, First Edition. Edited by Hideko Koshima.

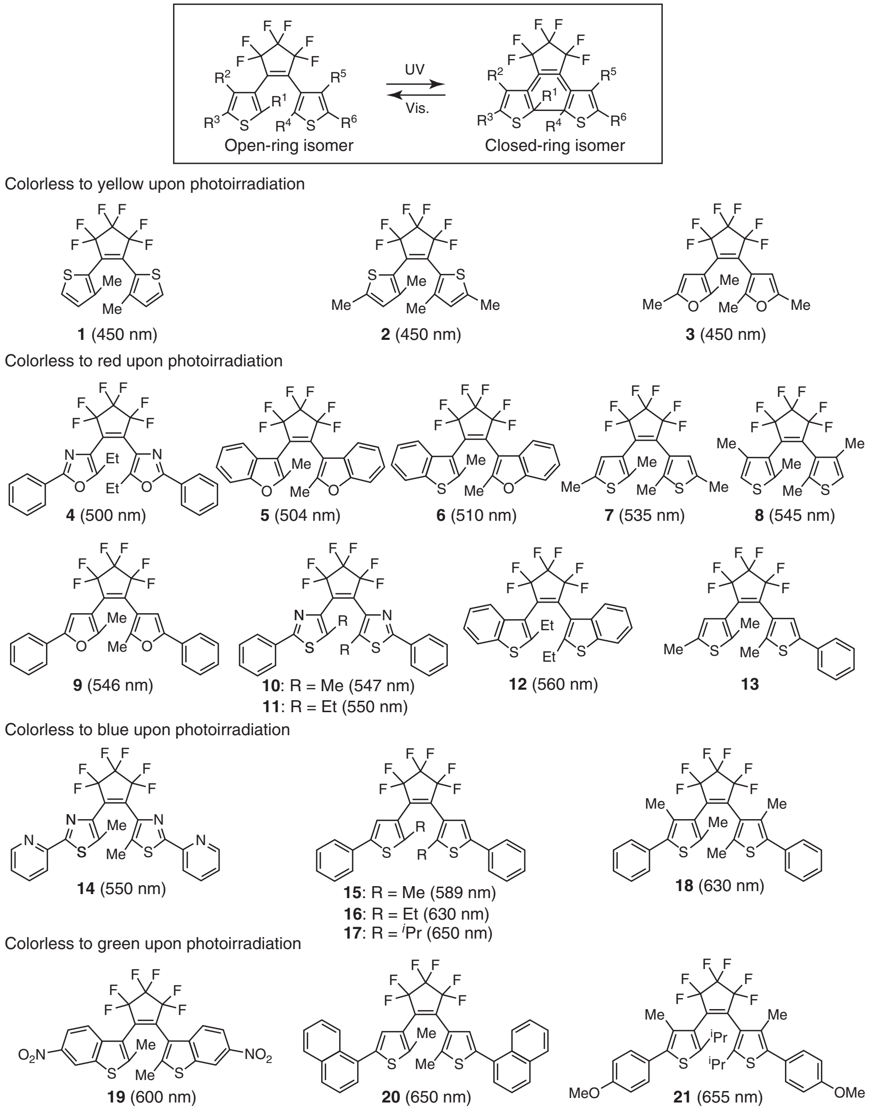


Figure 1.1 Typical examples of diarylethenes that underwent photochromism in the single crystalline phase. Maximum absorption wavelength of the photogenerated closed-ring isomers in crystals is shown in parentheses. When exposed to UV radiation crystals **1–3** turned to yellow, crystals **4–13** to red, crystals **14–16** to blue, and crystals **19–21** to green.

times [2]. There are many studies describing the photochromism of diarylethene crystals, including investigations that report multicolor photochromism [4], dichroism under polarized light [5], fluorescence [6], three-dimensional optical memory [7], diastereoselective cyclization [8], selective photochromic reaction under polarized light [9], theoretical studies [10], Raman spectroscopic studies [11], nanostructures [12], supramolecular architectures [13], nanocrystals [14],

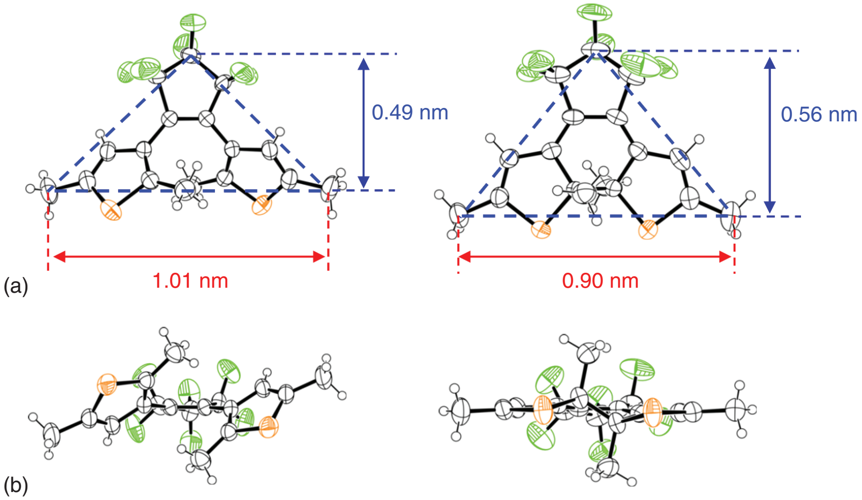


Figure 1.2 (a) Top and (b) side views of the geometrical structures of the open- and closed-ring isomers of 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene (**7**) in crystals. The two isomers were isolated and independently recrystallized. Source: Irie et al. 2014 [2b]. Adapted with permission from American Chemical Society.

polymorphism [9a, 15], phase transitions [15b, c], surface wettability [15a, 16], and molecular motion observed by X-ray crystallography [17]. The research on molecular motion observed by X-ray crystallography demonstrated that photochromic reactions of diarylethene molecules in the crystals are accompanied by a change in the unit cell dimensions because of a decrease in the molecular volume resulting from photoisomerization of the open-ring isomer to yield the closed-ring isomer as shown in Figure 1.2 [2b]. The height of the triangle shape increases from 0.49 to 0.56 nm and the base width decreases from 1.01 to 0.90 nm. The side view indicates that the thickness of the molecule is reduced. The change in the geometrical structure of diarylethene molecules plays an important role in photomechanical phenomena.

In 2001, the crystal surface of diarylethene **18** was found to exhibit a photoreversible surface morphology change [18]. The flat crystal surface formed a step with a height of approximately 1 nm upon UV light irradiation. The step was erased by irradiation with visible light. The crystal thickness decreased as a result of the photochromic isomerization of the open-ring isomer to yield the closed-ring isomer. Another surface, which is perpendicular to the surface that formed the step, exhibited a photoreversible valley formation. These reversible surface morphology changes are ascribed to photoinduced contraction in the direction of the long axis of each diarylethene molecule regularly packed within the single crystal. These results indicate that the molecular-scale structural change of individual molecules may induce the macroscopic mechanical movement of materials.

In this chapter, recent developments in the light-driven actuators based on photochromic diarylethene crystals are described.

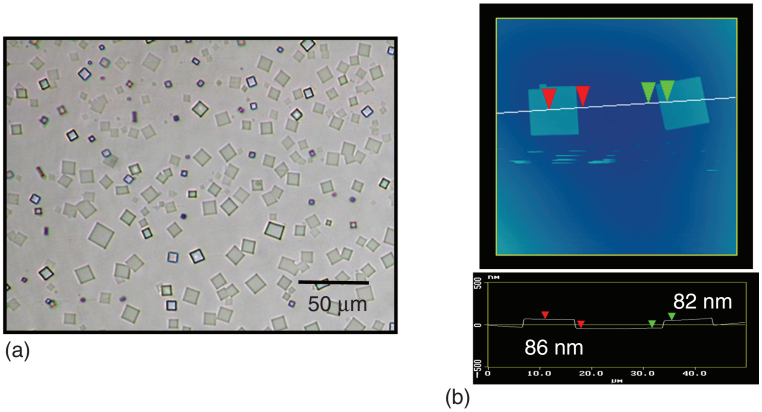


Figure 1.3 (a) Digital microscopic and (b) atomic force microscope (AFM) images for thin microcrystals of **16**.

1.2 Crystal Deformation Exhibiting Expansion/Contraction upon Photoirradiation

A first example of photoreversible macroscopic crystal deformation was a thin microcrystal of 1,2-bis(2-ethyl-5-phenyl-3-thienyl)perfluorocyclopentene (**16**) [19]. The microcrystals were prepared by sublimation on a thin glass plate under atmospheric pressure at 144 °C. A photograph of microcrystals composed of **16** is shown in Figure 1.3. The crystals have several tens of micrometers square in size with thickness of a few hundred nanometers. Upon irradiation with 365 nm light, the crystal turned blue and the blue-colored crystal returned to the initial colorless crystal form after irradiation with visible light. The conversion ratio in the crystal from the open- to the closed-ring isomers was followed by an infrared (IR) absorption microspectroscopy. IR absorption spectra for thin single crystal **16** were taken under polarized IR light to avoid an overlap of peaks. Figure 1.4 shows the IR spectral changes of crystal **16** upon irradiation with 365 nm light. The open-ring isomer in the crystal has two characteristic bands at 1260 and 1350 cm^{-1}. The band at 1350 cm^{-1} was split into two peaks upon UV light irradiation, whereas the band at 1260 cm^{-1} monotonously decreased. The closed-ring isomer has no absorption around 1260 cm^{-1}. The conversion ratio from the open- to the closed-ring isomers can be determined from the decrease of the band at 1260 cm^{-1}. Almost 70% conversion was observed at the photostationary state under irradiation with 365 nm light.

In general, crystals of different molecules have different unit cell parameters, space group, and packing in the lattice. Figure 1.5 shows the photographs of crystals for diarylethenes **16**, **11**, and **17** [19, 20]. A single crystal of **16** with a thickness of 570 nm was reversibly changed from a square-like shape with corner angles of 88° and 92° to a lozenge-like shape with corner angles of 82° and 98° upon alternating irradiation with UV and visible light. The photochromic reaction took place homogeneously in crystals because of their thin crystallized forms with a thickness of several hundred nanometers. Crystals of **11** and **17** have unit cell

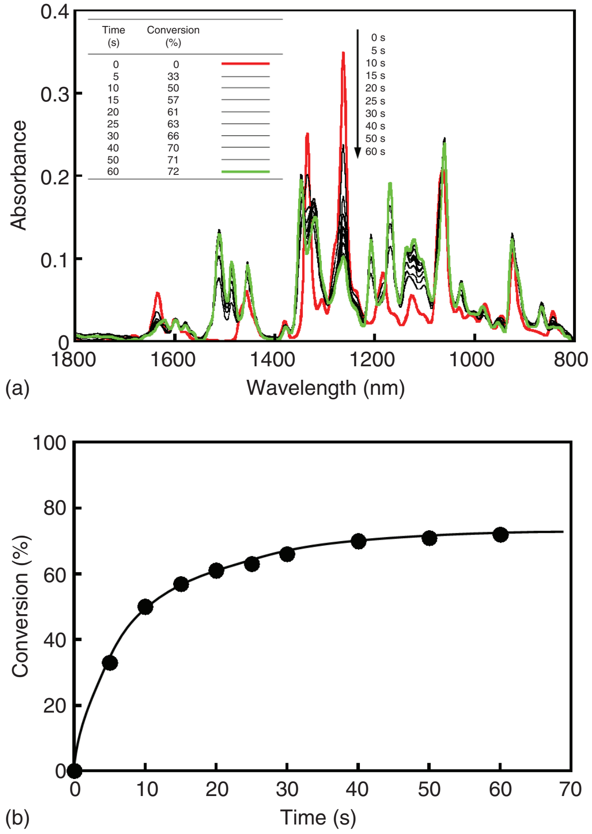


Figure 1.4 (a) IR spectral and (b) conversion change for thin microcrystal of **16** upon irradiation with 365 nm light. IR spectra were detected under polarized IR light. The polarization direction was set to the short axis in the molecule. Source: Kobatake et al. 2007 [19]. Adapted with permission of Springer Nature.

parameters similar to **16**. These diarylethenes have the same space group, i.e. *Pbcn*, as shown in Table 1.1. The molecular packings of **11** and **17** are also similar to that of **16**, as shown in Figure 1.6. Crystal **11** changed its color from colorless to red and its corner angles from 90° and 90° to 86° and 94°, and hence its shape from square to lozenge. Crystal **17** changed its color from colorless to blue and the corner angles from 83° and 97° to 81° and 99° upon irradiation with UV light. Crystals of **16**, **11**, and **17** exhibited a similar crystal shape deformation. These results indicate that the crystal shape deformation depends on the molecular packing of the molecules in the crystal and was not affected by difference in molecular structure.

1.3 Photoresponsive Bending

A first example of photoresponsive bending of diarylethene crystals was a rodlike crystal of 1,2-bis(5-methyl-2-phenyl-4-thiazolyl)perfluorocyclopentene (**10**) [19]. The crystal bent toward the incident UV light source when irradiated with UV light. The bending is attributed to a contraction in the direction of the crystal long axis and a gradient in the extent of the photoisomerization reaction at the crystal surface caused by high light absorbance. The rodlike crystal bent fast in

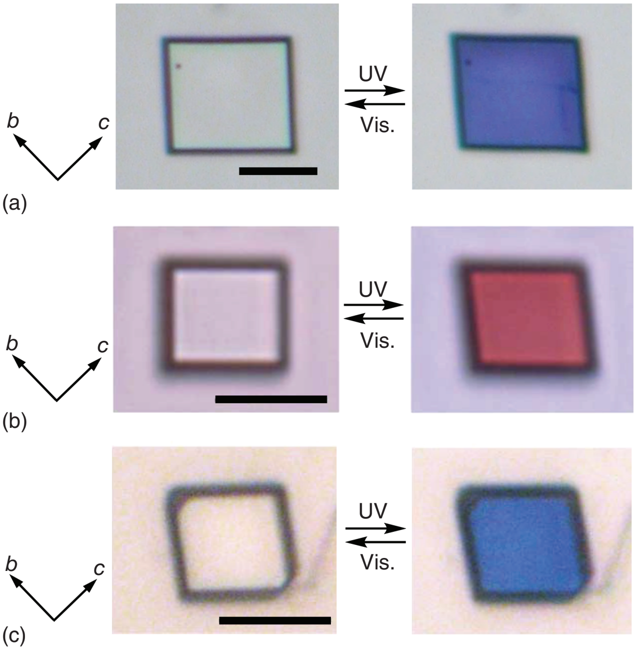


Figure 1.5 Photoinduced crystal shape deformation of crystals (a) **16**, (b) **11**, and (c) **17**. Scale bar is 10 μm. Source: Kobatake et al. 2007 [19, 20]. Adapted with permission of Springer Nature and the European Society for Photobiology, the European Photochemistry Association, and The Royal Society of Chemistry.

a few seconds timescale and could move a gold micro-particle that was 90 times heavier than the single crystal. Moreover, it could launch a tiny silica particle like a tennis ball. Thus, scaling down the crystal size allows achieving macroscopic mechanical responses.

The rodlike crystal of **10** (53 μm × 3 μm × 3 μm) was also used for measuring the response time of the bending because even low power single pulsed laser can induce the bending of the rodlike crystal [19]. As a light source, the pulsed laser of the third harmonics of Nd-YAG laser (355 nm, pulse width = 8 ns, power = 60 mJ/pulse) was used. The bending behavior induced by the single pulsed laser was measured using a high-speed camera with an image intensifier. The exposure time of each frame was 25 μs (40 000 frames s^{-1}). After irradiation with the single pulsed laser, the straight rodlike crystal bent, and the bending process was almost completed in one frame. This means that the response time of the bending shape change is around 25 μs or faster.

Various types of rodlike crystals of diarylethenes have been reported on photoresponsive bending. There are two types of the photoinduced bending behavior: bending away from the incident light and bending toward the incident light [21]. Figure 1.7 shows the molecular structures of crystals that exhibit photoinduced bending [19, 22–31]. When the long axis of the rodlike crystal expands upon UV light irradiation, the crystal bends away from the incident light. On the other hand, when the long axis of the rodlike crystal contracts upon UV light irradiation, the crystal bends toward the incident light.

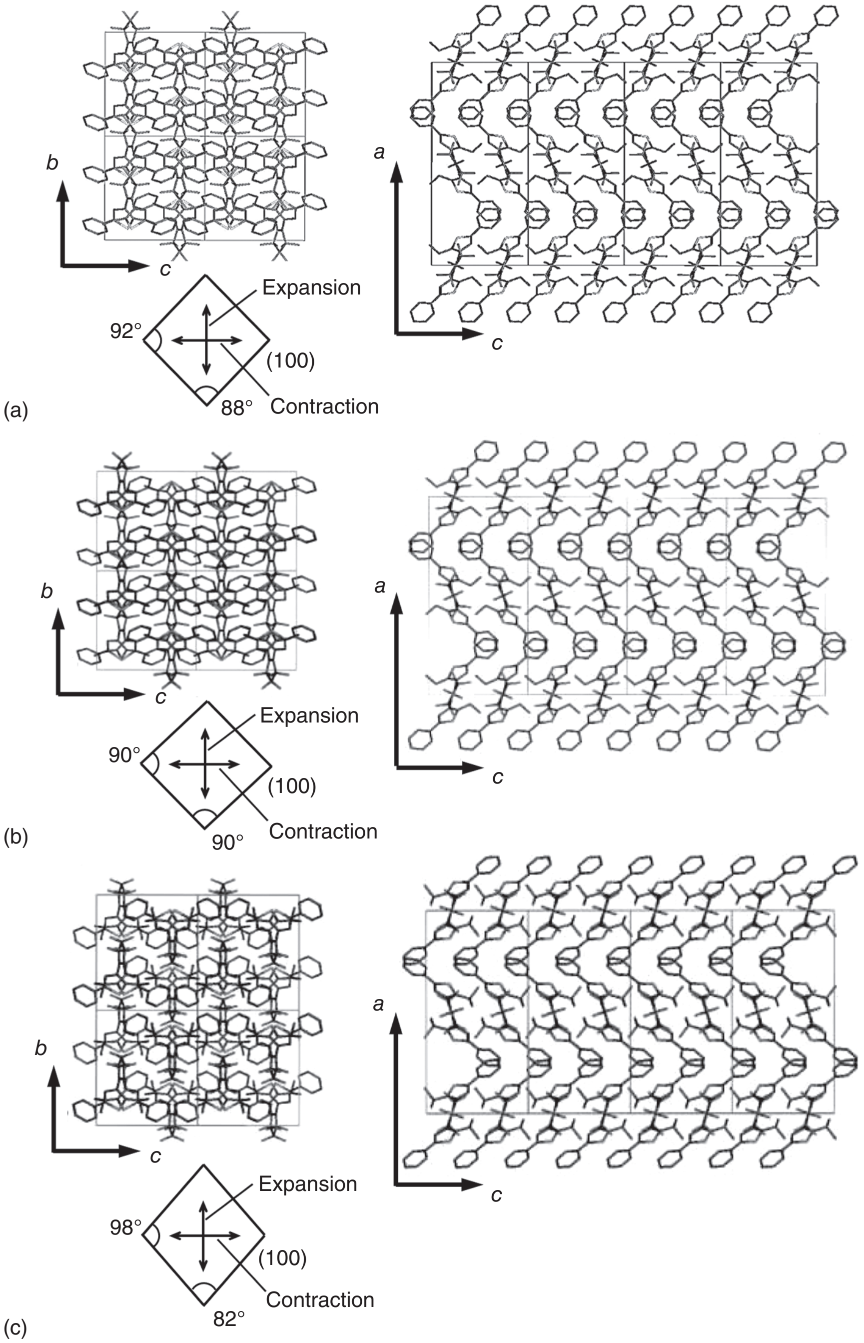


Figure 1.6 Molecular packing of crystals (a) **16**, (b) **11**, and (c) **17** viewed from (100) (left) and (010) faces (right). The arrows indicate the direction of contraction and expansion of the crystals upon UV irradiation. Source: Kobatake et al. 2007 [19, 20]. Adapted with permission of Springer Nature and the European Society for Photobiology, the European Photochemistry Association, and The Royal Society of Chemistry.

Table 1.1 X-ray crystallographic data for **16**, **11**, and **17**.

	16	**11**	**17**
Empirical formula	$C_{29}H_{22}F_6S_2$	$C_{27}H_{20}F_6N_2S_2$	$C_{31}H_{26}F_6S_2$
Formula weight	548.61	550.59	576.66
T (K)	123	123	123
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Pbcn*	*Pbcn*	*Pbcn*
a (Å)	22.332(5)	21.5461(15)	21.307(6)
b (Å)	10.991(2)	10.8096(8)	12.193(4)
c (Å)	10.601(2)	10.8098(8)	10.669(3)
V (Å^3)	2602.0(9)	2517.7(3)	2771.8(14)
Z	4	4	4
Density(cal.) (g cm^{-3})	1.400	1.453	1.382
Corner angles before UV irradiation (°)	88, 92	90, 90	83, 97
Corner angles after UV irradiation (°)	82, 98	86, 94	81, 99

The bending velocity of the photoresponsive bending crystals depends on the molecular structure and the crystal structure. Rodlike crystals of 1,2-bis(2-methyl-5-(4-(1-naphthoyloxymethyl)phenyl)-3-thienyl)perfluorocyclopentene (**22**) bends away from the incident light upon UV light irradiation [22]. It was found that the bending velocity depended on crystal faces subjected to UV light irradiation. Figure 1.8 shows the photoinduced bending behavior of crystal **22** upon irradiation with 365 nm light. When the (001) face was irradiated, the crystal bent slowly. In contrast, when the (010) face was irradiated, the crystal bent significantly fast. This is ascribed to the difference in the absorption coefficients and the photoreacted thickness of the different faces. The depth of the photoreaction in the vicinity of the crystal surface affects the bending velocity. Therefore, this result suggested that crystal thickness is a very important factor in bending behavior.

The dependence of the bending velocity on UV irradiation power was examined using a diarylethene crystal of **22** [23]. For their rodlike crystals, it was revealed that the initial velocity of curvature change (V_{init}) increased in proportion to the power of the incident UV light as shown in Figure 1.9. This result also suggests that the local strain owing to the individual diarylethene molecules structural changes acts cumulatively for the photomechanical bending behavior.

To understand the dependence of the bending velocity on crystal thickness, the bending behaviors of crystals **22**, **24**, and **34** with different thicknesses were investigated [23]. Figure 1.10 shows V_{init} as a function of the crystal thickness. The crystal bent significantly when it was thin. However, when the crystal thickness was 0.62 μm, the crystal could not bend. To explain this relationship, Timoshenko's bimetal model was introduced. The relation between V_{init} and the crystal

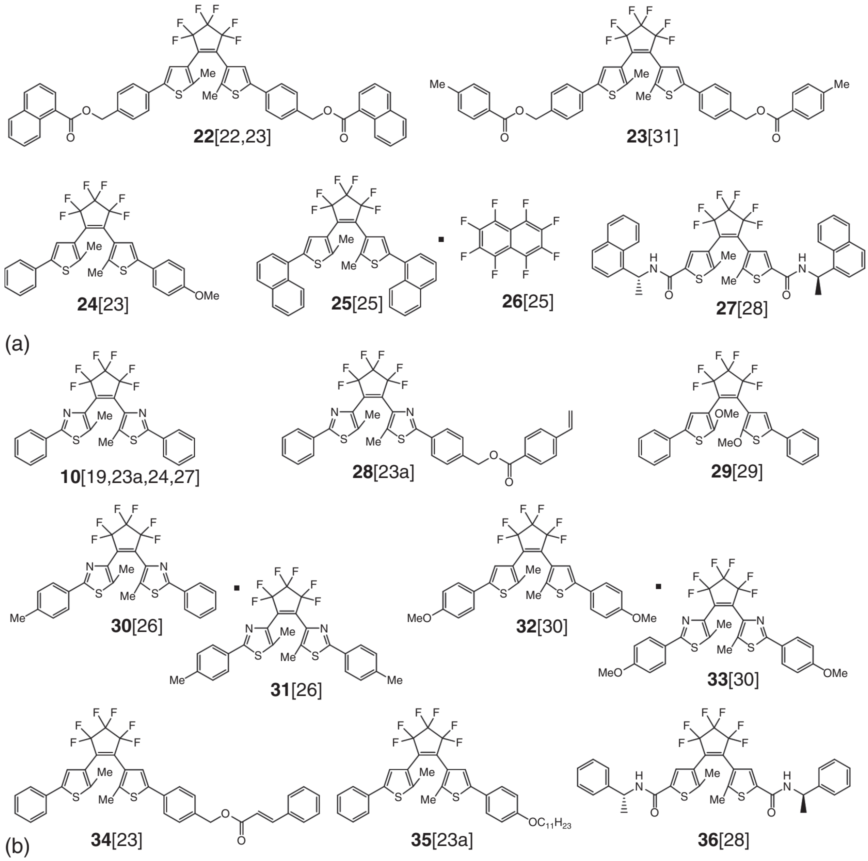


Figure 1.7 Photochromic diarylethene derivatives that exhibit the photoinduced crystal bending: (a) bending away from the incident UV light, (b) bending toward the incident UV light.

thickness was well explained by Timoshenko's bimetal model using two parameters. The depth of the photocyclization reaction in the crystal was defined to be h_2. The initial change in the actuation strain per second in a UV light intensity under the same condition was expressed as $\alpha_{2,\mathrm{init}}$. Timoshenko's bimetal model was applied to various diarylethene crystals and enabled quantitative evaluation of the potential photoinduced bending velocity among different crystals. Thus, it was revealed that h_2 and $\alpha_{2,\mathrm{init}}$ played important roles in determining the bending velocity.

1.4 Dependence of Bending Behavior on Irradiation Wavelength

Utilizing UV light with a different wavelength is expected to change h_2. To assess the effect of a change in h_2 for the photomechanical behavior, a rodlike crystal

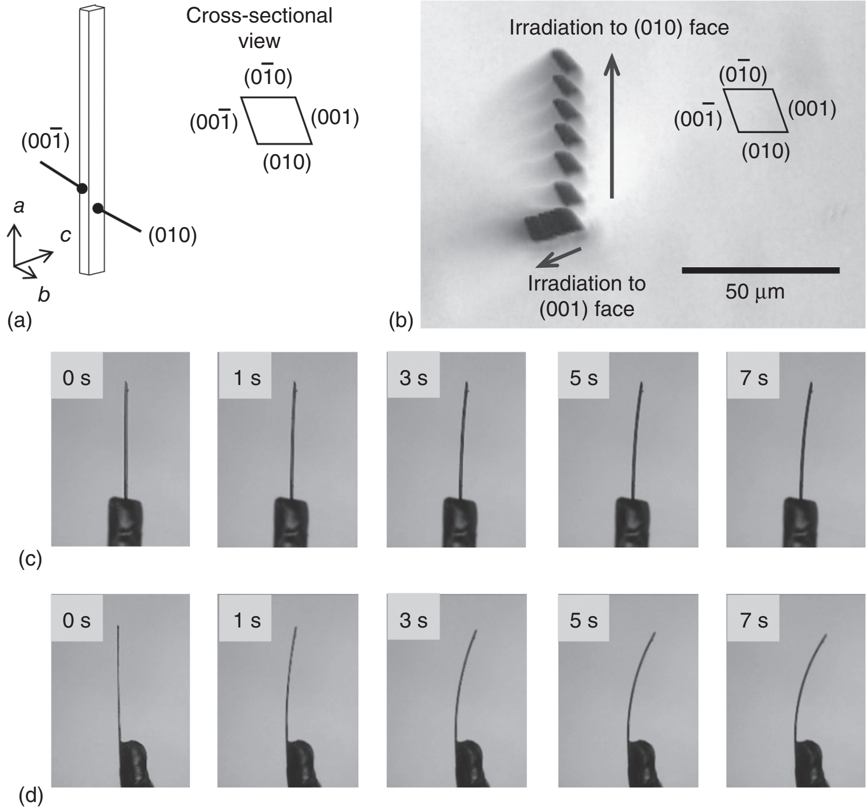


Figure 1.8 (a) Crystal shape and (b) photoinduced bending behavior of crystal **22** upon irradiation with 365 nm light to (c) the (001) face and (d) the (010) face. (b) Superimpose of the photographs observed from tip of the crystal. Source: Kitagawa and Kobatake 2013 [22]. Reproduced with permission of American Chemical Society.

of **10** was irradiated with different wavelengths of 365 and 380 nm light [24]. Figure 1.11 shows photographs of the bending behavior of the crystal. When irradiated with 365 nm light, the crystal bent toward the UV light source. In contrast, when irradiated with 380 nm light, the crystal first bent away from the incident light and then bent toward the light source. This is ascribed to the difference in the depth of the photochromic reaction from the crystal surface. When irradiated with 365 nm light, the photoisomerization of diarylethene molecules took place on only the crystal surface because of its high absorbance capacity. This indicates that the depth of photoisomerization from the crystal surface is very small relative to the crystal thickness and that the conversion of the photoreacted layer increases significantly. In contrast, when irradiated with 380 nm light, the photoisomerization of diarylethene molecules took place deep within the crystal because diarylethene has a low absorption at 380 nm compared with that at 365 nm. This indicates that, in this case, the depth of photoisomerization from the crystal surface was close to the crystal thickness, and the conversion of the photoreacted layer increased slowly. Upon UV light irradiation, photoisomerization

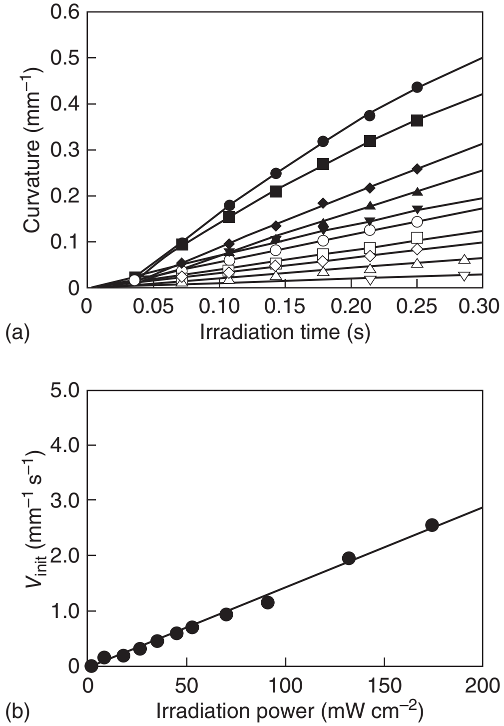


Figure 1.9 (a) Curvature change against UV irradiation time and (b) the initial velocity of curvature change (V_{init}) against power of the incident UV light for crystals **22** (crystal thickness: 6.7 μm). Power of the incident UV light is 174 (●), 132 (■), 91.0 (◆), 70.2 (▲), 52.7 (▼), 44.8 (○), 35.1 (□), 26.3 (◇), 17.6 (Δ), and 8.17 mW cm^{-2} (∇) for (a). Source: Hirano et al. 2017 [23b]. Reproduced with permission of American Chemical Society.

of diarylethene molecules in the crystalline phase from the open-ring isomer to the closed-ring isomer occurs randomly at first. As this occurs, there could be repulsion between the open-ring isomer and the photogenerated closed-ring isomer, which induces the expansion of the photoreacted layer. As the photoconversion of the diarylethene molecules increases, this repulsion disappears and van der Waals interactions between the closed-ring isomers induce the contraction of the photoreacted layer. When the depth of photochromic reaction is very small relative to the crystal thickness, the crystal cannot bend to a significant extent. In contrast, when the depth of the photochromic reaction is approximately half of the crystal thickness, the crystal can bend to a large extent. Therefore, upon irradiation with 365 nm light, the initial bending away from the light source could not be observed. On the other hand, upon irradiation with 380 nm light, the initial bending away from the light source was clearly observed. The proposed mechanism, shown in Figure 1.12, was well supported by the experimental results with respect to the crystal thickness and the change in the unit cell dimensions associated with the photochromic reaction.

1.5 Photomechanical Work of Diarylethene Crystals That Exhibit Bending

As mentioned previously, how to apply the photomechanical behavior to practical use turns out to be an important task. In this section, several

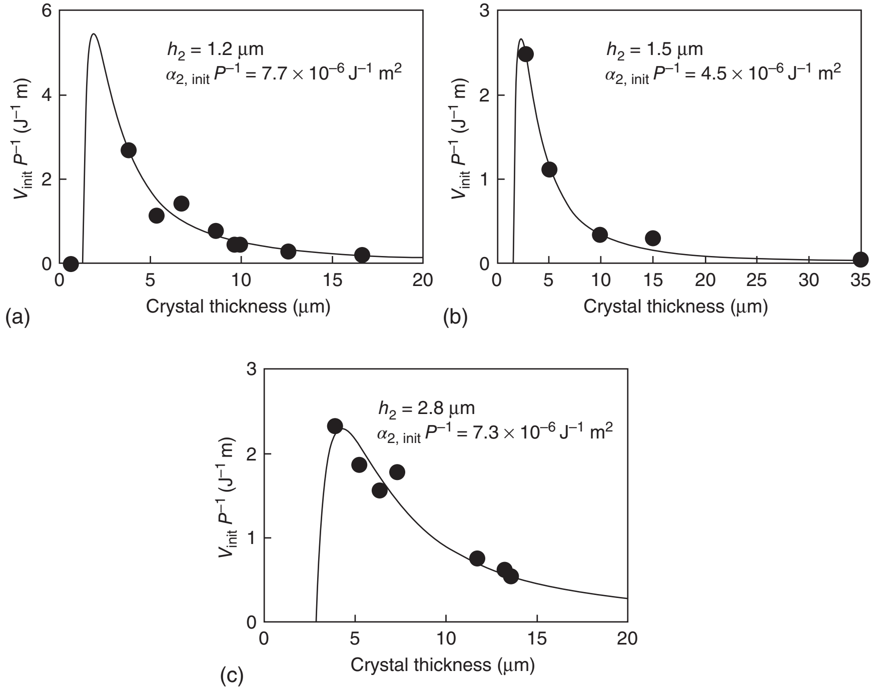


Figure 1.10 Initial velocity of curvature change (V_{init}) relative to the crystal thickness upon irradiation with UV light for diarylethene crystals (a) **22**, (b) **24**, and (c) **34**. The initial velocity is normalized according to the power of the light (P). Source: Hirano et al. 2017 [23b]. Reproduced with permission of American Chemical Society.

demonstrations using photomechanical behavior of diarylethene crystals were described.

Cocrystals composed of 1,2-bis(2-methyl-5-(1-naphthyl)-3-thienyl)perfluorocyclopentene (**25**) and perfluoronaphthalene (**26**) with a length of 1–5 mm exhibited photoreversible bending behavior over 250 times upon alternating irradiation with UV and visible light [25]. The crystals bent away from the incident UV light as a result of the elongation of the UV-irradiated thin surface layer, which corresponded to a change in the geometrical structure of the short axis of the diarylethene molecules from the open-ring isomer to the closed-ring isomer. The crystals were able to lift a heavy metal that was 200–600 times heavier than the crystals, as shown in Figure 1.13. The maximum stress in the crystals by photoirradiation was estimated to be 44 MPa, which is 100 times larger than that of muscle (~0.3 MPa). The Young's modulus of the crystal was measured to be 11 GPa. The relatively large Young's modulus enabled the crystals to carry out large mechanical work. Thus, the crystals could be used as "molecular crystal cranes."

Mixed crystals composed of 1-(5-methyl-2-phenyl-4-thiazolyl)-2-(5-methyl-2-*p*-tolyl-4-thiazolyl)perfluorocyclopentene (**30**) and 1,2-bis(5-methyl-2-*p*-tolyl-4-thiazolyl)perfluorocyclopentene (**31**) also exhibited more than 1000 reversible bending cycles upon alternating irradiation with UV and visible light without

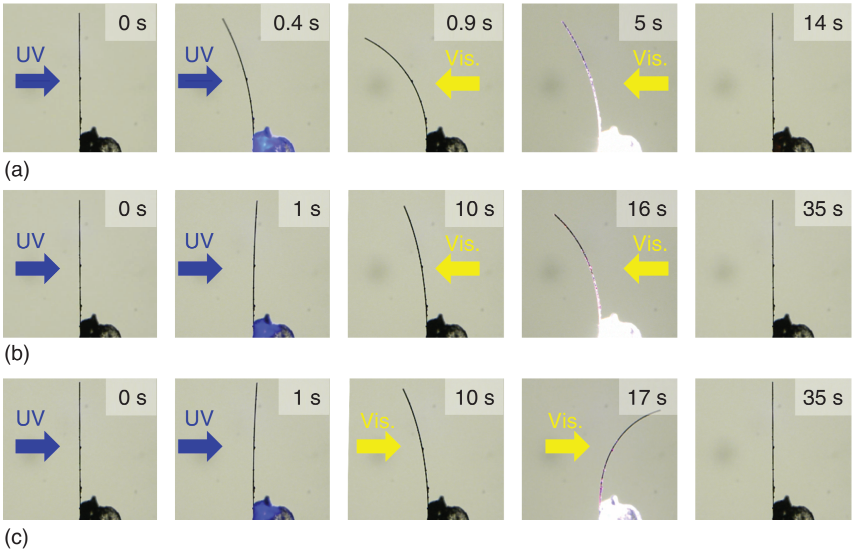


Figure 1.11 Photoinduced bending behavior of diarylethene crystal **10** upon irradiation with 365 (a) and 380 nm light (b and c) from the left side. The visible light was irradiated from the right side (a and b) and the left side (c). Source: Kitagawa et al. 2015 [24]. Reproduced with permission of the Royal Society of Chemistry.

any crystal destruction [26]. The crystal exhibited a bending motion across a wide temperature range from 4.6 to 370 K and even in water. The rodlike crystal bent toward the light source irrespective of the irradiation direction. The edge of the rodlike crystal could be rotated when the intensity of the UV and visible lights was controlled, which resulted in actual mechanical work to rotate a gearwheel, as shown in Figure 1.14. Thus, diarylethene crystals were used as “photoactuators.”

The bending behavior of a gold-coated crystal of **10** was investigated [27]. As a result of the large Young’s modulus of gold (83 GPa) compared with that of the diarylethene crystals, the gold-coated crystal tended not to bend as the thickness of the gold layer was increased. The relationship between the initial speed of the curvature change and the thickness of the gold-coated crystal was well explained by the extended bimetal model. When the thickness of the gold layer was 14 nm, the velocity of the bending motion was reduced by half. Furthermore, the photoreversible current ON/OFF switching of an electric circuit by the gold-coated diarylethene crystal was demonstrated, as shown in Figure 1.15. The current was able to flow in a stable manner even when the current value was over 30 mA; the current switching could be repeated over 10 cycles. Thus, gold-coated diarylethene crystals could be used as real “photoswitches” in the mesoscopic region.

1.6 New Types of Photomechanical Motion

The crystal shape change is ascribed to photogenerated anisotropic strain within the crystals. In most cases, the local shape change of each diarylethene molecule

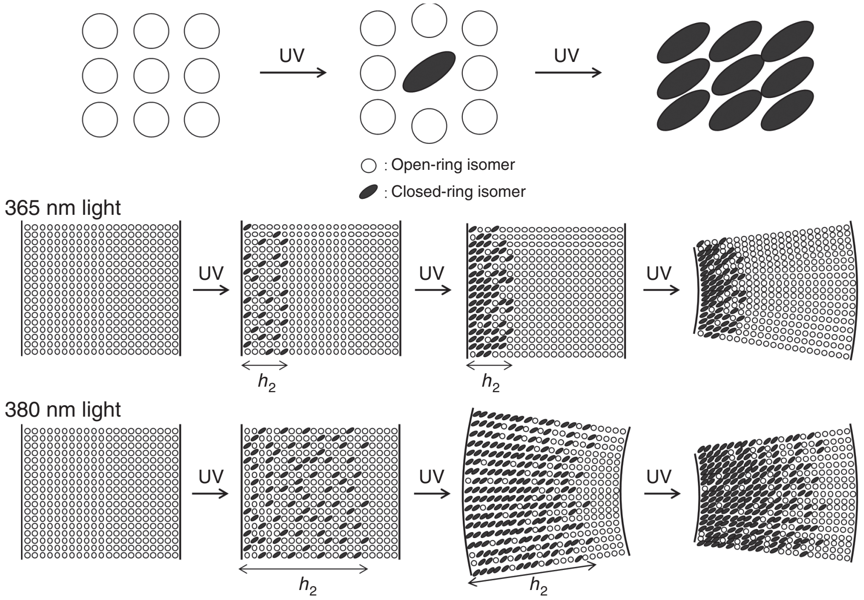


Figure 1.12 Schematic illustration of the mechanism for photoinduced crystal bending upon irradiation with 365 and 380 nm light. Source: Kitagawa et al. 2015 [24]. Reproduced with permission of the Royal Society of Chemistry.

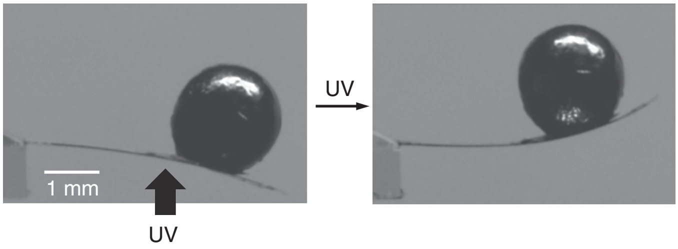


Figure 1.13 Photomechanical work of molecular crystal cantilevers made of **25**/**26** cocrystals. UV light was irradiated from the lower side of the crystal: 2 mm lead ball, 46.77 mg; crystal cantilever, 0.17 mg. Source: Morimoto and Irie 2010 [25]. Reproduced with permission of American Chemical Society.

contributes additively to the strain of the photoirradiated crystal [30]. However, a cooperative phase transition or domain formation induced by the photoisomerization may produce new types of photomechanical motion. Although the bending behavior is the most common photomechanical motion, the development of photoactuators exhibiting complex motion requires the investigation of new types of photomechanical motion. In the course of evaluating the initial bending speed of various diarylethene crystals, needle-like crystals of 1,2-bis(2-methyl-5-(4-(*p*-toluyloxymethyl)phenyl)-3-thienyl)perfluorocyclopentene (**23**) was found to exhibit unusual stepwise bending behavior, in which the bending rate changed significantly during continuous UV light irradiation,

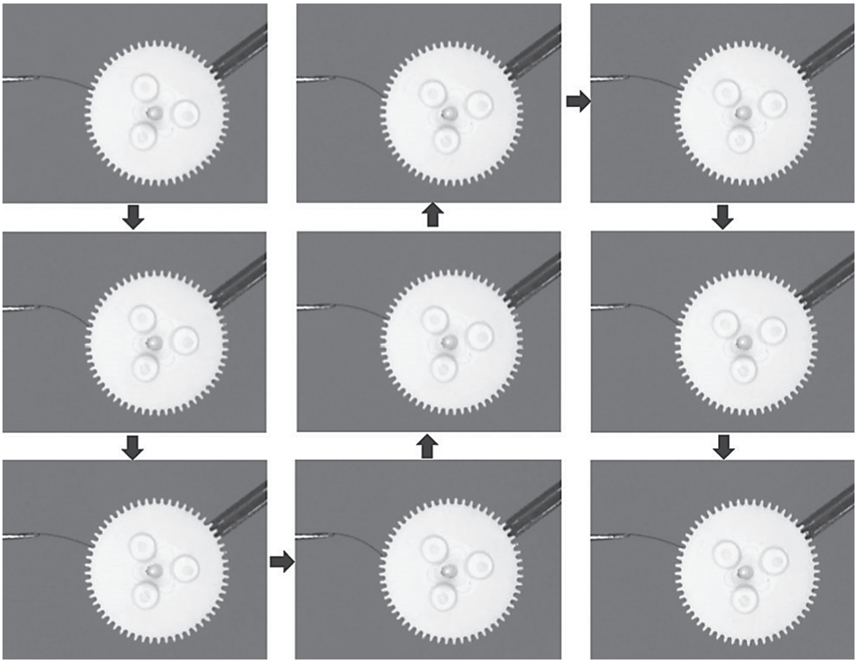


Figure 1.14 Gearwheel rotation operated by a light-driven molecular crystal actuator. The two-component mixed crystal containing **30** and **31** (**30** : **31** = 63/37) (1.3 mm × 60 μm × 12 μm) was fixed on the tip of a metal needle. The gear (diameter: 3.2 mm) was rotated by the crystal, which exhibited reversible bending upon alternating irradiation with UV (365 nm) and visible (>500 nm) light. Source: Terao et al. 2012 [26]. Reproduced with permission of John Wiley & Sons.

as shown in Figure 1.16 [31]. For the bending during the first step, it could be repeated over 100 cycles upon alternating irradiation with UV and visible light. On the other hand, the bending in the second step exhibited a different behavior after several cycles. Furthermore, delayed bending behavior was observed, in which the bending motion was continued even after the UV light was turned off during the second step. These results suggest that the bending during the second step may be ascribed to a change in the crystal packing, such as a phase transition. In fact, the powder X-ray diffraction pattern before and after many cycles of alternating irradiation with UV and visible light was different from each other. In this case, the phase transition was irreversible.

In contrast, crystals of 1,2-bis(2-methyl-5-(4-octyloxyphenyl)-3-thienyl)perfluorocyclopentene (**37**) were found to undergo a reversible thermodynamic single-crystal-to-single-crystal phase transition accompanying a change in crystal length, which was clarified by differential scanning calorimetry measurement, X-ray crystallographic analysis, and direct microscopic observation of the crystal length [32]. When UV irradiation was conducted on the rodlike crystal, the crystal exhibited an unusual photomechanical behavior. The crystal slowly bent away from the incident light at first and quickly bent away from the light source subsequently. After continuous UV light irradiation, the crystal suddenly

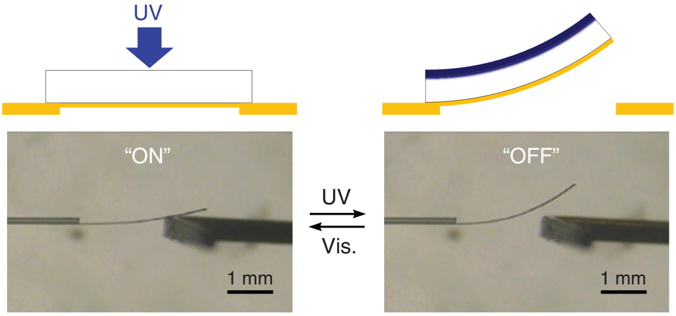


Figure 1.15 Photoreversible current switching using a gold-coated crystal of **10** upon alternating irradiation with UV and visible light. The crystal thickness is 6.2 mm. The gold thickness is 21 nm. Source: Kitagawa and Kobatake 2015 [27]. Reproduced with permission of The Royal Society of Chemistry.

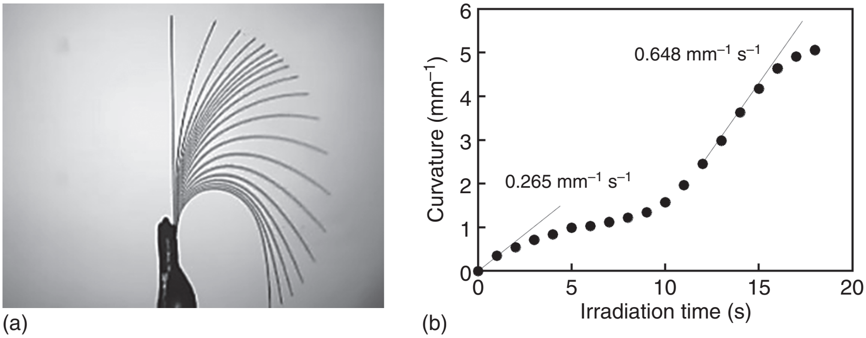
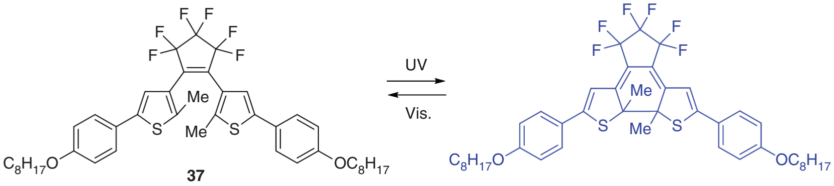


Figure 1.16 Stepwise photoinduced crystal bending of diarylethene **23** upon irradiation with UV light. (a) The photograph is a superimposition of 20 frames taken at intervals of one seconds. (b) Change in curvature relative to irradiation time with UV light. Source: Kitagawa et al. 2016 [31]. Reproduced with permission of The Royal Society of Chemistry.

returned to the initial straight shape as shown in Figure 1.17. From this detailed investigation, it was revealed that the mechanism of the unusual bending is based on the combination of the photochromic reaction and the phase transition. The photoirradiated crystal exhibited thermal bending behavior by changing temperature as shown in Figure 1.18. This is a new type of reversible mechanical material.

As a novel type of photomechanical behavior, ribbon-like crystals of 1-(2-methyl-5-(4-(1-naphthoyloxymethyl)phenyl)-3-thienyl)-2-(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**38**) were found to twist upon UV light irradiation, as shown in Figure 1.19 [33]. The twisted crystal retained its shape in the dark and returned to the initial straight shape upon irradiation with visible light. The photoreversible twisting could be repeated for more than 30 cycles by alternating irradiation with UV and visible light. Both types of twisting, which yield either left-handed or right-handed helices, occurred in almost equal amounts and the twisting direction depended on the face irradiated with UV light. When the $(0\bar{1}0)$ face was irradiated with UV light, the crystal twisted into



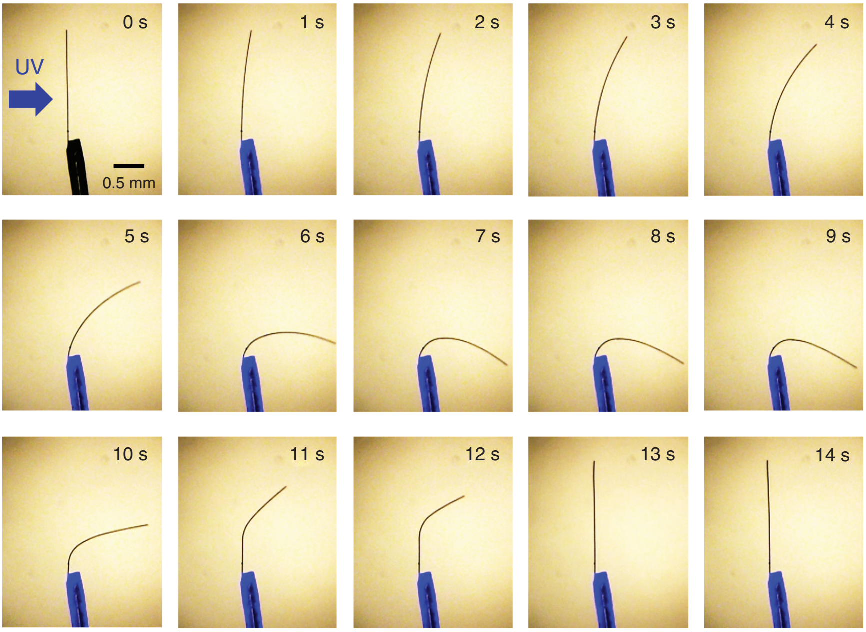


Figure 1.17 Photomechanical behavior of diarylethene **37**. UV irradiation was conducted from left side. Source: Kitagawa et al. 2017 [32]. Reproduced with permission of American Chemical Society.

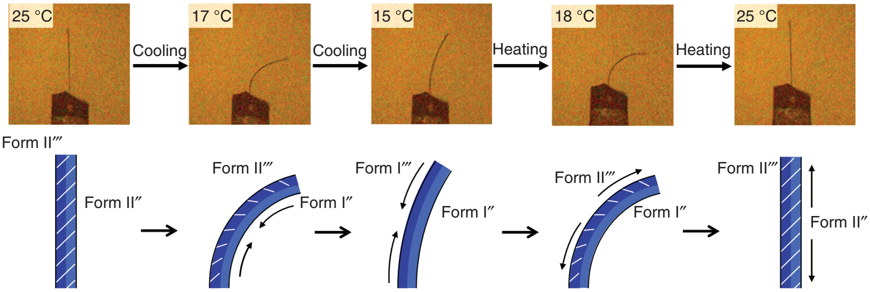


Figure 1.18 Bending behavior of the photoirradiated crystal **37** by changing temperature. The initial crystal was prepared by irradiation with UV light from left side. Source: Kitagawa et al. 2017 [32]. Reproduced with permission of American Chemical Society.

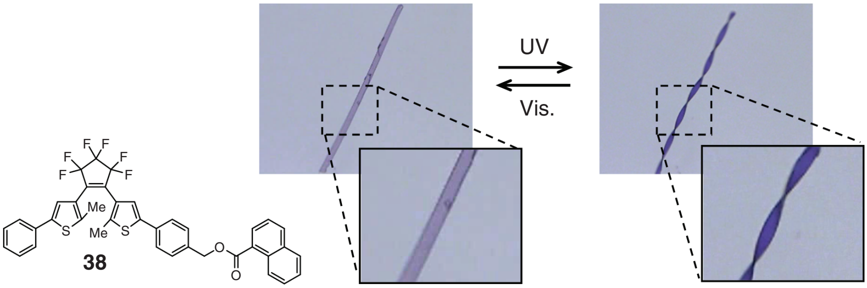


Figure 1.19 Photoinduced crystal twisting of diarylethene **38**. Source: Kitagawa et al. 2013 [33]. Reproduced with permission of John Wiley & Sons.

a right-handed helix. On the other hand, irradiation of the (010) face with UV light resulted in the crystal twisting into a left-handed helix. This is ascribed to the contraction of the crystal in the diagonal direction and a gradient in the photocyclization conversion that occurred below the crystal surface.

Moreover, it was found that the illumination direction affects the mode of the photomechanical twisting motion. The ribbon crystal of diarylethene **15** can be prepared by a sublimation method, while the recrystallization from organic solvents yields the block crystals. For the ribbon crystal, the effect of the illumination direction on the mode of photomechanical motion was investigated as shown in Figure 1.20 [34]. The definition of the illumination direction is depicted in the upper right side of the image. Upon UV light irradiation from the tip of the crystal (incident light angle = 0°), the crystal twisted into a helicoid shape. On the other hand, when UV irradiation was incident on the ribbon at larger angles, it gradually transformed into a cylindrical helix shape. Eventually, when the ribbon crystal was irradiated with an angle of 90°, the crystal exhibited bending rather than twisting. Thus, the incident light angle determines the mode of photomechanical motion. This might be due to the preferential excitation of differently oriented molecules within the crystal. In other words, the photoinduced strain tensor in the crystal, thus the mode of photomechanical deformation, can be controlled by exciting differently oriented molecules. This result suggests that the use of illumination angle to tune the mechanical response of photomechanical molecular crystals provides unique opportunities for the control of their motion.

1.7 Photosalient Effect

In addition to these photomechanical motions such as contraction, expansion, bending, and twisting, a photosalient behavior such as crystal jumping similar to the popping of corn has been also reported for some diarylethene crystals. First example of photosalient effect for diarylethene crystals has been reported for 1,2-bis(5-methyl-2-(2-pyridyl)-4-thiazolyl)perfluorocyclopentene (**14**) and 1,2-bis(2-ethyl-5-phenyl-3-thienyl)perfluorocyclopentene (**16**) [35]. Microcrystals of diarylethene **14** underwent jumping accompanied with photocyclization upon UV light irradiation. When the energy absorbed by the crystal reached

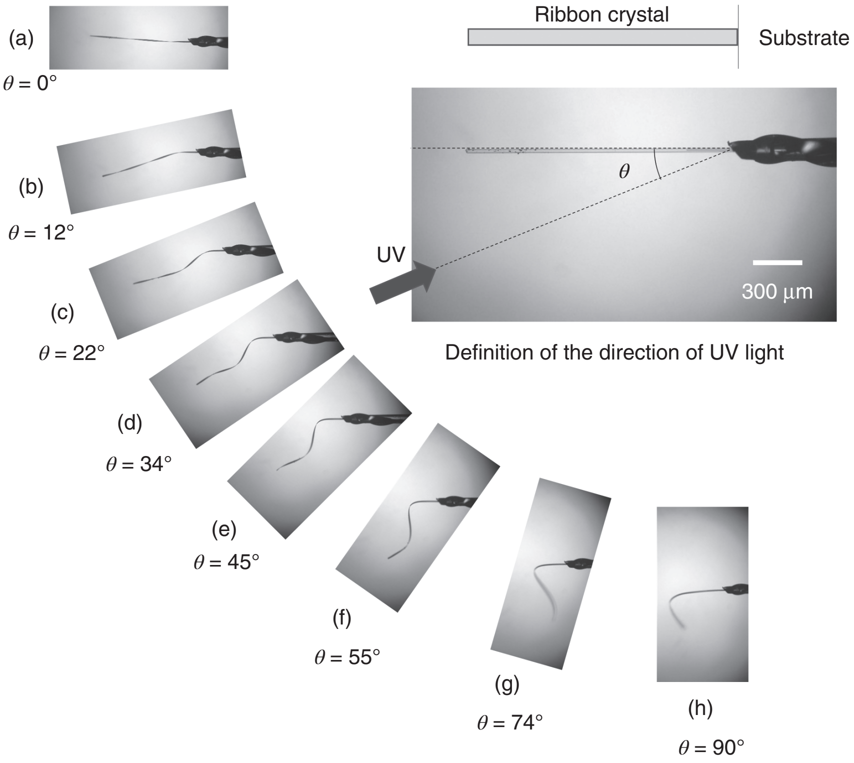


Figure 1.20 Different twisting motions, ranging from a helicoid to a cylindrical helix, of the ribbon crystal **15** depending on the angle of the incident light. Source: Kitagawa et al. 2018 [34]. Reproduced with permission of American Chemical Society.

about 10 μJ, the uniaxial stress induced in the crystal lattice relaxed through directional jumping. If the crystal was prevented from jumping, parallel and equidistant cracks appeared on crystal surfaces. These photomechanical effects could result from a Grinfeld surface instability [36].

Crystals of diarylethenes, 1-(2-methyl-5-(4-(phenylcarbarylmethyl)phenyl)-3-thienyl)-2-(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**39**) and 1-(2-methyl-5-(4-(benzylcarbarylmethyl)phenyl)-3-thienyl)-2-(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**40**), having urethane bonding unit in the molecular structure exhibited the photosalient effect by UV irradiation as shown in Figure 1.21 [37]. From X-ray crystallographic analysis, both crystals have intermolecular hydrogen bonding network at their urethane bonding units in the crystal, which suggests that the diarylethene molecules strongly interact with each other. The influence of crystal characters, such as size (area), thickness, and volume, on the initial speed of a fragment was not observed. The average speed and the kinetic energy for a crystal fragment were estimated to be $4.7\,\mathrm{m\,s^{-1}}$ and 3.2×10^{-12} J for **39** and $1.9\,\mathrm{m\,s^{-1}}$ and 0.50×10^{-12} J for **40**, respectively. The difference in the speed and energy might be due to the difference in the power of intermolecular interaction.

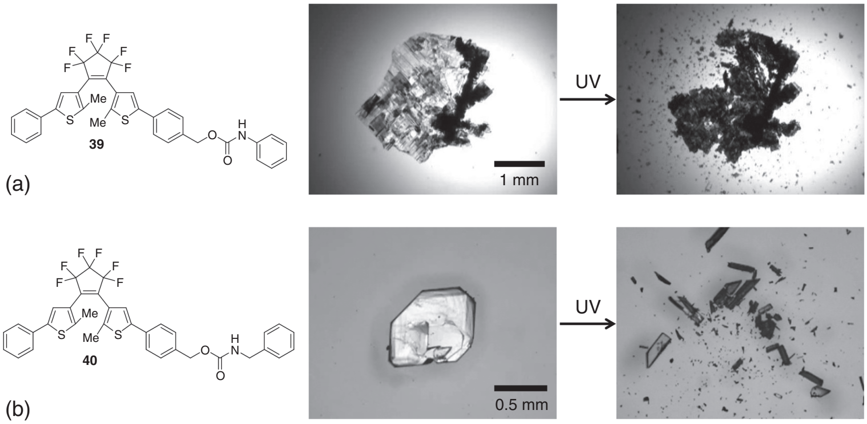


Figure 1.21 Optical photographs of diarylethene crystals (a) **39** and (b) **40** before and after UV irradiation. Source: Kitagawa et al. 2016 [37]. Reproduced with permission of American Chemical Society.

As another example, the photosalient effect of 1,2-bis(5-methyl-2-phenyl-4-thiazolyl)perfluorocyclohexene (**41**) was reported [38]. Crystals of **41**, prepared by a sublimation method under normal pressure, were found to have a hollow structure. Upon UV irradiation, the hollow crystal exhibited the photosalient effect, which burst the crystal into small pieces. The speed at which the broken crystal pieces travelled after the explosion was measured as 2.67 m s^{-1}. To mimic the behavior of "*Impatiens*," small fluorescent beads were inserted into the hollow crystal and exposed to UV light, which resulted in the scattering of the beads by deformation and bursting of the hollow structure as shown in Figure 1.22. This is the first example of the utilization of the photosalient phenomena.

1.8 Summary

In this chapter, recent developments in the light-driven actuators based on photochromic diarylethene crystals have been described. Molecular-scale structural changes of diarylethenes can induce macroscopic mechanical movement of the bulk crystals. The thin micro-sized diarylethene crystals exhibit contraction or expansion upon photoirradiation as a result of structural isomerization of the open-ring isomer to yield the closed-ring isomer. The rodlike crystals can bend away from the incident light or toward the incident light. This behavior occurs because of a gradient in the degree of photochemical conversion within the crystal caused by the high absorbance capacity of its surface. There are various types of photomechanical motions, such as contraction, expansion, bending, twisting, and jumping. These photomechanical behaviors are based on geometrical structure changes in the crystalline phase and can be applied to macro-sized light-driven actuators. In order to apply photoresponsive organic crystals as photomechanical materials to soft robots, microcrystals can be used as part of mechanical elements. Furthermore, combining existing materials with

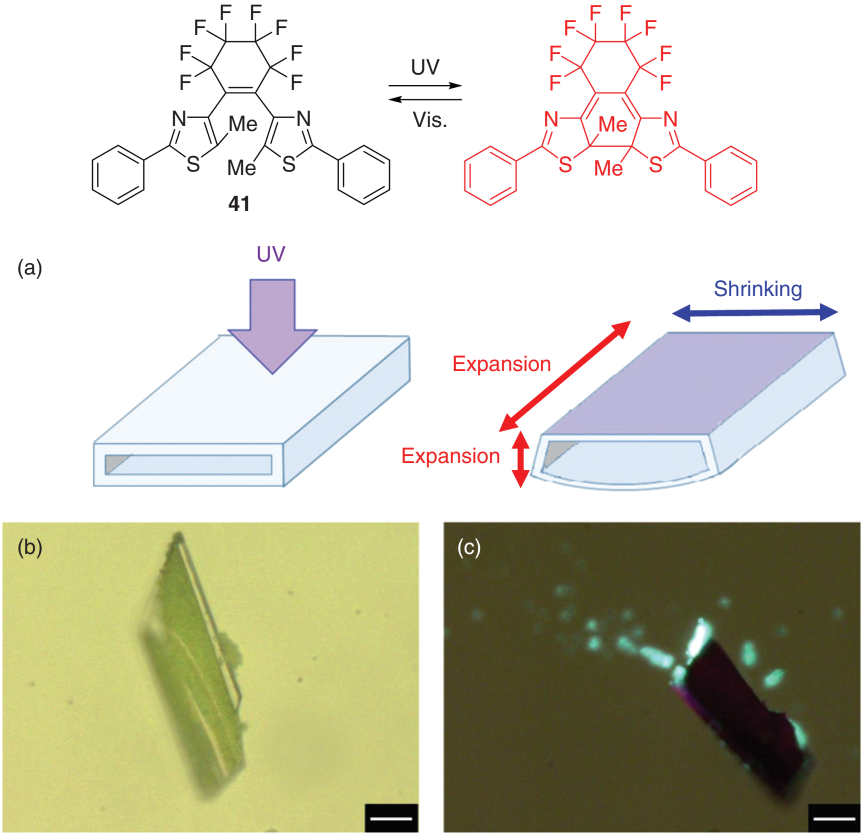


Figure 1.22 UV light-induced photosalient effect of a hollow crystal, mimicking *impatiens*: (a) deformation of the hollow crystal upon UV irradiation, (b) a hollow crystal packed with fluorescent polystyrene beads with 1 mm diameter, (c) UV-induced scattering of fluorescent beads. Scale bars = 20 μm. Source: Hatano et al. 2017 [38b]. Reproduced with permission of John Wiley & Sons.

photomechanical materials will create new functionality. It is expected to be applied to real soft robot parts by developing such materials in the future.

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