Photomechanical bending of salicylideneaniline crystals†

Hideko Koshima,*a Kyoko Takechi,a Hidetaka Uchimoto,a Motoo Shirob and Daisuke Hashizumec

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Platelike microcrystals of N-3,5-di-tert-butylsalicylidene-3-nitroaniline repeatedly bend and straighten upon alternate irradiation with UV and visible light. The mechanism of bending was elucidated by X-ray crystallographic analyses before and after photoirradiation.

Creating molecular-scale mechanical motion in response to chemical or physical stimuli and linking that motion to macroscale mechanical motion in a bulk material is of particular interest from both scientific and technological perspectives. However, artificial molecular mechanical systems, which are based on molecular-level shape changes, have not been linked to macroscale mechanical motion.1 Large-scale mechanical motion of molecular materials has been observed only in nematic elastomers, in which a photoinduced order–disorder phase transition was used as the driving force.2 Recently, mechanical bending of photochromic diarylethene crystals was reported, and the macroscale bending of the crystals was found to be caused by molecular-scale motion.3,4 Thereafter, several photomechanical crystals composed of anthracenes and azobenzenes have been reported to provide promising opportunities for artificial molecular machinery.5–9

Salicylideneanilines are typical photochromic compounds in the crystalline state (Scheme 1). Their photochromicity is based on the formation of colored species by photoinduced proton transfer.10,11 This communication describes long, platelike microcrystals of N-3,5-di-tert-butylsalicylidene-3-nitroaniline (1) in enol form that exhibit reversible bending upon alternate irradiation with UV and visible light. The bending mechanism is based on changes in crystal structure before and after photoirradiation.

Microcrystals of enol-1 were prepared by sublimation of crystalline powders in a small platinum pan covered with a silanated glass plate. Platelike microcrystals grew on the surface of the glass plate after heating to a temperature approximately 10 °C below the melting point (132 °C) and holding for several hours (Fig. S1, ESI†). X-Ray diffractograms of the microcrystals contained four peaks (Fig. S2a, ESI†), which were assigned to the 001, 002, 003, and 004 reflections based on consistencies with existing crystallographic data.12 The top surface of the platelike microcrystals was identified as the (001) face with its longitudinal direction along the a-axis, based on comparisons with platelike bulk crystals, which exhibit a (001) face along the a-axis.

Fig. 1a shows the frontal (001) face of a platelike enol-1 crystal (73 × 4.5 × 1.1 μm) with one end fixed to an adjacent crystal. When the (001) face was irradiated from the right at 365 nm (40 mW cm⁻²) with a UV-LED (Fig. 1b), the crystal bent away from the light to reach a maximum tip displacement angle of 45° after 5 s (Fig. 1c). Subsequent illumination with a halogen lamp equipped with a color filter (530 nm, 10 mW cm⁻²) returned the bend to its initial straight shape after 10 s (Fig. 1b).
A 2 s pulse of UV irradiation, with simultaneous and continuous illumination with visible light (>390 nm) from the above halogen lamp, bent the crystal to a displacement angle of 37°. When the UV source was blocked, the crystal returned to its initial straight form after 4.6 s. This reversible bending was observed over 200 cycles of alternating UV irradiation (2 s on, 5 s off) under continuous illumination with visible light (Fig. 1d and Video S1, ESI†). The bending motion was accompanied by a color change from pale yellow to reddish orange due to the formation of trans-keto-1 (Fig. S3a, ESI†). The reddish-orange crystal also returned to the initial pale-yellow color due to photochemical fading to the enol-I isomer (Fig. S3b, ESI†).

The bending motion of the microcrystals depended on both the intensity of UV and visible light. When a platelike microcrystal (50 × 6.3 × 2.1 μm; Fig. 2a) was irradiated at 365 nm at 5 to 40 mW cm⁻² for 30 s, the tip displacement angle increased from 9° to 25°, respectively, in proportion to the UV intensity (Fig. 2b and c). In the absence of UV radiation, the crystals straightened to their initial form after 500 to 1400 s. The lifetime of thermal fading from the straightened to their initial form after 500 to 1400 s. The time required to recover the initial straight form was also 42 days, k/C₀ 40 mW cm⁻² to 63 s upon illumination with 530 nm light at 10 mW cm⁻².

In the absence of UV radiation, the crystals straightened to their initial form after 500 to 1400 s. The lifetime of thermal fading from the trans-keto-1 to the enol-I isomer is very long (42 days, k = 2.8 × 10⁻⁷ s⁻¹ at 25 °C, Fig. 2a) was irradiated at 365 nm at 5 to 40 mW cm⁻² for 1 h (Fig. S4, ESI†). This is due to stabilization of the trans-keto-1 form by intermolecular hydrogen bonding and dimer formation between the N–H group of the trans-keto imine and the oxygen atom of the nitro group. However, the lifetime was dramatically shortened from 1400 s to 43 s with increasing visible light intensity up to 10 mW cm⁻² (Fig. 2d and e). This recovery time is comparable to the 63 s lifetime observed with 530 nm light, when the intensity of visible light was increased to 10 mW cm⁻².

The degree of tip displacement with platelike microcrystals increased with increasing aspect ratio (length/thickness). For example, maximum displacement angles of 25°, 52°, and 70° were observed with microcrystals having aspect ratios of 25 (50 × 6.3 × 2.1 μm), 71 (120 × 7.1 × 1.7 μm), and 132 (159 × 6.8 × 1.2 μm), respectively.

Notably, upon UV irradiation, a platelike crystal (120 × 7.1 × 1.7 μm) was able to flip a silica gel particle approximately 50-fold heavier than the microcrystal itself, suggesting that the mechanical force generated in these crystals is relatively large (Video S2, ESI†). Most of the platelike crystals prepared by sublimation adhered to the glass surface and were unable to bend freely. UV irradiation over the glass plate, however, bent most of the crystals away from the light source, stripping the stuck crystals from the glass surface (Video S3, ESI†). In contrast, crystals prepared on bare glass plates did not bend, indicating that silanation decreased the degree of interaction between the crystals and the glass.

Crystallographic analyses of a thin enol-I microcrystal (200 × 30 × 20 μm²) were performed at 123 K before and after successive UV irradiation at room temperature. A nearly constant unit cell size was attained after 1 h (Fig. S4, ESI†). The resulting crystal exhibited a disordered structure with contributions from both the enol-I and the trans-keto-I isomers at a ratio of 0.905(2):0.095(2) (details in ESI†). This is identical to the structures obtained following irradiation at 360 nm and following two-photon excitation at 730 nm.

Fig. 3a shows an ORTEP drawing of the disordered molecules. In the trans-keto-I molecule, the oxygen atom O(1) and the nitrogen atom N(1) are in a trans position with respect to the C(1′)–C(7′) bond. The bond lengths of C(2′)–O(1′), C(1′)–C(7′), and C(7′)–N(1′) were 1.305(9), 1.415(9), and

![Fig. 2](image-url) (a) A microcrystal (50 × 6.3 × 2.1 μm) is shown before and after irradiation with UV (365 nm) and visible light (530 nm). The scale bar is 10 μm. (b) The bending motion is dependent on the UV irradiation time. (c) Tip displacement angle is shown as a function of UV intensity. (d) The straightening motion is dependent on the visible irradiation time, and (e) the time to recover the initial straighness is shown as a function of visible light intensity.

![Fig. 3](image-url) (a) ORTEP drawings show the disordered structures of the enol-I (black) and trans-keto-I (red) isomers after irradiation at 365 nm at the 25% probability level. Hydrogen atoms except H(1) and H(1′) are omitted for clarity. (b) Molecular arrangements on the (001) face. AFM images show the (001) top surface of an enol-I microcrystal before (c) and after irradiation with (d) UV and (e) visible light.
1.349(9) Å, respectively, which differed significantly from those (1.355(4), 1.441(5), and 1.273(4) Å) of the enol-1 molecule. The C(8')-N(1')-C(7')-C(1') torsion angle of the trans-keto-1 was $-172.4(18)^\circ$ and the corresponding angle of the enol-1 isomer was $177.2(3)^\circ$. The phototransformation can occur through the motion of a pair of benzene rings analogous to the bicycle pedal motion of stilbenes and azobenzenes without requiring major structural changes. 14

The length of the $a$-axis in the unit cell increased by 0.42% from 6.0913(2) to 6.1171(4) Å (Fig. 3b). Hence, photoisomerization elongates the crystal length along the $a$-axis near the (001) crystal surface. In contrast, since no photoisomerization occurs in the absence of light, the unit cell dimensions remain constant at the non-illuminated surface, resulting in bending of the microcrystal away from the light source. When UV or visible (530 nm) irradiation is stopped, the reverse isomerization from trans-keto-1 to enol-1 brings the crystal back to its initial straight conformation.

The (001) surface of the enol-1 microcrystal was smooth before irradiation, as observed by atomic force microscopy (Fig. 3c). Small dents with a depth of 1.5 nm (0.3% of the total crystal thickness) appeared upon UV irradiation for 40 s (Fig. 3d). The overall surface morphology, however, remained constant. Subsequent irradiation with visible light for 180 s did not alter the surface morphology (Fig. 3e). These results suggest minimal molecular movement, such as a pedaling motion, during photoisomerization. This minimal movement allows the excellent repeatability of the reversible bending over as many as 200 cycles (Fig. 1d).

In conclusion, the photomechanical bending of platelike microcrystals of $N$-3,5-di-tert-butylsalicylidene-3-nitroaniline was repeated upon alternate irradiation with UV and visible light. The mechanism of bending was elucidated by X-ray crystallographic analyses.

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Notes and references