

Photoinduced Twisting of a Photochromic Diarylethene Crystal**

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Photoresponsive materials have been a topic of much attention in both industrial and academic research fields because photoirradiation offers a non-contact, non-destructive means of inducing a response.^[1–3] In particular, recent reports have described the development of photomechanical devices with photoresponsive organic crystals, such as diarylethene, anthracene, azobenzene, and furylfulgide.^[4–13]

Diarylethenes undergo thermally irreversible and fatigue-resistant photochromic reactions, even in the single-crystal phase.^[14] The shape of diarylethene crystals can be modulated solely by photoirradiation. A photoreversible step-and-valley formation can occur on diarylethene single-crystal surfaces upon alternating irradiation with ultraviolet (UV) and visible light, because of a slight change in molecular volume that occurs between the open- and closed-ring isomers during the photochromic reaction.^[15] This change in molecular volume plays an important role in other processes, such as bulk crystal deformation. Single microcrystals of diarylethenes have been found to exhibit rapid and reversible macroscopic changes in shape and size upon irradiation with UV and visible light.^[4–8]

Recently, 9-anthracenecarboxylic acid (9AC) crystals have been shown to twist upon UV light irradiation.^[11] 9AC can undergo a reversible [4+4] photocyclodimerization in the crystalline phase. Bardeen and co-workers have suggested that the crystal twisting is induced by generating interfacial strain within the microcrystal between unreacted monomer and photoreacted dimer regions. The crystal relaxes back to the original shape over the course of minutes, as thermal dissociation of the dimers returns them to their monomeric forms.

Herein, we report the photoinduced crystal twisting of a novel photochromic diarylethene crystal. The colorless needle-like crystals of diarylethene rapidly twisted, accompanied by a color change to blue upon irradiation with UV light. The twisted crystal relaxed back to its original shape in a few seconds under visible light irradiation. The photoreversible twisting of the crystal could be repeated over 30 cycles. The photoinduced crystal twisting was caused by contraction of the crystal in a diagonal direction, as can be

seen from a relationship between the face irradiated with UV light and the direction of the crystal twisting. Such photo-induced crystal twisting provides a new type of photomechanical actuator.

Figure 1 illustrates the structural transformation and the photoreversible single crystal twisting of 1-(2-methyl-5-(4-(1-naphthoxyloxymethyl)phenyl)-3-thienyl)-2-(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**1a**) upon alternat-

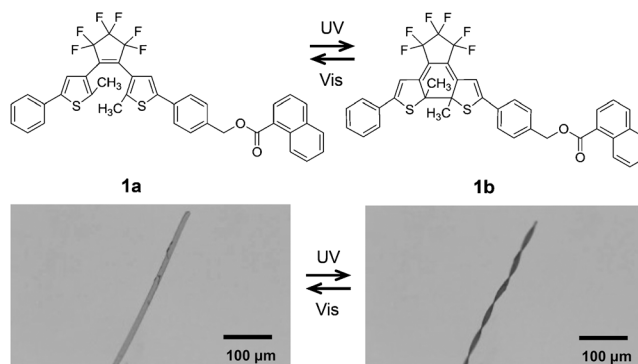


Figure 1. Chemical structures and photoreversible crystal twisting of diarylethene **1a** upon irradiation with UV ($\lambda = 365$ nm) and visible light ($\lambda > 500$ nm). A movie of the photoreversible twisting in real time is available in the Supporting Information (Video S1).

ing irradiation with UV ($\lambda = 365$ nm) and visible light ($\lambda > 500$ nm). The single crystal was prepared by recrystallization from an *n*-hexane/ether solution. The thickness, width, and length of the crystal are ca. 1.5 μm , 11 μm , and 320 μm , respectively. Upon UV light irradiation over the whole crystal, the molecules in the crystal underwent a photocyclization reaction from the open-ring isomer to the closed-ring isomer, and the crystal of **1a** rapidly twisted, accompanied by a color change of the crystal from colorless to blue. The twisting and color of the crystal was maintained in the dark. By irradiation with visible light, the blue color disappeared through a back reaction to regenerate the open-ring isomer and the twisted crystal relaxed back to its original shape in a few seconds. Such reversible twisting upon alternating irradiation with UV and visible light could be repeated over 30 cycles (Figure S1). These results revealed that the crystal twisting is induced by the photochromic reactions of diarylethene molecules in the crystal.

There are two directions of twisting, left-handed helix and right-handed helix. The helix that twists counterclockwise to the direction of the movement is referred to as a left-handed helix. The reverse is called a right-handed helix (Figure S2). To determine whether both helix types exist in this case, the crystals on the petri dish were irradiated with UV light, and the number of resulting left- and right-handed helical crystals

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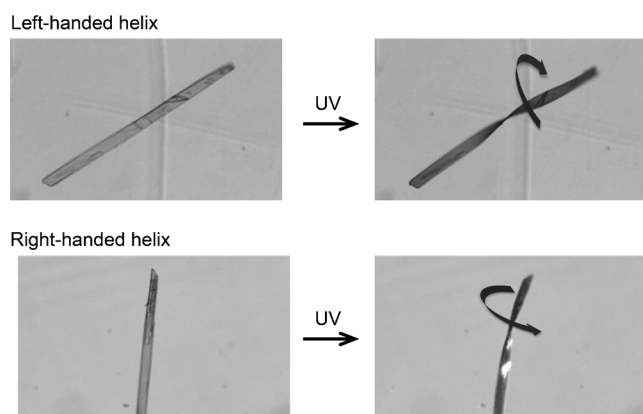


Figure 2. Photoinduced crystal twisting into left-handed and right-handed helices.

was determined. Both helix types were found, and in roughly equal amounts (Figure 2 and S3). It was noticed that the direction of twisting depends upon the face irradiated with UV light. However, half of all the crystals were not twisted. It is due to the fact that the twisting, or lack thereof, depends upon the crystal thickness.

Single-crystal X-ray crystallography of a crystal of **1a** showed a monoclinic crystal system and a space group of $P2_1$ (Table S1).^[16] The crystal is chiral, but the origin is due to a disorder of perfluorocyclopentene. Therefore, if the disorder is absent, the space group should be $P2_1/c$. Figure 3 shows the shape and the molecular packing of crystal **1a** before UV

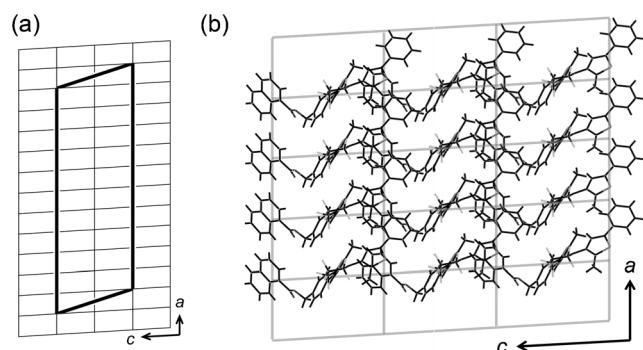


Figure 3. Molecular packing of crystal **1a**. The crystal shape (a) and molecular packing (b) of **1a** in the crystal viewed from the (0 -1 0) face are depicted. The crystal shape in (a) is shown by a bold line.

irradiation, as viewed from the (0 -1 0) face. The packing diagrams viewed from other surfaces are shown in Figure S4. The diarylethene molecules are regularly oriented to the direction of the *a* axis with a tilt angle of ca. 50°, and aligned perpendicularly to the (0 -1 0) face. All of the diarylethene molecules are fixed in a photoreactive antiparallel conformation, and the distance between the reactive carbon atoms in the thiophene rings is 3.50 Å. It is short enough for the diarylethene to undergo photocyclization in the crystalline phase.^[17]

The difference of the crystal surface on (0 1 0) and (0 -1 0) is distinguished by the shape of the crystal surface and the absorption anisotropy of the closed-ring isomer (Figure S5). When the (0 -1 0) face was irradiated with UV light, the crystal twisted into a right-handed helix. In contrast, the crystal twisted into a left-handed helix when the (0 1 0) face was irradiated with UV light, as shown in Figure S6 and Videos S1 and S2. When UV light irradiation was performed from both sides on (0 -1 0) and (0 1 0) faces on the whole crystal, it contracted (Figure 4). This result indicates that the

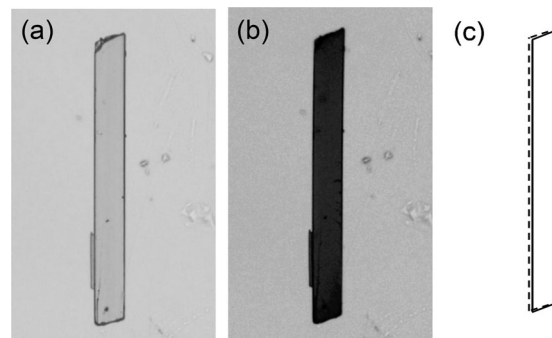


Figure 4. Shape of the contracted crystal. The colorless crystal (a) was irradiated with UV light to form the colored crystal (b). The colored crystal was produced with UV light irradiation from both sides on the crystal surfaces for a few minutes. The photoisomerization took place homogeneously in the crystal. c) The crystal shapes before (----) and after (—) UV light irradiation. The right edges of the colorless and colored crystals are superimposed.

crystal twisting was caused by the heterogeneity of the photochromic reaction in the thickness direction of the crystal because of the high absorbance of the crystal. Some diarylethene crystals thus far have been reported to cause the photoinduced reversible bending.^[4–8] In the present case, the contraction is considered to occur in the diagonal direction. When irradiated with UV light, the photoisomerization of the diarylethene molecules from the open-ring isomer **1a** to the closed-ring isomer **1b** occurs in the crystalline phase. The twisted thiophene rings become coplanar, and the thickness of each molecule is reduced. The closed-ring isomers in the photoirradiated crystal can stack with each other, resulting in changes in the cell dimensions. This change in cell dimensions causes the contraction or twisting of the crystal.

The change in cell dimensions upon UV light irradiation is generally confirmed by X-ray crystallographic analysis. We here determined the changes in the cell dimensions from the shape change of the contracted crystal after UV light irradiation (Figure 4). The crystal was irradiated with UV light from all of directions because of homogeneous photoisomerization. The coordinates on the four corners of the crystal before and after UV light irradiation was plotted in a rectangular coordinate system. When transforming from a rectangular coordinate system to an oblique coordinate system, the cell dimensions changed so that the coordinates might become the same in two different oblique coordinate systems. The cell parameters correspond to a change from $a = 6.10$ Å, $c = 11.36$ Å, and $\beta = 93.4^\circ$ to $a' = 5.98$ Å, $c' = 10.08$ Å,

and $\beta' = 96.5^\circ$, respectively. The a and c axes contracted as much as 2.0% and 11%, respectively, and the β angle enlarged as much as 3.3%. The shape of the unit cell viewed from the (0 $\bar{1}$ 0) face before and after UV light irradiation is shown in Figure S7. The contraction of the unit cell takes place in the direction of top-left to bottom-right when the unit cell was viewed from the (0 $\bar{1}$ 0) face. On the other hand, the contraction of the unit cell takes place in the direction of top-right to bottom-left when the unit cell was viewed from the (010) face. The photochromic reaction proceeds in a gradient to the thickness direction because of high absorption in the crystal. Therefore, the crystal can twist into a right-handed or left-handed helix depending on the contraction direction, as shown in Figure 5. There is an induction period of ca. 2 s until the crystal begins to twist (Figure S8). The strain required to

handed helix. The direction of the twisting depends upon the face irradiated with UV light. Furthermore, the direction of contraction in the unit cell was determined using the contracted crystal, which underwent a photocyclization reaction over the whole crystal by irradiation from both sides of the crystal surfaces. From these results, the twisting of the crystal requires both a gradient of photocyclization conversion in the thickness direction and the contraction of the crystal in the diagonal direction.

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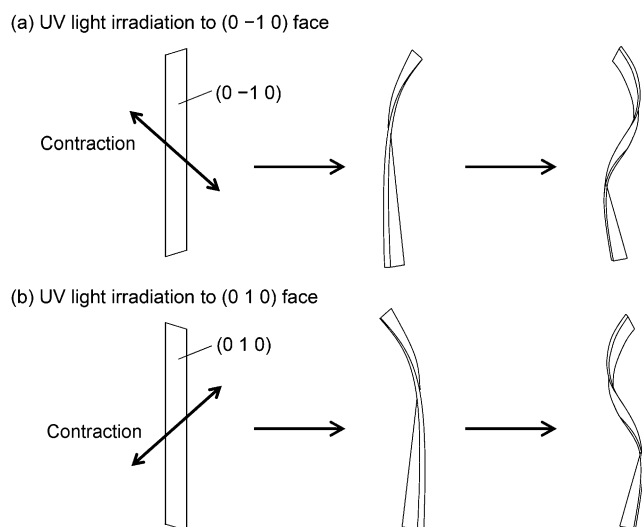


Figure 5. Relationship between the direction of twisting and the face irradiated with UV light. The crystal twists into a right-handed helix (a) or a left-handed helix (b). The arrows show the direction of contraction of the crystal surface.

perform the twist arises in this period. The photoirradiation time to the reversed side during the twisting is shorter than the period. The direction of twisting can be determined by the starting irradiation face.

In summary, we have shown photoinduced crystal twisting of novel diarylethene crystals. The photoreversible twisting of the diarylethene crystal could be repeated over 30 cycles by alternating irradiation with UV and visible light. The crystal twisting takes place in both a left-handed helix and a right-

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