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Photomechanical bending of 4-aminoazobenzene crystals

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ABSTRACT

Upon photoirradiation at 365 nm, platelike microcrystals of *trans*-4-aminoazobenzene quickly bend away from the light source, returning to their initial linear shape when irradiation was terminated. However, relative to the observations upon cessation of 365 nm irradiation, the bent crystals recovered their initial shape more rapidly when exposed to visible light (530 nm) irradiation.

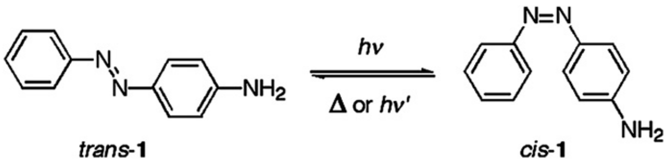
1. Introduction

Scientific and technological communities are interested in molecules that generate mechanical motion as a consequence of physical stimuli. In particular, interest exists in linking the motion to macroscale mechanical work of bulk materials. However, artificial molecular mechanical systems, based on molecular-level shape changes, have not been linked to macroscale mechanical motion of materials [1]. Large-scale mechanical motion of molecular materials was observed only in nematic elastomers, in which a photoinduced order–disorder phase transition is the driving force [2,3]. Recently, mechanical bending of diarylethene photochromic crystals was reported, with the macroscale bending of the crystals being caused by molecular motion [4–7]. Since then, several photomechanical crystals have been reported, thus, revealing potential opportunities for artificial molecular machinery [8–12].

We previously reported that platelike microcrystals of *trans*-4-dimethylaminoazobenzene bent upon irradiation with ultraviolet (UV) light and thermally returned to their initial shape upon ceasing irradiation [13]. We found that microcrystals of 4-aminoazobenzene *trans*-**1** bent reversibly upon alternate irradiation with UV and visible light (Scheme 1).

2. Experimental

4-Aminoazobenzene *trans*-**1** was obtained from Tokyo Chemical Industry Co., Ltd. and purified by recrystallization in methanol. Microcrystals of *trans*-**1** were prepared by sublimation on glass plates. Photoirradiation of microcrystals was carried out using a Keyence UV-400 UV-LED light source (365 nm, 0–50 mW/cm^2) and Asahi Spectra MAX-302 xenon light source (300 W). Ultraviolet–visible (UV–Vis) absorption spectra of the microcrystals and solutions were measured using a Hitachi U-2810 spectrophotometer. X-ray diffraction (XRD) measurements of the microcrystals were performed using a Rigaku RINT2 X-ray diffractometer. Surface morphology was observed in tapping mode using an SII SPA300 atomic force microscope (AFM). The bending motion of the microcrystals was observed using a Keyence VH-Z450 CCD microscope and recorded by video.



Scheme 1. Photoisomerization of 4-aminoazobenzene.

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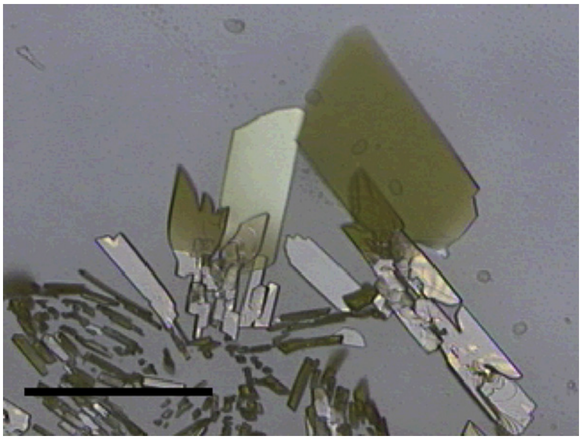

Fig. 1. Platelike microcrystals of *trans*-**1** grown on the surface of glass plate by sublimation. The scale bar is 100 μm.

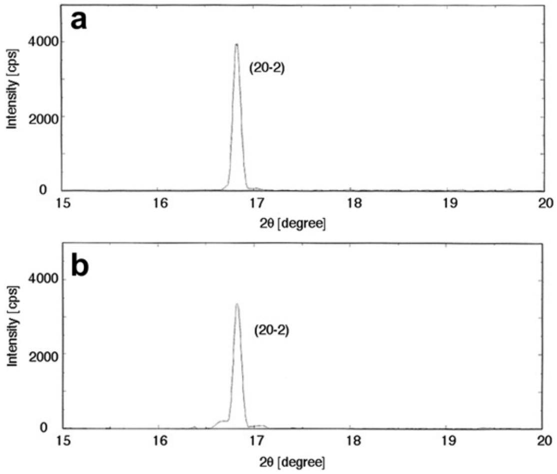

Fig. 2. X-ray diffraction profiles of *trans*-**1** microcrystals (a) before irradiation and (b) on maintaining UV irradiation.

3. Results and discussion

Platelike microcrystals of *trans*-**1** were obtained by sublimation on glass plates at ∼20 °C below the melting point (121–124 °C) of *trans*-**1** (Fig. 1). XRD measurements revealed only one sharp peak (Fig. 2a), which was assigned to the (20-2) face based on crystallographic data [14]. The top surface of the platelike microcrystals was identified as the (10-1) face in the longitudinal direction along the *b* axis, on the basis of comparisons with platelike bulk crystals, which exhibited a (10-1) face along the *b* axis.

Fig. 3a shows a piece of a platelike microcrystal ($200 \times 25 \times 1.2\ \mu m^3$) in which the lower portion was adhered to the glass surface and the upper portion was free. When the (10-1) surface was irradiated at 365 nm (40 mW/cm^2) from the left side, as indicated by the arrow in Fig. 3a, the crystal quickly bent away from the light, reaching a displacement angle of 34° after 0.5 s (Fig. 3b). Stopping the illumination resulted in the gradual return of the crystal to its initial linear shape after 4 min (Fig. 3c–f).

The microcrystal bending speed and displacement angle increased in proportion to the UV light intensity (Fig. 4). When the microcrystals were irradiated with 2.5 mW/cm^2, 8 s was required to reach the maximum displacement angle of 27°. When 50 mW/cm^2 was used, 2 s was required to reach the maximum displacement angle of 41°.

During UV irradiation, the melting point of *trans*-**1** microcrystals (121–124 °C) decreased to between 77 °C and 82 °C due to the coexistence of the *cis* isomer and returned to 121–124 °C when the irradiation was stopped, further demonstrating the reversibility of the isomerization.

The absorption spectrum ($\lambda_{max} = 375$ nm) of *trans*-**1** in benzene [15] changed upon UV irradiation at 365 nm for 30 s to that of *cis*-**1** (photostationary state) with two bands at $\lambda_{max} = 344$ and 442 nm, corresponding to (π,π^*) and (n,π^*) excitation, respectively (Fig. 5a). When irradiation was stopped for 10 min, the initial spectrum of *trans*-**1** in benzene was recovered, demonstrating thermal *cis*-to-*trans* isomerization. Visible light irradiation at 530 nm led to a faster recovery (1 min) to the initial *trans*-**1** spectrum. Thus, 4-aminoazobenzene **1** underwent reversible

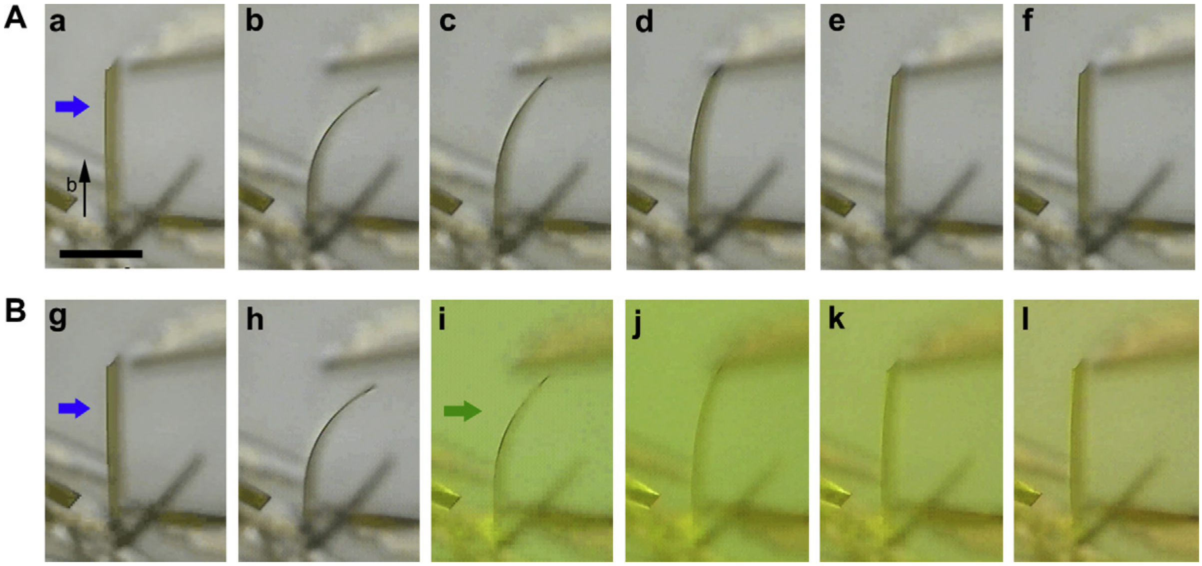

Fig. 3. Photomechanical bending of the *trans*-**1** microcrystal: (A) (a) before irradiation, (b) after UV irradiation from left side for 0.5 s, and stopping irradiation for (c) 10 s, (d) 60 s, (e) 120 s, (f) 240 s; (B) (g) before irradiation, (h) after UV irradiation from left side for 0.5 s, and after visible light (530 nm) irradiation from left side for (i) 2 s, (j) 14 s, (k) 30 s, (l) 60 s. The scale bar is 100 μm.

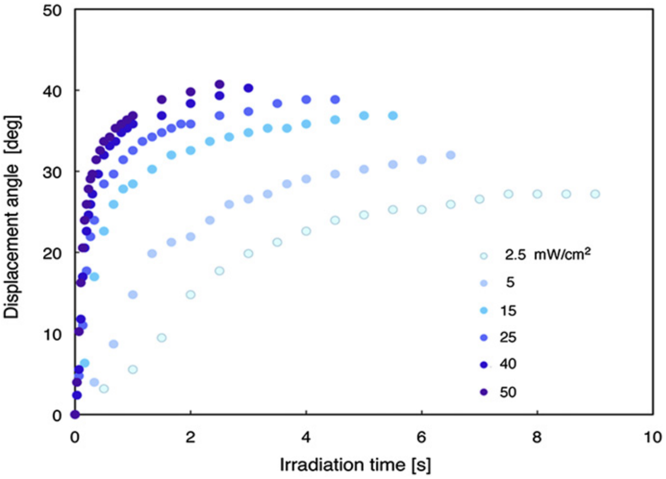

Fig. 4. Dependence of irradiation time of UV light on the displacement angle of the platelike microcrystal ($200 \times 25 \times 1.2$ μm^3) of *trans*-**1**.

photoisomerization between the *trans* and *cis* isomers in benzene via alternate irradiation with UV (365 nm) and visible (530 nm) light. In contrast, the absorption spectrum of *trans*-**1** microcrystals did not change after UV irradiation at 365 nm for 30 s (Fig. 5b), suggesting that the photoisomerization occurred near the crystal surface.

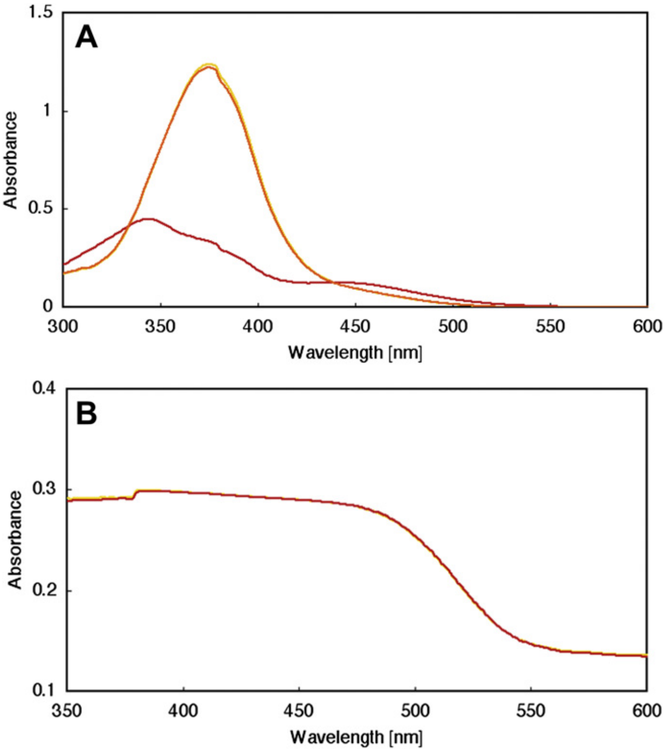

Fig. 5. (A) Absorption spectra of *trans*-**1** (0.05 M) in benzene before (yellow) and after UV irradiation at 365 nm for 30 s (red). Stopping irradiation for 10 min recovered the initial spectrum in benzene (red yellow). (B) Absorption spectra of the *trans*-**1** microcrystals before (yellow) and after UV irradiation for 30 s (red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

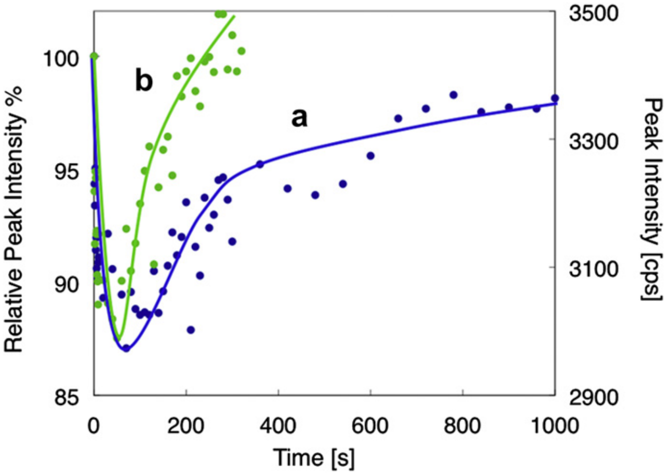

Fig. 6. Dependence of irradiation time on the XRD peak intensity of *trans*-**1** microcrystals. (a) Blue: UV light was irradiated for 60 s and then irradiation was stopped. (b) Green: UV light was irradiated for 60 s and then visible light at 530 nm was irradiated. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 6 shows the dependence of irradiation time on the relative XRD peak intensity of *trans*-**1** microcrystals. The (20-2) peak intensity decreased to 87% of the original value upon UV irradiation (40 mW/cm^2) for 60 s because of the *trans*–*cis* photoisomerization and deterioration in crystallinity (Fig. 2b). However, no shift of peaks or new peaks were observed in the XRD profile, even after continued irradiation, suggesting that the *cis*-**1** product did not form a new crystalline phase. After irradiation was stopped, the XRD peak intensity increased to 94% after 4 min and recovered after 15 min due to *cis*–*trans* thermal isomerization. In contrast, irradiation with visible light at 530 nm (10 mW/cm^2) recovered the initial intensity after 4 min due to *cis*–*trans* photoisomerization resulting from (n,π^*) excitation.

As discussed above, stopping the illumination returned the crystal to its initial linear shape after 4 min (Fig. 3f). In contrast, visible light irradiation for 1 min recovered the initial straight crystal (Fig. 3l), revealing that both bending and straightening of microcrystals were controlled by irradiation with UV and visible light.

The (10-1) top surface of the *trans*-**1** microcrystal was smooth before irradiation, as observed with an AFM (Fig. 7a). After UV irradiation for 10 s, uneven features appeared with a height of 3 nm and a relative roughness of 0.4% of the crystal thickness (840 nm) (Fig. 7b). The uneven features decreased slightly upon visible light irradiation at 530 nm for 10 min, but the initial smooth surface was not recovered (Fig. 7c).

In the *trans*-**1** crystal, the amino group of *trans*-**1** molecule is disordered in 50% occupancy and two independent planar molecules exist at a dihedral angle of 70.60° at the (10-1) face, forming two kinds of herringbone structures (red and blue) along the *b* axis (Fig. 7d–f) [14]. Upon UV irradiation, the planar *trans*-**1** molecules underwent photoisomerization to *cis*-**1** on the (10-1) crystal surface, resulting in an increased torsional conformation due to repulsion of two phenyl planes. Crystalline *cis*-azobenzene molecules normally exhibit a dihedral angle of 64.26° between the two phenyl planes [16]. The *trans*–*cis* photoisomerization elongated the unit cell length along the *b*, *a*, and *c* axes near the (10-1) crystal surface, giving rise to the uneven features. In contrast, the unit cell dimension remained constant at the nonirradiated surface, resulting in bending of the microcrystal.

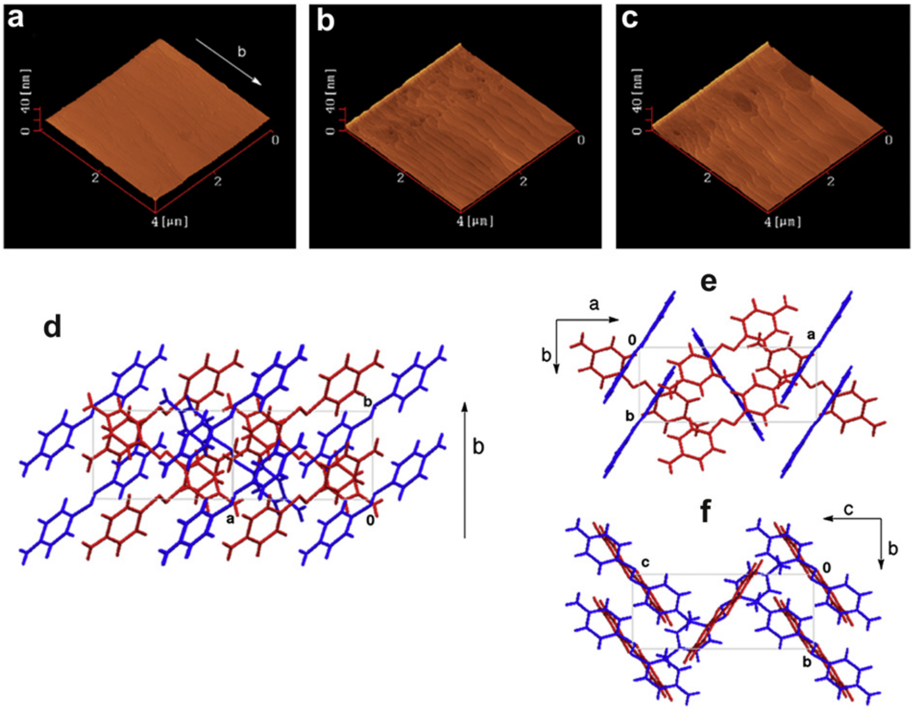

Fig. 7. An AFM image shows the (10-1) top surface of a *trans*-**1** microcrystal before (a) and after irradiation with (b) UV and (c) visible light. The molecular arrangement of the (d) (10-1), (e) (001), and (f) (100) faces is illustrated before irradiation.

4. Conclusions

Platelike microcrystals of *trans*-4-aminoazobenzene reversibly bend upon alternate irradiation with UV and visible light.

Acknowledgements

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