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Introduction

Stimuli-responsive crystal materials can change their chemical or physical properties in response to external stimuli, such as temperature, light, mechanical stress, electricity, pH, and so on,1-14 which has aroused great interest in materials science and engineering for their applications as actuators,^{15–18} sensors,¹⁹ switches²⁰ and biomimetic materials.²¹ The most widely used strategy to construct stimuli-responsive crystal materials is to take advantage of specially designed functionalities of molecules. For instance, macroscale photomechanical motions may arise from photoreactions of molecules such as trans-cis photoisomerization of azobenzene derivatives,^{5,6} photocyclization of diarylethenes,^{22,23}

Azobenzene crystal polymorphism enables tunable photoinduced deformations, mechanical behaviors and photoluminescence properties[†]

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Stimuli-responsive molecular crystals are fascinating for their potential as adaptive smart materials. However, achieving crystals that could respond to multiple stimuli and perform multiple functionalities simultaneously is still a challenging task. Herein, we report the fabrication and preparation of polymorphic crystals with multiple stimuli of a photoactive azobenzene derivative, trans-4-cyano-4'-oxethyl azobenzene (AzC₂). Different polymorphic forms of AzC₂ exhibit remarkable different photoinduced deformations, mechanical behaviors and photoluminescence properties. Upon UV irradiation, although both polymorphic forms undergo reversible photomechanical bending motions, Form I bent away from the light source while Form II bent towards the light source. Upon exertion of external mechanical stress, Form I tended to break whereas Form II exhibited elastic deformation. Furthermore, being excited at 325 nm, the block crystal of Form I exhibited a relatively strong green-yellow emission while a very weak red fluorescence emission was observed from the thicker Form II crystal. These different properties can be attributed to different molecular packings rather than molecular conformations. The present work provides an effective strategy to construct multiple stimuli-responsive crystal materials with potential applications in actuators, switches and sensors.

> and photodimerization of anthracenes.^{2,24} However, most of these kinds of crystal materials are generally responsive to one stimulus or possess one responsive mode. Moreover, the complicated synthesis of these different molecules also increases the production cost, which apparently limits their practical applications.

> To enhance the versatility and extend multifarious applications of such materials, researchers have developed multi-stimuli responsive and multi-functional crystal materials.²⁵⁻³⁰ Recently, the synthesis of cocrystals via non-covalent interactions has been proved to be an effective strategy for developing multi-stimuli responsive and multi-functional crystal materials.31,32 Naumov et al. reported a cocrystal with thermally twistable, photobendable, elastically deformable and self-healing properties by the co-crystallization of 4,4'-azopyridine with probenecid.33 However, it could be a difficult and time-consuming task to find appropriate host molecules and guest molecules to synthesize the target cocrystal with ideal properties. Also, the stability of the cocrystal could be another issue when the weak strength of the non-covalent interactions is considered.³⁴ In comparison, manipulating crystal polymorphs of the same functional molecules by regulating the conformation and packing during the crystal nucleation and growth processes is more convenient and efficient. Generally, the solid-state structure of functional molecules plays an important role in their performance, and some polymorphs may exhibit

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significantly different properties like colors,³⁵ mechanics,^{36,37} luminescence^{38–40} and electrical features.³⁷ Under appropriate conditions, crystalline polymorphs could undergo a single-crystal-to-single-crystal (SCSC) phase transition,^{22,31,40,41} which provides the potential for making multi-stimuli responsive and multi-functional crystal materials by manipulating different polymorphs of the same compound. However, development these kinds of crystalline materials has been scarcely reported.

Azobenzene derivatives are among the most promising candidates to prepare multi-responsive crystal materials due to their superior characteristics. First, they exhibit a quick and reversible trans-cis photoisomerization, in which a large difference in geometric shapes and molecular sizes often exists between the isomers, leading to macroscale deformation in bulk. A variety of molecular crystals of azobenzene derivatives have been prepared to undergo various photomechanical deformations.42-45 Recently, we reported mono-component molecular crystals of 4-cyano-4'pentyloxy azobenzene with multi-directional deformation ability.46 Second, the multitude and moderate intermolecular interactions in the molecular structures of azobenzene derivatives make them potential candidates for designing elastic crystals.^{36,47} However, mechanical behaviors of azobenzene crystals under mechanical stress are also rarely studied. Third, azobenzene derivatives are often non-fluorescent due to photoisomerization. Nevertheless, relatively weak fluorescence has been occasionally observed when photoisomerization is suppressed in the crystalline state,48-50 as a result of crystallization-induced emission (CIE).51,52 Herein, we report two crystal polymorphs of 4-cyano-4'-oxethyl azobenzene (AzC₂), exhibiting remarkable difference in photomechanical deformation, mechanical properties and luminescence. This work may inspire more investigations on constructing multiple stimuliresponsive crystal materials through polymorph manipulation.

Results and discussion

Crystal growth and structural analysis of polymorphs

As shown in Fig. S1 (ESI⁺), trans-AzC₂ was synthesized in 84% yield.⁴⁶ Here, AzC₂ was selected as one representative example for several reasons: (1) its electrons are easily excited because of the stronger conjugation from the push-pull structure, (2) its para-substituents are stable enough to resist chemical reactions during experiments, (3) the oxethyl chain acts as the end-group for acquiring free space that permits isomerization, and the chain flexibility is easily controlled to avoid the formation of conformational polymorphs. Fig. 1 shows the crystallization of trans-AzC₂ by sublimation on quartz slide-generated microcrystals with plate habits, while microcrystals with good needle habits were obtained through epitaxial crystallization on the (100) surface of the KBr substrate. More details on crystallization and characterization are given in the ESI.[†] X-ray diffraction analyses confirm that the two crystalline habits correspond to different polymorphs, hereafter referred to as Form I (plate crystal) and Form II (needle crystal) (Table S1, ESI[†]). Both of them belong to the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit. The molecules in the



Fig. 1 (a) Molecular structure and photoisomerization of AzC₂. (b) Optical microscopy images of the plate-like Form I crystals and (c) needle-like Form II crystals. The scale bar is 100 μ m. (d) Comparative PXRD patterns of two polymorph crystals. Crystal packing in (e and f) Form I and (g and h) Form II.

two forms have almost identical conformation (Fig. S6, ESI⁺). However, they adopt significantly different packing patterns to have different cell parameters. As shown in Fig. 1e, the molecules in Form I are $\pi \cdots \pi$ stacked (3.44 and 3.47 Å) in alternately anti-parallel patterns along the *c*-axis. Then, the stacked columns are connected by C-H···H intermolecular interactions to form parallel tapes along the $[\bar{1}02]$ direction. The adjacent tapes are connected via very weak dispersion interactions to further form a herringbone arrangement (Fig. 1e and f). In Form II, on the other hand, the molecules are $\pi \cdots \pi$ stacked (3.36 Å) in parallel patterns along the a-axis. Then, the stacked columns are connected by C-H···N, C-H···C and C-H···O along the *c*-axis in a middle-to-middle way to form a crossing structure, which is further expended along the *b*-axis via $C-H \cdots N \equiv C$ and C-H···H intermolecular interactions (Fig. 1g and h). Their dominant surfaces were indexed based on SEM observations, combined with the results of preferred orientation from PXRD and the calculated Miller indices based on crystallographic data (Fig. S8 and S9, ESI[†]).^{32,53}

In order to investigate their structural stability, two polymorph crystals were grinded and heated from 25 °C to 120 °C. No obvious peak shifts were observed in the variabletemperature PXRD patterns in Fig. S11 (ESI†), indicating that both polymorph crystals have good thermal stability. Moreover, even after continuous grinding for 10 min, the crystal structure of both polymorphs did not change, indicated by their PXRD patterns before and after grinding (Fig. S12, ESI†). This means that the external force of grinding does not affect the crystal structure. Both polymorphs are relatively stable and cannot transform to each other, due to their far different molecular packings. These characteristics make these two polymorphs exhibit completely different properties under the same stimulus conditions.

Photomechanical deformation

Like other azobenzene derivatives, AzC2 exhibited reversible isomerization upon irradiation with UV light and thermal relaxation (Fig. S13 and S14, ESI⁺), which played an important role in photomechanical deformation. When the main microcrystal surface of Form I and Form II was exposed to the same UV irradiation, respectively, photomechanical deformations were observed in both forms, but in opposite direction. Form I bent away from the light source, while Form II bent towards the light source. As shown in Movie S1 (ESI⁺) and Fig. 2a, one end of the plate-like microcrystal of Form I (size: 2926 μ m \times 228 μ m \times 10 μ m) is free while the other end is fixed to a syringe needle. Upon photoirradiation of the (020) surface from the left front with UV light (365 nm, 150 mW cm⁻²), the microcrystal quickly bent away from the light source to reach a maximum tip displacement of 346.64 µm within 0.2 s. Subsequent removal of the illumination resulted in the immediate return of its initial shape. A similar reversible sequence of motions in opposite direction was observed for the needle-like microcrystal of Form II (size: 2847 μ m \times 27 μ m \times 24 μ m). It bent towards the light source to reach a maximum tip displacement of 295.45 µm within 1 s when UV light irradiated the (012) surface from the left front (Movie S2, ESI[†] and Fig. 2b). After the irradiation was terminated, the crystal of Form II instantly regained its original straight shape. Both the reversible photomechanical bending and unbending motions were repeated more than 20 cycles (Fig. S15, ESI[†]) without any detectable fatigue observed. During irradiation, the temperature of the two polymorphic microcrystals did not apparently increase, which excluded the possibility of photothermal effects contributed to photomechanical deformations (Fig. S16, ESI[†]). Additionally, the directions of UV irradiation did not affect the photomechanical behaviors of the two polymorphic microcrystals, and photoirradiation for longer durations did not lead to any more significant deformation of the two polymorphic microcrystals either (Fig. S17, S18 and Movies S3, S4, ESI[†]).

Photoinduced bending has been the most frequently reported motion of mechanical molecular crystals so far,¹⁰ and it has been ascribed to the so-called bimetal mechanism.⁵⁴ Generally, the bending direction depends on the nonuniform change in the crystal unit volume caused by the change of molecules on the



Fig. 2 Photoinduced reversible deformation: (a) one plate-like Form I microcrystal bent away from the light source upon irradiation on the (020) face, and (b) one needle-like Form II microcrystal bent towards the light source upon irradiation on the (012) face.

irradiated surface upon photoirradiation. However, it is difficult to determine the structure after isomerization because this photochemical reaction often occurs in a range of only a few microns on the surface and the products have very short half-lives. Powder X-ray diffraction (PXRD) is one of the most powerful methods to identify and characterize the subtle variations of lattice in the surface. As shown in Fig. 3a and b, all the PXRD characteristic peak intensities of Form I and Form II microcrystals decreased and broadened upon continuous illumination of UV light, indicating that microstrain was generated in both crystal lattices due to photoisomerization.5,6 In addition, the peak positions of Form I slightly shifted to larger angles, while the peak positions of Form II slightly shifted to smaller angles. These results suggest that the interplanar spacing of the irradiated surfaces contracts in Form I while expands in Form II upon UV irradiation (Bragg's law, Equation 1 in the ESI[†]). Particularly, new peaks appeared at $2\theta = 6.36^{\circ}$ in Form I while new peaks appeared at $2\theta = 16.42^{\circ}$ in Form II, suggesting that a new crystalline phase formed in both polymorphs on photoisomerization.

This was further confirmed by the AFM measurements of surface topological changes in the two crystal polymorphs. As shown in Fig. 3c and e, smooth top surfaces were clearly observed for the as-prepared crystals in both polymorphisms. Upon UV irradiation, crinkle-like features appeared on both crystal surfaces with an increased roughness from 0.193 to 3.86 nm in Form I (Fig. 3d), and from 0.091 to 7.11 nm in



Fig. 3 Change of crystal structure and surface topology of two polymorphic microcrystals upon UV irradiation at room temperature: PXRD patterns of (a) one plate-like Form I crystal and (b) one needle-like Form I crystal before and during irradiation, respectively. AFM images of the (020) surface of one plate-like Form I crystal (c) before illumination, and (d) upon irradiation with 365 nm light during measurements. AFM images of the (012) surface of one needle-like Form II crystal (e) before illumination, and (f) upon irradiation with 365 nm light during measurement.

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Form II (Fig. 3f). These results suggested that the molecular arrangement in each polymorph becomes disordered on the short-range length scale in the irradiated areas.⁵ In addition, Form II has a rougher surface compared to Form I. The narrower and higher crinkle-like feature of Form II indicates that its photoisomerization ability is better than that of Form I. These phenomena are consistent with Raman experimental results (Fig. S14, ESI[†]).

Then, the possible mechanisms of photomechanical bending behaviors of these polymorphic microcrystals are discussed below. According to the results of molecular simulations, the length, width and thickness of the *trans*-AzC₂ molecule on the (020) face of Form I increased by 30.26%, and decreased by 9.03% and 36.33%, respectively, after photoisomerization (Fig. S19a–d, ESI†). This should produce an expansion along the *c*-axis and lead to the crinkle topologies as surface bucking occurs to release the strain, which agrees well with the results of the AFM measurements (Fig. 3d). This also produces a contraction along the *b*-axis, which is consistent with the decreased *d*-spacing observed by PXRD (Fig. 3a). The overlay of packing arrangements of *trans*- and *cis*-AzC₂ is given in Fig. 4a. Hence, the irradiated microcrystal surface would expand in the direction along the microcrystal growth, and contract in the direction along the cross-section to induce a



Fig. 4 Schematic illustration of the reversible photoinduced bending motion of two polymorph crystals. (a) Overlaid molecular packing of Form I (blue) and *cis*-isomer (green) on the (020) face and perpendicular to the (020) face, respectively. (b) Overlaid molecular packing of Form II (red) and *cis*-isomer (green) on the (012) face and perpendicular to the (012) face, respectively. The colored arrows indicate the direction of dimension changes. For clarity, all hydrogen atoms are omitted.

bending deformation away from the light source. On the other hand, on the (012) face of Form II, the length and width of the *trans*-AzC₂ molecule decreased by 23.39% and 24.40%, respectively, while the thickness increased by 10.34% upon photoisomerization (Fig. S19e–h, ESI†). This should produce a contraction on the irradiated (012) surface, and expands in the direction normal to it (Fig. 4b), which is consistent with the increased *d*-spacing observed by PXRD and the crinkle topologies of AFM (Fig. 3b and f). As a result, the photoinduced bending motion occurs towards the light source.

Mechanical behaviors

As mentioned above, the two polymorphs exhibit distinct photoinduced deformation behaviors upon photoirradiation. Interestingly, the two crystal polymorphs also exhibited different elastic mechanical properties. Upon application of external mechanical stress, Form I tends to break while Form II underwent elastic deformation.

As shown in Fig. 5a, the two ends of one plate-like Form I crystal were bound to double-sided adhesive tape. Then, an external force was applied at the middle of the major surface (020) of Form I, and the crystal instantly broke into two pieces (Movie S5, ESI†). Considering that the acicular Form II has two main crystal surfaces, we tested them separately. When an external force was applied perpendicular to the (012) surface, a semi-circular arc formed without any detectable fracture and crack observed simultaneously. This process was found to be reversible as the crystal straightened immediately upon withdrawal of the force (Fig. 5b and Movie S6, ESI†). This sequence can be repeated many times. Besides, a similar elastic bending deformation was observed when poked on the (020) surface of the same Form II crystal (Fig. 5c and Movie S7, ESI†), indicating that Form II has two-dimensional elastic mechanical properties.

Moreover, it was found that the elastic mechanical behavior of Form II is related to the crystal size. As shown in Fig. 5d and Movie S8 (ESI[†]), the much thinner crystal of Form II can easily



Fig. 5 (a) Brittle breaking of Form I crystal. Elastic bending of the same Form II crystal from (b) the (012) face and (c) the (020) face. (d) Plastic deformation of the much thinner Form II crystal.

exceed the threshold of elastic deformation and undergo plastic deformation when subjected to an external force. It was clearly observed that the thinner acicular crystal was elongated along its longest axis when it bent into an arc shape upon exerting pressure. Upon removal of external force, the deformed crystal gradually and slowly returned to its original shape but cannot be completely recovered, which is quite different from the fragmentation of Form I. However, the crystal would break into two pieces rather than deform permanently when it was bent beyond a threshold limit.

The surface morphology of Form II crystals was characterized by scanning electron microscopy (SEM), as shown in Fig. 6. The straight region of the crystals has a smooth surface, and one terminal is thicker than the other due to the growth direction of the crystals. In contrast, when one crystal was bent to the critical point of fracture, the thickness of the bent section in the middle was 12.66 μ m, which is narrower than the straight section in both terminals. In addition, stretching stripes appeared on the surface of the bent section, while the straight sections still remained smooth. These results indicate that the lattice of Form II is elongated parallel to the long axis of the acicular crystal and compressed in the vertical direction during bending deformation.

It is expected that both elongated and compressed deformations of the lattice of Form II crystals would influence the strength of the intermolecular interactions, which can be examined by micro-Raman spectroscopy at the molecular level (Fig. 7).⁴⁷ The strength of the $\pi \cdots \pi$ stacking interactions was probed by the position of the out-of-plane δ (C-N=N) mode⁵⁵ at 1146 cm⁻¹. Its intensity decreased on the convex (cx) side relative to the straight section, indicating that the $\pi \cdots \pi$ interactions become weaker after bending deformation, possibly in response to the expansion on the cx side. On the other hand, its intensity did not increase much on the concave (cc) side, probably because this mode is much more sensitive to tensile stress than to compression. The strength of the C-H···N and C-H···C



Fig. 6 SEM images of one bending Form II crystal (a) and the corresponding magnification (b-d).



Fig. 7 (a) An optical microscopy image showing one bent Form II crystal and the locations where the micro-Raman spectra were recorded (crosses). (b) Raman spectra were recorded for the concave (cc), convex (cx) and straight (s) regions of the bent Form II crystal.

interactions between the layers was probed by the position of the in-plane $\delta(C-N=N)$ mode at 1132 cm⁻¹. Its intensity increased simultaneously on the cx and cc sides relative to the straight section, demonstrating that the C-H···N and C-H···C interactions become stronger after bending deformation, which is consistent with contraction between the layers during the bending process.

To further investigate the relationship between the crystal structure and the mechanical property quantitatively, nanoindentation tests were performed on both polymorphs. In Form I, the elastic modulus and hardness of the (020) surface are 199.16 \pm 23.81 MPa and 15.71 \pm 8.06 MPa, respectively (Fig. 8a), which are consistent with those of the previously reported organic molecular materials.⁵⁶ The occurrence of popins is possibly due to a sudden slip during the breaking of the Form I crystal. Form II is comparatively softer in nature. Its elastic modulus is 5.42 \pm 1.88 MPa and its hardness is only



Fig. 8 Representative load-depth (P-h) curves obtained from nanoindentation on (a) the (020) face of Form I and (b) the (012) face of Form II crystals.

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 1.74 ± 0.45 MPa (Fig. 8b), which are in the same order of magnitude as those of soft materials such as rubber.⁵⁷ Furthermore, the elastic modulus of Form I is about 40 times higher than that of Form II, and its hardness is about 10 times higher than that of Form II. These results indicate that the molecular arrangement has a significant influence on the elastic mechanical properties of the crystals. Obviously, the cross-molecular arrangement makes the crystals more flexible than the layered arrangement. Considering that the mechanical properties along the long axis of the crystal growth are not suitable for nanoindentation tests, we measured the elastic modulus of Form II by stretching three individual single crystals (see Table S5, ESI⁺) by dynamic mechanical analysis (DMA). The storage modulus was found to be in the range of 14.479-16.159 MPa, and the loss modulus was in the range of 3.745–11.070 MPa. The loss tangent $(\tan \delta)$ was determined to be 0.259-0.685, suggesting that most of the energy generated by the external force is stored as potential energy, while another small part is dissipated as thermal energy during stretching. These results are consistent with the phenomena of plastic deformation of the thinner crystal in Form II.

Such difference in elastic mechanical properties can be attributed to the weak intermolecular interactions, which can be visualized by the independent gradient model (IGM) method, used in the cluster of the central molecule with other surrounding molecules within 3.8 Å. As shown in Fig. 9, the intermolecular interactions around the central molecule (yellow) are divided into three parts along the orthogonal direction, respectively: forming $\pi \cdots \pi$ stacking with the top and bottom molecules (purple), forming tape stacking with the molecules on the side (blue), and forming a slip plane with the head and tail molecules (pink). The large green sections of the isosurface should be interpreted as dispersion interactions, and the blue sections should be considered as hydrogen bond interactions. Obviously, the crystal of Form I shows high anisotropy, and the intermolecular interactions parallel to the poked (020) surface (Fig. 9a and b) are significantly greater than those perpendicular



Fig. 9 Visualization of intramolecular interactions of (a–c) Form I and (d–f) Form II. The intermolecular interactions around the central molecule (yellow) are divided into three parts along the orthogonal direction and investigated respectively: (a and d) forming $\pi \cdots \pi$ stacking with the top and bottom molecules (purple); (b and e) forming tape stacking with the molecules on the side (blue); (c and f) forming a slip plane with the head and tail molecules (pink). The large green sections of the isosurface should be interpreted as dispersion interactions, and the blue sections should be considered as hydrogen bond interactions.

to it (Fig. 9c). Particularly, there is a distinct blue region on the isosurface of the tape stacking. The Form I molecules are tightly connected along the (020) surface, resulting in a layered structure, which may account for the high elastic modulus and hardness of nanoindentation. As these layers are weakly interconnected, they can therefore break irreversibly when the crystals are stressed in the direction vertical to the molecular layers. In contrast, the Form II molecules are connected isotropically by moderate interactions (Fig. 9d-f). The isosurfaces of the three directions are all large green sections with some small blue areas. These interactions are weak enough to achieve free molecular motion for releasing the stress during deformation, yet strong enough to reform after the removal of external force. The flexibility makes the elastic modulus and hardness of Form II much smaller than those of Form I. The same conclusion can be drawn from the energy framework analysis: the interactions in Form I are highly anisotropic (Fig. S21a, ESI⁺) and the interactions in Form II are almost isotropic (Fig. S21b, ESI[†]).

Photoluminescence behaviors.

In addition to the different photoinduced deformations and mechanical properties, the two different polymorphs also exhibited different photoluminescence behaviors. Generally, crystals with a higher crystallinity have a narrower full width at half maximum (FWHM) of the characteristic peaks in their PXRD. Here, we chose the crystals with a higher crystallinity by comparing the FWHM to suppress the isomerization of AzC_2 molecules as much as possible, so as to investigate the photoluminescence behavior of both polymorphs.

As mentioned above, molecular azobenzene is a non-emissive π -conjugated group since the energy associated with the excited state is mainly dissipated for photoisomerization instead of emission.⁴⁸⁻⁵⁰ In order to investigate the ability of photoisomerization, the absorption spectra of AzC_2 in the free state (solution) and the crystalline state were characterized before and after irradiation, respectively. In THF, the free AzC2 compound underwent effective trans-to-cis isomerization upon UV irradiation (Fig. S22a, ESI[†]). The maximum absorption peak at 365 nm quickly decreased and shifted to 325 nm, and the peak at 448 nm increased after 3 s of UV irradiation (80 mW cm⁻²), corresponding to the $(\pi \rightarrow \pi^*)$ and $(n \rightarrow \pi^*)$ excitation, respectively. Compared to the free state, the UV-vis absorption spectra of the block Form I and thicker Form II crystals after irradiation remained almost unchanged before and after irradiation (Fig. S22b and c, ESI[†]). These results indicate that the ability of isomerization of the azobenzene crystals with higher crystallinity is suppressed since large conformational change requires sufficient free space.

In this case, however, weak photoluminescence was detected in both polymorphic crystals with higher crystallinity. Interestingly, far different fluorescence emission properties were observed from Form I crystals and Form II crystals due to their different molecular packings (Fig. 10a and b). Green-yellow photoluminescence was observed from Form I crystals under UV irradiation with emission maxima at 564 nm (the absolute fluorescence quantum yield $\Phi_{\rm PL} = 5.79\%$, $\lambda_{\rm ex} = 325$ nm) (Fig. 10c, blue solid line). In comparison, Form II crystals exhibited a very weak red emission Journal of Materials Chemistry C



Fig. 10 Fluorescent microscopy images of (a) Form I crystals and (b) Form I crystals with higher crystallinity. (c) Absorption and photoluminescence spectra displayed as solid and dashed lines, respectively.

at 616 nm ($\Phi_{\rm PL}$ = 1.53%) (Fig. 10c, red solid line) under the same irradiation condition (λ_{ex} = 325 nm). The CIE 1931 chromaticity diagrams (Fig. S23, ESI[†]) indicate that the coordinate of Form I is (0.402, 0.597) and that of Form II is (0.683, 0.317), respectively. There is a blue-shift for the absorption spectrum of Form I crystals (Fig. 6c, blue dash line) compared with that of Form II crystals (Fig. 6c, red dash line), which is consistent with the stronger π - π stacking structures in the Form I crystals. Furthermore, both polymorphs exhibit very large Stokes shifts (256 nm for Form I and 303 nm for Form II), which may be because the nonradiative process makes them lose parts of the excitation energy. Obviously, the Stokes shift of Form II crystals is larger than that of Form I crystals. In the meanwhile, the $\Phi_{\rm PL}$ of Form I crystals is about 4 times higher than that of Form II crystals, indicating that the luminescence ability of Form I crystals is better than that of Form II crystals. A possible reason for the difference in luminescence between these two polymorphic crystals is that the extent of photoisomerization of Form I is lower than that of Form II due to its fewer void space along the two orthogonal directions (Fig. S24, ESI[†]). Therefore, the non-radiative process of Form I is possibly lower than that of Form II, thus exhibiting a higher radiative phenomenon.

Conclusions

In summary, the influence of crystal polymorphs of an azobenzene derivative (AzC_2) on the photoinduced deformation, mechanical behaviour and photoluminescence properties was studied. By regulating the crystallization conditions, two crystal polymorphs of herringbone structure Form I and crossing structure Form II were successfully developed and prepared. These two crystal polymorphs show a remarkable difference in photomechanical bending motions, elastic mechanical properties and photoluminescence under the same stimulus. These distinct mechanical

and optical behaviors were attributed to different molecular packings rather than molecular conformations. Upon UV irradiation, the thin microcrystals of Form I bent away from the light source while Form II bent towards the light source, because the photoisomerization-induced lattice changes on the irradiated surface are different in both polymorphs. Upon exertion of mechanical stress, Form I tends to break whereas Form II exhibits elastic deformation, and the elastic modulus of Form I is about 40 times higher than that of Form II, owing to remarkable different intermolecular interactions generated by different molecular packings. Furthermore, when the isomerization of AzC₂ molecules is suppressed in the crystalline state, the block crystal of Form I exhibits a relatively strong greenyellow emission while a very weak red fluorescence emission was observed for the thicker Form II crystal under the same irradiated conditions. Moreover, the crystal structure of each polymorph is stable at high temperatures and even after continuous grinding for 10 min, which increases the durability of the crystals in practical applications. The results in this work provide an effective strategy for designing and preparing multiple stimuli-responsive crystal materials towards desired potential applications.

Conflicts of interest

There are no conflicts to declare.

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