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Photochromic Actuators

Light-Driven Molecular-Crystal Actuators: Rapid and Reversible Bending of Rodlike Mixed Crystals of Diarylethene Derivatives**

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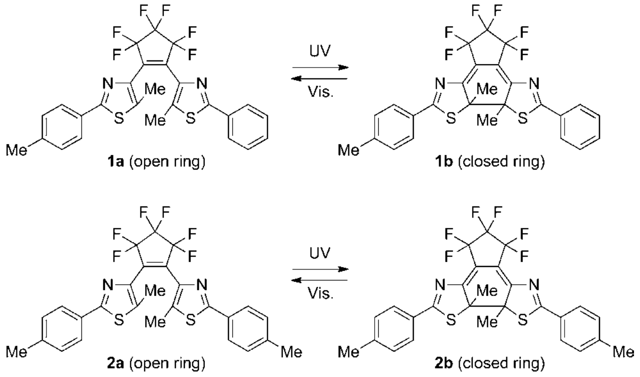
Piezoelectric crystals are useful in industrial and consumer applications because of their special characteristics: they can be bent by electricity. But the crystals require a wire connection so that the electricity can be supplied. This wire connection prevents their use in water and reduction of their size to the micrometer scale. Herein, we report on wireless molecular-crystal actuators, which work upon photoirradiation. Rodlike mixed crystals of 1-(5-methyl-2-phenyl-4-thiazolyl)-2-(5-methyl-2-*p*-tolyl-4-thiazolyl)perfluorocyclopentene (**1a**) and 1,2-(5-methyl-2-*p*-tolyl-4-thiazolyl)perfluorocyclopentene (**2a**; Scheme 1) with sizes ranging from micrometers to millimeters were found to exhibit rapid, reversible, and fatigue-resistant bending upon alternate irradiation with UV (365 nm) and visible (> 500 nm) light.



Scheme 1. Photochromism of diarylethenes **1** and **2**.

Various types of artificial molecular muscles have been reported, such as rotaxanes,[1–7] catenanes,[8–12] polymer films and gels,[13–16] conductive polymers,[17] liquid-crystal elastomers,[18–21] molecular crystals,[22–26] and nanotubes.[27] Although the supramolecular systems (e.g., bistable rotaxanes and catenanes) exhibit musclelike sliding motion at the molecular level, the movement fails to be effectively linked to macroscopic motion of materials. Polymer artificial muscles primarily depend upon the response of bulk materials rather than upon individual molecular behavior. It is a challenge to construct molecular materials that perform macroscopic mechanical motion that stems from stimuli-responsive geometrical structure changes of individual molecules.

In previous reports,[22] we demonstrated that photochemical geometrical structure changes of individual diarylethene molecules in crystals induced changes in molecular packing and alignment, resulting in the anisotropic deformation of the bulk crystals. For example, a rodlike crystal of 1,2-bis(5-methyl-2-phenyl-4-thiazolyl)perfluorocyclopentene exhibits reversible bending upon alternate irradiation with UV and visible light.[22a] For practical applications, the crystal actuators should have sufficient durability and substantial mechanical properties. The above single-component diarylethene crystal lacks this durability and breaks in less than 100 deformation cycles. To improve fatigue resistance, we prepared a platelike two-component cocrystal composed of 1,2-bis(2-methyl-5-(1-naphthyl)-3-thienyl)perfluorocyclopentene and perfluoronaphthalene.[22d] The cocrystal exhibits reversible bending for up to 250 cycles. During the course of the study on such multicomponent crystals it was found that the durability is further improved by mixing two diarylethene derivatives, **1a** and **2a**, in a crystal. The bending can be repeated more than 1000 times without any crystal damage, and the crystals exhibit light-driven bending in all directions toward the UV light source in wide temperature range from 4.6 K to 370 K. Moreover, the photogenerated maximum stress of the crystals was found to be comparable to that of piezoelectric crystals.

Microcrystals were prepared by recrystallization from ethanol. Platelike crystals are mainly formed from the ethanol solution containing only **1a**. When **2a** is added to the solution in amounts exceeding 30 mol %, formation of rodlike crystals becomes dominant. In the ethanol solution containing equimolar amounts of **1a** and **2a**, rodlike crystals composed of both **1a** (63 mol %) and **2a** (37 mol %) grew. The rodlike two-component mixed crystals bend toward UV (365 nm) light sources and become straight upon irradiation with visible (> 500 nm) light, while the shape of the single-component crystals of **1a** remains unchanged. The surface skin layers were peeled off the crystals (see Figure S1 in the Supporting Information). When the content of **2a** in the mixed crystals was increased over 60 mol %, the photostimulated bending was suppressed, and the bending was not observed for the rodlike crystal of **2a**. Figure 1 shows the bending cycles of the rodlike mixed crystal (1.3 mm × 25 μm × 13 μm) containing both **1a** and **2a** (**1a**:**2a** = 63/37) upon

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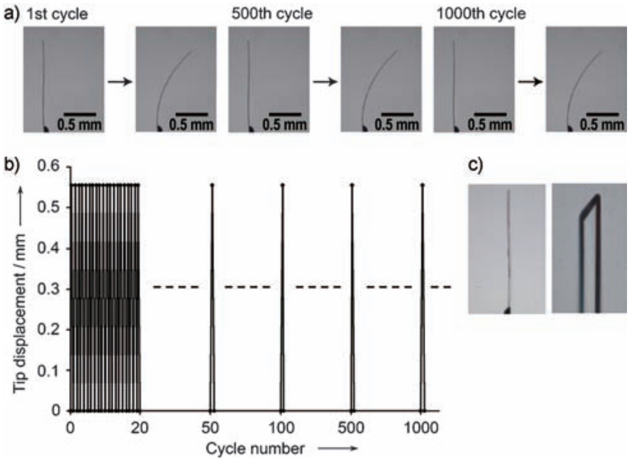

Figure 1. Reversible bending of a rodlike two-component mixed crystal of **1a** and **2a** (**1a**:**2a** = 63/37) upon alternate irradiation with UV (365 nm) and visible (>500 nm) light. a) Pairs of photographs of the crystal (1.3 mm×25 μm×13 μm) showing the 1st, 500th, and 1000th cycles. b) Tip displacement of the crystal during reversible bending. c) An approximately 10× (left) and 80× (right) expanded photograph of the crystal after the 1000th cycle. The surface of the crystal remained clear even after 1000 bending cycles, and no damage was observed.

alternate irradiation with UV and visible light. The edge of the rod reversibly moved as much as 0.56 mm upon photoirradiation, and the bending could be repeated more than 1000 times. The surface of the crystal remained clear even after 1000 cycles, and no damage was discerned, as shown in Figure 1 c, right.

The melting point of the mixed crystals depends on the ratio of the two components. It showed the minimum of 131 °C at the molar ratio of 1:1 and increased when the content of one of the components increased (see Figure S2 in the Supporting Information). X-ray crystallographic analysis of the mixed crystals indicates that the crystal system and space group are the same as for the single-component crystal of **1a**, even when the content of **2a** is as large as 60 mol % (see Table S1 in the Supporting Information). The low melting point of the crystal containing equal molar amounts of the two component molecules suggests that intermolecular interaction among the component molecules is weakened in the mixed crystals. The weakened intermolecular interaction is considered to favor the macroscopic mechanical motion and improve the durability of the crystals.

The rodlike crystal has a rectangular (or distorted hexagonal) cross-section, as shown in Figure 2 a. The rod was irradiated from the right, lower, and left sides with UV and visible light, and bending behavior was monitored. The rodlike crystal bends toward the UV (365 nm) light source irrespective of the irradiation direction, as shown in Figure 2 b and Movie S1 in the Supporting Information. The bent rodlike crystal returns to a straight position upon irradiation with visible (>500 nm) light. When the light intensity of UV and visible light is controlled, the edge of the rodlike crystal exhibits rotation movement, as shown in Figure 2 c and Movie S2 in the Supporting Information. The bending is ascribed to a gradient in the extent of photoreaction caused by high absorbance of the crystal.

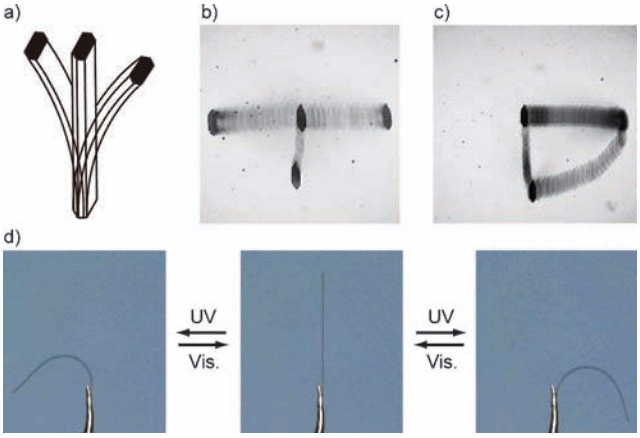

Figure 2. Bending of the rodlike two-component mixed crystal containing **1a** and **2a** (**1a**:**2a** = 63/37) in all directions. a) Schematic illustration of the bending rodlike crystal. b) The crystal (1.3 mm×40 μm×15 μm) was irradiated from the right, lower, and left sides with UV (365 nm) and visible (>500 nm) light, and movement of the rodlike crystal edge was monitored. The edge moved toward the UV light source and then returned to the original position upon irradiation with visible light. c) First, the crystal was irradiated from the lower side with UV light, and then from the right side with controlled-intensity UV and visible light. The edge of the crystal exhibited rotation. d) Reversible curling to a hairpin shape upon irradiation with UV light (crystal length: 3.0 mm). The crystal kept the crystalline state even after the curling and returned to the original straight shape upon irradiation with visible light. See also Movies S1, S2, and S3 in the Supporting Information.

Contraction of the irradiated part of the crystal results in bending toward the light source, as in bimetals. The bending irrespective of the irradiation direction indicates that contraction of the surface region takes place along the long axis of the rod. To confirm the bending mechanism, in situ X-ray crystallographic analysis was carried out. X-ray crystallographic data before and after UV (365 nm) light irradiation, and after subsequent visible (>500 nm) light irradiation, are shown in Table S2 in the Supporting Information. Upon irradiation with UV light for 10 s, 6.1 % of component diarylethene molecules convert from the open- to the closed-ring isomers, and the cell length of *b* axis shows a small but significant decrease (0.12 %). The lengths of the *a* and *c* axes increase by 0.23 and 0.09 %, respectively. Upon visible-light irradiation, the cell parameters return to the initial values. The *b* axis corresponds to the long axis of the rodlike crystal (see Figure S3 in the Supporting Information). The decrease of the length of the *b* axis explains the contraction of the irradiated surface region and accounts for the bending toward the UV light source. Shrinkage by 0.12 % is the average change of the bulk crystal lattice when the average conversion reaches 6.1 %. The photoreaction upon UV (365 nm) light irradiation is limited to the surface layer of the crystal because of high absorbance of the crystal in the UV region. Most of the bulk crystal remains unchanged. On the other hand, X-ray crystallographic analysis measures the bulk crystal. Therefore, the conversion in the surface region is considered to be over a few tens of percent, and the *b* axis shrinks over 0.5 %. Shrinkage of 0.5 % is enough to induce the large bending.[28] The decrease of the length of the *b* axis is ascribed to the changes of molecular packing and alignment, as reported.[22]

The rodlike crystal that was 3.0 mm long showed curling into a hairpin shape upon irradiation with UV light, and the shape remained stable after switching off the light (Figure 2d and Movie S3 in the Supporting Information). The crystal remained crystalline even after the curling and returned again to its straight shape upon irradiation with visible light. The curling and recovery to the straight shape could be repeated many times while crystallinity was maintained. The two-component crystal is flexible.

A noticeable feature of the molecular-crystal actuators is the performance at low temperature. The crystal was cooled to 4.6 K in a cryostat and irradiated with UV (365 nm) and visible (> 500 nm) light. The rodlike crystal exhibits light-driven bending even at 4.6 K (Figure 3a). The bending behavior was monitored using a high-speed camera (Vision Research, PhantomV710; Figure S4 in the Supporting Information). The crystal already showed bending in the first frame after irradiation with pulsed laser light (355 nm, 8 ns pulse width). The exposure time of each frame is five microseconds. Therefore, the light-driven bending takes place in less than five microseconds at 4.6 K. Polymer artificial muscles, such as polymer gels, conductive polymers, and liquid-crystal elastomers, are rather slow-acting (typically in seconds to minutes), and the working temperature must be above the glass-transition temperatures.[18] The present molecular-crystal actuators are superior to the existing polymer muscles in their response time (< 5 μs) and their wide range of working temperature (4.6 K < *T* < 370 K). Another characteristic feature of the molecular-crystal actuator is light-driven bending motion in water. Figure 3b shows the photostimulated reversible bending of the rodlike crystal in water. The bending behavior is similar to that observed in air.

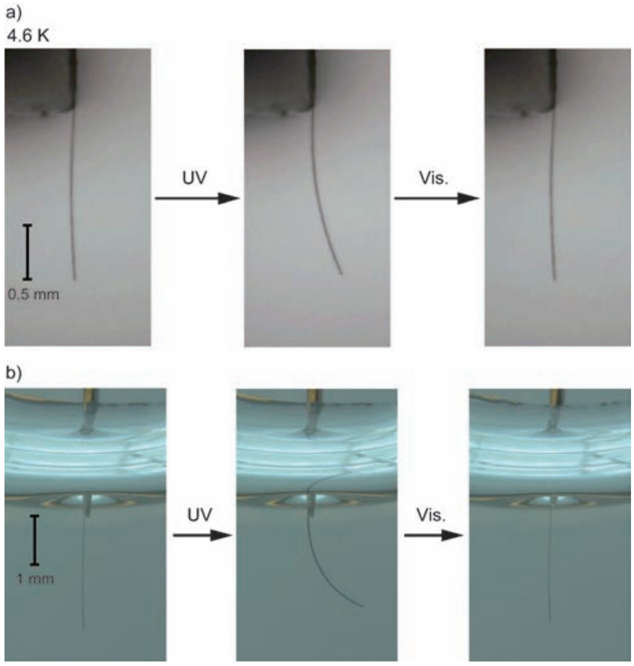

Figure 3. Bending of the rodlike two-component mixed crystal containing **1a** and **2a** (**1a**:**2a** = 63/37) at 4.6 K and in water. a) Reversible bending of the crystal (1.5 mm × 20 μm × 10 μm) upon irradiation with UV (365 nm) and visible (> 440 nm) light at 4.6 K. The crystal was fixed to a copper sample holder in a cryostat. b) Reversible bending of the rodlike crystal (2.3 mm × 30 μm × 15 μm) in water upon irradiation with UV and visible light.

The rodlike crystal can bring about gearwheel rotation (Figure 4 and Movie S4 in the Supporting Information). Upon UV light irradiation, the crystal bends and hits the gear, resulting in rotation of the gear. The crystal returns to the straight shape upon controlled irradiation with UV and visible light. Then, irradiation with UV light bends the crystal and again induces the rotation of the gearwheel. The cycles can be repeated many times. This is actual photomechanical work of the rodlike crystal.

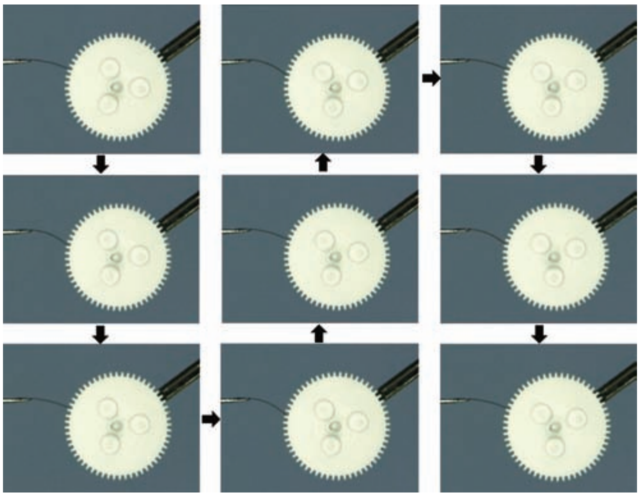

Figure 4. Gearwheel rotation operated by a light-driven molecular-crystal actuator. The two-component mixed crystal containing **1a** and **2a** (**1a**:**2a** = 63/37) (1.3 mm × 60 μm × 12 μm) was fixed on the tip of a metal needle. The gear (diameter: 3.2 mm) was rotated by the crystal, which showed reversible bending upon alternate irradiation with UV (365 nm) and visible (> 500 nm) light. See also Movie S4 in the Supporting Information.

We also tried to use the rodlike crystal to lift a metal load (see Movie S5 and Figure S5 in the Supporting Information). The rodlike crystal (2.5 μg) was fixed at the edge of a glass plate as a cantilever arm, and a metal weight (2.2710 mg) was loaded onto the rod. The weight is 908 times heavier than the crystal. Upon irradiation with UV (365 nm) light, the weight was lifted as high as 0.10 mm. The tiny rodlike crystal, which weighs only 2.5 μg, performs lifting work as large as 2.2 nJ.

This mechanical work is ascribed to a large Young's modulus of the crystal materials. The modulus of the crystal was measured by means of a manual beam-bending test to be as large as 8.5 GPa (see Figure S6 in the Supporting Information). This value is much larger than those of typical polymer materials (ca. 1 GPa)[29] and similar to other organic crystals.[30] The large Young's modulus enables the crystal to generate strong force and carry out large mechanical work. It is possible to estimate the maximum stress generated by UV irradiation from the photostimulated bending of the crystal cantilever beam (see Figure S7 in the Supporting Information). The maximum stress was estimated to be 56 MPa, which is 180 times larger than that of muscles (ca. 0.3 MPa) and comparable to that of piezoelectric crystals, such as lead zirconate titanate (PZT, ca. 50 MPa). The robust light-driven molecular-crystal actuators having substantial mechanical properties comparable to piezoelectric crystals and can be potentially used in various micro- and nanomechanical applications.[31]

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[31] CCDC 770597, 770598, 770599, 770600, 770601, 770602, 770603 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.