

Mechanical Motion of Azobenzene Crystals upon Photoirradiation

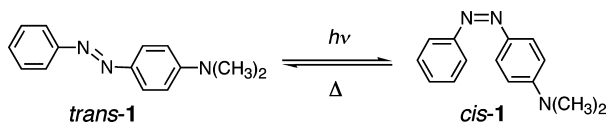
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Synthetic molecular machines based on the conversion of changes in molecular geometry to mechanical motion in macroscale materials are interesting from the perspective of basic research and offer a wide range of potential applications. Such machines are amenable to remote operation with external stimuli such as photon impingement and do not require direct contact. Supramolecular machines have been reported but have not been linked to macroscale mechanical motion in bulk materials.¹ Numerous solid-state reactions in molecular crystals have been developed in recent decades,^{2,3} and crystalline photoreactions are often accompanied by molecular motion, causing morphological changes at crystal surfaces.^{4–6} Irie and co-workers⁷ first reported rapid, reversible bending in rod-shaped microcrystals of photochromic diarylethene upon photoirradiation, thereby linking molecular-level shape changes to macroscale mechanical motion in crystals. Bardeen and co-workers⁸ demonstrated irreversible and reversible shape changes in rod-shaped nanocrystals of anthracene carboxylates by photodimerization. These types of photoreactive crystals have been suggested for the development of molecular machines.⁹

Azobenzenes are typical chromophores that undergo *trans*–*cis* photoisomerization. Azobenzene-containing elastomer films bend upon photoirradiation, and this effect has been applied in the fabrication of a photodriven plastic motor¹⁰ and a high-frequency photodriven polymer oscillator.¹¹ In this communication, we report that platelike microcrystals of *trans*-4-(dimethylamino)azobenzene (*trans*-1) exhibit reversible bending upon irradiation with UV light.



Microcrystals of *trans*-1 were prepared by sublimating crystalline powders in a glass tube oven under vacuum. Platelike microcrystals (several hundred micrometers in length) grew on the edges and surface of the glass plate after heating to a temperature near the melting point (114 °C) for several hours [Figure S1 in the Supporting Information (SI)]. X-ray diffraction (XRD) measurements revealed three sharp peaks (Figure S2a in the SI), which were assigned to the (002), (004), and (006) faces on the basis of consistencies with crystallographic data.¹² The top surface of the platelike microcrystals was identified as the (001) face with its longitudinal direction along the *a* axis, on the basis of comparisons with platelike bulk crystals, which exhibited a (001) face along the *a* axis.

Figure 1a shows a piece of a platelike microcrystal ($525 \times 280 \times 5 \mu\text{m}^3$) whose lower portion was fixed to the glass surface and whose upper portion was free. The (001) surface was irradiated at 365 nm ($5 \text{ mW}/\text{cm}^2$) from the right rear, as indicated by the arrow in Figure 1a. Shape changes in the crystal were observed with a CCD microscope and recorded by video. Upon irradiation, the

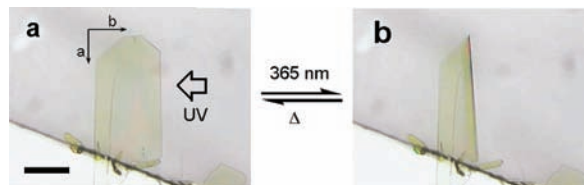


Figure 1. The (001) face of the platelike *trans*-1 microcrystal (a) before and (b) after UV irradiation from the right rear (indicated by the arrow labeled “UV”). The scale bar is 200 μm .

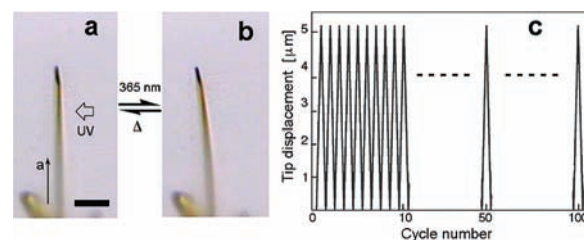


Figure 2. Bending of a narrow, platelike crystal of *trans*-1, as shown by a comparison of images acquired (a) with and (b) without UV irradiation. The scale bar is 20 μm . (c) Graph showing the repeatability of the reversible bending over as many as 100 cycles.

crystal quickly bent forward in the direction opposite the light source, reaching maximum deflection after 0.5 s (see Figure 1b and video 1 in the SI). The maximum deflection angle was quite large, leading to the formation of a semicircle of $\sim 180^\circ$ along the *b* axis. When the illumination was stopped, the crystal returned to its initial flat shape after 30 s (Figure 1a). The observed mechanical motion was reversible over repeated cycles of UV irradiation. Irradiation of the front face of the crystal induced backward bending, demonstrating that both bending directions were possible (see video 2 in the SI).

A narrow, platelike crystal ($70 \times 5 \times 1 \mu\text{m}^3$) with one end fixed to another crystal was subjected to repeated bending (Figure 2a). As described above, comparison with bulk crystals showed that the (001) plane was oriented perpendicular to the surface of the glass plate with the longitudinal direction along the *a* axis. When subjected to UV irradiation at the (001) surface, the crystal bent in the direction opposite the light source, reaching a maximum deflection of $5 \mu\text{m}$ after 0.2 s, as measured at the end of the crystal (see Figure 2b and video 3 in the SI). The degree of deflection along the *a* axis was considerably smaller than that along the *b* axis (Figure 1b). The bent crystal returned to the initial, straight form 3.8 s after the illumination was stopped. This reversible bending was observed over 100 cycles of alternating UV irradiation (2 s) and darkness (5 s) (Figure 2c).

The absorption spectrum of platelike microcrystals of *trans*-1 after irradiation at 365 nm revealed a slight decrease in absorbance at $\lambda_{\text{max}} = 400 \text{ nm}$ relative to that before irradiation (Figure S3 in the SI). This spectral change was similar to that of *trans*-1 in

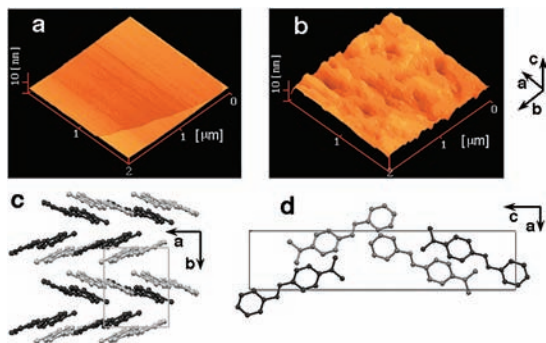


Figure 3. AFM images of the (001) top surface of a *trans*-1 microcrystal (a) before and (b) after UV irradiation and illustrations of the molecular arrangements of the (c) (001) and (d) (010) faces before irradiation.

benzene due to photoisomerization to *cis*-1. The ^1H NMR spectrum of *trans*-1 microcrystals that had been irradiated for 1 min was measured in benzene- d_6 and exhibited singlet peaks at 2.35 and 2.23 ppm, corresponding to the $\text{N}(\text{CH}_3)_2$ protons of the *trans* and *cis* isomers with a 160:1 relative intensity (Figure S4 in the SI). This provided unambiguous evidence of *trans*–*cis* photoisomerization in the crystalline state.¹³ The estimated yield of the *cis* isomer was $\sim 1\%$ based on the decay of absorbance in benzene. The *cis* isomer almost disappeared after 30 min as a result of *cis*–*trans* thermal isomerization. During UV irradiation, the melting point of *trans*-1 microcrystals (113–114 °C) decreased to 66–80 °C because of the coexistence of the *cis* isomer and returned to 113–114 °C when the irradiation was extinguished, further demonstrating the reversibility of the isomerization. To our knowledge, *trans*–*cis* photoisomerization of azobenzene chromophores has not been observed in the crystalline state because of the large geometric changes that would be required in such densely packed crystal lattices. However, we confirmed the occurrence of photoisomerization near the surface of *trans*-1 microcrystals.

The (001) top surface of the *trans*-1 microcrystal was smooth before irradiation, as observed by atomic force microscopy (AFM) (Figure 3a). After UV irradiation for 5 s, uneven features appeared along the *a* axis with a height of 10 nm and a relative roughness of 1% of the crystal thickness (900 nm) (Figure 3b). The uneven features slightly decreased in the dark after 1 h, but the initial smooth surface was not recovered. The relative XRD peak intensities for the microcrystals quickly decreased to 93% upon UV illumination for 5 s, likely because of both the *trans*–*cis* photoisomerization and the deterioration in crystallinity (Figure S2b in the SI). After the irradiation was stopped, the diffraction peaks increased to 97% of their initial intensities after 30 s, and recovered completely after 15 min, as a result of the *cis*–*trans* thermal isomerization and the recovery of crystallinity. However, no new peaks were observed in the XRD profile, even after continued irradiation (Figure S2c in the SI), suggesting that the *cis*-1 product did not form a new crystalline phase.¹⁴

In the *trans*-1 crystal, the planar molecules are arranged almost perpendicularly at the (001) face to form a herringbone structure along the *a* axis (Figure 3c).¹² Upon UV irradiation, the planar *trans*-1 molecules undergo photoisomerization to *cis*-1 on the (001) crystal surface, resulting in an increased torsional conformation due to repulsion of the two phenyl planes. Crystalline *cis*-azobenzene molecules normally exhibit a dihedral angle of 64.26° between the two phenyl planes.¹⁵ The *trans*–*cis* photoisomerization elongates the unit cell length along the *b* and *a* axes near the (001) crystal surface, giving rise to the uneven features. In contrast, since there is no photoisomerization in the absence of light, the unit cell dimensions remain constant at the nonilluminated surface, resulting in bending of the microcrystal. Furthermore, the molecular interactions between the neighboring herringbone structures are weak, as seen in the packing arrangements at the (001) and (010) faces (Figure 3c,d). Therefore, the uneven features along the *b* axis are sharper than those along the *a* axis (Figure 3b). This leads to a drastic bending motion along the *b* axis (Figure 1) relative to the small crystal bending observed along the *a* axis (Figure 2).

In conclusion, the mechanical bending of platelike microcrystals of *trans*-4-(dimethylamino)azobenzene upon UV photoirradiation was observed.

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Supporting Information Available: Figures S1–S4 and three videos of mechanical bending. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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