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Photoinduced Topographical Surface Changes and Photoresponse of the Crystals of 7-Methoxycoumarin

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Photoinduced topographical changes due to the dimerization reaction were observed on the surface of a single crystal of 7-methoxycoumarin, upon deep UV (254 nm) light irradiation. Upon 365 nm irradiation, a step or valley formation was observed on the crystalline surface depending on the surface index. As a function of UV light wavelength, the depth of dimerization thickness changes. After intensive UV irradiation, photosolient phenomena of the crystal were observed. As a result of sublimation from granular crystals of 7-methoxycoumarin, several kinds of shaped crystals, including thin rod-shaped crystals, hollow cone-shaped crystals, and crystalline capsules were formed. Photoinduced bending due to the dimerization reaction was observed in the thin rod-shaped crystals. The hollow crystals showed photosolient phenomena upon UV irradiation. The bending and photosolient phenomena, previously reported for several kinds of diarylethene crystals, were also observed for 7-methoxycoumarin crystals. Unlike the case of diarylethene crystals, however, we found photoinduced amorphization on a coumarin crystal surface as well as reverse bending with prolonged irradiation of 365 nm light.

Introduction

The dramatic photoresponse of organic crystalline systems has received much attention in the development of photo-actuators and soft robots.¹⁻⁸ In these organic crystalline systems, diarylethenes, which exhibit thermally stable photochromic performances with high fatigue resistance,^{9,10} showed a remarkable photoresponse in the crystalline system. The formation and deformation of steps and valleys on a diarylethene single crystalline surface,¹¹ followed by photoinduced bending phenomena,¹²⁻¹⁵ photoinduced crystal growth,¹⁶⁻²² and photosolient phenomena²³⁻²⁵ of the diarylethene crystals were reported. Such cases of photoresponse have also been observed for other organic crystals of photoresponsive molecules, including walking and rolling locomotion of chiral azobenzene crystals,²⁶ salicylideneaniline crystals,^{27,28} photomechanical bending, peeling and oscillatory behavior of biological flagella of anthracene derivatives,²⁹⁻³⁴ and bending behavior by [2+2] dimerization reaction of a phenylbutadiene.³⁵ Here, we report the photoresponse of the crystal of 7-methoxycoumarin. The dimerization reactions of coumarin derivatives in crystalline states have already been

reported.³⁶⁻⁴¹ In particular, the photochemistry of 7-methoxycoumarin in the crystalline state has been extensively studied, and the results reveal that the reactive double bonds are rotated by 67.5° with respect to each other, with the center-center distance between the double bonds being 3.83 Å. In spite of this unfavorable arrangement, photodimerization occurs in the crystalline state, yielding syn head-to-tail dimer as the only product.⁴⁰ However, those studies focused on the photodimerization reaction in the crystal without observing the changes in the crystals' shapes. Therefore, the photoinduced topographical changes and mechanical motions of the crystals are not well-known. Accordingly, we examined the photoresponse and mechanical motion of the crystal, as well as the crystal growth of 7-methoxycoumarin on the crystalline surface.

Results and Discussion

Experiments were done on the dimerization reaction of 7-methoxycoumarin (**1**) (Fig. 1), and the crystals used in these experiments were prepared as follows. The bulk crystals of **1** were formed by recrystallization from benzene solution. Thin rod-shaped and hollow-cone-shaped crystals were prepared by sublimation

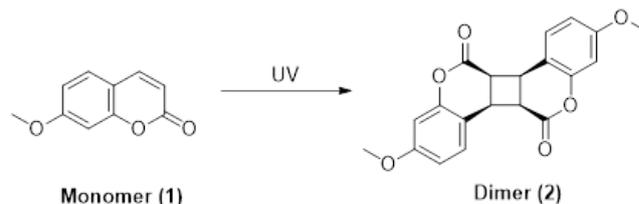


Fig. 1. Photoinduced dimerization of 7-methoxycoumarin.

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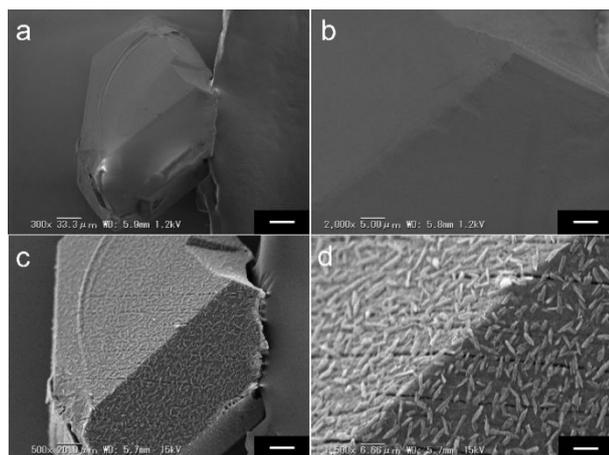


Fig. 2. Photoinduced topographical changes on single crystalline surfaces of 7-methoxycoumarin (**1**) (a), (b) before UV irradiation, (c), (d) after UV (254 nm) irradiation for 1 h, (b) and (d) are extended images of (a) and (c), respectively. Scale bars: 33.3 μm for (a), 5.00 μm for (b), 20.0 μm for (c) and 6.66 μm for (d).

based on a previous paper.²⁵ The crystals were all colorless and transparent. Upon UV irradiation, each crystal showed a photoresponse specific to its crystalline shape as it changed from transparent to opaque. Upon UV (254 nm) irradiation to the single crystals of **1** at room temperature, the flat crystalline surface (Fig. 2a, c) was covered with many small rectangular protrusions whose average lengths and widths are around 5 and 1 μm , respectively (Fig. 2b, d). We observed the FT-attenuated total reflection (ATR) IR spectra of the crystalline surface before and after UV irradiation, and a new band assigned to the C=O stretching vibration of lactone moiety in dimer **2** was observed at 1745 cm^{-1} . The shift to the higher frequency from that of **1** is due to the loss of conjugation accompanied with the conversion from **1** to **2** (Fig. S1).^{37, 38} In order to ascertain the molecular structure of the photoproduct, the crystals after UV irradiation were dissolved in the mixture of benzene and ethyl acetate (9/1 v/v). In order to isolate the photodimer **2**, the photoproduct was separated on preparative TLC with the same solvent mixture as eluent. The single crystals of **2** were obtained by recrystallization from benzene solution. The X-ray analysis data of **1** and the photoproduct **2** are listed in Table 1 (ORTEP images are shown in Fig S2), and the molecular structure of **2** is shown in Fig. 3. The structure was the same as that reported in solid state under UV

	1 _{low temp.}	2 _{low temp.}
<i>T</i> / K	143(2)	143 (2)
Chemical formula	C ₁₀ H ₈ O ₃	C ₂₀ H ₁₆ O ₆
Formula weight	176.17	352.34
crystal system	triclinic	orthorhombic
space group	<i>P</i> -1	<i>Pbcn</i>
<i>a</i> / Å	6.8212 (3)	14.6312 (7)
<i>b</i> / Å	13.3401 (5)	12.0469 (6)
<i>c</i> / Å	18.5886 (7)	18.6651 (10)
α / °	80.8654(17)	90
β / °	89.4342 (17)	90
γ / °	81.6705(16)	90
<i>V</i> / Å ³	1652.26 (11)	3289.9 (3)
Volume for a molecule (Å ³)	206.53	411.24
<i>Z</i>	8	8
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>))	0.0574	0.0511
<i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.1321	0.1336
<i>R</i> ₁ (all data)	0.0663	0.0535
<i>wR</i> ₂ (all data)	0.1396	0.1368
CCDC	2061357	2061358

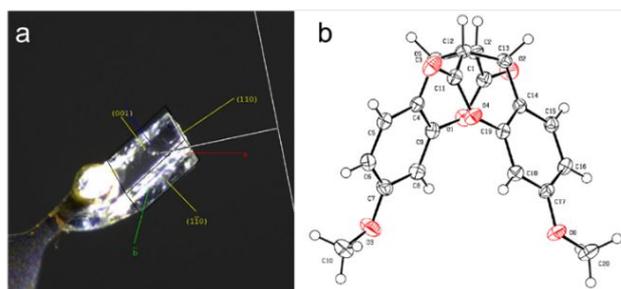


Fig. 3. X-ray analysis of the molecular structure of photodimer (**2**).

Table 1. Crystal data of monomeric 7-methoxycoumarin (**1**) and its dimer (**2**) recrystallized from benzene solution.

light irradiation in the previous studies.³⁶

It is well known that the photo-dimer **2** reverts to monomers upon deep UV irradiation in the solution. This was easily confirmed because the absorption band of photo-dimer **2** around 250 nm disappeared, which is the absorption window of **1** (Fig. 4a). In contrast, the absorption bands of **1** and its dimer **2** in the crystalline state overlapped as shown in Fig. 4b. Monomer **1** and the photogenerated **2** also have absorbance at 254 nm, which implies that complete photocontrol cannot be applied to revert the monomers. Therefore, only photoinduced dimerization is applicable in the crystalline state.

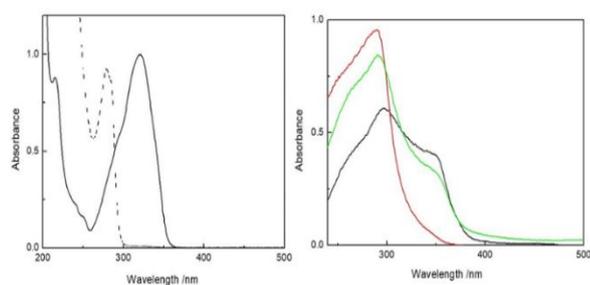


Fig. 4 Absorption spectra of **1** and **2** in solution and crystalline states (a) Transmission absorption spectra of **1** (solid line) and **2** (broken line) in methanol, (b) Reflection absorption spectra of crystalline powders of **1** (black line), **2** (red line), and **2** after 254 nm light irradiation (green line).

In order to clarify the mechanism of topographical changes, we measured the XRD of the crystals of **1** before and after UV irradiation. The reflection peaks observed at 9.7°, 19.3°, and 27.0° for a single crystal of **1** decreased dramatically upon UV irradiation (Fig. 5). This indicates that the photogenerated grain protrusion structure on the surface is amorphous. The molecular volume of dimer **2** is nearly twice that of monomer **1** (Table 1), indicating that the volume change in the system should be negligible. In the crystalline state, monomer

1 is located nearly parallel to the *ac* plane (Fig. S3a) and densely packed. The distances between the reactive carbon atoms for monomers were 3.593 and 4.126 Å, respectively. This agrees with Schmidt's rule, which shows that photoreactions can proceed in solid state when the distance between the active carbon atoms is less than 4.2 Å.⁴² During the dimerization of **1**, molecules of **1** rotated and

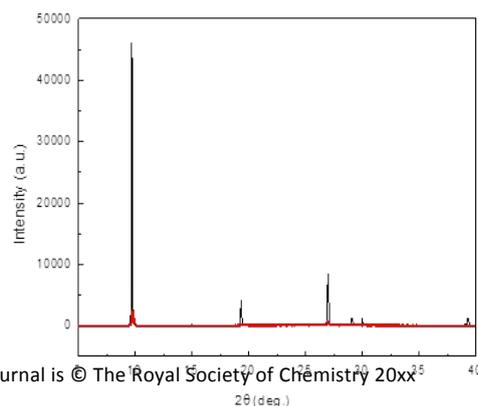


Fig. 5 XRD spectra of crystals of **1** before (black line) and after (red line) UV irradiation for 1 h at room temperature.

underwent the dimerization reaction with *syn* head-to-tail orientation³⁶ to form **2**, where the dihedral angles between two coumarin moieties is around 40° (Figs. 3 and S3). Due to the large structural changes that accompany molecular ordering, the large disordering induces amorphization with the volume expansion upon UV irradiation. Thus, topographical changes were produced on the crystalline surface. This is very different from the previously reported

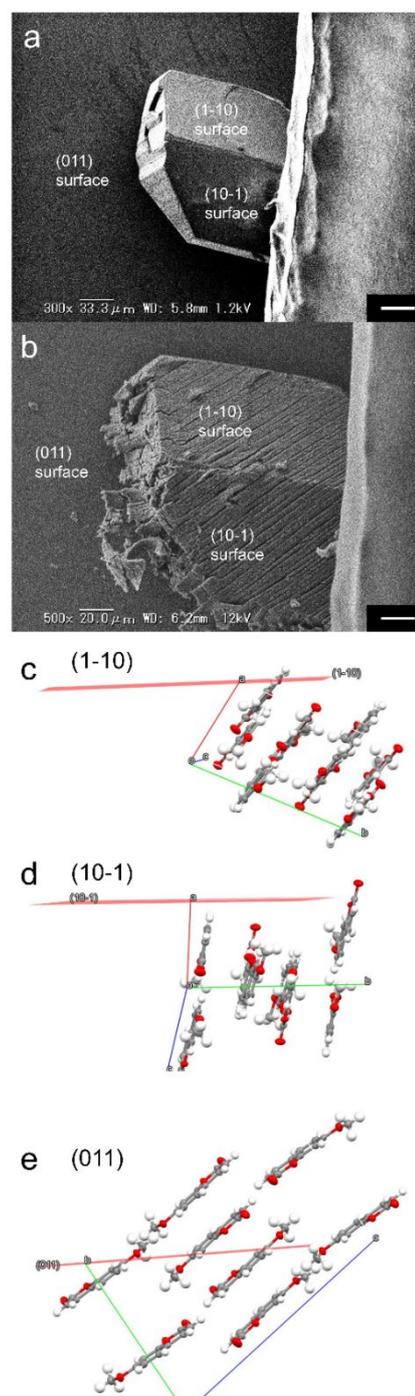


Fig. 6. Photoinduced cracks generated upon 365 nm light irradiation at -35 °C on a single crystal of **1**. (a) SEM image of the crystal of **1** before UV irradiation. (b) SEM image of the crystal of **1** after UV (254-365 nm PU-21) irradiation for 1 h. (c-e) Molecular alignments on crystalline surfaces of (1-1 0) (c), (1 0-1) (d), and (011) (e). The angles between the aromatic ring surface of 7-methoxycoumarin and each crystalline surface (indicated by red line) were 55°(c), 80°(d), and 35°(e). Scale bars: 33.3 μm for (a), 20.0 μm for (b).

photoinduced topographical changes in diarylethene crystals in which a reversible photoreaction proceeds while maintaining the crystalline state.¹⁷⁻²²

Then we irradiated the crystals of **1** with 365 nm light, which corresponds to the tail of the absorption band of **1** in crystalline state. This light reaches deeper into the crystal, in comparison to the case using 254 nm light; the absorbance of **1** at 254 (0.65) and 365 nm (0.04) is shown in methanol solution in Fig. 4a. Note that the photogenerated dimer **2** has little absorption at 365 nm. Prolonged irradiation with 365 nm light induced the photodimerization of the crystal to a deep level from the surface. Upon 365 nm light irradiation, the formation of steps and valleys was observed on the crystalline surface. It is interesting to compare this result with the previously reported step and valley formation for a diarylethene crystal below the glass transition temperature (T_g).¹¹ As for the crystals of **1**, no T_g was observed from the DSC measurement, indicating that no phase transition occurs at those temperatures (Fig. S4). The surfaces of a single crystal of **1** was flat before UV irradiation (Fig. 6a). After UV (365 nm) irradiation for 1 h to the crystal at -35 °C, cracks or valleys were observed on the (1 -1 0) and (1 0 -1) surfaces, while the generation of a step-like random structure was observed on the (0 1 1) surface (Fig. 6b). From X-ray analysis of the single crystal of **1**, the coumarin molecules were aligned as shown in Figs. 6c-e.

Upon UV irradiation, a planar molecule of coumarin **1** undergoes a dimerization reaction (Fig. 1) to form a bulky dimer molecule (Fig. 3), which disturbs the alignment. Thus, cracks were generated along the molecular layer. The topographical changes were different depending on the surface. On the (1 -1 0) and (1 0 -1) surfaces, deep valley structures were generated, while surface crystals were peeled off in the form of flakes on the (0 1 1) surface upon UV irradiation (Fig. 6b). Considering the alignment of the plane molecule of **1**, the angles of the molecular alignment of the aromatic rings to the surfaces are around 55°, 80°, and 35° for the (1 -1 0), (1 0 -1) and (0 1 1) surfaces, respectively. For comparison, we consider the previous works of Irie *et al.*, which reported the photoinduced morphology changes on the surfaces of a diarylethene single crystal. In their system, upon UV irradiation, one surface has a valley structure when the long axis (direction of aromatic ring) of the molecules is perpendicular to the surface, while another surface shows step-like structure when the long axis is parallel to the surface. Considering the previous results, the topographical changes observed for crystalline surfaces of **1** are consistent with the previous work on such changes in diarylethene crystals.¹¹ Due to the different transparency of dimer **2** in the condensed state at 254 and 365 nm, remarkably different topographical changes were observed depending on the wavelengths of irradiated the UV light.

It is noteworthy that remarkable photosolient phenomena of the crystals of **1** were observed even at room temperature, when we used stronger UV light (365 nm LED, 1 W cm⁻²) (Supporting Information Movie 1).

Photoinduced bending phenomena were also observed for a thin crystal of **1**. Thin crystals of **1** were prepared according to our previous papers.^{14,35} One of the obtained thin crystals was irradiated

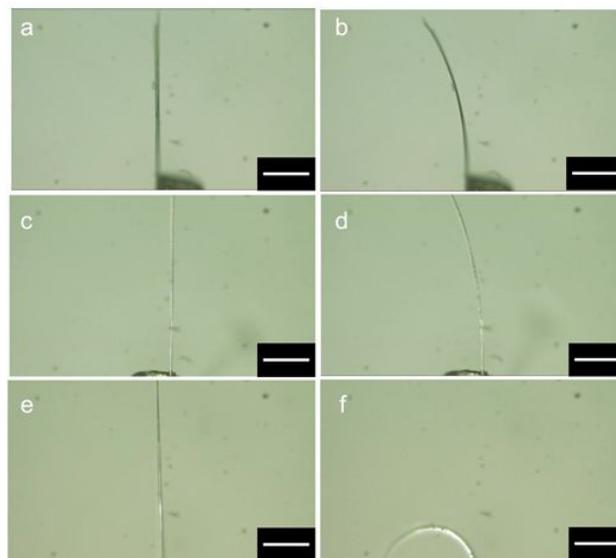


Fig. 7. Photoinduced bending phenomena of thin crystals of **1** prepared by sublimation. (a, c, e) before UV irradiation, (b) after 254 nm light (0.07 W cm⁻²) irradiation for 60 s, (d) after 365 nm light (0.07 W cm⁻²) irradiation for 60 s, (e) after 365 nm light (1 W cm⁻²) irradiation for 7 s. Crystal dimensions, length 378 μm, width 19.5 μm, thickness 7.3 μm for a and b, length 440 μm, width 14.3 μm, thickness 5.9 μm for c and d, length 428 μm, width 5.3 μm, thickness 4.3 μm for e and f, Scale bars: 100 μm for all figures).

with 254 nm light from the right side, and smooth bending was observed within 60 s (Fig. 7a, b, Supporting Information Movie 2). This is due to the photoinduced expansion resulting from the photoreaction on the surface of the crystal. The phenomena were clarified by X-ray analysis of a single crystal of **1**. The long axis of the crystal extends along the *a*-axis of the unit cell. Upon UV irradiation to the crystal, the *a*- and *b*-axes expanded while the *c*-axis contracted (Tables 2 and S1).

Here, wavelength-dependent photoinduced bending modes were observed. Upon 254 nm irradiation from the right side of a thin crystal, a bending phenomenon was observed within 60 s (Fig. 7a, b) (Supporting Information Movie 3). Upon irradiation with 365 nm light with the same light intensity, more moderated bending was observed within the same irradiation period (Fig. 7c, d). The difference is attributable to each reaction depth depending on the irradiation wavelength (Fig S5, 6). The similar dependence was always observed more than 10 crystals. Kobatake *et al.* also reported the relationship of the thickness of the photo-reacted layer and the bending speed in thin crystals of diarylethenes.⁴³ They reported that the thinner the photo-reacted layer, the faster the bending speed was. In our system, the bending speed of **1** is faster when the crystal was irradiated at 254 nm with the same light intensity. The depth of the reaction layer under 254 nm light irradiation is estimated to be

shorter compared to that under 365 nm light irradiation as described above. Upon irradiation with much stronger UV (365 nm) irradiation, dramatic bending was observed within 7 seconds (Fig. 7e, f). By

increment of unit cell volume. The quality of the crystal decreased after additional 10 min irradiation with the light. The long axis of the rod-shaped thin crystal is along the *a*-axis of the unit cell; therefore,

Table 2. Crystal data of **1** before and after 400 nm light irradiation with rate of change of the unit cell (ORTEP images are shown in Fig S7).

	1 before UV irr.	1 400 nm 10 min
<i>T</i> / K	298(2) K	298(2) K
Chemical formula	C ₁₀ H ₈ O ₃	C ₁₀ H ₈ O ₃
Formula weight	176.16	176.16
crystal system	triclinic	triclinic
space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> / Å	6.8137(3)	6.8504(8) (+0.54%)
<i>b</i> / Å	10.6743(5)	10.7265(13) (+0.54%)
<i>c</i> / Å	12.4313(6)	12.3293(15) (-0.82%)
α / °	108.1891(16)	107.962(4)
β / °	95.2297(15)	95.521(4)
γ / °	95.2045(15)	95.436(4)
<i>V</i> / Å ³	848.11(7)	850.38(18) (+0.27%)
Volume for a molecule (Å ³)	212.03(2)	212.60(4)
<i>Z</i>	4	4
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>))	0.0627	0.0708
<i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.1625	0.1792
<i>R</i> ₁ (all data)	0.0868	0.1105
<i>wR</i> ₂ (all data)	0.1625	0.2183
CCDC	2074689	2075129

continuous irradiation with the UV light, the bent crystal reverted to its original shape, but it broke in the process (Supporting Information Movie 4, Fig. S7). The reverse movement is due to the progress of photodimerization in the whole crystal. Therefore, such phenomena were also observed when UV light was irradiated from the opposite side to the bent crystals of **1**.

To clarify the mechanism of the bending phenomena, we compared the X-ray analysis data of single crystals of **1**, before and after UV irradiation. In order to proceed the dimerization reaction in the whole crystal, 400 nm light corresponding to the absorption edge was irradiated to the crystal of **1** while rotating the crystal.⁴⁴ The irradiation was carried out at room temperature. The results are summarized in Table 2. Due to the different measuring temperature, polymorphism was observed. Upon 400 nm light irradiation for 10 min, the *a*- and *b*-axes elongated, while the *c*-axis shrank with an

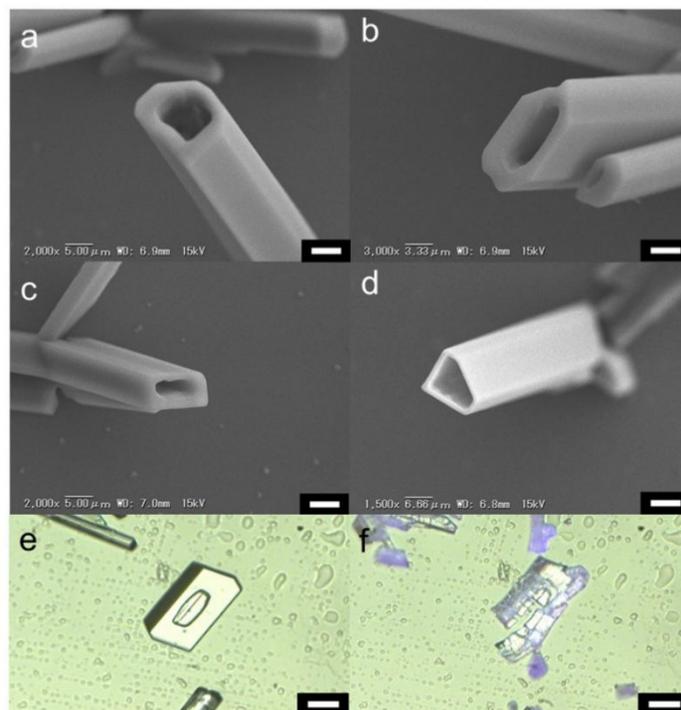


Fig. 8. Hollow crystals and a crystalline capsule of **1** prepared by sublimation. (a), (d) $\times 2000$, scale bar = 5.00 μm . (b): $\times 3000$, scale bar = 3.33 μm . (d) $\times 1500$, scale bar = 6.66 μm . (e, f) scale bar = 20.0 μm .

UV irradiation to the thin crystal of **1** induced bending away from incident UV light through expansion of the photo-irradiated side. The photodimerization efficiency ($\sim 10^{-2}$)³⁹ is much lower compared with those (~ 1.0) of diarylethenes,³⁴ but the expansion ratio is much larger than those of diarylethene crystals. Thus, remarkable photoinduced bending was observed for a coumarin crystal of **1**.

Surprisingly, several kinds of hollow crystals of **1** were generated by sublimation (Figs. 8a-d). The formation of such hollow crystals was also observed for a diarylethene derivative.²⁴ The photoresponsive crystals with hollow structure have a potential for photo-triggered scattering of included substances. A crystalline structure with a single side opened, and these hollow crystals extended from the substrate. This is a feature of the Iwanaga model,^{38,39} by which we previously explained the formation mechanism of diarylethene hollow crystals. Due to the structural hindrance to bending, the hollow crystals were initially elongated along the *a*-axis of the crystal, followed by scattering into small pieces or jumping away from view upon UV irradiation; this shows a photosalient effect (Supporting Information Movies 5,6). Coincidentally, crystalline capsules were also obtained (Fig. 8e). The crystalline structures of these hollow crystals and capsules are estimated to be the same as that of bulk crystals due to having the same XRD spectra. They also showed photosalient phenomena (Figs. 8f, S8, Supporting Information Movie 7) as we previously observed in a diarylethene crystalline system.⁴⁵ Organic crystalline

capsules were also very recently reported using 9-methylanthracene-1,2,4,5-tetracyanobenzene and naphthalene-1,2,4,5-tetracyanobenzene.⁴⁶ Such crystalline capsule systems will receive attention for their potential to offer new photoresponsive functions in the near future.

Conclusions

Photoinduced topographical changes on the crystalline surface of 7-methoxycoumarin were observed. The photoreaction in the crystalline state was irreversible owing to the overlapping of absorption bands between the monomer and the photo-dimer in the crystalline state. Rectangular protrusions formed on the crystalline surface upon 254 nm light irradiation. In contrast, valley formation and a phenomenon in which a crystalline surface peeled off in the form of flakes were observed upon 365 nm irradiation. This difference based on the wavelength of UV light is due to the depth of photodimerization from the crystalline surface. In both cases, the crystallinity decreased by UV irradiation. Thin rod-shaped crystals and hollow crystals were prepared by sublimation. Upon UV irradiation to the rod-shaped crystals, bending phenomena were observed. Through continuous UV irradiation or irradiation from the opposite side of the crystal, recovery to the straight shape was observed occasionally. Upon 254 nm irradiation, the crystal slowly bent, while dramatic bending followed by recovery from bending and breaking of the crystal were observed upon 365 nm irradiation. In the hollow crystals, photosolient phenomena of the structure were observed after elongation of the crystal. All of these shape changes are attributed to the phase changes from crystal to amorphous. As a result, versatile photo-responses were observed for crystals of 7-methoxycoumarin during the dimerization reaction. This study provides a promising example of photoinduced responses from organic molecular crystals as reported for photochromic diarylethene crystalline systems. Furthermore, this work inspired us to explore the photoresponse possibilities in a wide range of crystals of photoreactive compounds.

Experimental

Methods

Melting points were measured with a micro melting point apparatus, Yanaco MP-500D. Absorption spectra of the solutions were monitored with the Hitachi U-4150 spectrophotometer. Perkin Elmer DSC8500 was used for DSC measurement with temperature elevated at a rate of 10 °C / min. KEYENCE digital microscope VHX-500, equipped with microscope stage VH-S30, zoom lenses VH-S1, and VH-Z450, and lens attachment VH-Z20, was used to monitor the photoinduced topographical changes, photoinduced bending, and photosolient phenomena. For the UV light irradiation, KEYENCE UV-400, UV-50H ($\lambda = 365$ nm, 1 W cm⁻¹), AS ONE Handy UV Lamp LUV-6 (100 V, $\lambda = 365$ nm, 1378 μ W/cm⁻¹ at 4 mm) and Spectroline model 280C/J (100 V, $\lambda = 313$ nm, 852.6 μ W/cm⁻¹ at 4 mm) was used for monitoring the dimerization by ¹H NMR. Topcon hand lamps PU-21 (100 V, $\lambda =$

250-400 nm, 905.1 μ W/cm⁻¹ at 4 mm, Fig. S6), Fi-51s (100 V, $\lambda = 254$ nm 1559 μ W/cm⁻¹ at 4 mm, 832.9 μ W/cm⁻¹ at 5 cm) and Fi-5L (100 V, $\lambda = 365$ nm, 1623 μ W/cm⁻¹ at 4 mm, 800.0 μ W/cm⁻¹ at 5 cm) were used.

The 7-methoxycoumarin was purchased from Tokyo Chemical Industry Co., Ltd. Block crystals (triclinic) of **1** were prepared by recrystallization from the benzene solution. The thin rod-shaped (thickness: ~20 μ m), hollow cone-shaped, and capsule-shaped crystals of **1** (triclinic) were obtained by sublimation under normal atmosphere on hotplates KPI Models HP-19U300P and HP-19U300, for 100 min at 80 °C, which is about 40 °C below the melting point (117-121 °C) of **1**. After that process, the crystals were cooled to room temperature.

Crystal data of **1** and **2**

X-ray crystallographic analyses of the single crystals of **1** and **2** were performed with an X-ray diffractometer (Bruker AXS, D8 QUEST) with Mo K α radiation ($\lambda = 0.71073$ Å). The temperature of the crystals was controlled with a temperature controller (Japan Thermal Engineering, JAN 2-12). The diffraction frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The cell constants were determined by global refinement. The data were corrected for absorption effects using the multi-scan method (SADABS). The structure was solved by the direct method and refined by the full-matrix least-squares method using the SHELXL-2014 program.⁴⁷ The positions of all hydrogen atoms were calculated geometrically and refined by the riding model.

Crystal data of **1**. C₁₀H₈O₃, triclinic, *P*-1, *a* = 6.8212(3) Å, *b* = 13.3401(5) Å, *c* = 18.5886(7) Å, $\alpha = 80.8654(17)^\circ$, $\beta = 89.4342(17)^\circ$, $\gamma = 81.6705(16)^\circ$, *V* = 1652.26(11) Å³, *Z* = 8, *D*_{calcd} = 1.416 Mg m⁻³, *R*₁ (*I* > 2 σ (*I*)) = 0.0574, *wR*₂ (*I* > 2 σ (*I*)) = 0.1321, *T* = 143(2) K; CCDC 2061357.

Crystal data of **2**. C₂₀H₁₆O₆, orthorhombic, *Pbcn*, *a* = 14.6312(7) Å, *b* = 12.0469(6) Å, *c* = 18.6651(10) Å, $\alpha = \beta = \gamma = 90^\circ$, *V* = 3289.9(3) Å³, *Z* = 8, *D*_{calcd} = 1.423 Mg m⁻³, *R*₁ (*I* > 2 σ (*I*)) = 0.0511, *wR*₂ (*I* > 2 σ (*I*)) = 0.1368, *T* = 143(2) K; CCDC 2061358.

XRD data of powder diffraction

XRD spectra of powder crystals of **1** before and after UV irradiation for 1 h at room temperature was measured on a Rigaku RINT2000.

Author contributions

All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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