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A Diarylethene Cocrystal that Converts Light into Mechanical Work

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Abstract: The photomechancial effect of a rectangular plate two-component cocrystal composed of a photochromic diarylethene derivative, 1,2-bis(2-methyl-5-(1-naphthyl)-3-thienyl)perfluorocyclopentene (**1o**), and perfluoronaphthalene (**FN**) has been examined. The crystal of **1o·FN** with the size of 1−5 mm in length exhibits reversible bending motion upon alternate irradiation with ultraviolet (UV) and visible light. The reversible bending could be repeated over 250 times. *In situ* X-ray crystallographic analysis revealed that the deformation of the crystal is due to the elongation of the *b*-axis of the unit cell, which corresponds to the long axis of the plate crystal, induced by the shape change of component diarylethene molecules upon photocyclization. The bending motion was observed even at 4.7 K, and dynamic measurement of the bending proved that the anisotropic expansion of the crystal takes place in the microsecond time scale at the low temperature. Molecular crystal cantilevers made of **1o·FN** can lift metal balls, the weight of which is 200−600 times heavier than the weight of the crystal, upon UV irradiation. The maximum stress generated by UV irradiation was estimated to be 44 MPa, which is 100 times larger than that of muscles (∼0.3 MPa) and comparable to that of piezoelectric crystals, such as lead zirconate titanate (PZT) (∼50 MPa).

Introduction

It is a long-standing ambition for chemists to construct molecular systems which exhibit mechanical movement based on geometrical structural changes of individual molecules induced by external stimuli and have the systems perform mechanical work.[1] In biological systems, molecular-scale movements of actin−myosin proteins are artfully linked to macroscale motion of muscles.[2] Although elaborate design and synthesis of various types of molecular machines,[3] such as molecular shuttles,[4] molecular muscles,[5,6] molecular elevators,[7] and molecular rotors (e.g., molecular compasses and gyroscopes)[8−12] has been extensively studied and their machine-like motions are well characterized using NMR, X-ray diffraction, and other instruments, an attempt to link the molecular-scale motions of these man-made devices to macroscale movement of materials is limited. Stoddart et al.[6] prepared microcantilever beams coated on one side with a monolayer of bistable rotaxane molecules

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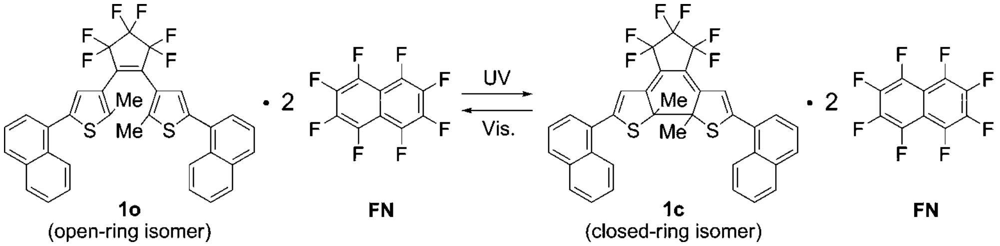
Scheme 1. Photochromic Reaction of **1o·FN** Cocrystal[a]



[a] The diarylethene molecule undergoes a reversible cyclization reaction from the open-ring isomer (**1o**) to the closed-ring isomer (**1c**).

and successfully demonstrated that the beams reversibly bend by the addition of chemical oxidants and reductants. The effect was, however, too small to be practically used, and the bending behavior is repeated only for a few tens of cycles. Any certain methodology how to rationally assemble the molecular machines to perform macroscale mechanical work has not yet been developed.[13] On the other hand, various types of polymers, hydrogels, and carbon nanotubes have been reported to transfer molecular phenomena into macroscale movement of the materials.[14−18] The movement, however, relies not on individual molecular behavior but on the response of bulk materials. The photoinduced contraction of liquid-crystal elastomers, for example, is attributed to the order−disorder phase transition of the liquid-crystal materials.[14−16]

In a previous paper,[19] we reported that the surface morphology of a photochromic diarylethene single crystal reversibly changes upon alternate irradiation with UV and visible light. This result implies that the macroscale crystal shape follows the shape changes of component diarylethene molecules. In other words, the changes of molecular shape can be linked to the macroscale shape of materials in densely packed crystals. Based on this view, we prepared small-size single crystals (10−100 μm) of photochromic diarylethenes and demonstrated that the bulk crystal shape changes upon photoirradiation.[20] Now it is generally accepted that small size photoreactive molecular crystals change their shape and size upon photoirradiation.[21−28] Although densely packed crystals are proved to be useful to link the molecular-scale events to macroscale movement of materials, the crystals so far examined are too small and fragile to be used in real world applications.

Here we report on photoinduced mechanical movement of a two-component cocrystal composed of 1,2-bis(2-methyl-5-(1-naphthyl)-3-thienyl)perfluorocyclopentene (**1o**) and perfluoronaphthalene (**FN**) (Scheme 1).[29] The molecular crystals with the size of 1−5 mm in length reversibly bend upon alternate irradiation with UV and visible light. The millimeter-size crystals exhibit outstanding performance as light-driven actuators in the real macroscopic world and enable us to study the deformation mechanism in detail by the use of *in situ* X-ray crystallographic analysis.

Results and Discussion

1 undergoes reversible isomerization between open- and closed-ring isomers, **1o** and **1c**, by alternate irradiation with UV (365 nm) and visible ($\lambda > 440$ nm) light in solution as well as in the cocrystal of **1o·FN** (Scheme 1).[29,30] The cocrystal was prepared by slow evaporation of a hexane solution of a mixture of **1o** and **FN** (1:2 molar ratio). The shape of the crystal is a thin plate with rectangular faces, as shown in Figure 1a (typically 1−5 mm in length, 0.2−1.5 mm in width, and 10−50 μm in thickness). Figure 1a also shows the molecular packing of the cocrystal determined by X-ray crystallographic analysis. The crystal is composed of **1o** and **FN** in the ratio of 1:2, and the aryl−perfluoroaryl interaction[31] between the naphthalene rings of **1o** and **FN** propagates into the direction of the *c*-axis and makes stacking column structures. The large rectangular faces of the crystal correspond to (1 0 0) and (−1 0 0), and the long and short edges are parallel to *b*- and *c*-axes, respectively. **1o**

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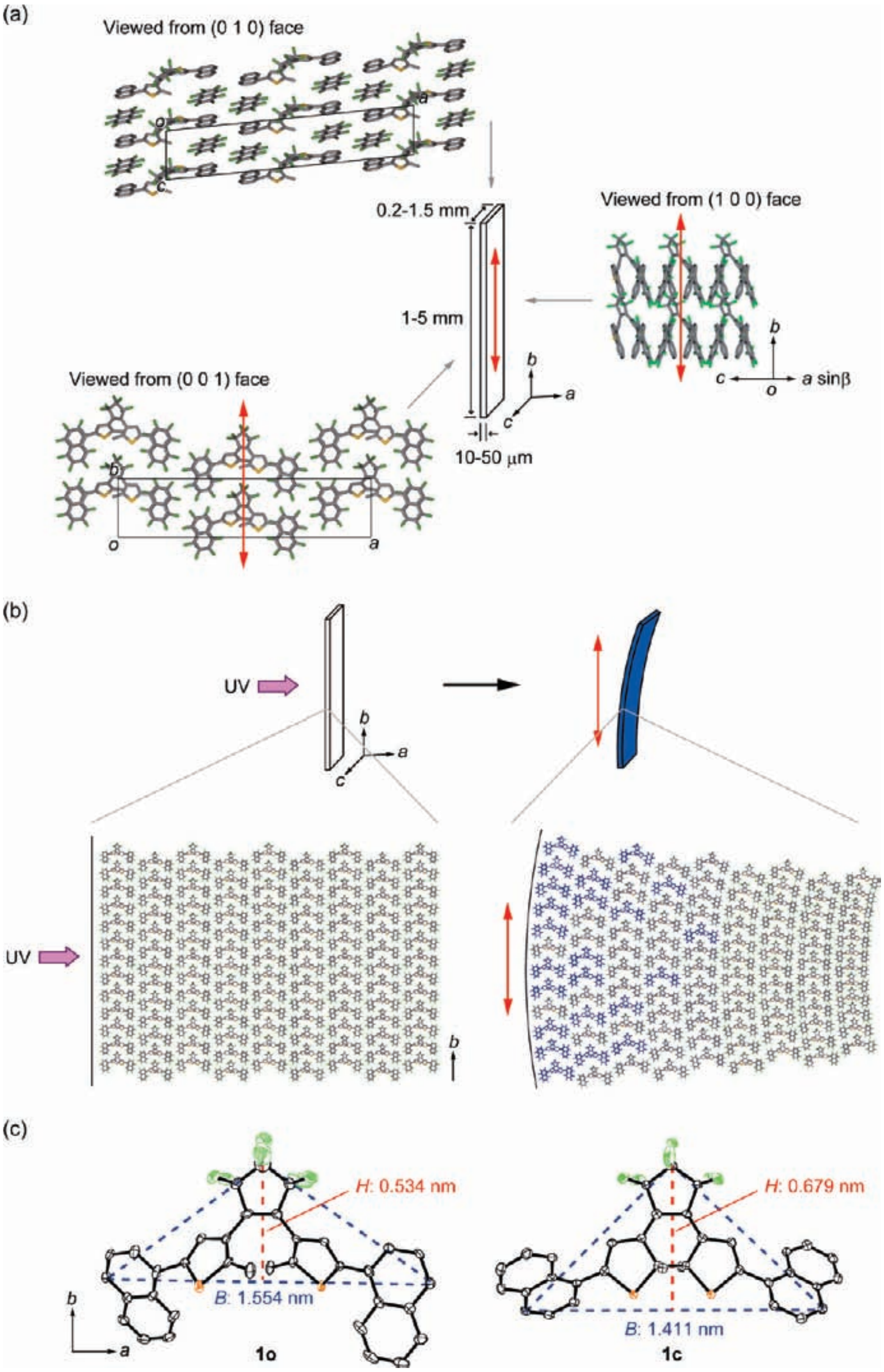

Figure 1. (a) Illustration of a typical crystal shape of the cocrystal of **1o·FN** and molecular packing diagrams viewed from the (1 0 0), (0 1 0), and (0 0 1) faces. The red arrow indicates the direction of the anisotropic elongation of the crystal, which is parallel to the *b*-axis, upon UV irradiation. (b) Schematic illustration of the photoinduced bending. The blue molecules are photogenerated closed-ring isomers in the crystal. (c) ORTEP drawings of **1o** in the cocrystal of **1o·FN** and **1c** in the crystal of the isolated and independently recrystallized closed-ring isomer. One of two conformers in the crystal of **1c** was shown (see Figure S2 in the Supporting Information). Hydrogen atoms were omitted for clarity. *H* is the height of the triangle shape (broken blue line), and *B* is the base width of the shape.

molecules are fixed in an antiparallel conformation,[32] and the distance between the two reacting carbon atoms in the thiophene rings (3.47 Å) are short enough for the diarylethene to undergo photocyclization in the crystalline phase.[33] The cocrystal changes the color from colorless to blue upon UV irradiation, and the blue color disappears upon visible light irradiation.[29]

The rectangular plate crystal shows photoinduced bending, as shown in Figure 2 (see movie files ja105356w_si_002.avi and ja105356w_si_003.avi in the Supporting Information). Upon irradiation with UV (365 nm) light from the right side of the crystal, the crystal turns blue and bends, moving away from the light source, as shown in Figure 2a. The bending ceases when the illumination light is switched off and the crystal keeps

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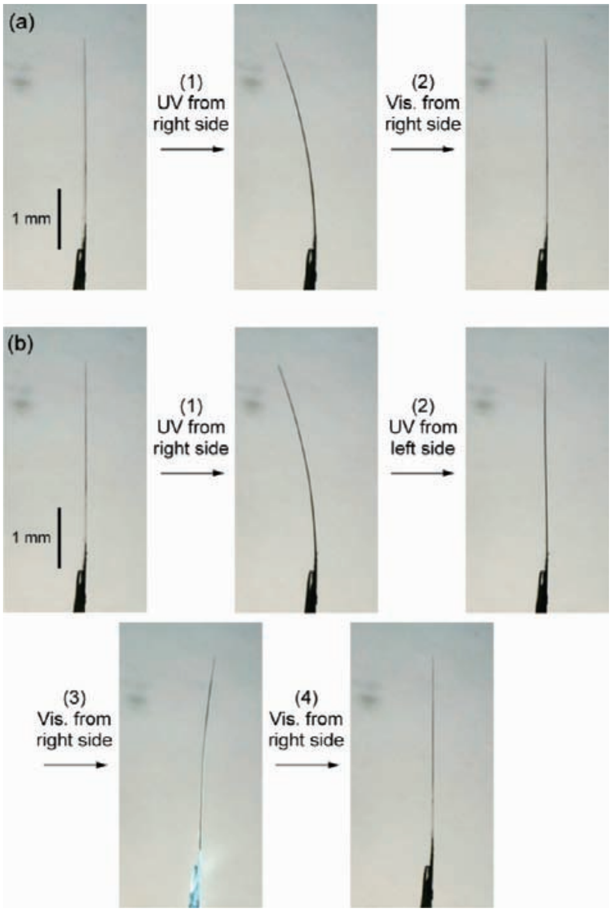

Figure 2. Reversible bending of a cocrystal of **1o·FN** (3.1 mm × 0.5 mm × 20 μm) induced by irradiation with UV (Keyence UV-400 with UV-50H, 365 nm, 30 mW/cm^2) and visible (Asahi Spectra MAX-302, $\lambda > 440$ nm) light. (a) (1) Upon irradiation with UV light from the right side, the crystal bent, moving away from the light source, and then (2) returned back by visible irradiation. (b) The crystal (1) first bent by UV irradiation from the right side and (2) second straightened by UV irradiation from the left side. (3) Upon irradiation with visible light from the right side, at first the crystal bent toward the light source and then (4) became straight after further irradiation.

the bent shape in the dark. When the bent crystal is irradiated with visible ($\lambda > 440$ nm) light from the right side, the blue color disappears and the crystal returns to the original straight shape. The photoisomerization of component diarylethene molecules takes place only in the surface thin layer, because of the high absorbance and inner filter effect of the dense crystal. The UV (365 nm) light cannot penetrate deep into the crystal. Therefore, bending is ascribed to the gradient of the degree of photoisomerization of the diarylethene molecules in the crystal. The UV irradiated surface thin layer is expected to be elongated, and the plate crystal bends, moving away from the UV light source, as observed in bimetals. Figure 1b shows the schematic illustration of the photoinduced bending.

Figure 2b shows the effect of visible light illumination. The crystal is irradiated with UV light from both sides and then irradiated with visible light from the right side. At first, the crystal bends toward the light source and then becomes straight. The bending toward the visible light source as observed in Figure 2b is well explained by the gradient of closed-ring isomers in the crystal. The reversible bending motion upon irradiation with UV and visible light can be repeated more than 250 times, as shown in Figure 3. Even after 250 cycles, no damage to the crystal could be observed.

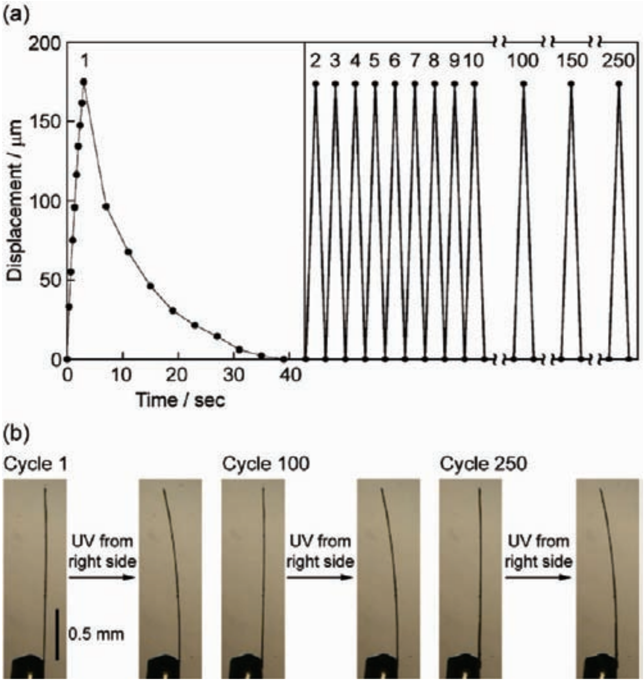

Figure 3. Reversible bending of a cocrystal of **1o·FN** (1.7 mm × 0.2 mm × 10 μm) by alternate irradiation with UV (365 nm) and visible ($\lambda > 440$ nm) light. (a) Tip displacement of the crystal during the reversible bending. (b) Photographs of the crystal in the 1st, 100th, and 250th cycles of the reversible bending.

It is generally believed that most photoreactive crystals tend to collapse as the reaction proceeds. The local stress accompanying the photodecarbonylation of diphenylcyclopropenone, for example, efficiently converts the crystals into a fine powder of diphenylacetylene and carbon monoxide.[34] The magnitude of the local stress, however, depends on the structural mismatch between reactants and products. In the present diarylethene crystal, the difference between the open- and closed-ring isomers is rather small. Therefore, the crystal can preserve the three-dimensional order by small adjustments in the unit cell. The perfluoronaphthalene−naphthalene interaction[31] is also considered to play an important role as buffer stacking layers in the crystal.[35] The $\pi-\pi$ interactions absorb the strain energy by adjusting their intermolecular distances and keep the crystal packing stable even after large deformation.

Elongation of the UV irradiated part was directly confirmed by *in situ* X-ray analysis of UV irradiated crystals (see Figure S1 in the Supporting Information). Upon UV irradiation, residual electron-density peaks appeared near sulfur atoms of the open-ring isomer **1o**. The new peaks are reasonably ascribed to sulfur atoms of the photogenerated closed-ring isomer **1c**.[36] The occupancy ratio of the peaks indicates **1o**/**1c** = 87:13. The change of the cell parameters upon photoirradiation is sum-

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Table 1. Crystal Data for **1o·FN**

	1o·FN (before irradiation)	**1o·FN_UV−UV** (after UV irradiation)	**1o·FN_UV−UV−vis** (after visible irradiation)
formula	$C_{55}H_{22}F_{22}S_2$	$C_{55}H_{22}F_{22}S_2$	$C_{55}H_{22}F_{22}S_2$
formula weight	1164.85	1164.85	1164.85
T/K	93(2)	93(2)	93(2)
crystal system	monoclinic	monoclinic	monoclinic
space group	$C2$	$C2$	$C2$
a/Å	37.113(6)	37.055(7)	37.105(7)
b/Å	8.4961(15)	8.5204(17)	8.4981(16)
c/Å	7.3282(13)	7.3284(14)	7.3282(14)
α/deg	90	90	90
β/deg	95.987(3)	95.687(3)	95.980(3)
γ/deg	90	90	90
V/Å^3	2298.1(7)	2302.4(8)	2298.1(7)
Z	2	2	2
ρ_{calc}/g cm^{-3}	1.683	1.680	1.683
goodness-of-fit on F^2	1.069	1.114	1.055
R_1 ($I > 2\sigma(I)$)	0.0528	0.0759	0.0540
wR_2 ($I > 2\sigma(I)$)	0.1413	0.1957	0.1415
R_1 (all data)	0.0551	0.0784	0.0562
wR_2 (all data)	0.1464	0.1998	0.1466

marized in Table 1. After UV irradiation, the *b*-axis is elongated as much as 0.29% and the *a*-axis is contracted as much as 0.16%, while the *c*-axis remains constant (**1o·FN_UV−UV** in Table 1). When the crystal is bleached with visible light, the residual electron-density peaks disappear and the cell parameters recover to the original ones (**1o·FN_UV−UV−vis** in Table 1). Thus, the deformation of the crystal upon UV irradiation is certainly explained by the UV-induced elongation of the *b*-axis, which corresponds to the long axis of the plate crystal.[37]

To investigate the origin of the cell parameter change, the geometrical structural change of the component diarylethene molecule upon UV irradiation was examined. Figure 1c shows the structures of the open- and closed-ring forms represented as ORTEP drawings. The structure of the open-ring isomer was determined by X-ray analysis of the cocrystal before UV irradiation, while that of the closed-ring isomer was obtained by the analysis of the crystal of the isolated and independently recrystallized closed-ring isomer (see Table S1 and Figure S2 in the Supporting Information). We assumed that the geometric parameters derived from the rigid structure of the independently recrystallized closed-ring isomer are valid except the conformation of the naphthyl side groups for the structure that is formed *in situ* in the crystal of the open-ring isomer. The two isomers differ in the geometrical structure, as shown by the triangle shape (broken blue line). The height H increases from 0.534 to 0.679 nm, and the base width B decreases from 1.554 to 1.411 nm upon photocyclization reaction. A similar change of the triangle shape of the diarylethene molecule is also confirmed by *in situ* X-ray crystallographic analysis (see Figure S1b in the Supporting Information). H in the UV-irradiated crystal (**1o·FN_UV−UV**), which is an average structure of the open-ring isomer (**1o**) and the photogenerated closed-ring isomer (**1c**) (**1o**/**1c** = 87:13), is longer than that in the crystal before irradiation (**1o·FN**), while B is shorter. The diarylethene molecules align with keeping the longitudinal height direction in parallel to the *b*-axis in the crystal packing (see the molecular packing viewed from the (0 0 1) face in Figure 1a). Each diarylethene molecule reversibly changes the triangle shape upon UV and visible light irradiation. The height increase by photocyclization forces the densely packed molecular layers to expand, resulting in the elongation of the *b*-axis. The contraction of the *a*-axis is also explained by the change of the triangle shape, i.e. the decrease of the base width. The geometrical structural changes of individual molecules are amplified in the crystal to cause the macroscale crystal movement (Figure 1b). It was proposed in previous papers[20] that cofacial packing of photogenerated thinner-shaped closed-ring isomers allows the molecules to be stacked one-by-one, resulting in the anisotropic contraction of the crystal. This stacking mechanism cannot be applied to the present cocrystal, because not contraction but elongation of the UV irradiated area was observed.

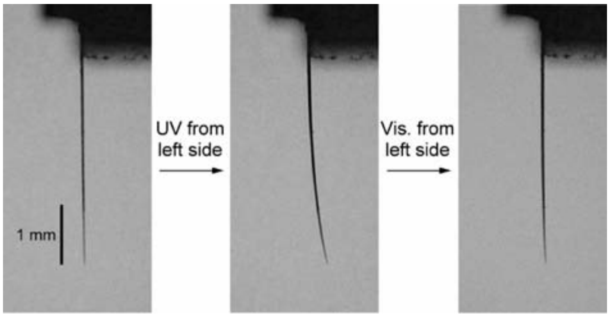

Figure 4. Reversible bending of a cocrystal of **1o·FN** (3.5 mm × 0.4 mm × 30 μm) induced by irradiation with UV (365 nm) and visible ($\lambda > 440$ nm) light at 4.7 K. The crystal was fixed to a copper sample holder in a cryostat.

The photoinduced bending was observed even at extremely low temperature. The crystal was fixed to a copper sample holder in a cryostat with optical windows and cooled down to 4.7 K under helium-gas atmosphere. Upon irradiation with UV light, the crystal turned blue and bent, moving away from the direction of the incident light, as shown in Figure 4 (see movie file ja105356w_si_004.avi in the Supporting Information). After switching off the illumination, the crystal ceases the bending and keeps the bent shape over one hour in the dark at the low temperature. This result indicates that the bending is not due to surface heating by the incident light but due to photochemical reaction of diarylethene molecules in the crystal. Upon irradiation with visible light, the blue color of the crystal slowly disappears and the bent crystal returns to the original straight shape.

The bending dynamics after irradiation with pulsed laser light (355 nm, 8 ns pulse width, 30 mJ/pulse) was followed using a high-speed camera (Vision Research, Phantom V710) at 295 K as well as at 4.7 K, as shown in Figure 5. The photoisomerization of diarylethene molecules in the crystal is complete during the laser pulse (8 ns).[38] We tried to measure how fast the mechanical movement of the crystal follows. Figure 5 shows the photographs of the bending. At both temperatures, the crystal shows bending in the first frame after irradiation with the laser pulse, although the bending is small due to the low photon dose in the single laser pulse. The exposure time of each frame is 5 μs. Therefore, the light-driven bending takes place in less than

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(37) The bending angle of a crystal can be expressed as "$\tan \theta \approx \nu/l = l\Delta\varepsilon/2h$", where θ is the angle, ν is the displacement of the tip, l is the length, h is the thickness, and $\Delta\varepsilon$ is the strain. Very small elongation of the surface thin layer, around 0.4% elongation, is enough to induce the bending as much as 22° in a crystal with 2-mm length and 10-μm thichness.

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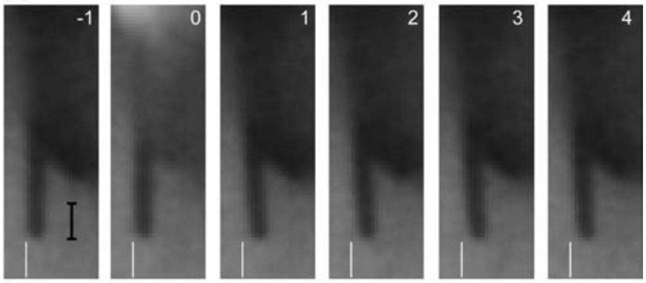
(a) 295 K



(b) 4.7 K

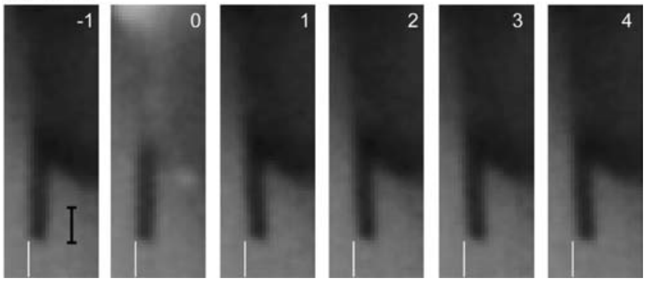


Figure 5. Bending dynamics of a cocrystal of **1o·FN** after irradiation with a laser pulse at (a) 295 K and (b) 4.7 K. The crystal (100 μm × 30 μm × 10 μm) was fixed to a copper sample holder in a cryostat. The black scale bars are 50 μm. The exposure time of each frame was 5 μs (200,000 frames/s). The numbers in the photographs are frame numbers. The laser pulse (Spectra-Physics INDI-40-10, wavelength 355 nm, pulse width 8 ns, pulse energy 30 mJ/pulse) was irradiated from the left side. The bright spot in frame 0 was the fluorescence from the attached anthracene crystal, which emitted when the laser pulse was irradiated. The white lines were added as markers to appreciate the bending better.

5 μs at 295 K as well as at 4.7 K. The very rapid movement of the crystal at 4.7 K suggests that the contribution of the slow relaxation process in the lattice is negligible.

As noted in the introductory part, our ambition is to link the shape changes of molecules to macroscale mechanical movement of materials and have the materials perform mechanical work. We tried to use the photoinduced bending crystal to lift heavy metal balls. A rectangular plate crystal was fixed at the edge of a glass plate as a cantilever arm, and a 2-mm lead ball was loaded onto the crystal, as shown in Figure 6a. The crystal and the ball weigh 0.17 mg and 46.77 mg, respectively. The weight of the lead ball is 275 times heavier than that of the crystal. Upon irradiation with UV light from below, the heavy ball was lifted as high as 0.95 mm (see movie file ja105356w_si_005.avi in the Supporting Information). Figure 6b shows another example of weight lifting of a steel ball (see movie file ja105356w_si_006.avi in the Supporting Information). A 3-mm steel ball (110.45 mg) was loaded onto a crystal plate (0.18 mg), and the crystal was irradiated with UV light. The weight of the ball is 614 times heavier than that of the crystal. Even such a heavy steel ball is lifted upon irradiation with UV light. The former example shows that the cantilever arm performs lifting work and the amount of the work is as large as 0.43 μJ. The latter example indicates that the force which is generated by UV irradiation is larger than 1.1 mN. The crystals, which weigh less than 0.2 mg, can generate a strong force and perform large mechanical work.

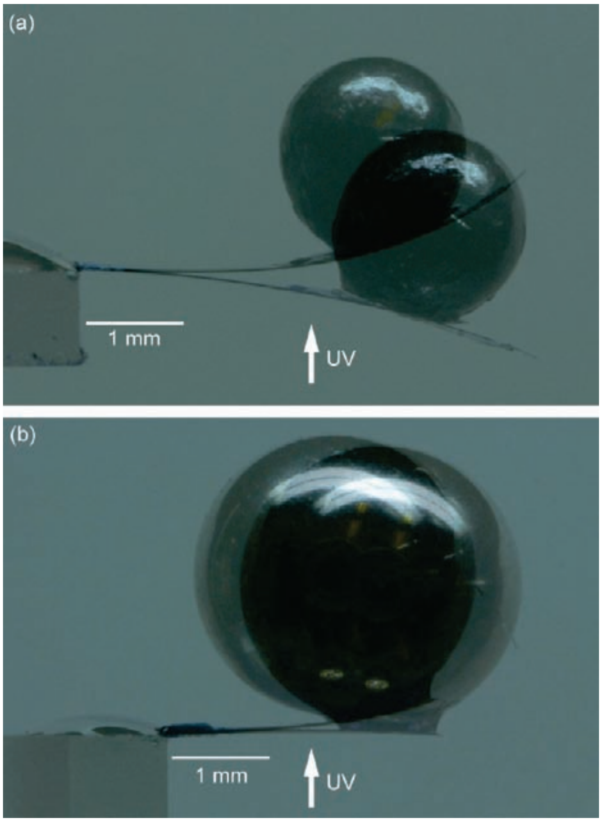


Figure 6. Photomechanical work of molecular crystal cantilevers made of **1o·FN**. The photographs before and after irradiation with UV (365 nm) light were superimposed. Illumination of UV light was carried out from the lower side of the crystal: (a) 2-mm lead ball, 46.77 mg; crystal cantilever, 0.17 mg; (b) 3-mm steel ball, 110.45 mg; crystal cantilever, 0.18 mg.

The work and force are ascribed to a large elastic modulus of the crystal materials. The modulus of the crystal was measured to be as large as 11 GPa by means of a manual beam-bending test[39] (see Figure S3 in the Supporting Information). This is much larger than those of typical polymer materials (~1 GPa)[40] and comparative to other organic crystals.[41] The large elastic modulus enables the crystal to generate a 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[39,42] (see Figure S4 in the Supporting Information). The maximum stress was estimated to be 44 MPa, which is 100 times larger than that of muscles (~0.3 MPa) and comparable to that of piezoelectric crystals, such as lead zirconate titanate (PZT) (~50 MPa).

Conclusions

In conclusion, the cocrystal of **1o·FN** exhibits photoreversible, rapid, and durable bending behavior upon irradiation with UV and visible light in the wide temperature range from 4.7 to 295 K. X-ray crystallographic analysis revealed that the bending deformation of the crystal is due to the anisotropic expansion

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of the crystal lattice induced by the shape change of the component diarylethene molecules upon photocyclization. The present cocrystal links the geometrical structural changes of molecules in the molecular world to macroscale movement of the materials and performs the mechanical work in the macroscopic world. The light-driven crystal actuators, which remotely work without wire connection, potentially find various applications in micro- and nanomechanics, such as manipulation of biological cells and light-driven valves in microreactors.

Experimental Section

1o and **1c** were synthesized by methods reported previously.[43] **FN** was purchased from Tokyo Chemical Industry. Single crystals of **1o·FN** were prepared by slow evaporation of a hexane solution of a mixture of **1o** and **FN** in a molar ratio of **1o**/**FN** = 1:2. Single crystals of **1c** were prepared by slow evaporation of an acetone solution of **1c**.

Photographs and videos of the crystals were recorded with a digital camera (Sony, HDR-CX7) connected to microscopes (Nikon, E600 POL or Leica, MS5) or a digital microscope (Keyence, VHX-900). UV irradiation was carried out using a UV-LED irradiation system (Keyence, UV-400 with UV-50H; wavelength 365 nm). Visible irradiation was carried out using a xenon-lamp irradiation system (Asahi Spectra, MAX-302). The wavelength of the light was selected by passing the light through cutoff filters.

X-ray crystallographic analysis was performed on a CCD-based X-ray diffractometer (Bruker AXS, SMART APEX) with Mo Kα radiation ($\lambda = 0.71073$ Å). The crystals were cooled with a low temperature controller (Japan Thermal Engineering, TC-190CP-CS-K). The data were collected as a series of ω-scan frames, each with a width of 0.3°/frame. The crystal decay was monitored by repeating the 50 initial frames at the end data collection and analyzing the duplicate reflections. Data reduction was performed using SAINT software, which corrects for Lorentz and polarization effects and decay. The cell constants were determined by the global refinement. The structure was solved by direct methods using SHELXS-90[44] and refined by full-matrix least-squares on F^2 using SHELXL-97.[45] The positions of all hydrogen atoms were calculated geometrically and refined by the riding model.

Extremely low temperature experiments were carried out under helium-gas atmosphere in a cryostat (Oxford Instruments, Optistat CF static). The temperature was monitored with a RhFe sensor near the sample and controlled with a temperature controller (Oxford Instruments, ITC-503S).

Pulsed laser irradiation was carried out using a Nd:YAG laser system (Spectra-Physics, INDI-40-10). The third harmonics (wavelength 355 nm) selected by a dichroic mirror was used. The bending behavior after irradiation with a single laser pulse was recorded with a high-speed camera (Vision Research, Phantom V710).

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Supporting Information Available: Five movie files showing crystal bending motions (AVI); X-ray crystallographic files (CIF) for **1o·FN**, **1o·FN_UV−UV**, **1o·FN_UV−UV−vis**, and **1c**; *in situ* X-ray crystallographic analysis of **1o·FN** (Figure S1); X-ray crystallographic analysis of **1c** (Table S1 and Figure S2); and measurement of Young's modulus and maximum stress (Figures S3 and S4). These materials are available free of charge via the Internet at http://pubs.acs.org.

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