

Photothermal high-speed crystal actuation and the simulation

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Mechanically responsive organic materials have attracted attention from perspective of both basic research and applications in smart actuators and soft robots [1]. We have developed many mechanical crystals such as azobenzene [2] and salicylidenealine [3], mainly based on photoisomerization. However, photoisomerization has some disadvantages for crystal actuation, such as a limited number of photoisomerizable crystals, slow actuation speed, and no actuation of thick crystals. Here we report photothermally driven fast-bending actuation and simulation of a salicylideneaniline derivative crystal with an *o*-amino substituent in enol form (enol-1).

X-ray crystallographic analysis revealed that enol-1 crystal belonged to the space group, $P2_1$, showing that the enol-1 molecule is achiral but forms chiral crystal. The molecules were connected weakly through the intermolecular hydrogen bond chains in a two-fold helical manner to form the herringbone structure along the *b* axis (Figure 1a, b). Absorption spectra of a thin enol-1 crystal revealed that enol-1 crystal exhibited fast photoisomerization from enol to *trans*-keto form ($\tau=0.9$ s) by UV light and fast back-isomerization ($\tau=4.2$ s) from *trans*-keto to enol form.

Under UV light irradiation, the thin ($<20\mu\text{m}$) crystals bent away from the light source quickly (in a few seconds) by photoisomerization. In contrast, the thick ($>20\mu\text{m}$) crystals bent very quickly (in several milliseconds) due to the photothermal effect, finally achieving 500-Hz high-frequency bending by pulsed UV laser irradiation. We propose a possible mechanism in which photothermally driven bending is caused by a non-steady temperature gradient in the thickness direction. The temperature gradient was calculated based on a one-dimensional non-steady heat conduction equation, resulting in the successful simulation of bending via the photothermal effect and the elucidation of the proposed mechanism (Figure 1c). Most materials that absorb light show their own photo-thermal effects. The creation of crystal motion via the photothermal effect will expand the designability and versatility of mechanical crystals in the future.

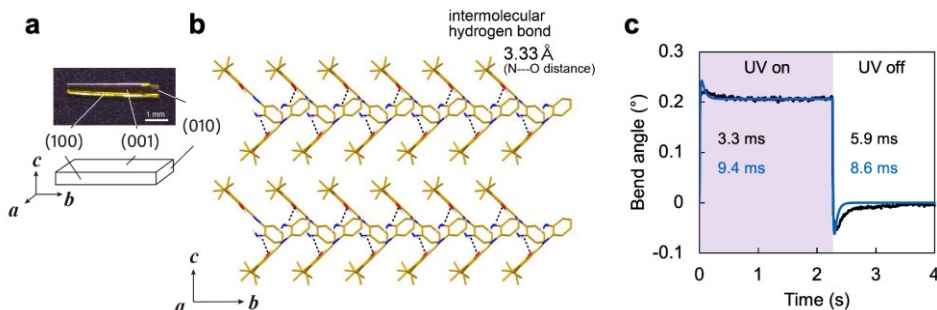


Figure 1. (a) Face indices of enol-1 crystal. (b) Two-fold helical arrays formed via intermolecular hydrogen chain along the *b* axis on the (100) side face. (c) Time dependence of measured (black) and simulated (blue) bend angle. The numbers indicate time constants.

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