

Mechanical Bending and Modulation of Photoactuation Properties in a One-Dimensional Pb(II) Coordination Polymer

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ABSTRACT: With emergent research on stimuli responsive materials, dynamic crystals are at the forefront of investigation. However, research on the mechanical properties of coordination polymers (CPs) is still in its infancy. Elastic deformation induced by pressure and photoactuation are rare occurrences in CPs, let alone their combination in a single CP. Here, we report a one-dimensional (1D) CP comprising PbBr₂ chains with 3-fluoro-4'-styrylpyridine arms showing excellent elasticity and photomechanical properties. A slender crystal can be bent to make a circle and write different shapes with restoration of original shape upon removal of the applied force. In addition, photomechanical properties triggered by [2+2] cycloaddition of the olefinic ligand can be modulated easily by variation of the crystal sizes. Crystals with bigger width show destructive photosalient effects while the smaller ones show plastic deformation like bending, twisting, curling etc. upon UV irradiation. This example provides avenue for designing CPs for multi-stimuli responsive actuating properties.

INTRODUCTION

In recent years, great efforts have been made to mimic nature artificially for fabricating actuators that can work with accuracy in response to external stimuli by transduction of energy.¹⁻⁴ Mechanically responsive actuators hold tremendous potential for their use in smart medical devices, artificial muscles, flexible electronics etc.^{1, 5-7} A new class of macroscopic crystals also known as “soft crystals” exhibit mechanical movements induced by pressure, heat, and light which often results in hopping, splitting, bending, curling, coiling, twisting, swimming of the crystals.^{1, 8-26} With the upsurge of dynamic crystals, several examples of mechanically flexible crystals have been reported in the literature showing elastic and plastic deformation upon the application of an external force.²⁷⁻³⁴ Apart from actuation by mechanical force, photomechanical actuation is of great advantage due to its remotely controlled process.^{25, 35-37} Examples of flexible crystals and photomechanical actuators have been reported separately in the literature where most of them are organic crystals.^{1, 2, 5, 27} However, multi-stimuli responsive crystals are rarely encountered in the literature.^{1, 8, 13, 38} In general, fabrication of multifunctional materials demands the combination of several functionalities for imbibing multiple properties. Designing single component smart materials that can perform multiple functions in response to different stimuli is a challenge in fundamental chemistry as well as materials fabrications.

Apart from their catalytic, magnetic, and optical properties, coordination polymers (CPs) have recently been explored for their mechanical flexibility and photoactuation properties.^{35, 38, 39} Elasticity^{38, 39} and plasticity⁴⁰ have been investigated in one-dimensional (1D) CPs having similar

structures. Similarly, photoactuating CPs showing photosalient effect^{35, 41} and photomechanical motions⁴² have been reported in separate literature articles. However, CPs showing multi-stimuli responsive behavior are rarely observed.^{4, 38} Most importantly, modulation of the actuation properties in a single crystalline material is a great challenge and it has been achieved only in organic crystals.^{43, 44} Controlled modulation of mechanical responsiveness in CPs can pave their way to emerging applications in wearable technology and tissue engineering etc. Multistimuli receptive actuators based on CPs can outshine organic counterparts due to their additional properties originating from the metal centers.

In this paper we report a 1D CP of Pb(II), [PbBr₂(3F-spy)₂] (3F-spy = 3-fluoro-4'-styrylpyridine) which not only shows great mechanical flexibility but also modulated photoactuation properties. The presence of anisotropic weak interactions along the crystal lattice facilitates the restoration of crystal deformation upon removal of external force, enabling slender crystals to show mechanical elasticity. In addition, macroscopic crystals show a wide range of photoactuating properties depending on their sizes. Violent photosalient effects such as jumping, breaking, splitting effects as well as bending, twisting, curling etc. have been observed in the 1D CP. To the best of our knowledge, we are not aware of any CP showing such multi-actuation properties.

RESULTS AND DISCUSSION

Structural Analysis. The 1D CP [PbBr₂(3F-spy)₂] **1**, was synthesized as single crystals by slowly evaporating a DMF solution containing 1:2 molar ratio of PbBr₂ and 3F-spy. Single crystal structure at 295(2) K reveals that **1**

crystallized in the monoclinic space group $P2_1/c$ with $Z = 2$. The asymmetric unit constitutes half the formula of the compound. The Pb(II) atom occupies the crystallographic center of inversion and has octahedral geometry from two 3F-spy ligands coordinating via N atoms and four bridging bromide ions. The 3F-spy ligands are flanked in *trans* positions. The bridging bromide ions bind neighbouring Pb(II) atoms forming $Pb(\mu\text{-Br})_2$ chains which propagate along the *a*-axis. All the 3F-spy ligands are arranged parallel in their respective side of the $Pb(\mu\text{-Br})_2$ chain in a *head-to-head* manner (Figure 1, Figure S3-S5). The distance between the centers of the olefin bonds of the styryl groups is 4.175 Å (*a*-axis length), which falls in the upper limit of the required distance (4.2 Å) satisfying Schmidt's topochemical criteria⁴⁵ for the [2+2] cycloaddition reaction in the solid state upon UV irradiation.^{46,47} This could lead to the formation of another 1D dimerized structure upon UV light irradiation.

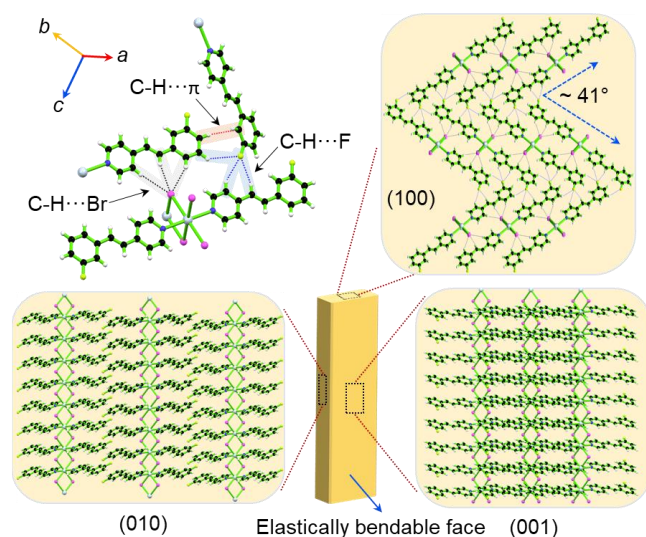


Figure 1. Weak interactions between neighboring groups and crystal packing as seen perpendicular to the crystal faces.

Elastic Bending. Elastic³⁹ and plastic⁴⁰ bending have been reported in 1D CPs having similar ribbon like structures. Elasticity is observed when “strong” interchain interactions prohibit the formation of stable interwoven networks upon the application of mechanical force.^{39,40} We tested this interesting elastic deformation on slender crystals of **1** as it also possesses the key structural prerequisite.³⁹ After fixing one end of the crystal, with the help of a metal needle the other end of the crystal was bent along the crystal length, *i.e.*, by applying the force perpendicular to the 1D chains. When the force was applied on the (010) plane, crystals broke immediately, while flexible bending was observed when poked on the (001) face. Macroscopic elastic crystal deformation occurred to a great extent without any fracture and the bent crystal underwent transient recovery upon withdrawal of the external force. This could be repeated for several times in both the directions indicating great flexibility of the crystals (Figure 2a, Video SV1). With the help of Paratone oil we tried to bend the crystals to such an extent that we could write a few letters with them (Figure S7). Interestingly, a full circle could be made with a typical slender crystal (4 mm × 23 μm × 15 μm) indicating excellent flexibility of the

CP. A crystal of ~4 mm length could be flexed into a loop of ~0.5 mm radius (circumference 3.14 mm) (Figure S8, Video SV2). Further, a “critical radius” of ~0.2 mm was attained before the crystal broke (Video SV2). Elastic bending strain $\epsilon = h/2R$ (where *h* is the thickness of the crystal and *R* is the radius of the circle) was calculated for several crystals and the average bending strain was found out to be ~1.3%, which is higher than reported elastic CPs.³⁹

Mechanism of Bending. Diffraction images were collected before and after bending experiments at several positions of the crystals. Sharp diffraction peaks with similar cell data prior to bending suggested that long range ordering in the crystal is restored without any substantial damage even after repeated bending experiments (Figure S10, Table S3). This indicates reversible reconfiguration of the local environment at the bent/curved positions due to supramolecular interactions (Figure 1). However, diffraction spots of a crystal under a tensile state could not be indexed. As per the previous reports, elastic deformation is a consequence of the gradient of stretching to compression from the outside to the inside of a bent crystal.^{28,32,38,39} Slight displacement of the molecules at the bent position results in the diffused diffraction pattern (Figure S10), unsuitable for indexing. However, consensus of this crystal being single is very clear as proven by previous examples.⁷

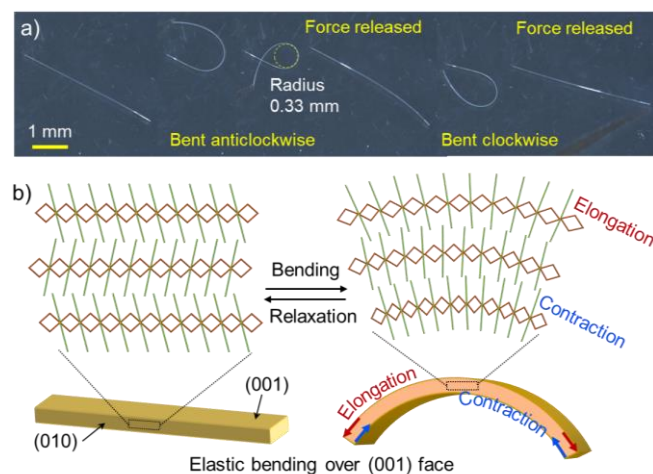


Figure 2. (a) Single crystal of **1** showing elastic bending upon application of an external force. (b) Plausible mechanism of elastic bending.

Elastic bending in 1D CPs of Cd(II) has been explained in terms of supramolecular interactions.³⁹ Similarly, in our case, all 1D polymeric chains are interlinked together by C-H...F and C-H...Br(Pb) interactions perpendicular to the crystal elongation *i.e.*, crystallographic *a*-axis (Figure 1 and Table S2). Due to the presence of such “strong” interactions between the neighboring chains, an interchain network is formed throughout the crystal. Thus, 1D chains are interlocked, preventing a slippage and further plastic deformation upon application of an external force. However, it is important to mention that both elastic²⁸ and plastic⁴⁰ bending have been reported in the absence of slip planes. Anisotropic distribution of supramolecular interactions in the crystal lattice facilitates mechanical flexibility in the macroscopic crystals, as observed in elastic crystals of copper(II) acetylacetonate complex²⁸, and Cd-

based 1D CPs³⁹. In addition, the Pb(μ -Br)₂ unit is highly tensile as seen from the data collected at 100(2) K (Figure S4). Similar structural motif in a CP showed temperature dependent reversible flexibility.²³ So the application of an external force compel the units to stretch on the outer arc and compress on the inner arc of a bent crystal, thus constraining the ligands to accommodate accordingly (Figure 2b). The neighbouring 1D chains are slanted at $\sim 41^\circ$ to each other and can adjust reversibly as seen from the packing perpendicular to (010) plane (Figure 1). Hence, elastic bending is only feasible over the (001) plane and the pristine structure is reinstated upon removal of the mechanical force (Figure 2b). Apart from the structural interactions, thickness of the (010) plane was found to be an important parameter for the mechanical bendability of the crystals.

Photoreactivity. Aimed at achieving a multifunctional CP, the inclusion of a photoreactive olefinic ligand was deliberate. As per the structural arrangement in the 1D CP, the styryl groups of 3F-spy ligands are expected to undergo [2+2] dimerization upon UV irradiation to form cyclobutane rings. When single crystals of different dimensions were irradiated under UV light (360 nm) using MAX-350 with a 300 W xenon light source, various photomechanical effects of the crystals were observed, which subsided within few minutes. Crystal residues were dissolved in DMSO-*d*₆ for ¹H NMR spectral analysis. Integration of the peaks revealed that the signal of pyridyl protons of 3F-spy at 8.57 ppm decreased and new peaks at 8.34 ppm and 4.61 ppm evolved, which are ascribed to pyridyl protons and cyclobutane protons of *rctt*-3F-ppcb (*rctt*-3F-ppcb = *rctt*-1,2-bis(4'-pyridyl)-3,4-bis(3'-fluoro-phenyl)cyclobutane) respectively. The photoconversion of 3F-spy to *rctt*-3F-ppcb was calculated to be 49% indicating [2+2] cycloaddition reaction was the driving force for the photomechanical effects. Complete photodimerization of the ligands occurred after 15 min of UV irradiation resulting in the formation of a new 1D CP **2** (Figure 3).

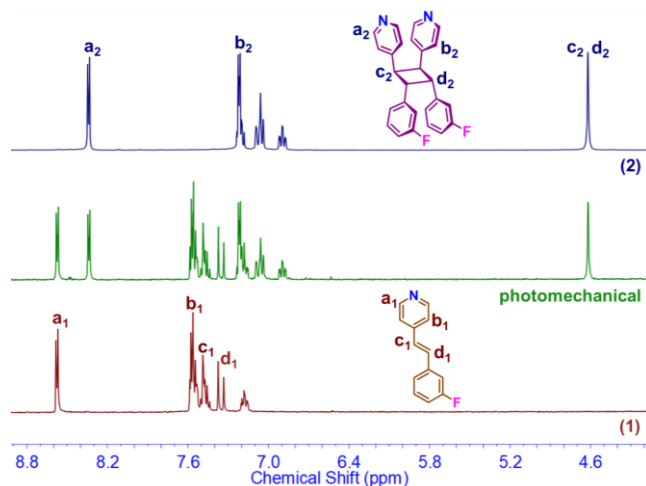


Figure 3. ¹H NMR spectra of **1**, **1** after showing photomechanical effects and the dimerized CP **2**. Relevant proton peaks are assigned.

In our previous work, we could obtain the single crystal structures of partial photoconverted and 100% dimerized product of a photosalient CP.³⁵ In this case, such attempts

were unfruitful as the crystals could not be indexed due to deterioration of the single-crystal quality. The PXRD pattern of **2** closely matches with that of **1** with peaks shifting to the lower angles, which suggests a lattice expansion after the photoconversion (Figure S1). Our attempts to solve the structure from the powder data is not successful.

Modulation of Photoactuation. After our successful attempt at understanding the photosalient effect and photomechanical motions in a 1D CP³⁵, here we try to modulate the photoactuation properties in different dimensions of slender crystals. Naumov *et al.* have explained various photomechanical effects of crystals in terms of several factors including crystal size/shape and surface strain tensor.¹⁻⁵ Modulation of photoactuation properties have been achieved in some organic crystals,^{43,44} but controlled modulation of such properties in CPs is not reported. In order to rationalize and successfully modulate different photomechanical motility, we grew crystals of several distinguished dimensions. Instead of pure DMF as the crystallization solvent, different ratios of DMF and MeCN resulted in the formation of long single crystals of different width and thickness. We were able to grow at least four different crystal dimensions and investigated their photomechanical behavior in detail under a microscope equipped with a high-resolution camera.

Crystals with width \times thickness larger than $85 \mu\text{m} \times 45 \mu\text{m}$ mostly showed violent photosalient effects, exhibiting jumping and splitting of crystals during 90 s UV irradiation (Figure 4a-c, Video SV3). Initially bending along the crystal length occurred when the crystals were irradiated perpendicular to the (001) face. Crystals with smaller width started splitting and breaking after 20 s, while bigger ones took 5 s more. In general, continuous stress relaxation in the absence of an induction period results in bending while rapid stress relaxation after an induction period leads to breaking, jumping of the crystals.⁵ Prolonged irradiation resulted in explosion of all the crystals into fragments and the fragmented crystals jumped to move away from the visual field of the microscope with few portions left on the glass slide (Figure 4a, Video SV3). Most fragmentation occurred along the (100) plane following the bending along the longest crystallographic face *i.e.*, (001) plane. Scattered fragments showed only $\sim 29\%$ photodimerization after the end of violent PS effects. Similar observations have been made in other photosalient crystals, where percentage conversion is small for the observed effects.^{20, 48} This is possibly related to a sudden anisotropic expansion in the unit cell during dimerization or heterogeneous product distribution in the crystal as explained in our prior work.³⁵ Formation of cyclobutane rings between neighbouring 3F-spy ligands cause high strain in Pb(μ -Br)₂ units resulting the disruption of PbBr₂ chains that propagate along the *a*-axis.

In general, bending was observed in crystals of width \times thickness below $65 \mu\text{m} \times 25 \mu\text{m}$. Elaborate photobending experiments were conducted by irradiating single crystals glued to a glass fiber. Irradiation on (001) or (00 $\bar{1}$) plane resulted in bending of the crystal away from the light source (Figure 4d, Video SV4). Initial irradiation results in the formation of a product phase on the irradiated surface, thus generating a strain gradient between two faces. Flexibility of PbBr₂ chains accommodate the strain by facilitating bending along the crystal length. A slender crystal ($3.2 \text{ mm} \times 31 \mu\text{m} \times 16 \mu\text{m}$) would bend to a great extent forming a

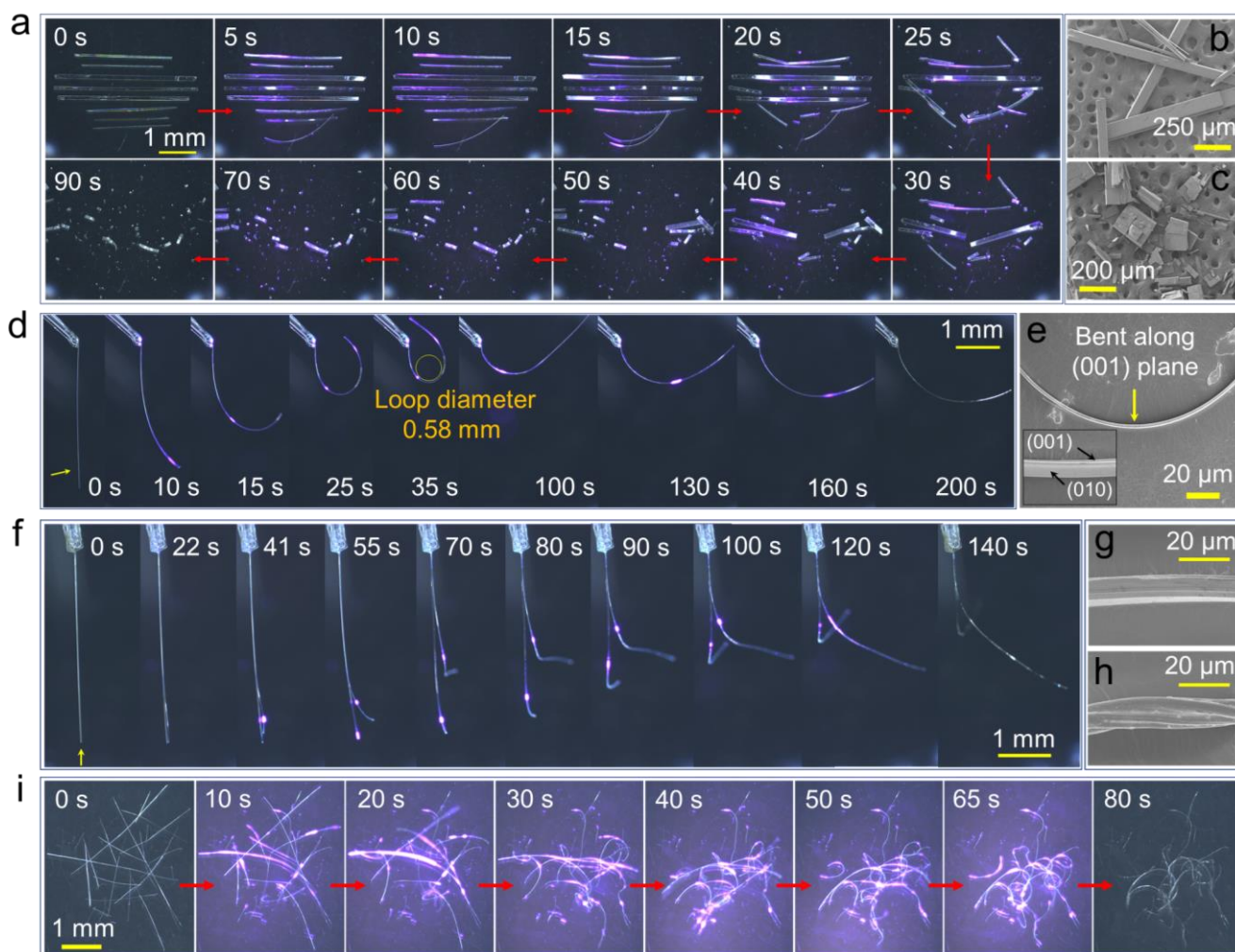


Figure 4. (a) Photosalient effect in thicker crystals of **1**. SEM images of crystals (b) before (c) after PS effect. (d) Photoinduced crystal bending. (e) SEM image of a bent crystal after UV irradiation. (f) Photoinduced crystal splitting and twisting. SEM images of crystal (g) before and (h) after photoinduced twisting. (i) photoinduced curling of fiber crystals.

loop (diameter 0.58 mm) after 30 s. However, upon continued UV exposure the crystal undergoes a slow release of internal strain by bending backwards (Figure 4d, Video SV4). Although it seems like an elastic motion, the crystal undergoes a plastic deformation due to [2+2] photocycloaddition. SEM image of a bent crystal after UV irradiation clearly shows plastic bending over the (001) face (Figure 4e). Because of higher flexibility, longer crystals (>3 mm) tend to bend backwards after completing a loop while relatively shorter ones (< 2 mm) just moved away from the light source to a bent position. In general, irradiation on the upper half (free end) of the crystal generated faster response and the movement was minimal when the other end sticking to the glass rod was exposed. Also, when the crystals underwent bending away from the UV light, it was turned off at the middle and the irradiation direction was reversed to bend the crystal back to its original position (Figure S11, Video SV5).

Splitting of crystal along its length was observed when it was irradiated by a pointed beam from the UV light source at the tip *i.e.*, (100) plane (Figure 4f). It took more than 20 seconds for any observable effect possibly due to the exposure of smaller surface area to UV light. Dimerization on the (100) face created strain in the parallel 1D chains slanted $\sim 41^\circ$ to each other, and the crystal split along the longest crystal dimension *i.e.*, parallel to (001) face to release the surface strain. Further, bending and twisting of the split portions were observed during 140 s irradiation time (Figure 4f, Video SV6). Hence the position of the UV irradiation is an important aspect for the induced photomechanical effects. Apart from bending, twisting of the crystal is fascinating. When free-standing crystals were irradiated over glass slide, pronounced jumping, and bending happened, while crystals were also seen to twist. 60 s UV irradiation resulted plastically deformed bent and twisted crystals (Figure S12, Video SV7). SEM images of pristine crystal and photoinduced twisted crystal highlight the change (Figure 4g-h).

Further, reducing crystal width \times thickness below $18 \mu\text{m} \times 10 \mu\text{m}$ resulted in long fiber crystals. Photoinduced curling was peculiar in such crystals. Crystals underwent bending along the length from one end or both the ends to form plastically curled crystals (Figure 4i, Video SV8). Crystals interweaved with each other and the conglomerate looked like curly hair. Generally, crystals of smaller thickness showed better curling compared to relatively bigger ones. A bunch of fiber-like crystals placed over one another immediately curled and intertwined together upon UV irradiation to form tangled bunch of fibers (Figure S13, Video SV9). Curling of crystals have been studied in organic crystals^{17, 43, 49, 50} and no such photomechanical behavior has been reported in CPs. Transduction of energy for performing observable work is of great importance for actuating materials. So, we tasked a bunch of slender crystals in performing mechanical work by moving a glass rod ~ 10 times higher than their weight upon UV irradiation (Figure S14, Video SV10). This is a clear demonstration of the conversion of light energy to mechanical energy.

CONCLUSION

In summary, a 1D CP was found to be showing dual stimuli responsive actuation properties. Comparison of structural arrangements with previous examples of CPs assisted in rationalizing the elasticity of slender crystals. Presence of anisotropic supramolecular interactions facilitates crystal bending over (001) plane only. Diffused diffraction peaks at the bent position could not be indexed due to the stressed structure. However, a relaxed crystal retained the same cell parameters as that of a pristine one, confirming the reversible reconfiguration. In addition to this, our rational inclusion of an olefinic ligand in the CP, enabled us to study photomechanical actuation properties triggered by [2+2] cycloaddition reaction. In general, the stress generated in the crystal during the photochemical reaction results in various photomechanical motions depending on the strain tensor and crystal thickness. Modulation of photoactuation properties has been manifested in organic crystals. Addition of metal component in the crystal has not resulted in such varied response under UV illumination. We could successfully modulate the photoactuation properties of the CP by varying crystal thickness. Violent photosalient effects were prevalent in wider crystals, while photobending, twisting, curling etc., were observed in slender crystals of smaller width. Crystal splitting could be seen in bendable crystals depending on the position of light irradiation. Such actuation properties have seldom been reported in CPs. This example can provide important new insights for rationally designing multi-actuator materials which can conveniently convert energy into mechanical work. Control and manipulation of actuation properties will provide avenue for accuracy and precision in such applications.

ASSOCIATED CONTENT

Supporting Information.

Experimental details, crystallographic data, PXRD, TGA, optical microscopic images (PDF)

Crystallographic data in cif format (CIF)

Video SV1: Elastic bending

Video SV2: Mechanical bending

Video SV3: Photosalient effects

Video SV4: Photoinduced bending

Video SV5: Light direction dependant bending

Video SV6: Photoinduced splitting and twisting

Video SV7: Photoinduced bending and twisting

Video SV8: Photoinduced curling

Video SV9: Photoinduced curling

Video SV10: Photoinduced work by crystals

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Notes

The authors declare no competing financial interest.

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