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Photoinduced multi-directional deformations were first achieved with plate-like crystals of 4-cyano-4'-pentyloxy azobenzene. Upon UV irradiation, three separate types of photomechanical motions (bending towards and away from a light source, and fully bi-directional motions) were observed at different temperature regimes, which demonstrate that the critical temperature could have a great influence on the direction of motion, and could enrich the applications of the photochromic crystalline materials.
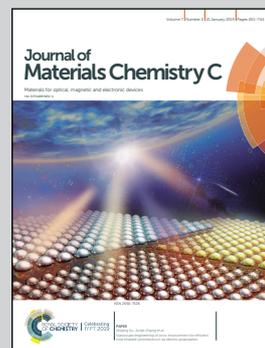
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PAPER

Photoinduced multi-directional deformation of azobenzene molecular crystals†

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Developing biomimetic stimuli-responsive materials to imitate movements found in plants and animals has been a very exciting research field in materials science and engineering. However, achieving multiple forms of motion with a mono-component material is still extremely challenging. Here, photoinduced multi-directional deformations were firstly achieved with plate-like crystals of 4-cyano-4′-pentyloxy azobenzene (AZ). Upon irradiation of UV light, three separate types of photomechanical motions are observed in different temperature regimes: Firstly, a rapid and reversible photomechanical bending away from the light source was achieved when the temperature was kept below the melting point of *cis*-AZ (MPCA). Secondly, photoinduced bending towards the light source was observed when the temperature was higher than the melting point of MPCA. Thirdly, fully bidirectional motions were achieved in the temperature regime below but near the melting point of MPCA, due to a competition between photoisomerization-induced volume expansion and phase-transition caused volume contraction, aided by a photothermal effect. The light-directed multi-directional motions of the same crystal sample under the same photoirradiation conditions enabled by temperature tuning demonstrated here signify a new and versatile class of photocontrollable mono-component molecular crystals and provide a novel level of control of operation for photomechanical actuators by combination of photoisomerization and photothermal effects.

Introduction

In nature, motion in response to sunlight is an important prerequisite for the basic function of many living things. For example, positive phototaxis of most plants (such as sunflowers) directs them to grow towards the sun, whereas negative-phototaxis demonstrating animals (such as snails) dislike illumination and move backwards in response to sunlight. Developing biomimetic stimuli-responsive materials that similarly capture these movements towards or away from a light source has been a very exciting research field in materials science and engineering.[1,2] Recently, one-dimensional or two-dimensional ordered condensed state materials with photoresponsive characteristics have aroused wide interest due to their ability to directly convert light energy into mechanical work, known as photomechanics.[3–15] While some of the earlier studied systems were based on polymers or liquid crystals (LCs), photomechanical motion in several different varieties of molecular crystals has been studied more recently, as the high degree of molecular order in crystals can magnify the effects of local stresses caused by local molecular perturbations.[16–23] Compared with soft materials such as LC elastomers,[24–26] photomechanical crystalline materials exhibit a more rapid energy transfer, faster response and relaxation.[27,28]

Azobenzene and its derivatives are some of the most typically employed photochromic molecules, as they exhibit a quick and reversible *trans–cis* isomerization. A big difference in geometric shape and molecular size often exists between the *trans*- and *cis*-isomers, which can be harnessed to produce macroscale mechanical motion in the bulk arising from microscopic molecular shape changes.[27–30] However, nearly all the reported azobenzene class crystals can only respond to light in one direction (asymmetric illumination) and possess only one direction of photomechanical motion either towards or away from a light source, which limits their applications. Previous work has mainly been focused on photoinduced volume changes of the irradiated crystalline near-surface regions, yet it has neglected the influence of phase changes

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J. Mater. Chem. C, 2019, 7, 503–508 | 503

of crystals, possibly due to concern over the destruction of the crystal structure and the difficulty of providing local temperature control. In addition to photoisomerization, azobenzene derivatives can also exhibit photothermal effects leading to elevated temperatures concurrent with the photoirradiation.[31,32] Combining these two effects together, advanced photoactuators have been fabricated by incorporating azobenzene groups into polymer systems, where each of the two components (backbone and side chain) exhibits a competing effect.[33–35] But, it still remains a challenge to combine photoisomerization and photothermal effects to achieve complex motion control of simple single-component materials.

In this paper, photoinduced multi-directional motions of monocomponent crystals under the same irradiation conditions but at different temperatures were achieved with plate-like crystals of 4-cyano-4′-pentyloxy azobenzene (AZ). The molecular mechanisms underlying the photomechanics were systematically investigated from the viewpoints of molecular arrangement, phase states, and limitations of the crystal lattice size. The volume expansion in the irradiated near-surface regions was controlled by UV light to isomerize the AZ, and temperature control could induce a local phase change to trigger photo-contraction. Thus, the volume expansion caused by the photoisomerization of AZ enabled the crystals to bend away from a light source, while the volume contraction induced by the phase transition caused the crystals to bend towards the light source. By elaborately adjusting the order and relative magnitude of these two competing effects, with both light and heat, sophisticated complex bending, recovery, and then opposite-directional re-bending of AZ crystals was accomplished by controlling the competition between photoisomerization and photothermal effects upon irradiation of one beam of single-wavelength light.

Results and discussion

Characterization of the AZ crystals

The synthesis and characterization of the compound are given in the ESI† (Scheme S1 and Fig. S1). As shown in Fig. 1b, the photoisomerizable dye forms good plate-like crystals, and its molecular arrangement was analysed by single crystal X-ray diffraction (SXRD). The top surface of the plate-like crystals was identified as the (200) Miller plane based on crystallographic data (Fig. S2, ESI†), with its vertical direction along the a-axis. There is an angle of 42.9° between trans-molecules and the (200) surface (Fig. 1c), and a dihedral angle of 36.4° exists between two independent neighbouring molecules, forming a herringbone structure along the a-axis (Fig. 1d).

The melting point of trans-AZ (MPTA) was observed at 108 °C in its DSC curve (Fig. S5a, ESI†). To evaluate the thermal properties of the cis-isomers, the crystals were kept at 80 °C and exposed to 365 nm UV light for 2 min, and then quenched in liquid nitrogen. Thus, a new gentle endothermic peak appeared at 74–83 °C in Fig. S5b (ESI†), which can be assigned to the melting point of cis-AZ (MPCA). Detailed experimental information and PXRD data are also provided in Fig. S5 (ESI†). Since the melting point gap between the two isomers is large,
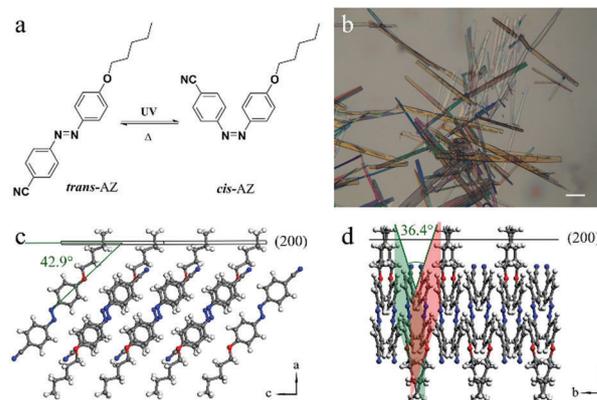

Fig. 1 (a) Molecular structure and photoisomerization of AZ, and (b) optical microscope images of the plate-like trans-AZ crystals. The scale bar is 200 μm. The molecular arrangements of the (200) surface viewed from (c) the b-axis and (d) the c-axis.

the temperature for photomechanical studies can be divided into two regions: (1) below the melting point of MPCA, where both trans- and cis- molecules are in the solid state, and (2) above the melting point of MPCA but below the melting point of MPTA, where cis-AZs melt into liquid yet trans-AZs maintain the solid state. Under the same photoirradiation conditions, the crystals should thus exhibit a different photomechanical response in each of the two different temperature regions.

Motion 1: reversible bending away from the light source

Polarizing optical microscopy (POM) was used to investigate the photoinduced deformation of the AZ crystals, with one end free and the other end fixed to the glass surface. As shown in Fig. 2a and Movie S1-1 (ESI†), upon photoirradiation of the (200) surface from the left front with UV light (365 nm, 500 mW cm^{-2}) at 0 °C, the crystals quickly bent away from the light source to reach a maximum tip displacement of 52 μm within 0.2 s (Fig. 2b). Photoirradiation for longer durations did not lead to any further
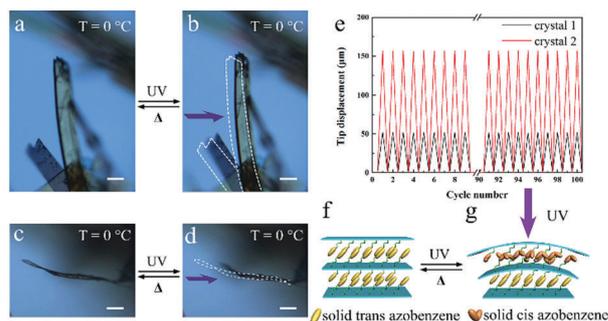

Fig. 2 Photoinduced reversible bending motion of the plate-like trans-AZ crystals at 0 °C: (a) before irradiation and (b) after UV irradiation of the (200) surface from the left front. Another narrow plate-like trans-AZ crystal (c) before irradiation and (d) after UV irradiation of the (200) surface from the left front. The incident direction of light is indicated by the arrow, and the scale bar is 100 μm. (e) The repeatability of the bending motion of the two crystals can be observed over 100 cycles. (f and g) Schematic illustration of the reversible bending motion away from the light source. Only a limited number of layers is shown for simplification.

504 | J. Mater. Chem. C, 2019, 7, 503–508

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significant deformation of the crystals. Subsequent removal of the illumination resulted in the immediate return to its initial shape. This reversible bending motion backwards from the light irradiation is marked as Motion 1. A similar reversible sequence of motions was also observed for narrow plate-like crystals, which bent away from UV light to reach a maximum tip displacement of 157 μm within 1.5 s (Movie S1-2, ESI† and Fig. 2c, d). These differences in bending magnitude demonstrate that the crystal morphology and the thickness could somewhat affect the degree of tip displacement of Motion 1 but would not affect the bending direction. Both the reversible bending motions were repeated over more than 100 cycles (Fig. 2e) without any detectable fatigue observed. The photomechanical bending process of the crystals was observed to depend on the light intensity. When a crystal was exposed to UV light with variable intensity ranging from 50 to 500 mW cm^{-2} at 0 °C, the maximum tip displacement increased linearly from 4 to 52 μm, in proportion to the light intensity (Fig. S6, ESI†).

Motion 1 of the crystals was also investigated at different temperatures in range (1) (below MPCA). Under the same photoirradiation conditions, there were no obvious changes observed in the level and direction of the bending motion when the temperature was set below 45 °C. When increasing the temperature from 45 to 70 °C, the maximum tip displacement decreased with increasing temperature (Fig. S7, ESI†), which can be ascribed to the thermally enhanced *cis*-to-*trans* back-isomerization leading to a lower concentration of *cis*-isomers in the photostationary state.

Generally, the molecular geometric deformation caused by photoisomerization of azobenzene leads to macroscopic shape changes, yet the bending direction is also often influenced by the molecular arrangement on the irradiated crystal surfaces.[36,37] When azobenzene molecules lie parallel with the irradiated surface, volume contraction is generally produced, resulting in a bending motion towards the light source.[33] Conversely, volume expansion is observed when azobenzene molecules lie perpendicular to the irradiated surface, leading to a bending motion away from the light source.[27] Thus, powder X-ray diffraction (PXRD) and AFM measurements were used to investigate the structural changes in molecules and crystals upon photoisomerization, relative to their orientation to the crystal face.[38] As shown in Fig. 3a and b, all the PXRD peak intensities decreased, and the peak positions slightly shifted to higher angles on continuing illumination of UV light. Taking the (200) crystal face as an example, the peak intensity decreased to 72% of the original value, while the full width at half maximum and peak area increased slightly, likely due to the *trans–cis* photoisomerization and a corresponding deterioration of crystallinity. Meanwhile, it was found that the 2θ angle shifted from 4.820° to 4.980° and the *d*-spacing decreased from 18.316 Å to 17.730 Å, indicating that parts of the unit cell structure had been re-arranged significantly upon photoirradiation. When the irradiation ceased, the original PXRD patterns appeared (Fig. 3c). The parametric variations of other crystal faces are listed in Table S2 (ESI†). During the photoirradiation, no new PXRD peaks appeared, suggesting that the *cis*-isomers did not form a new crystalline phase in this temperature region. This was further confirmed by the
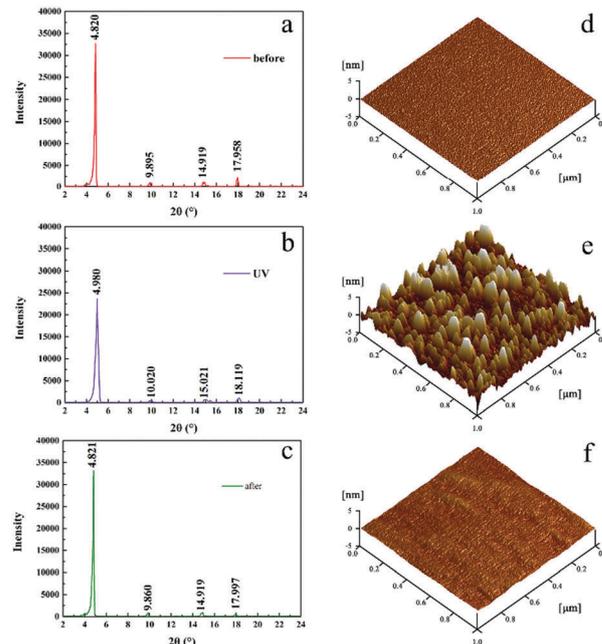

Fig. 3 The change of crystal structure and surface topology of the plate-like *trans*-AZ crystals upon UV irradiation at room temperature: PXRD patterns of the *trans*-AZ crystals (a) before irradiation, (b) on maintaining 365 nm ultraviolet irradiation, and (c) after stopping UV irradiation. AFM images of the (200) surface of one *trans*-AZ crystal (d) before illumination, (e) upon irradiation with 365 nm light during measurement, and (f) after stopping illumination.

measurement of surface topological changes with AFM. As presented in Fig. 3d, a smooth top surface was clearly observed for the as-prepared crystals. Upon UV irradiation, crinkle-like features appeared on the crystal surface with increased roughness from 0.193 to 1.36 nm (Fig. 3e), suggesting that the molecular arrangement becomes disordered on the short-range length scale in the irradiated areas. After irradiation, these surface crinkles decreased in size and finally disappeared (Fig. 3f).

Considering the molecular arrangement, the change in crystal cell structures, and the surface topological changes in the irradiated parts, a possible model is proposed in Fig. 2f and g to rationalize the mechanism of Motion 1. Under the UV illumination, the planar ordered *trans*-AZs isomerize into V-shaped *cis*-AZs requiring a larger dimension in the plane of the crystal face than that of the rod-like *trans*-AZs. This should produce an expansion along the *b*- and *c*-axes and lead to the crinkly topologies as surface bucking occurs to relieve strain, which agrees with the results of the AFM measurements. Since the *cis*-AZs pack to a smaller dimension in the vertical axis than the *trans*-AZs, the increase in the packing density should cause a contraction along the *a*-axis, which is consistent with the decreased *d*-spacing observed by PXRD. Hence, the irradiated surface would be expected to expand in the direction along the face, and contract in the direction normal to it, while the unit cell dimension remained invariant at the non-irradiated surface. The molar extinction coefficient of the AZ groups is high, with absorbance values typically on the order of 10 s per micrometer,[3,4] so it can be assumed that all the light is

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J. Mater. Chem. C, 2019, **7**, 503–508 | 505

effectively absorbed in the first several hundred nanometers, representing a near-surface volume region of morphology changes below the surface receiving the irradiation. Thus, mechanical stress produced in this near-surface region is transmitted into the inner dark regions of the crystal, leading to a bending motion away from the light source, which is similar to a so-called bimetal mechanism.[39] It is worth noting that the physical connection between each layer relies on the intermolecular forces between alkyloxy chains rather than covalent bonds. Thus, the AZ molecules are limited in the crystal lattice although they are isomerized upon photoirradiation, which guarantees the reversibility of the photoinduced deformation. However, there still exists a component of mechanical stress between the layers that could not be transmitted but will instead relax by sliding,[40] leading to a photomechanical motion with only a slight deformation but a fast speed.

Motion 2: incompletely reversible bending towards the light source

When the temperature was set in range (2) (above the melting point of MPCA but below the melting point of MPTA), the crystals exhibited a different photomechanical behaviour, as shown in Movie S2 (ESI†). Upon irradiation of the (200) surface from the left with UV light (365 nm, 100 mW cm^{-2}) at 85 °C (Fig. 4a), the crystal gradually bent towards the light source, which was accompanied by the appearance of a dark-coloured liquid drop on the irradiated surface, appearing to deepen the colour of the entire crystal (Fig. 4b). After stopping the illumination, the crystal partially returned to its initial state, along with the liquid drops partially disappearing (Fig. 4c). This photoinduced bending towards a light source is marked as Motion 2. Here, a parameter F is introduced to quantitatively describe the bending degree of the crystal, which can be calculated by the following equation:

$$F = \frac{L_0 - L}{L_0}$$

where L_0 and L are the linear lengths of the crystal before and after the deformation, respectively. Under the same irradiation conditions, the F value increased with increasing temperature (Fig. S8, ESI†).

Similarly, AFM analysis was used to evaluate the change in the crystal surface topology upon photoirradiation. Compared with the smooth surface before irradiation (Fig. 5a), a significantly rougher surface was observed (the roughness increased from 0.597 to 3.13 nm), as shown in Fig. 5b. When the illumination was stopped and the crystallinity presumably restored, the photoinduced deformation, however, did not completely recover.

Obviously, the mechanism of Motion 2 is substantially different from that of Motion 1; it is not photoisomerization-induced volume expansion, but instead derives from a photoinduced change in phase (from solid crystalline to isotropic liquid). Accordingly, this light-directed process can be divided into two steps: firstly, the *trans*-AZs in the near surface irradiated region are isomerized into *cis*-isomers (Fig. 4e), which then immediately undergo an isothermal phase transition from solid to liquid. This undoubtedly destroys the crystal structure and
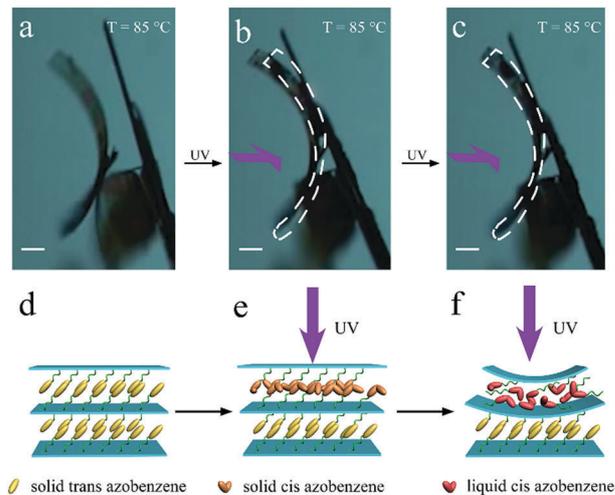

Fig. 4 Photoinduced incompletely reversible bending motion of the crystals at 85 °C: (a) before irradiation, (b) upon photoirradiation of the (200) surface from the left, and (c) returning to its initial shape after stopping the illumination. The incident direction of UV light is indicated by the arrow, and the scale bar is 100 μm. (d–f) Schematic illustration of the mechanism proposed for the bending motion towards the light source. Only a limited number of layers are shown for simplification.
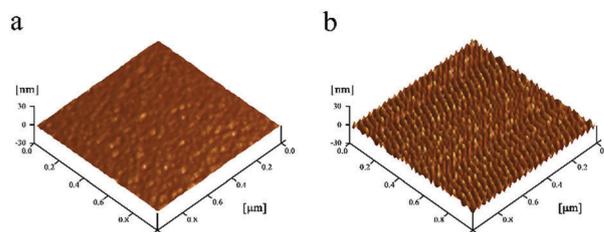

Fig. 5 AFM images of the (200) surface of a *trans*-AZ crystal (a) before illumination, and (b) recovery after UV irradiation (365 nm, 100 mW cm^{-2}) at 85 °C.

enables the *cis*-AZs to break the confinement of the crystal lattice and move randomly on the irradiated surface. Thus, volume contraction occurs in this region near the surface of the crystal while the not irradiated opposite face remains unchanged, causing the crystal to bend towards the light source, as shown in Fig. 4f. Following the melting of the upper surface, *cis*-AZ molecules in the liquid state flow away and a new surface layer gets exposed to light and is again melted away. This is possibly why the bending towards the light source has a higher curvature but a lower speed than Motion 1. After stopping the illumination, *cis*-AZs back-isomerize thermally to *trans*-isomers, which are then recrystallized into ordered crystalline phases after 1 min. Due to the random thermal motions in the intermediate process, the crystal structure before and after the photoirradiation is different (Fig. 4a and c). As a result, the crystal cannot completely recover to its initial shape.

To eliminate the possibility of macroscopic deformation caused by crystal cells sliding at high temperatures, AZ crystals were ground up and heated from 25 °C to 100 °C. No obvious changes were observed in the PXRD data shown in Fig. S9 (ESI†),

indicating that the *trans*-AZs have high thermal stability. Therefore, the synergistic effect of a sufficient temperature and irradiation of UV light is a prerequisite for Motion 2.

Motion 3: bidirectional bending motion upon photoirradiation

Then, the photoinduced bidirectional bending motion of *trans*-AZs was investigated. This interesting phenomenon has been observed in diarylethene crystals by combining photochromic reaction and a reversible single-crystal-to-single-crystal phase transition upon changing the wavelength of incident light.[42,43] Here, we are focusing on a combination of photoisomerization of azobenzene and its crystal-to-isotropic phase transition induced by photothermal effects. Azobenzene chromophores are well known to increase their temperature after they are exposed to UV light with high intensity, so the contribution of photothermal effects also needs to be considered. As shown in Fig. 6, the temperature of crystals increased rapidly from 25 °C to 84 °C within 5 s upon photoirradiation (500 mW cm^{-2}), then they remained at a constant temperature when the irradiation time reached 10 s. The highest temperature recorded was higher than the MPCA.

To combine photothermal effects with photoisomerization, the photoresponsive behaviours of *trans*-AZ crystals were investigated at 70 °C (near but below the MPCA). As shown in Fig. 7 and Movie S3 (ESI†), when the (200) surface was continuously exposed to UV light (365 nm, 500 mW cm^{-2}) from the left, the crystals first bent away from the light source (Fig. 7b), then returned to their initial position (Fig. 7c), and next bent towards the incident light (Fig. 7d). This bidirectional bending motion is marked as Motion 3.

Here, UV light was not turned off when the crystals returned to their original position, which is very different from all the previously-reported phenomena and also different from Motion 1 and Motion 2. Generally, the recovery process of crystals requires another stimulus, such as thermal-back-isomerization by stopping irradiation[27] and irradiation at different wavelengths.[19,20,38,41] This bidirectional bending motion can be rationalized as follows: firstly, *trans*-to-*cis* photoisomerization induces volume expansion in the irradiated near-surface region, leading the crystals to bend away from the light source (Fig. 7e and f), which is consistent
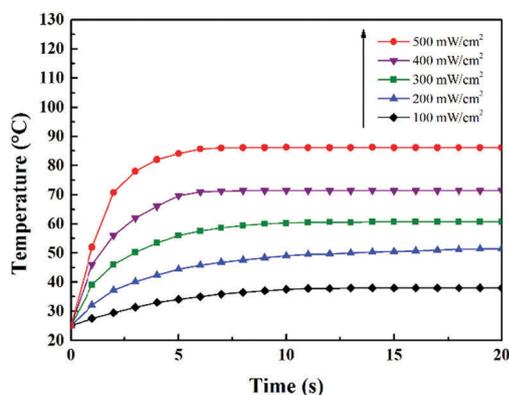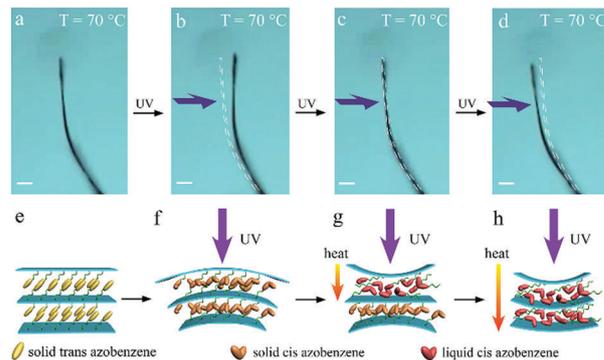
Fig. 7 Photoinduced bidirectional bending motion upon photoirradiation of the crystal at 70 °C: (a) before irradiation, (b) upon continuous photoirradiation of the (200) surface from the left, the crystal first bent away from the light source, then (c) returned to its initial position, and (d) next bent towards the incident light. The incident direction of UV light is indicated by the arrow, and the scale bar is 100 μm. (e–h) Schematic illustration of the bidirectional bending motion upon irradiation of UV light. Only a limited number of layers are shown for simplification.

with Motion 1. Secondly, with continuous light irradiation, the temperature of the irradiated upper surface increases up to the melting point of MPCA, causing the *cis*-AZs exposed to the light to melt. Thus, volume contraction of the upper irradiated surface occurs. Meanwhile, the *cis*-AZs not exposed to the light (far below the surface) remain solid. These expansions and contractions of volume have a competitive relationship, so when they are at equilibrium, the crystal will return to its initial shape (Fig. 7g). Finally, when the temperature is higher than the melting point of MPCA due to photothermal effects, the volume contraction of the irradiated surface region gradually assumes the leading role, resulting in the crystals bending towards the light source (Fig. 7h). Essentially, the difference between Motion 2 and Motion 3 is just in the way that the thermal energy is introduced and conducted away. The temperature of the whole crystal is uniform in Motion 2. However, in Motion 3, the thermal energy was transferred into the interior of the crystal layer by layer through the UV irradiation.

Conclusions

In summary, using a very simple method and without sophisticated molecular design, plate-like AZ crystals were successfully fabricated. The volume change of the irradiated crystal surfaces at different temperatures enabled the crystals to exhibit photoinduced multi-directional motions. When the temperature was controlled below the melting point of MPCA, a rapid and reversible bending away from the light source was realized due to photoisomerization induced volume expansion. When the temperature was well above the melting point of MPCA, a photoisomerization induced phase transition from crystal to isotropic phases caused volume contraction in the irradiated surface regions, leading the crystals to bend towards the light source. When the temperature was set below but near the melting point of MPCA, the crystals underwent a bidirectional deformation process. They first bent

Fig. 6 Change of temperature of crystals as a function of time upon irradiation with 365 nm UV light.

away from the incident light and then returned to their initial position, and then next bent towards the light source, due to the competition between photoisomerization-induced volume expansion and phase transition-caused volume contraction. This study provides a further illustration of the versatility of these AZ molecular crystals as complex photoresponsive systems and confirms that photoinduced multi-directional mechanical modes can be achieved by a combination of photoisomerization and photothermal effects. This work is also a rare demonstration of the critical effect in which temperature could have a great influence on the direction of motion, enabling photochromic crystalline materials to be utilized as a critical temperature indicator and light-driven biomimetic swimmer, which is currently under study.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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