Perspective

Mechanoresponsive Flexible Crystals

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ABSTRACT: Flexible crystals have gained significant attention owing to their remarkable pliability, plasticity, and adaptability, making them highly popular in various research and application fields. The main challenges in developing flexible crystals lie in the rational design, preparation, and performance optimization of such crystals. Therefore, a comprehensive understanding of the fundamental origins of crystal flexibility is crucial for establishing evaluation criteria and design principles. This Perspective offers a retrospective analysis of the development of flexible crystals over the past two decades. It summarizes the elastic standards and possible plastic bending mechanisms tailored to diverse flexible crystals and analyzes the assessment of their theoretical basis and applicability. Meanwhile, the compatibility between crystal elasticity and plasticity has been discussed, unveiling the immense prospects of elastic/plastic crystals for applications in biomedicine, flexible electronic devices, and flexible optics. Furthermore, this Perspective presents state-of-the-art experimental avenues and analysis methods for investigating molecular interactions in molecular crystals, which is vital for the future exploration of the mechanisms of crystal flexibility.

KEYWORDS: *Mechanical response, plastic deformation, elastic deformation, flexible crystals*
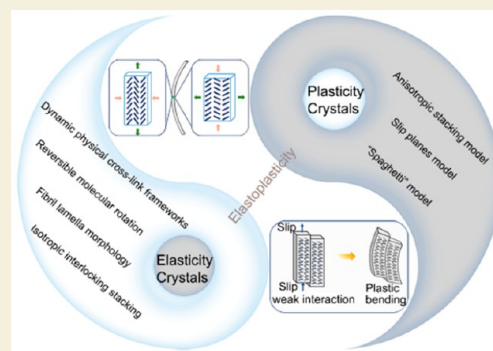
1. INTRODUCTION

Stimuli-responsive materials can efficiently convert external input into both microscopic and macroscopic changes,[1−7] which may manifest in various forms including magnetic, piezoelectric, ferroelectric effects, optical properties, and even the deformation of crystal shape.[8−16] Mechanical stimuli are a kind of representative external stimulation that can trigger the transformation of crystal properties.[17−21] As a reliable and environmentally friendly stimulation, mechanical forces can alter the electronic states of chemical bonds, resulting in changes in chemical reactivity, optical properties, electrical conductivity, magnetic response, and other properties.[22−24] Molecular crystals with special molecular packing could exhibit remarkable mechanoresponsive deformation without losing its integrity under mechanical forces, showing outstanding flexibility.[25−29] Functional molecular crystals with mechanical flexibility have potential powerful applications, such as in wearable devices and flexible optoelectronic devices.[19,30−33] The stress-induced response of molecular crystals to shape deformation is another new feature recently realized by molecular and crystal structure design strategies.[34] Mechanoresponsive flexible crystals can convert mechanical energy into other forms of energy, such as electrical or magnetic energy which is a key feature of many smart functional materials.[1,35−37] The mechanical deformation of a molecular crystal depends on the type of atom, ion or molecule, the molecular arrangement and the strength of the intermolecular interactions.[30,38] Understanding of the important role of weak intermolecular interactions within crystal packing and designing new solids with optimized mechanical properties are both essential for developing flexible molecular crystals.[2]

During the rise of flexible crystals for nearly two decades, researchers have made significant progress in understanding their unique properties and exploring their potential applications. Some mechanisms based on molecular packing have been proposed in an attempt to explore the origins of molecular crystal flexibility.[25,27,28,39−42] However, there is still no universally applicable set of general guidelines capable of providing guidance for the design of molecular crystals with specific functions. In this Perspective, we retrospectively examined the rise and development of mechanoresponsive flexible molecular crystals and analyzed the flexibility mechanisms specific to different types of flexible crystals. Moreover, the broad applications prospects, the experimental avenues, and the methods for investigating molecular interactions are discussed. It is aimed to review the recent advances in mechanically flexible molecular crystals and provide a theoretical basis for the development of this emerging cross field.
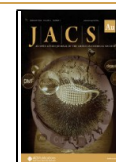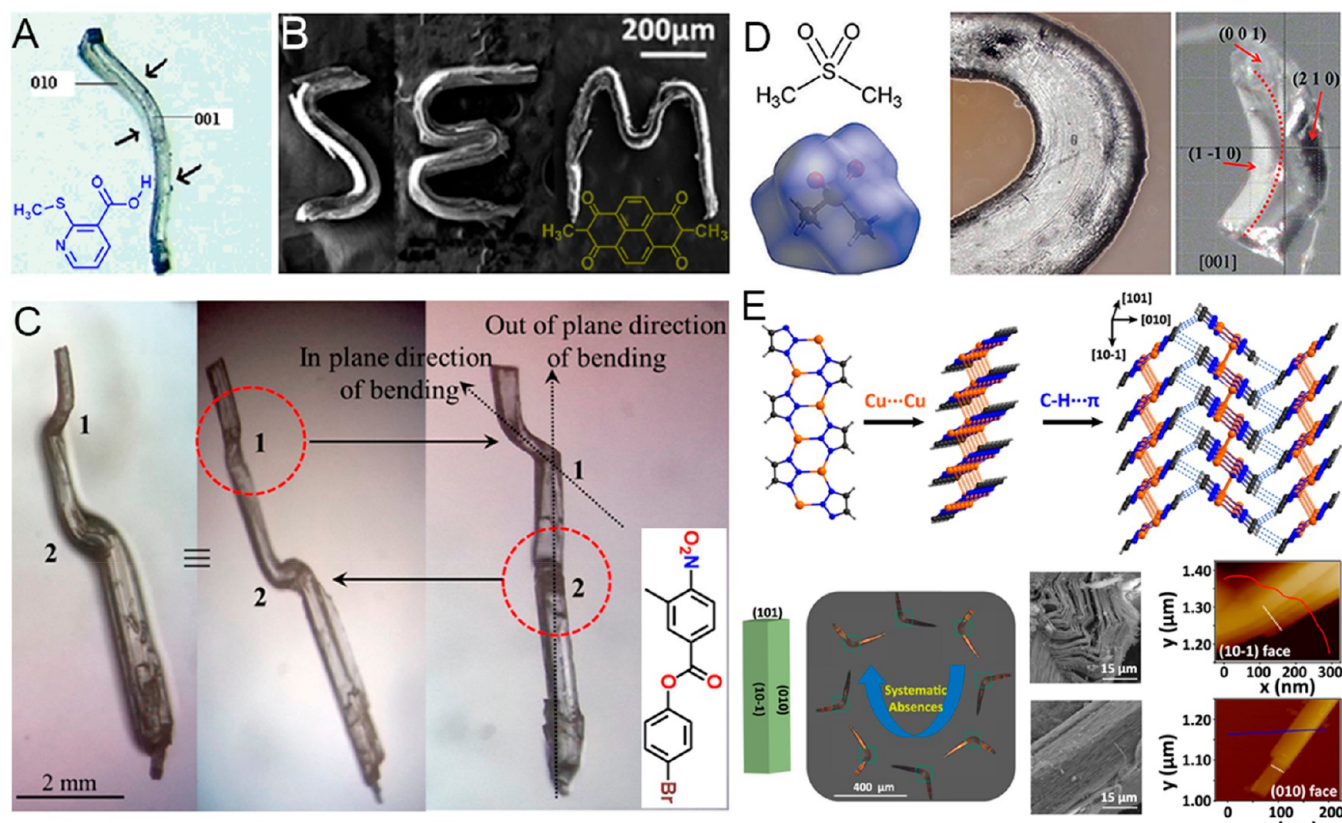
Figure 1. Mechanical plastic crystals. (A) 2-(Methylthio)nicotinic acid crystal bent on the (010) face. The arrows show the point of impact of forceps and needles. The polarizing microscopic images on the (10−1) face and SEM images showed the changes of the bending section. Reproduced from ref 26. Copyright 2006 American Chemical Society. (B) Plastic bending of N-substituted naphthalene diimide derivatives with methyl-vdW groups. Reproduced from ref 48. Copyright 2016 American Chemical Society. (C) 2D plastic bending of the crystal achieved by introducing C−H···O interactions into 1,4-dibromobenzene. Reproduced from ref 49. Copyright 2017 American Chemical Society. (D) Anisotropic packed dimethyl sulfone crystal exhibits plastic bending along the (1−10) crystal plane. Reproduced with permission from ref 50. Copyright 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (E) Crystal structures and morphology of Cu-Trz. The blue lines represent the C−H···π interactions and the orange dash lines represent the Cu···Cu interactions. Reproduced with permission from ref 42. Copyright 2022 The Authors, Published by Springer Nature.

2. PLASTIC AND ELASTIC DEFORMATION

The mechanically induced deformation of molecular crystals can be classified into elastic deformation and plastic deformation, depending on the ability to recover the initial shape after removing the applied force.[25,34,40] Plastic deformation is defined as molecular crystal deformation caused by mechanical stress that is unable to recover its original shape after removing the force.[34,43] In contrast, elastic deformation refers to the ability of crystals to deform when subjected to mechanical force, and can regain their original shape without permanent deformation after the force is released.[40]

2.1. Plastic Deformation

Plastic deformation can be achieved by layering molecular crystals to form plates which can slide along each other.[26,39,44] Unlike typical molecular crystals, which are prone to break or fracture when applying stress, plastic crystals generally retain their diffraction ability and the integrity of single crystals after bending.[40]

2.1.1. Organic Plastic Crystals. In 2005, Reddy et al. studied the plastic bending of an organic crystal 2-(methylthio)nicotinic acid.[25] When pressure was applied by a needle on the (010) face of the crystal, it demonstrated plastic deformation and was prone to bending (Figure 1A).[26] However, when pressure was applied to the (001) and (00−1)

faces, the crystal underwent brittle fracture. This highlights the anisotropic nature of crystal plasticity, where the mechanical response of a crystal depends on its crystallographic orientation. After studying many bendable crystals, the authors tried to establish a correlation between the crystal plastic bending behaviors and their stacking patterns.[26,45] They proposed that the sufficient and necessary condition for crystal bending was the presence of a considerable variation in the strength of intermolecular interaction in the orthogonal direction.[26]

More detailed theoretical models and mechanical experiments on plastically bendable crystals have demonstrated that the bending mechanism might involve the separation of the bending regions into flexible layers.[39,46,47] It is proposed that these flexible layers slip over each other through the reorganization of weaker intermolecular interactions, leading to the formation of domains with slightly altered lattice orientations.[39,46,47] Based on this model, in 2016, Reddy et al. utilized a structural configuration featuring weak interaction and introduced active slip planes to enable plastic bending (Figure 1B).[48] Their approach involved leveraging various supramolecular weak interactions, including van der Waals (vdW) interactions and hydrogen bonds, to form slip planes. Afterward, by introducing orthogonal C−H···O interactions and manipulating halogen bonds, the researchers were able to
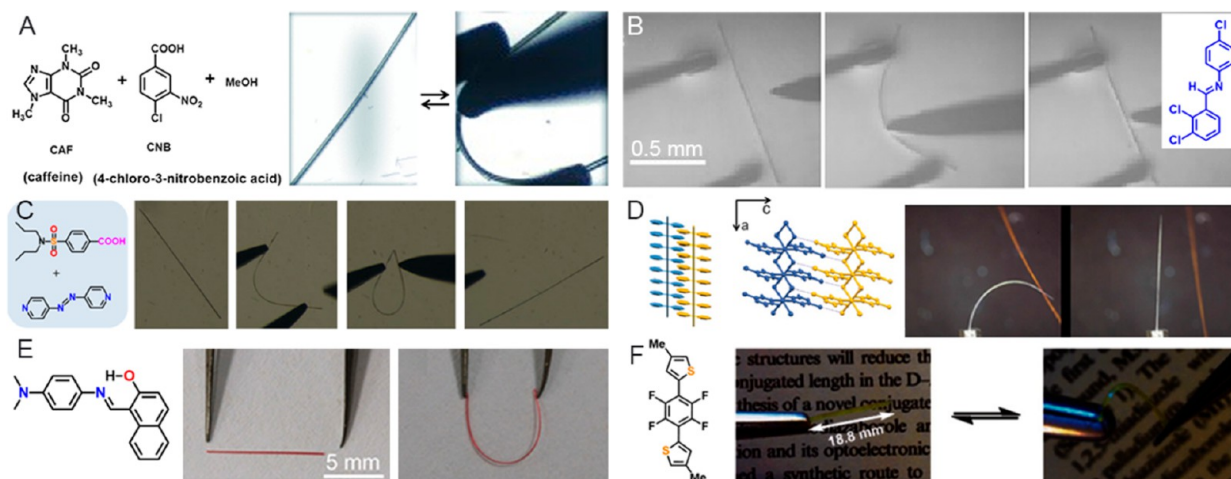
Figure 2. Mechanical elastic crystals. (A) Preparation of the elastic cocrystal of methanol, caffeine, and 4-chloro-3-nitrobenzoic acid. Reproduced with permission from ref 27. Copyright 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (B) Elastic bending of Schiff base crystals with abundant intermolecular interactions. Reproduced with permission from ref 28. Copyright 2015 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (C) Elastic bending of the cocrystal formed by probenecid and 4,4′-azopyridine. Reproduced with permission from ref 60. Copyright 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (D) The elasticity of 1D cadmium(II) halide polymer crystal. Reproduced with permission from ref 61. Copyright 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (E) High elasticity of the (*E*)-1-(4-(dimethylamino)phenyl)iminomethyl-2-hydroxyl-naphthalene crystal. Reproduced with permission from ref 62. Copyright 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (F) Elastic crystal of tetrafluorophenyl derivative with slip planes. Reproduced with permission from ref 63. Copyright 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

transform the plastic bending of a common 1,4-dibromobenzene crystal from one-dimensional (1D) to two-dimensional (2D) (Figure 1C).[49] Moreover, the crystal exhibited three-dimensional (3D) plastic properties due to the presence of cross-slip planes in two directions, allowing it to undergo twisting deformations under mechanical stress.

In recent years, a growing number of plastic crystalline materials have been reported, and some of them are proposed to involve an isotropic packing topology in their mechanisms. Thomas et al. reported a plastic crystal based on dimethylsulfone with a symmetrical molecular structure (Figure 1D).[50] Different from the previous mentioned organic plastically bendable crystals whose molecular packing is susceptible to anisotropy,[26,51] the unit cell of dimethyl sulfone crystal has almost equal crystal axes and are highly symmetric. By analyzing the intermolecular interaction energy, experimental X-ray charge density analysis, and variable temperature neutron diffraction and adopting the model energies and energy framework tool, the authors proposed that the plastic ability of this crystal originates from H···H dihydrogen interactions and differences in electrostatic complementarity between molecular layers. The combined method used in this study also provides a new method for exploring the mechanism of crystal flexibility.[52,53]

2.1.2. Coordination Polymer (CP) Plastic Crystals.

Mechanically flexible coordination polymers (CPs) have only been discovered very recently. In 2020, Bhattacharya et al. reported an mechanically plastic 1D coordination polymer.[41] The single-crystal CP, $[Zn(\mu\text{-}Cl)_2(3,5\text{-dichloropyridine})_2]_n$, exhibited mechanical plastic bending responses when subjected to a stress that was perpendicular to the CP chains. However, there are no slip planes in the molecular packing and the bending stress is accumulated between CP chains rather than within them. Thus, a named "the spaghetti model" was proposed to rationalize this mechanical flexibility. This model emphasizes the interwoven network formed by the CP chains when the crystal bents.

Another family of 1D CPs demonstrated the impact of supramolecular interactions on plastic deformation.[54,55] Pisacic et al. explored the role of intermolecular interactions in the flexibility of 1D Cd(II) coordination polymer.[54] Its mechanical response primarily depends on the relative importance of specific and directed interactions rather than interlocking of adjacent molecules. The team subsequently further investigated the flexibility origins of two-dimensional anisotropic Cd(II) coordination polymers.[56] It was showed that even small changes in the tilt angle between adjacent layers of CPs could significantly impact crystal morphology and the intermolecular interactions. An increase in interaction energy in the orthogonal direction and the rational design of weak molecular interactions wavy arrangement of building units would result in weakening crystal bending ability, accounting for the flexible anisotropy.

During the bending of CP crystals, the mechanical force is predominantly dissipated through dynamic regulation of weak intermolecular interactions. The coordination skeleton formed by strong coordination bonds is usually less affected. Weak intermolecular interactions typically exist in the adjacent lamellar molecules that are connected by strong, oriented bonds. Based on the particular distribution of interactions, the crystal can adapt to applied strain permanently by slip molecular layers.[57] Bu, Li et al. recently reported a plastic Cu-Trz (Trz = 1,2,3-thiadiazole) crystal, in which the molecular chains are tightly stacked by Cu···Cu interactions to form layered motifs (Figure 1E).[42] Adjacent layers form a 3D supramolecular structure in a herringbone arrangement through C−H···π interactions. The spatially resolved analysis of short-range molecular forces reveals that the strong coordination bonds and the adaptive C−H···π and Cu···Cu interactions synergistically lead to the delamination of the local structures and consequently the associated mechanical bending.

2.2. Elastic Deformation

In comparison to the covalent interatomic interactions in alloys and ceramics, the intermolecular interactions present in molecular crystals are relatively weak. Furthermore, the brittleness of molecular crystalline materials is positively correlated with their degree of crystallinity. Thus, it is often challenging to achieve both flexibility and crystallinity, which greatly hinder the practical applications of molecular crystalline materials.[27]

2.2.1. Mechanical Elasticity. The investigation of elastic molecular crystals started from eutectic crystals. In 2012, Reddy et al. reported a needle-like cocrystal consisting of three components (caffeine, 4-chloro-3-nitrobenzoic acid, and methanol), which demonstrated elastic bending under external stress (Figure 2A).[27] Structural analysis revealed that the molecules were staggered to form an interlocking structure without slip planes, preventing the relative slip of molecules. Additionally, multiple weak and dispersive interactions effectively buffered the external mechanical stress applied to the crystal. When the external stress was applied to the crystal, the molecules on both sides of the bending arc would move collectively in a coordinated but opposite manner, which is manifested as inner contraction and outer expansion. Later, Ghosh et al. investigated elastic behaviors of N-benzylideneaniline Schiff base series (Figure 2B).[28] They summarized their structural characteristics as molecules stack into interlocked structures with various weak and dispersed interactions.[28] It is believed that the elasticity of crystals comes from the staggered 3D interlocking structures and multiple scattered weak interactions.[58] Since then, many more elastic crystals have been reported, featuring common structural characteristics. For example, Anoop et al. attempted to use this model to explain the elasticity origin of the azine group functionalized (E)-3-(hydrazonomethyl)benzene-1,2-diol crystal.[59] Naumov et al. also ascribed the elasticity of the cocrystal formed by probenecid and 4,4′-azopyridine to its isotropic interlocking stacking (Figure 2C).[60] Đaković et al. commented that the elasticity of 1D cadmium(II) halide polymer was closely related to its isotropic interlocking structure (Figure 2D).[61] Zhang et al. reported several flexible Schiff base crystals with abundant hydrogen bonds and ascribed their flexibilities to the molecular stacking pattern in the crystals (Figure 2E).[62,64,65]

As the number of examples of elastic crystals increases, the understanding of the elasticity mechanism is no longer limited to interlocking stacking modes. Hayashi et al. reported that an elastic crystal of tetrafluorophenyl derivative actually possesses slip planes (Figure 2F).[63] When undergoing mechanical bending, the molecular chain on the sides of slip planes occurs opposite expansion and contraction. The contact angle of molecules on both sides of the slip planes is changed, but the relative position of the molecules did not change. Hayashi et al. pointed out that rigid planar molecules were conducive to the formation of slip planes and promoted the elastic properties of crystals.[66] McMurtrie et al. prepared a single crystal of Cu acetylacetone complex with anisotropic intermolecular interactions.[40] With relatively strong π-superposition in one dimension and only weakly dispersive interactions in other dimensions, the molecular structure is not interlocked. The high π-electron-density structure allowed the molecules to be sufficiently redirected without damaging the integrity of the crystal. It is important for the molecules to reversibly reorganize so that the interior of the crystal could compress along the arc and subsequently expand in the orthogonal direction. Recently, Huang et al. reported a racemic fluorenol-carbazole elastic crystal with distinct slip planes.[67] The interlayer slip and intramolecular perturbation enabled the energy storage and dispersion, ensuring the structural integrity of crystal. The crystal effectively absorbs strain energy and prevents the generation and expansion of cracks.

2.2.2. Pseudoelasticity. Some special molecular crystals exhibit pseudoelastic characteristics, which undergo a reversible solid-state phase transition under the stimulus of mechanical force. Takamizawa et al. observed that terephthalamide crystals exhibit superelasticity driven by even small shear stress, producing macroscopic motions with high repetition and high energy storage efficiency (Figure 3A).[68]
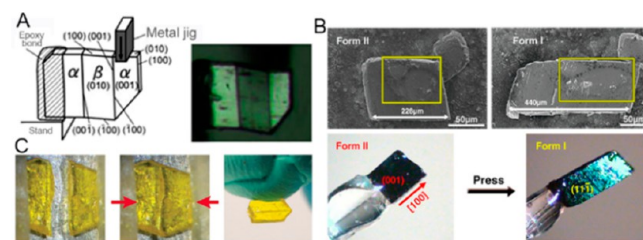

Figure 3. Superelastic crystals. (A) The terephthalamide crystal exhibits pseudoelasticity with phase transitions under mechanical stress. Reproduced with permission from ref 68. Copyright 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (B) CuQ2-TCNQ crystal shows phase transition induced elongation under mechanical press. Reproduced from ref 69. Copyright 2014 American Chemical Society. (C) Self-healing of the dipyrazolethiuram disulfide crystal under mechanical stress. Reproduced with permission from ref 70. Copyright 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Upon mechanical stress, the terephthalamide crystal underwent a transition from the α- to the β-phase with morphological deformation. After the stress was removed, the curved crystal spontaneously returned to its initial state. Tao et al. reported an eutectic crystal, 7,7,8,8-tetracyanoquinodimethane-p-bis(8-hydroxyquinolinato) copper(II) (CuQ$_2$-TCNQ, Figure 3B).[69] When subjected to mechanical stimulation, the crystal exhibited elastic deformation due to its phase transition along the crystallographic a-axis. The macroscopical length of the crystal was doubled, and the thickness was reduced to 1/2. Interestingly, such a phase transition could also be induced when the crystal is heated rapidly to increase its defects.

Some crystals are equipped with self-healing properties under mechanical stress through the recombination of dynamic chemical bonds. The typical example of a mechanically self-healing crystal is the dipyrazolethiuram disulfide crystal reported by Naumov et al. (Figure 3C).[70] The self-healing was caused by the rearrangement of the S−S bonds at the crack interface. During the breaking of the crystal, the S−S bonds would undergo homogeneous breaking, and the free radical would delocalize between the two sulfur atoms. When the broken crystals are pressed together, the free radical interacts with neighboring sulfur atoms to form new S−S bonds, and self-healing occurred. The compression test showed that the healing rate of the crystal could reach nearly 7% of that of the initial state. The team further investigated the reversible reaction between boric acid and borate esters and applied it to the preparation of self-healing crystals.[71] The self-healing property of the crystal was ascribed to the highly dynamic

borate bonds, which was achieved through borate ester metathesis and transesterification reactions. At the same time, the crystal exhibited flexibility and dynamic responses, such as bending, twisting, and curling.

2.3. The Combination of Elasticity and Plasticity

In general, the plasticity of organic crystals is primarily due to the anisotropic packing mode, while elastic crystals are often characterized by isotropic packing. It is often regarded that elasticity and plasticity are incompatible in one crystal. However, in rare cases, some crystalline materials demonstrate both elastic and plastic deformation. Zhang et al. reported an organic crystalline material, 6,6′-((1E,1′E)-hydrazine-1,2-diylidenebis(ethan-1-yl-1-ylidene))bis(3-methylphenol), with both elastic and reconfigurable plastic twisting capabilities.[72] The crystal displayed elastic bending ability on the (001) and (010) planes, maintaining this 2D bending ability even at −196 °C. When shear stress was applied in opposite directions to both ends of the crystal, it underwent a twisting deformation. Under stress, the twisted crystal could be straightened and twisted in the opposite direction, and this plastic distortion could be repeated multiple times without fracturing the crystal (Figure 4A). Moreover, the twisted crystal retained its elastic
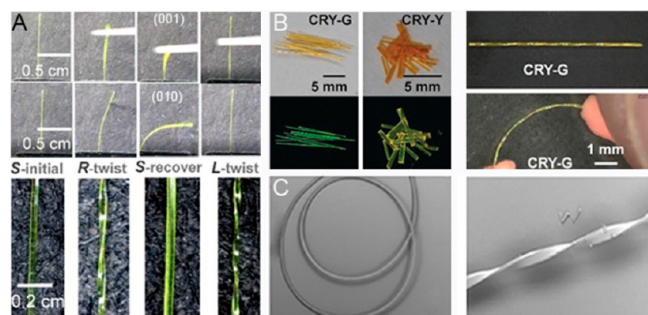

Figure 4. Crystals with both elasticity and plasticity. (A) 2D elastic bending and reconfigurable plastic twisting of 6,6′-((1E,1′E)-hydrazine-1,2-diylidenebis(ethan-1-yl-1-ylidene))bis(3-methylphenol) crystal. Reproduced with permission from ref 72. Copyright 2022 Wiley-VCH GmbH. (B) Plastic twisting and elastic bending of (E)-1-(((3,5-dimethoxyphenyl)imino)methyl)naphthalene-2-ol crystals. Reproduced with permission from ref 73. Copyright 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (C) Elastic bending plastic twisting of (E)-2-((4-(trifluoromethoxy)phenyl)imino)methyl-6-methoxyphenol crystal. Reproduced with permission from ref 75. Copyright 2023 Elsevier Ltd.

bending characteristics. The analysis of molecular stacking revealed that the crystal elasticity arised from π−π interactions and intermolecular hydrogen bonding, while the twisting deformation was due to the presence of double slip planes. Additionally, the short distance deviation of the molecules and the partial retention of hydrogen bonds kept the twisted crystal in a metastable state, enabling it to maintain its deformed shape throughout the distortion process.

Recently, some crystals demonstrated both plastic twisting and elastic bending under different modes of external forces. It indicates that different external force modes can affect the accumulation of molecules in different crystal directions. The Schiff base crystal, (E)-1-(((3,5-dimethoxyphenyl)imino)-methyl)naphthalene-2-ol shows plastic helical twisting under twisting forces and elastic bending under bending forces (Figure 4B).[73] Under controlled ambient humidity conditions, the crystal can undergo crystallization into two distinct phases.

Both phases demonstrate elastic bending ability, with the wider and narrower faces of Cy-G being capable of bending, while only the wider face of Cy-Y can be bent. Furthermore, the Cy-G can be twisted into a spiral shape under torsional force, and the spiral crystal retains its ability to bend elastically. This suggests that plastic deformation and elastic deformation can coexist and are compatible with each other in this crystal system. Another similar example is (E)-4-(3-(5-methoxy-1-methyl-1H-indol-3-yl)acryloyl)benzonitrile crystal, which could be plastically twisted along the direction perpendicular to its growth to form both left-handed and right-handed morphologies when the twist forces were applied at both ends of the crystal tips in the opposite direction.[74] The crystal simultaneously displays elasticity, which is not significantly affected by the plastic twisting of the crystal. (E)-2-((4-(Trifluoromethoxy)phenyl)imino)methyl-6-methoxyphenol crystal could retain the ability of elastic bending even after severe twisting deformation (Figure 4C).[75] Furthermore, twisted crystals could be bent freely in any direction due to the twisted shape, thus achieving the transition from 2D to 3D elastic bending. The analysis of crystal structure showed that the multiplanar elastic bending and plastic twisting of the crystal were guaranteed by the abundant intermolecular interaction and the unhindered molecular rotation.

3. THE MECHANISMS OF PLASTIC AND ELASTIC DEFORMATION

Flexible deformation, which includes both plastic and elastic deformations, plays a crucial role in determining the mechanical behavior of materials. The flexibility of materials is also an important factor affecting their performance in various applications, such as structural materials, electronic devices, biomedical implants, etc. Understanding the mechanism behind flexible deformation is essential for optimizing the design and manufacture of flexible crystals. Scientists and engineers have made significant progress in elucidating the mechanisms of plastic and elastic deformation, paving the way for the development of new materials with advanced mechanical properties.

3.1. Mechanisms of Plastic Deformation

For plastic crystals, irreversible deformation will occur to offset the external stress when subjected to an external force. Deformation may be the result of molecular layer/column slip. The irreversibility of molecular motion may be accompanied by the broken and reformation of interacting bonds.[76] Crystals deforming under mechanical stress usually have planes parallel to each other, which are defined as curved planes.[25] When the crystal was subjected to mechanical stress perpendicular to the pair of parallel planes, these planes will become nonplane and the crystal will bend. In the exploration of the origins of plasticity, researchers initially believed that crystal bending was due to the anisotropic stacking of internal molecules. That is, the strong interaction and weak interaction were arranged nearly vertically in the molecular packing, which was a necessary and sufficient condition for crystal bending.[25,77] Further researches concerning the origins of the plastic deformation complemented the concept of the slip planes.[39] Although the origins of crystal plasticity are still debated, it is undeniable that the plastic bending of organic crystals is closely related to the unbalanced interaction and the slip molecular layers. The model of anisotropic stacking and slip planes can explain the plastic mechanism of most crystals, especially
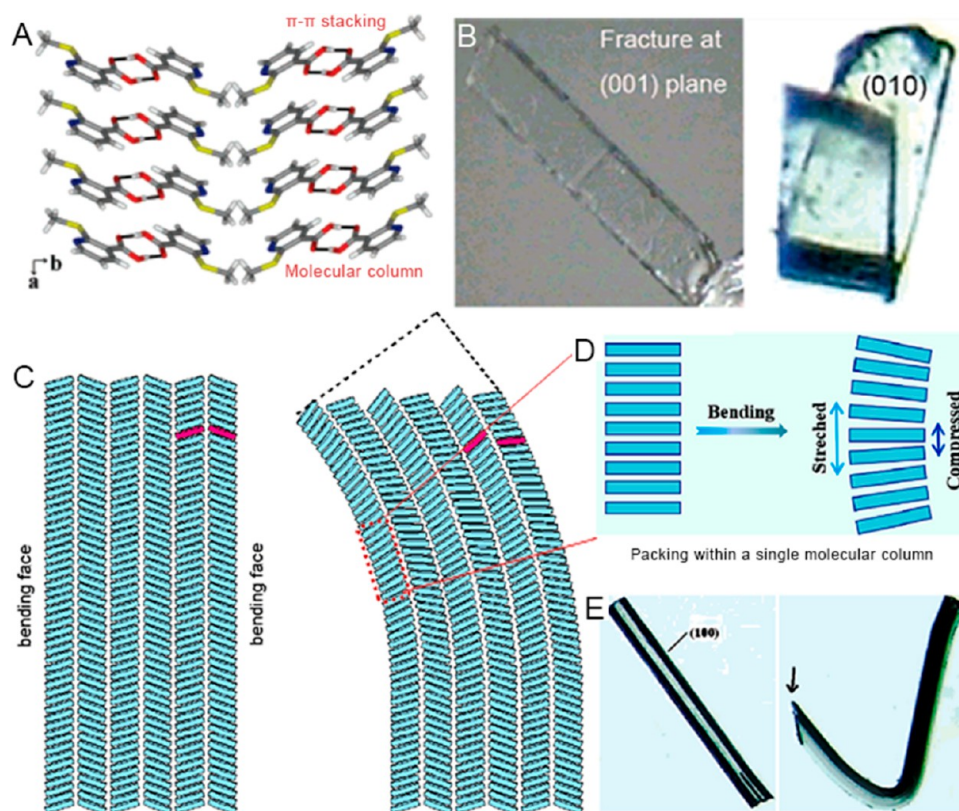
Figure 5. Anisotropic packing model mechanism of plastic deformation. (A) Stacking of dimers along the longest crystal dimension. Notice the weak Me···Me interactions and $\pi-\pi$ molecular stacking. (B) 2-(Methylthio)nicotinic acid crystal fracture at the (001) plane and bent on the (010) face. (C) Half-planed surface plots of undeformed and deformed crystals. Comparing the stacked blocks marked in red shows the change in the relative position of the molecules due to the bending model. (D) Lateral expansion and internal contraction of local $\pi-\pi$ accumulation in a single molecular column. (E) Bending results in an angle change in the position of the crystal tip. Reproduced from ref 26. Copyright 2006 American Chemical Society.

organic molecular crystals. However, new mechanisms still need to be explored for crystals without potential slip planes, especially for coordination polymer crystals.

3.1.1. Anisotropic Stacking Model. The exploration of plastic mechanism began with the 2-(methylthio)nicotinic acid crystal.[25] The crystal exhibited variable degrees of macroscopic response when mechanical stress was applied to different crystal planes. Based on this phenomenon, the authors ascribed the plastic bending of organic crystals to the molecular stacking pattern. With the analysis of the molecular stacking models of numerous plastic crystals,[78] it was proposed that a crucial requirement for crystal bending plastically is the significant anisotropy in the strength of the intermolecular interaction in the orthogonal direction. To explain the underlying cause of plastic bending in crystals, researchers put together a structural model that takes into account the highly anisotropic packing (Figure 5).

Molecular stacking can take different forms, such as head-to-head or head-to-tail arrangements. The critical aspect is that strong and weak interactions are distributed almost vertically throughout the stacking process, forming molecular columns along with the strong interactions (Figure 5A). On one hand, this stacking pattern is conducive to anisotropic responses to external stimuli (Figure 5B). On the other hand, it is obvious that the relative slip of molecules proceeds along the direction of weak force first, resulting in the plastic deformation. When a crystal is subjected to external mechanical stress perpendicular to the direction of the weak interactions, the molecular

columns will bend, respectively, resulting in the dislocation of the head-to-tail or head-to-head positions between adjacent molecular columns, or a change in their distance (Figure 5C and D). Correspondingly, the angle between the direction of the molecular column and its cross-section will change from a right angle to an acute angle macroscopically (Figure 5E). For the interior of a single molecular column, the bending process inevitably leads to a change in $\pi-\pi$ stacking. That is, contracting on the inside of the bending area and expanding on the outside (Figure 5D). The thickness of the organic crystal and the length of the molecular columns undergo almost no change under the double variation within and between the molecular columns, which is different from the plastic deformation of metal materials.[78]

3.1.2. Slip Planes Model. The slip plane model is a development of the anisotropic model. It highlights that the plastic bending is achieved by separating the curved parts into flexible layers. The molecular layers slip along the weak interaction to realize the reorganization of weak intermolecular interactions, generating domains with slightly different lattice orientations. The direct macro evidence for the existence of slip planes was first attempted by using scanning electron microscopy (SEM) and atomic force microscopy (AFM).[39] It was observed that there were layers with an average thickness of 3.2 μm formed on the curved plane after the bending of the hexachlorobenzene crystal. Each layer further formed multiple ridges with widths less than 1 μm. These layers were absent in the straight part of the crystal and evolved during the bending
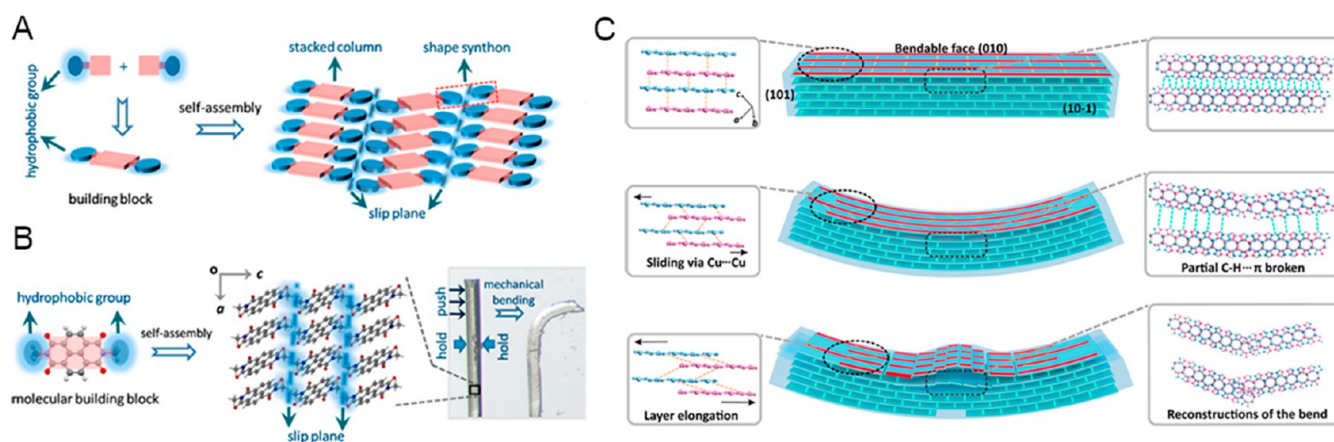
Figure 6. Slip plane model mechanism of plastic deformation. (A) Strategy of preparing plastic crystals by strong interaction and weak interaction is introduced. (B) Slip planes and plastic bending of naphthalene diimides derivatives. Reproduced from ref 48. Copyright 2016 American Chemical Society. (C) Schematic representation of the process of the fracture and recombination of intermolecular interactions during the plastic bending of the Cu-Trz crystal. Reproduced with permission from ref 42. Copyright 2022 The Authors, Published by Springer Nature.

process. The slip plane model reveals the plastic deformation nature of molecular crystals: molecules slip to achieve the fracture and reorganization of weak intermolecular interactions. This mechanism has significant guiding implications for designing plastic molecular crystals, including both organic crystals and metal coordination compound crystals. It provides a strategy for fabricating mechanically plastic crystals by introducing both strong and weak interactions into the structure (Figure 6A).[48] The incorporation of strong interactions and weak interactions is expected to achieve the desired plasticity for molecular crystal. Based on this strategy, Reddy et al. successfully prepared a series of plastic naphthalene diimides derivatives by introducing spherical vdW groups.[48] The spherical hydrophobic groups were assembled via shape complementarities (shape synthesizers) to form low-energy slip planes, promoting molecular flexibility (Figure 6B). Meanwhile, the central aromatic core groups tend to pack together in parallel through $\pi-\pi$ stacking. The dispersion of spherical vdW groups can facilitate the formation of slip planes in the structure with a minimum adhesion energy, enabling molecules to slide under mechanical stress.

The slip plane model reveals the plastic deformation nature of molecular crystals: molecules slide to achieve the fracture and reorganization of weak intermolecular interactions. The study of plastic bending mechanism of Cu-Trz crystal by Bu et al. further supports this view (Figures 1E and 6C).[42] When the crystal is bent, the adjacent CPs would slide over each other due to the relatively weak interchain Cu···Cu interactions, resulting in layer expansion in the bent section. Meanwhile, the slipping of the CPs causes concurrent weakening and even possible breakage and reconstruction of a large number of C−H···π bonds, leading to significant sliding between adjacent layers. Upon further bending, slipping is not enough to fully counterbalance the mechanical stress, so that the breakage of the CPs occurs in the inner region. This drastic change leads to the complete disruption of a large amount of C−H···π bonds and the corresponding detached adjacent layers in the bent section.

The slip plane model mechanism is to a great extent universal and has significant guiding implications for designing plastic molecular crystals, including both organic crystals and metal CP crystals. However, there are certain limitations for the model when applied to some molecular crystals that have

no anisotropic packing. For instance, the isotropic packed plastic molecular crystal, dimethyl sulfone, exhibit remarkable plasticity has no obvious slip planes.[50] Its plasticity comes from the H···H dihydrogen interactions and differences in the electrostatic complementarity between molecular layers. This indicates that the possession of slip planes is not always a necessary condition for plastic bending.

3.1.3. "Spaghetti" Model. New mechanism models have to be developed to explain the plastic mechanism of metal−organic hybrids. The plastic crystal of 1D CP, $[Zn(m\text{-}Cl)_2(3,5\text{-dichloropyridine})_2]_n$ (Zn-CP), crystallized in the square space group of $P\bar{4}b2$ and contains a 1D CP chain along the crystallographic c-axis.[41] Due to the crystallographic symmetry, the molecular arrangements along the crystal $(1−10)$ and $(−1−10)$ planes are exactly the same, and accordingly, it exhibits 2D irreversible plastic bending. In contrast, when the crystal is stressed along plane (001) parallel to the CP chain, a brittle fracture is observed. During mechanical deformation, no detectable displacement was observed in the Raman spectrum. The lattice vibration analysis of the bending process by terahertz time domain (THz-TD) spectroscopy revealed that all but two of the low-frequency bands (<3 THz, 100 cm^{-1}) were lost in the THz-TD spectrum upon bending. The result is identical to the AFM analysis in indicating that the long-range order is compromised during the bending of the crystal, although it remains macroscopically intact.

Unlike the previously reported plastic mechanism crystals, Zn-CP does not have the necessary conditions to form slip planes. In fact, most of the flexible CP crystals hardly contain the necessary slip planes required by the slip planes model. Therefore, a new mechanism has been proposed to explain the source of plasticity in such CPs, namely the "Spaghetti" model (Figure 7). In this model, the molecules stack to form "spaghetti" roots along a chain of CPs that are dominated by the central atoms of the metal. CP chains form parallel clusters, and the molecules pack and grow along these chains' direction. When the mechanical stress was applied vertically to the CP chains (the "spaghetti"), bending stress accumulates only between the chains, rather than within them. As a result, the clusters of CP chains move and become interwoven, accompanied by the fracture and reconstruction of weak interactions. During the bending process, small angular grain boundaries distribute widespread throughout the structure,
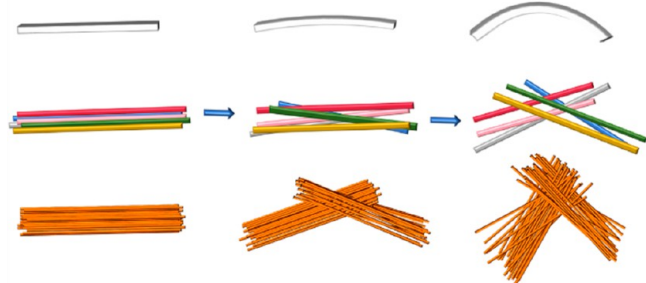
Figure 7. "Spaghetti" model mechanism of plastic deformation. Schematic representation of the "spaghetti" model for the bending of the Zn-CP crystal. Note that each bundle of straws represents a cluster of CP chains. Referenced from 40.

compromising the long-range crystallinity and ultimately resulting in the formation of a powdery structure. The "Spaghetti" model indicates that plastic deformation is primarily driven by breaking the interactions between CP chains. Therefore, plastic deformation is more beneficial when the energy loss of the CP interchain displacement is low. Because of the relatively weak interchain interactions, a stable interweaving network readily forms when the crystals are subjected to mechanical deformation.

DFT calculation comparing elastic CPs and plastic CPs suggest that the CP chains in the plastic CPs are more prone to separate, providing a theoretical foundation for the spaghetti model.[61] Further researches have shown that the model had a certain universality.[79] The crystals form interwoven CPs networks as they bend, resulting in the separation of the CP chains.

3.2. Elastic Deformation Mechanism

Mechanical deformation in molecular crystals is usually ascribed to their stacking characteristics and the presence of intermolecular interactions. The reversible rearrangement of molecules stacking is a necessary condition to maintain elasticity.[80] The fact that crystals can completely recover without any fracture after multiple cycles of loading and unloading stresses indicates the micro self-healing properties of elastic crystals.[76] When subjected to pressure in a specific direction, crystals regulate and buffer external stress through multiple weak and dispersed interactions, thereby avoiding crystal fractures and facilitating the adaptation to induced strain during elastic deformation processes.[27,28,49,67] There
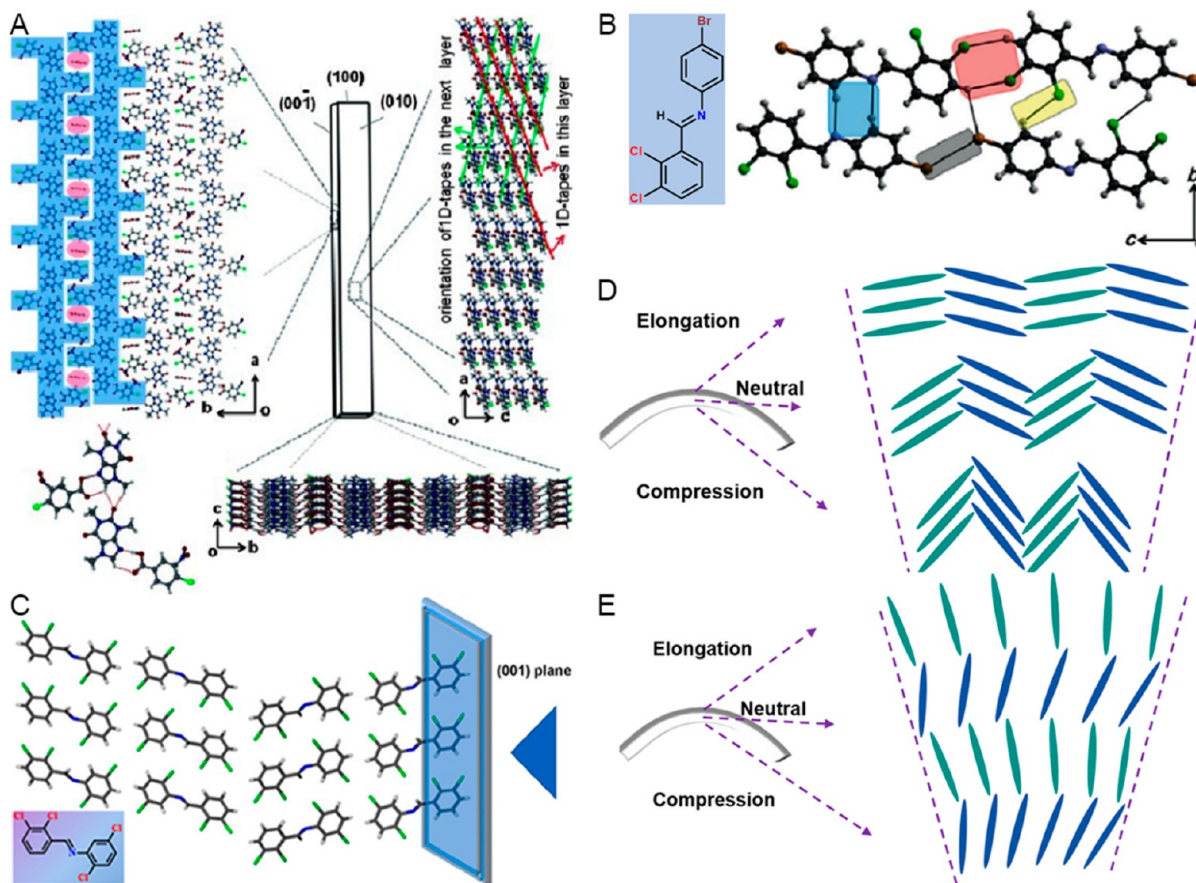

Figure 8. Interlocking stacking model mechanism of elastic deformation. (A) Crystal ternary eutectic packing in interlocking of the comb-like 2D sheets (blue) and the formation of channels (red) with disordered methanol along the crystallographic c-axis. Formation of dimers by caffeine and 4-chloro-3-nitrobenzoic acid occurs through O−H⋯N and C−H⋯O interactions; the caffeine molecules form 1D tapes. Views perpendicular to (100) and the 2D layers in (010). Reproduced with permission from ref 27. Copyright 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (B) 2,3-Dichlorobenzylidine-4-bromoaniline crystal stack forms a herringbone stacking. Reproduced with permission from ref 28. Copyright 2015 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (C) (E)-1-(2,3-Dichlorophenyl)-N-(2,5-dichlorophenyl) methanimine crystal stack forms a nearly parallel chain-like structure. Reproduced from ref 84. Copyright 2019 American Chemical Society. (D) First elastic bending mechanism model of interlocking stacking. The change in the angle of herringbone stacking leads to expansion and contraction at the crystal bend. (E) Change in the π−π plane distance causes expansion and contraction at the crystal bend.
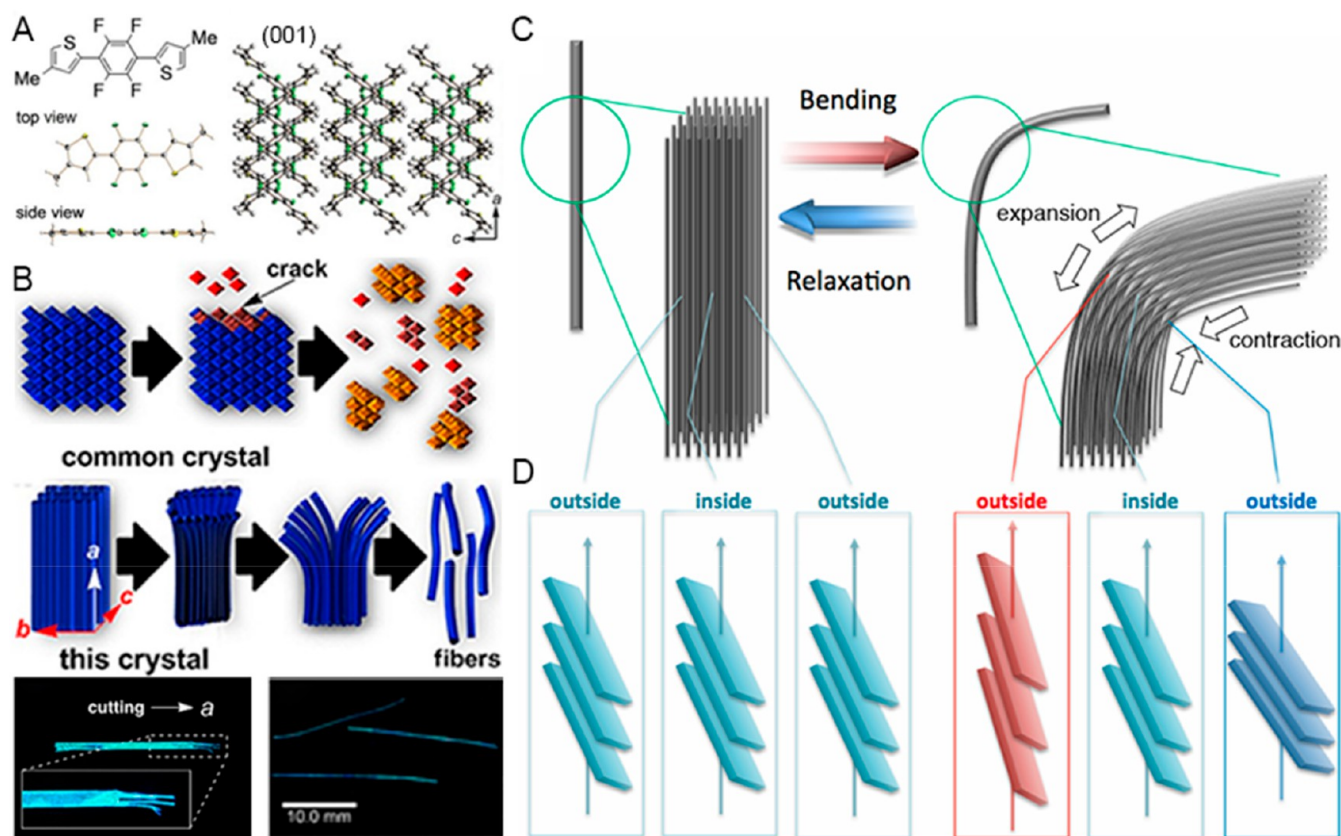
Figure 9. Fibril lamella morphology model mechanism of elastic deformation. (A) Molecular structure of BMTP and its molecular columns formed by stacking. (B) Illustration of the common organic crystal breakage and the process of BMTP single crystal's mechanically induced splitting into fibrous layers when applied stress. Reproduced with permission from ref 66. Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (C) Schematic representation of the fiber structure change on bending process. (D) Schematic representation of the distance change between molecules. Reproduced with permission from ref 89. Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

have been many attempts to establish a set of standards based on crystal packing analysis to effectively explain the elasticity of crystals, and thus provide guidance for designing elastic crystals, including isotropic interlocking stacking model,[27,28] fibril-lamella morphology model,[63,66] reversible molecular rotation model,[30,40] and dynamic physical cross-linking model.[67] Although there are still limitations for these models in understanding the crystal elasticity, it is certain that the origins of crystal elasticity cannot be separated from the buffer of molecular stacking patterns and weak dispersed intermolecular interactions.[81−83]

3.2.1. Isotropic Interlocking Stacking Model. In the early exploration of the relationship between elasticity and molecular stacking, researchers intuitively proposed an isotropic interlocking stacking model based on the study of ternary eutectic formed from caffeine, 4-chloro-3-nitrobenzoic acid, and methanol in a 1:1:<1 ratio.[27,28] Elastic crystals are considered to be packed isotropically with weak interactions across all three dimensions, with interlocked structural characteristics.[27] The ternary eutectic forms a herringbone arrangement along the (010) crystal plane, while it stacks into an interlocking zigzag pattern along the (00−1) crystal plane (Figure 8A). From the (100) crystal plane, the adjacent molecules form an interlocking stacking arrangement through hydrogen bonding. Schiff bases possess abundant intermolecular interactions, which facilitate interlocking stacking. 2,3-dichlorobenzylidine-4-bromoaniline molecules arrange (Figure 8B).[28] The (E)-1-(2,3-dichlorophenyl)-N-(2,5-dichlorophen-

yl) molecules stack in almost parallel chain-like structures (Figure 8C).[84] The molecules form long chains in the same direction, and the chains are attracted to each other through intermolecular interactions, forming parallel stacking.

According to the isotropic interlocking stacking model, the elastic properties of crystals should satisfy two conditions: isotropic weak molecular interactions and cross-interlocking structures.[28] The interlocking structure of elastic crystals inhibits molecules from slip against each other, which effectively resists irreversible plastic deformation.[39,85] The interlocking packing pattern enables compression or stretching of the distance between molecules within a specific range, allowing for varying degrees of deformation on the inside and outside planes during crystal bending. This mechanism can be described as two distinct processes with the specific stacking of the crystal determining which mechanism is operative. The first mechanism involves molecular rotation, which alters the angle of the herringbone pattern, thereby either compressing or expanding the interlocking structure (Figure 8D).[28,86] The second mechanism involves the modulation of the distance between the $\pi-\pi$ planes, resulting in the elongation and compression necessary to induce bending (Figure 8E).[61,87,88] The existence of the interlocking stacking structure was confirmed through the examination of several elastic crystals, including specific halogen-substituted aromatic molecules and Schiff base molecules.[39,61,80,84,87] According to the isotropic interlock stacking hypothesis, the elasticity properties of crystals are determined by three factors: isotropy in the
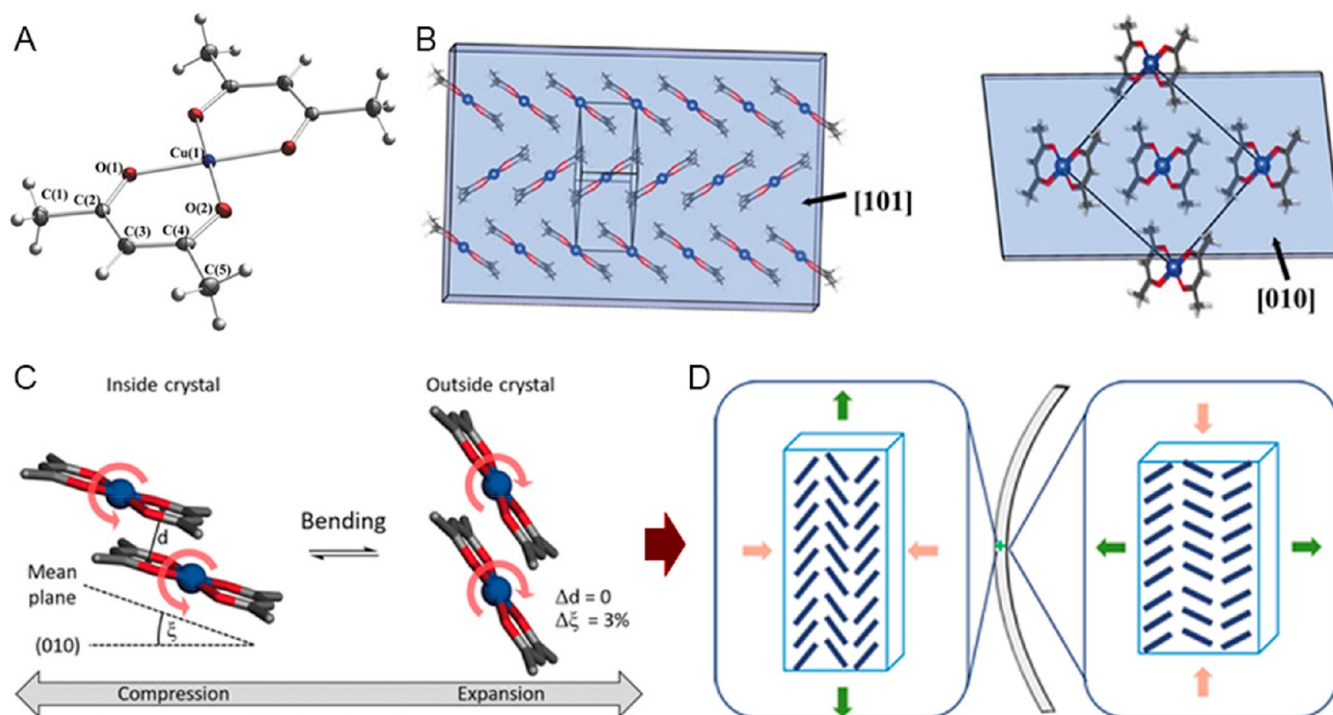
Figure 10. Reversible molecular rotation model mechanism of elastic deformation. (A) Molecular structure of $[Cu(acac)_2]$. (B) Crystal structure of unbent $[Cu(acac)_2]$ viewed along the $[101]$ and $[010]$ directions. (C) Schematic representation of the reversible molecular movement mechanism as applied to $[Cu(acac)_2]$. (D) Schematic representation of compression and expansion for the molecular staking, resulting in the bending of the crystal. Reproduced with permission from ref 90. Copyright 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

stacking, the lack of slip planes, and the interlocking or interleaved arrangement.[80] The multiple intermolecular interactions extend throughout the entire crystal, providing a "structural buffer" that promotes the reversibility of bending.[81] Despite a few exceptional cases that deviate from the model,[49,50,56] it is indeed beneficial to design of elastic molecular crystals following the principles: avoiding the presence of slip planes, achieving nearly isotropic crystal packing, and incorporating an interlocking structure.

3.2.2. Fibril Lamella Morphology Model. In the realm of molecular crystals, the existence of slip planes is necessary for crystal plasticity. This characteristic stabilizes the permanent displacement of the molecular layer and prevents the restoration of the original shape.[39,85] To achieve elasticity, it is imperative that the crystal structure contain no slip planes. However, Hayashi et al. reported a particular elastic molecular crystal, 1,4-bis[2-(4-methylthiophenyl)]-2,3,5,6-tetrafluoro-benzene (BMTP).[63] The crystal features a fibrous lamellar morphology with remarkable elasticity, while there are slip planes due to the slip accumulation of flat molecules. The alternating π-conjugated structure with tetrafluorobenzenes and thiophene nuclei provide a rigid center, resulting from the interaction between $S\cdots F$ and $F\cdots H$ (Figure 9A).[89] The molecules assemble in slip stacked arrays, with the rigid π-plane serving as the main body, which was described as fibril lamella morphology.[66] The centimeter-sized crystals demonstrated substantial mechanical splitting (Figure 9B). It may decompose into finer fibers while still maintaining elastic behaviors.[61,89] Hayashi et al. hypothesized that extended π-conjugated molecules suitable for elastic organic crystals require a planar conformation, a rigid structure, and controlled intermolecular interactions for face-to-face slip-stacking.[66] Figure 9C depicts a schematic diagram of the fibril lamella

morphology model.[66] The crisscrossed stacking structure between the fiber bundles serves to prevent the wires from slip under stress and deformation, thus preserving the structural integrity.[66,89] Upon stress, the $\pi-\pi$ interstacking molecules slide along the rigid π-plane over a short length range and then return to their original length upon relaxation. The slip of the π-planes inhibits effective energy transfer between molecules. The molecular filaments on either side of the bending arc of the fiber lamellae crystal undergo opposite expansions and contractions (Figure 9D).[89] The interlamellar zigzag molecular wires interlock with each other to prevent slippage between the fibers. For a single fiber bundle, the distance between atoms within the outer side increases at the bend, accompanied by the distance decreases in the inner side. The distance between the two π planes, however, remains unchanged.

While this model is well applied in a few examples, it is considered a more suitable mechanism for flexible crystals with mechanical-induced splitting characteristics.[91] Furthermore, the model provides valuable insights into the enhancement of planarity and rigidity of constituent molecules and facilitates the preparation of flexible fiber form crystal materials.

3.2.3. Reversible Molecular Rotation Model. To achieve elastic crystal bending, some reversible rearrangement of molecules within the crystal is necessary to meet expansion and contraction. Earlier studies mostly supported the isotropic interlocking stacking hypothesis. However, there are some special examples that do not fit this model, suggesting the hypothesis does not serve as a general criterion for the elasticity of crystals.[30] Clegg et al. discovered an elastic crystal of copper(II) acetoacetate ($[Cu(acac)_2]$) with an anisotropic stacking structure (Figure 10A and B).[30,90] Using micro-focusing synchronous X-ray diffraction technology, they
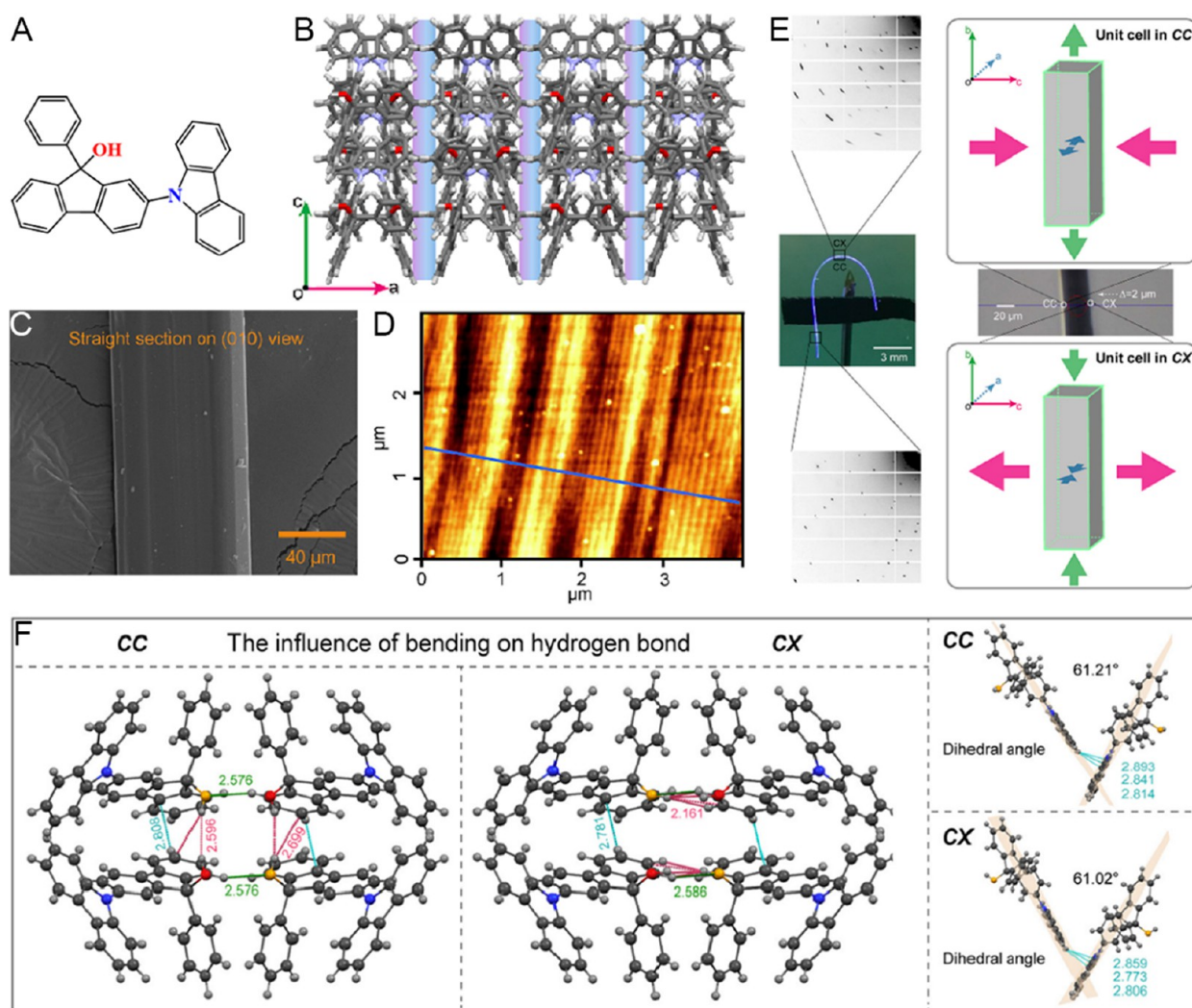
Figure 11. Dynamic physical cross-link frameworks. (A) Molecular structure of PhOH-Cz. (B) PhOH-Cz molecules accumulate to form molecular layers along the (010) crystal face, with colored rectangles indicating areas of weak molecular interaction. (C, D) SEM and AFM images of the PhOH-Cz crystal along the (010) crystal face. The layered structure can be clearly observed, corresponding to the accumulation of microscopic molecules. (E) XRD patterns of U-shaped bent crystals at bent and straight regions (left) and microscopic images of a bent section in U-shaped crystal. Side section view of the trajectory of the line map from the cx to cc area in the crystal. Diagram of the structural perturbation along the crystallographic *a*-, *b*-, and *c*-axes in the unit cell. The corresponding blue, green, and pink arrows in (E) represent slight changes along the different axes. (F) Crystalline structure and molecular packing of the bent PhOH-Cz crystals at the cc and cx points. Reproduced with permission from ref 67. Copyright 2022 Elsevier Inc.

analyzed the changes in the molecular arrangement within the crystal and identified a mechanism for the crystal's elastic flexibility at atomic resolution, namely, the reversible molecular rotation model. The molecules in the crystal rotate reversibly, allowing for the required mechanical compression and expansion (Figure 10C).[40,90] This hypothesis emphasizes that the only criterion for an elastic crystal is that the molecules must be able to recombine reversibly. This is necessary for the crystal to compress internally and expand externally along the arc, and accordingly expand and contract separately in the orthogonal direction (Figure 10D).[40,90,92] In a sense, this molecular rotation is more advantageous than molecular planes sliding past each other during strain. This allows stress to be dissipated into the interactions between molecules. The different strengths and types of intermolecular interactions in crystals can influence how molecules rearrange themselves to create macroscopic bending. Obviously, there are some elements consistent with some previous hypotheses,

such as the existence of 1D molecular chains, the morphology of fiber layers, the apparent alteration in center-to-center $\pi-\pi$ separation, and the variation in the angle between two columns of π-molecular motion. The reversible molecular rotation model attributes the different responses of the inner and outer sides to molecular rotation and does not restrict the properties of the molecular motion and the packing characteristics of the crystal. In this context, the hypothesis is general. However, it does not provide enough guidance on how to design elastic flexible crystals.

3.2.4. Dynamic Physical Cross-Link Frameworks. The advancement of elastic conjugated crystals in the field of elastic optoelectronics primarily relies on the capability to establish dynamic noncovalent networks and optimize intermolecular arrangements and photophysical processes.[27,34,93] Elasticity, as a microscopic reversible mechanism, requires dynamic and reversible weak interactions to allow for energy absorption and release.[28,94,95] Huang et al. developed and synthesized a
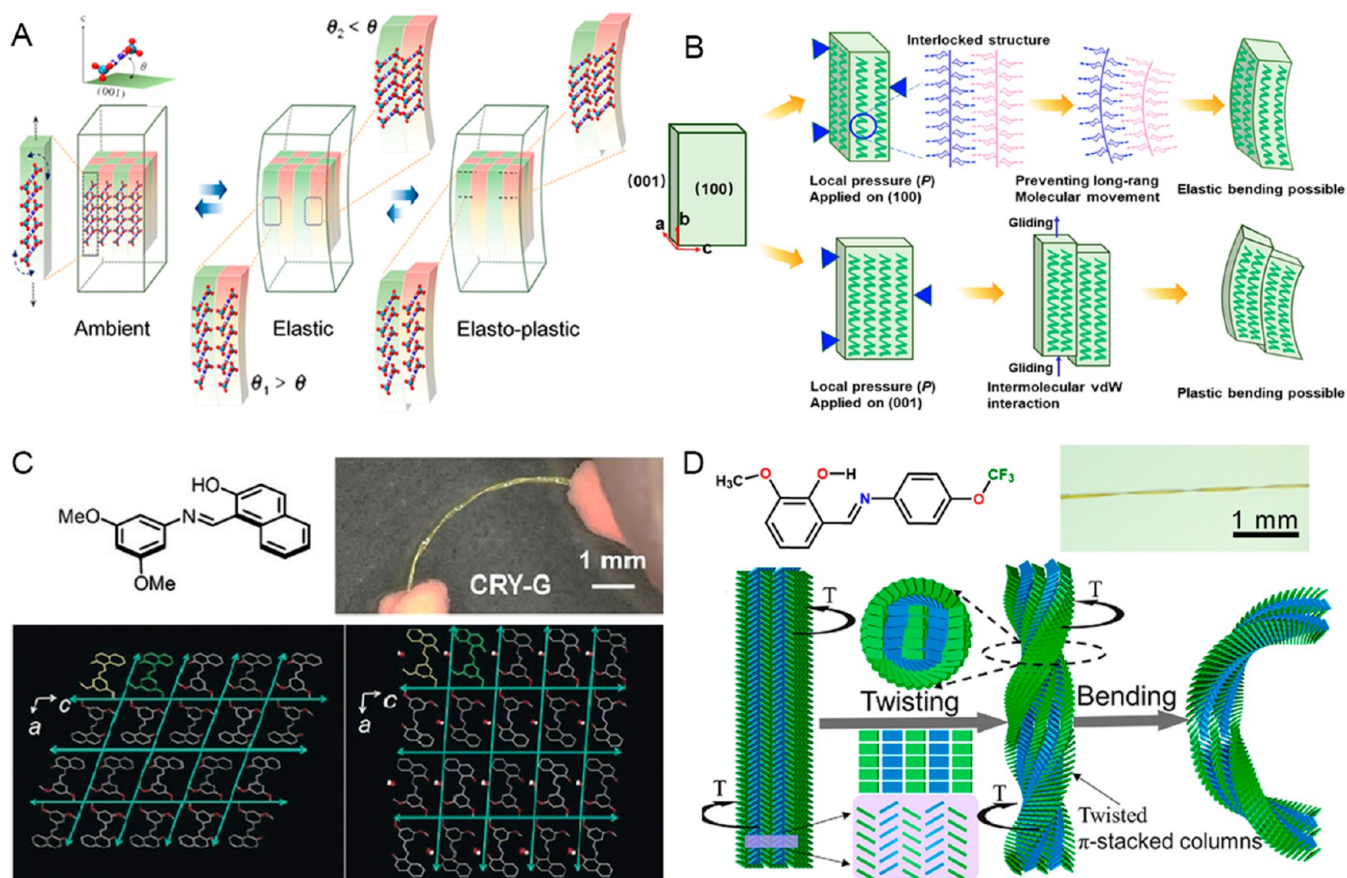
Figure 12. Flexible mechanism of elastic-plastic combination. (A) Schematic illustration of the proposed elasto-plastic bending mechanism of the dimethylammonium perrhenate ionic salt crystal. The reversible rotation of the molecule causes elastic bending of the crystal. However, when the degree of molecular rotation exceeds a certain limit, the molecular columns slide relative to one another, leading to irreversible plastic bending. Reproduced with permission from ref 97. Copyright 2022 2021 Wiley-VCH GmbH. (B) Diagram of elastic and plastic bending of anisotropic response types and their results at different structural levels. (C, D) Two crystals with both elastic bending and plastic twisting responses and their molecular structures and packing patterns. The packing of the molecules creates potential slip planes with cross arrangements, which can allow for molecular slip and relative motion, leading to plastic twisting of the crystal. Reproduced with permission from ref 73, Copyright 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim; ref 75, Copyright 2023 Elsevier Ltd. All rights reserved.

racemic conjugated material called PhOH-Cz (Figure 11A).[67] The crystals assembled into layered nanorods, and the layered nanostructures were firmly attached to create flexible single crystals (Figure 11B-11D). Microfocusing synchronous X-ray diffraction (XRD) spatial resolution structure analysis revealed that during the bending process, the layered nanostructures cross-linked by noncovalent hydrogen bonds underwent short-range molecular motion (Figure 11E and F). Furthermore, microregion infrared and Raman results revealed the dynamic and reversible properties of supramolecular hydrogen bonds interaction under mechanical stimulation.

The elasticity of the crystal can be ascribed to the structural perturbations that arise between the layered molecules as well as the dynamic and reversible recombination of hydrogen bonds. Fundamentally, the dynamic physical cross-linking framework of PhOH-Cz provides sufficient buffering capacity. Hydrogen bonds are particularly suited to build reversible physical cross-links in organic crystals because of the programmable self-recognition of their point-to-point interactions.[45,96] The layered structure provides a physical platform for rapid intermolecular mechanical energy transfer in tightly packed crystal structures, allowing the crystals to bend under an external stress. The contraction and elongation of interlayer and intralayer molecules are ascribed to the recombination of

C−H···O, O−H···π, and C−H···π, and hydrogen bonds. The dynamic physical cross-linking framework hypothesis suggests that anisotropic zigzag topologies favor the elasticity and that these anisotropic interactions (alternating weak and strong interactions within a zigzag column) allow the accumulation of external stresses applied within the crystal. Interlayer slip and intralayer perturbations facilitate energy storage and dissipation, prevent brittle fracture, and preserve the integrity of the conjugated crystals.

3.3. Mechanisms of Elastic-Plastic Deformation

So far, the majority of the mechanically flexible crystals reported concentrate on the extreme elastic or plastic types, and the connections between the various deformable crystals are relatively less studied. In recent years, crystals with both elastic and plastic deformations have gradually been discovered gradually. They demonstrate a transition from macro-elastic bending to macro-plastic bending,[98] and even the coexistence of elastic-plastic deformation.[73,74,99] It shows that the mechanisms of elasticity and plasticity are related to rather than isolated from each other.

The bendable ionic salt crystal, dimethylammoniumperrhenate, demonstrated intriguing elastic-plastic behavior. Within the bending strain (ε) limit of 1%, the crystal remained elastic,
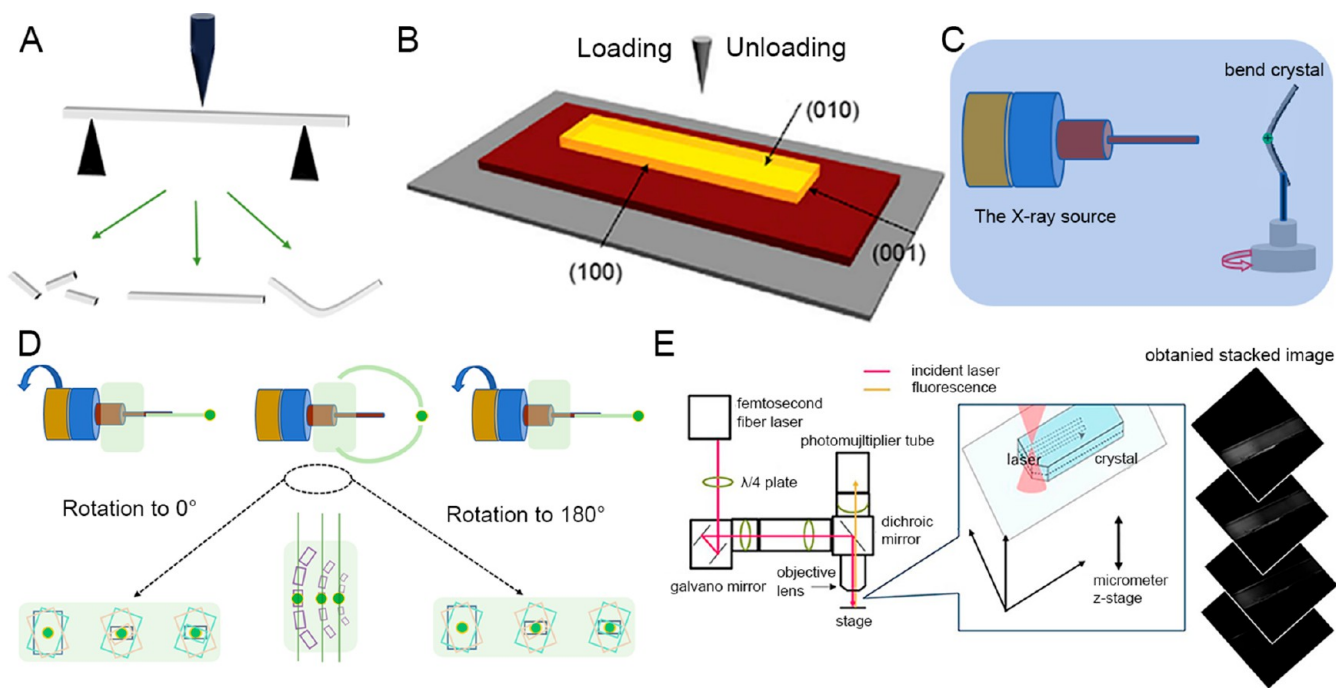
Figure 13. Characterization methods for crystal flexibility. (A) Three-point bending method proves the crystal flexibility. (B) Schematic diagram of nanoindentation technology. Reproduced with permission from ref 67. Copyright 2022 Elsevier Inc. (C) SCXRD characterization of the integrity of the bending crystals. Reproduced with permission from ref 27. Copyright 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (D) Schematic representation of narrow φ-scans (yellow circles indicate X-ray beams perpendicular to the page). (E) Optical configuration of MPFM. Reproduced from ref 111. Copyright 2023 American Chemical Society.

even during multiple bending cycles. Permanent plastic bending deformation was observed when the ε exceeded 1%. Such an elastic-plastic behavior has been also observed in organic crystals.[98] The transition from elasticity to plasticity is a gradual process; therefore, it is reasonable to assume that localized molecular rotation promotes elastic bending. The molecular rotation increases progressively and ultimately results in slip (plastic deformation) of the crystal layers at higher strains (Figure 12A).[97] This unique crystal structure necessitates that the weak interactions satisfy two concurrent conditions. First, the interaction must prevent the bending planes from slip during elastic bending, and second, it must also provide opportunities for slip during plastic bending.[98]

Another type of elastoplastic compatibility is the anisotropic response. Zhang et al. synthesized organic crystals using a stoichiometrically controlled cocrystallization method. The crystals manifested both elastic and plastic properties on different crystal planes (Figure 12B).[99] The anisotropic mechanical response in these organic crystals arises from the anisotropic arrangement of molecules within the crystal structure. The presence of interlocking cross-linked packing allows for elastic deformation, while the existence of potential slip planes permits plastic deformation. Molecular stacking in various crystal directions can be influenced by diverse external forces. As a result, a crystal can undergo both plastic spiral twisting and elastic bending, sometimes concurrently, depending on the external force applied. Zhang et al. reported several organic crystals possessing both plastic twisting and elastic bending properties (Figure 12C).[73,74] The reversible change of $\pi-\pi$ stacking is primarily responsible for the elastic bending, whereas an irreversible molecular slip leads to plastic twisting. To achieve plastic twisting, the crystal must possess slip planes that cross each other. Additionally, the deformation process typically entails the destruction and subsequent recombination of the hydrogen bonds. The $\pi-\pi$ packing, responsible for the elastic bending, is less influenced during the crystal twisting process. It has been recently reported that a crystal based on (E)-2-((4-(trifluoromethoxy)phenyl)imino) methyl-6-methoxyphenol exhibits multiplanar elastic bending and plastic twisting capabilities. This crystal has the ability to bend freely in any direction even after undergoing severe twisting, enabling a transition to three-dimensional elastic bending.[75] The existence of a cross-slip plane is a prerequisite for crystal twisting. During the twisting process, the twisting force (T) is tangential to the cross-section of the crystal, while the $\pi-\pi$ interaction is perpendicular to the cross-section along the crystal long axis. The twisting force applied to the $\pi-\pi$ interaction is relatively small, which prevents the breaking of the $\pi-\pi$ interactions and destruction of the π-stacking column. As a result, the two adjacent molecules within a π-stacking column can rotate relative to each other, allowing the entire π-stacking column to twist into a helical structure. This twisted shape creates an interlocking molecular stacking structure, enabling three-dimensional elastic bending (Figure 12D).[75]

4. CRYSTAL FLEXIBILITY MEASUREMENT

Understanding the correlation between crystal structures, particularly intermolecular interactions, and their mechanical properties is necessary for rational design and synthesis of flexible crystals with optimal mechanical properties.[80,100] To control the mechanical properties of molecular crystals, it is crucial to comprehend not only the strength of the intermolecular interactions but also the 3D molecules packing. Visualization and analysis of crystal assembly assist in isolating the distinctive mechanical responses associated with the molecules packing.[101]

4.1. Characterization Methods for Crystal Flexibility

To investigate the flexibility of the crystals, various methods have been proposed for characterizing flexible molecular crystals. *Three-points bend test* is the most conventional and convenient analytical method for characterizing crystal flexibility (Figure 13A). This well stablished mechanical test is widely used not only in molecular crystals but also in metals, polymer materials, and composite materials. The stress−strain curve is commonly used to provide elastic data.[40,3,30,102] The clear linear relationship between stress and strain not only reveals the elastic properties of a material, but also allows for the calculation of the elastic modulus using Hooke's law.[103] However, the traditional stress−strain measurement technique is limited by the size of sample.

As an alternative, *Nanoindentation* provides a more accurate and reliable method for characterizing the plane hardness and elastic modulus of crystals, thereby enabling precisely quantify of crystal flexibility.[2,104] *Nanoindentation* enables the linkage from molecular level properties, such as crystal stacking, (supra)molecular interactions, and inherent anisotropy, to macro events, such as layer migration, polymorphism, and solid-state reactivity (Figure 13B).[39,40,67,100] However, in practice, the presence of crystal defects and measurement errors usually leads to deviations between the measured elastic modulus and the true value. To mitigate this issue, a small number of areas can be selected for multipoint *Nanoindentation* testing during the experiment.[105]

It is necessary to analyze the change of crystal during the bending process for providing intuitive pieces of evidence of flexibility mechanisms. *Single crystal X-ray diffraction* (SCXRD) is an important method for characterizing whether the integrity of crystal remains intact during the bending process (Figure 13C).[27] SCXRD utilizes X-rays to illuminate the crystal to obtain information about its structure by analyzing the diffraction pattern produced by the interaction of X-rays and the crystal lattice. SCXRD can characterize the integrity of crystal and lattice changes before and after bending, by analyzing the presence and changes in the shape of diffraction points.[27,79] The presence of diffraction spots indicates that the periodicity of the crystal is largely preserved during the bending process. While the elongation of diffraction spots suggests that the molecules in the crystal lattice have moved away from their ideal position due to the stretching or compressing.[27] The changes in the diffraction points before and after bending indicate whether the crystal can return to its original microstructure after deformation. However, SCXRD has high requirements for crystal quality and size and may not be able to accurately characterize disordered structures after bending. Therefore, alternative techniques may be necessary to determine the structure of the curved crystals.

The development of *synchrotron* sources has undoubtedly provided a new way for analyzing the structure of curved crystals (Figure 13D).[106] Spatially resolved structure analysis using synchrotron radiation microfocus X-ray diffraction provides a mean to analyze the internal structural changes of crystals with atomic-scale resolution.[40,107,108] This technique can be used to determine the existence of slip planes in plastic-bent crystals,[39,42] and even to solve the crystal structure of elastically bent crystals.[67] As such, it provides key evidence for the mechanisms of crystal flexibility. At the molecular level, the effect of bending on molecular interactions can be studied by spatially resolved linearly polarized microinfrared and micro-Raman spectroscopy.[79,109,110] Spatially resolved infrared and Raman Spectra may provide clear evidence about the different influences of bending on halogen−halogen interactions on both sides of curved crystals.[39,42]

There has been a lack of analysis of the deep interior regions of crystals; therefore, physical properties based on molecular arrangement and lattice stability cannot be studied. *Multi-photon excited fluorescence microscopy* (MPFM) is an effective nondestructive 3D luminescence imaging technique that utilizes the principle of laser scanning microscopy.[111] The technique is commonly used in biomaterials to obtain clear 3D images of the inside of tissues and organs.[112−114] It can be used to distinguish the surface and volume luminescence of molecular crystals with a size of tens of microns. Changes in intramolecular interactions of molecular crystals may alter energy levels, resulting in unique optical properties of molecular crystals. Spectroscopic study of their internal body properties can promote the understanding of the essence of molecular crystals.[111] Recently, Suzuki et al. performed 3D MPFM imaging of the elastic molecular single crystal of 1, 4-bis (4-methylthiono-2-yl)-2,3,5, 6-tetrafluorobenzene (Figure 13E).[111] The results showed that the molecular interactions in the elastic crystal were controlled by mechanical shape changes of the crystal through elongation or bending, which demonstrated the potential of MPFM in the study of flexible molecular crystals.

4.2. Characterization of Intermolecular Interactions

Analysis of molecular interactions has played an important role throughout the development of flexible crystals. Research into the mechanisms of flexible crystals generally focuses on understanding the crystal packing through intermolecular interactions. Since the development of *Kitaigorodsky's packing principles* and *Desiraju's supramolecular synthons,*[115] several methods have been proposed to explain crystal molecular packing.[52] The *Hirschfeld surface analysis* method provides a visual basis for the analysis of molecular interactions.[116,117] Treating molecules as organic entities fundamentally changes the discussion of molecular interactions by enabling the unbiased identification of all the close contacts between them. It provides a direct understanding of the interactions between molecules in the crystal by mapping the electrostatic potentials of molecules onto the Hirschfeld surface.[49,82,118−120] Some practical computation of the Hirshfeld surface have been developed.[121,122] Based on the Hirshfeld calculation methods, the CrystalExplorer soft-ware visualizes molecular interactions as 2D fingerprint plots which contains functions of distance: d_e, d_i, d_{norm} and fingerprint plots.[121,123] d_i and d_e are the distances from the Hirshfeld surface to the nearest nucleus inside the surface and outside the surface, respectively. The fingerprint is highly sensitive to the immediate environment of the molecule and is unique to a given molecule for a particular polymorphic form. The coordinate system composed of d_i and d_e provides rich information including the type and strength of intermolecular interactions. Therefore, the 2D fingerprint plots provide direct evidence of intermolecular interaction for crystal flexibility. However, while the Hirschfeld surface can provide some quantitative information on molecular inter-actions, the method is still largely qualitative.

Density functional theory (DFT) is the most widely used method for studying the electronic structure of multielectron systems.[124] It has become a powerful research tool in the fields of chemistry, biology, and materials science. DFT has been widely applied to analysis of the noncovalent interactions of

molecular crystals (i.e., hydrogen bonding, dispersion interaction, dipole effect, etc.), which determine the crystal structure and properties.[125] However, the approximate standard density functions (DFs) used in electronic structure theory often fail to provide an adequate description of long-range ordered dispersion interactions.[126] Therefore, there are different dispersion correction strategies proposed to improve the existing DFT methods.[109,126−130] The dispersion-corrected density functional theory has shown great potential in the calculation of the dispersive interactions and lattice energies of organic crystals and supramolecular complexes.[130−132] Recently, a new density functional called Chemistry Functional 2022 with Damped Dispersion (CF22D) was developed,[124] which uses physical descriptors, extensive databases, and supervised learning strategies to optimize the damping dispersion term in molecular mechanics. The energy functional of CF22D has two kinds of terms: a DFA term and a molecular mechanics term representing the damping dispersion,

$$E^{CF22D} = E_{DF} + E_{disp}$$

where the E_{DF} is an exchange-dependent term,

$$E_{DF} = \frac{X}{100} E_X^{HF} + E_{nxc} + E_c$$

and E_{disp} is a molecular mechanical term, often referred to as the damped dispersion term,

$$E_{disp} = -\frac{1}{2} \sum_{AB} \frac{C_6^{AB}}{C_{AB}^6} f_{d,6}(r_{AB})$$

$$f_{d,6}(r_{AB}) = \frac{1}{1 + 6(r_{AB}/(S_{r,6}R_0^{AB}))^{-14}}$$

in which the parameters have been clearly defined in the relevant computational literature.[124,133] By using a flexible function form, combined with a global hybrid nonseparated meta general gradient approximation that depends on electron density and occupied orbitals, along with a damping dispersion term that depends on geometric structure, CF22D achieves greater chemical universality than previous functions. CF22D provides a universally reliable prediction of noncovalent interactions by simultaneously optimizing both the form of the density functional and the parameters of the molecular mechanics damping dispersion term. Furthermore, CF22D is not only able to accurately predict binding energy near equilibrium distance but can also provide reliable predictions for weak interactions at long distances.

Turner et al. proposed an *Energy framework* model that combines efficient calculations of precise internal molecular interaction energies with the molecular crystal topology.[52] The basis of the *Energy Framework* is the intermolecular interaction energy, which is obtained from unperturbed molecular wave functions. The energy of intermolecular interactions is typically expressed in terms of four key components: electrostatic, polarization, dispersion, and exchange repulsion:

$$E_{tot} = E_{ele} + E_{pol} + E_{dis} + E_{rep}$$

The energy between a pair of molecules is represented by a cylinder connecting the center of the molecular mass, and the cylinder radius is proportional to the magnitude of the interaction energy. The cylinders that make up the frame represent the relative strengths of the molecules in different directions.

The *Energy Framework* mode is notable for its low computational cost and efficient calculation time, facilitating the evaluation of the interaction topology of a large number of molecular crystal structures with relatively high accuracy.[52,134] By comparing the *Energy Framework* of molecular crystals, the anisotropic or isotropic energy distributions can be visually observed, thus providing reliable evidence for the crystal flexibility mechanism.[50] It has direct practical applications in exploring the mechanical properties of crystals. The method is particularly useful in identifying the anisotropy of interactions in molecular crystals as molecular columns or layers can be readily visualized and analyzed. It provides a comprehensive and intuitive way to understand the underlying mechanisms governing the mechanical properties of crystals.[50] The accurate and efficient calculation of model interaction energies, in conjunction with visualization through energy frames, offers a powerful new tool for quantitatively exploring both molecular crystal interaction energies and crystal structures. As a result, this method is highly valuable for gaining deeper insights into the fundamental characteristics of crystalline materials.[47,53,67,84,100]

5. APPLICATION PROSPECTS OF FLEXIBLE CRYSTALS

The recent discoveries of numerous flexible crystals break the understanding of the rigidity and fragility of molecular crystals, which created opportunities for the basic research and practical applications of molecular crystals. The elastic modulus of flexible molecular crystals (mostly between 1−25 GPa) lies between inorganic hard materials and polymeric soft materials, which is undoubtedly a great advantage of this material.[135−137] In contrast to hard inorganic materials, the presence of weak intermolecular interactions in flexible molecular crystals allows for maintaining integrity under external stimulus.[3,5,136] Compared with those of polymer soft materials, the ordered arrangement of crystals facilitates their structural characterization. The dynamic processes of crystals can be characterized and studied in situ by various techniques.[39,40] The observations on the atomic level of the responsive processes of crystals have deepened the understanding of the flexible mechanism. The operability of molecular crystal is also one of its advantages.[48] Especially for organic molecular crystals, one can rationally design molecules and even effectively adjust the intermolecular interactions by changing the functional groups of the building blocks, so as to realize the transition between different response behaviors of crystals under external stimuli. Moreover, molecular crystals often feature polymorphism that the molecules crystallize in different space groups under different crystallization conditions, which enriches the stimuli-responsive behaviors of molecular crystals.[8,138] Therefore, researchers can analyze the differences of the interactions between molecules according to the different stacking forms and inductively determine the origin of their flexibility, which further provides a theoretical basis for the controllable preparation of flexible molecular crystals. With highly ordered aggregation structure, flexible crystals might be engineered to exhibit fascinating optical, electrical, and mechanical properties, promising their potential flexible electronics and actuation applications. On account of the broad applications prospect in the fields of information sensing,[139−142] biomedicine,[25,86,143−147] wearable devices,[32] laser media,[148,149] fluorescence detection,[150] renewable biomass resources development,[151] etc., flexible crystals have attracted increasing attention from academia and industry.

5.1. Pharmaceutical Industry

Understanding the correlation between mechanical properties and crystal structure is beneficial for chemists in developing drug formulas. The pharmaceutical industry needs to fully consider factors such as active ingredient content, liquidity, stability, metabolic rate, granulation, and grinding characteristics.[143,147,152,153] The flexibility of solid drugs affects their crushing, granulation, and preparation. Enhancing the mechanical properties can remarkably improve the efficiency of postprocessing. In-depth study of the mechanisms of flexibility of molecular crystals is highly beneficial to promoting the compatibility, compressibility, and tablet properties of drugs. Shastri et al. studied the compressibility of three blend compounds prepared by flexible crystals and lamotrigine (Figure 14A).[154] The capping tendency indicates the elasticity of the blend material, showing that the elasticity of the blend is not conducive to compressibility. When the compression force is released, the material shows a tendency to rebound, resulting in the self-destruction of compaction.[154] Among them, the LCA blend material with the best plasticity has the highest

compaction strength at the maximum residence time. Moreover, the hardness of the three compacted materials with brittleness, LVNA, LVNB and LVNC, is almost the same. It shows that plasticity and brittleness are suitable for pharmaceutical manufacturing.[154]

The applications of crystal engineering to the design of active pharmaceutical ingredients (APIs) allows for the optimal combination of materials with important physicochemical properties, such as solubility, dissolution rate and bioavailability.[155] It also allows for the adjustment of mechanical properties such as grindability and plannability in industrial-scale pharmaceutical production.[156−159] Drug cocrystals have been shown to improve the physicochemical properties of drugs.[160] Researches have shown that the preparation of APIs and eutectic salt devices can effectively adjust their mechanical properties.[155] Moreover, it has been demonstrated that the transformation of single-component compounds into multicomponent plastic crystals can adjust the physicochemical properties and powder flow of active pharmaceutical ingredients, thereby improving the plateness.[161]

5.2. Flexible Optical Waveguide

Flexible molecular crystals have emerged as a promising platform for optical waveguides owing to their highly ordered anisotropic lattices. In particular, the anisotropic properties make flexible molecular crystals attractive candidates for applications in optics.[34] High-quality crystal structures can provide lateral confinement of light, thereby lowering the laser threshold.[162] Elastic organic crystals can bend the path of light while maintaining ordered stacking of molecules, which is beneficial for optical signal transmission with excellent flexible optical waveguide properties.[34,142,149,163−166] For example, Zhang et al. realized optical waveguides in straight and bending states using elastic monobenzene molecular crystals with red fluorescence emission. Owing to the high elasticity, the optical loss coefficient of bending crystals is almost the same as that of straight crystals (Figure 14B).[149]

Flexible molecules with certain degrees of freedom and low energy conformations are likely to adopt different conformations, leading to conformational polymorphism. Polymorphism has been revealed as a potential design strategy for altering both the optical and mechanical properties of molecular crystals. Based on the polymorphism of molecular crystals, optical waveguide crystals with different mechanical responses can be prepared to adapt to different conditions.[65,73,167] Feiler et al. demonstrated how the mechanical properties of organic photoluminescent materials could be modulated by controlling polymorphism.[138] Beneficial from its plasticity and bright luminescence, the crystalline phase with plastic bending ability exhibits the characteristic of a flexible optical waveguide. Zhang et al. even prepared a flexible optical waveguide crystal with both elasticity and plasticity. The crystal, (E)-1-(((3,5-dimethoxyphenyl)imino)methyl)naphthalen-2-ol, exhibited plastic twisting under torsional force and elastic bending underbending force.[73] Based on this, a new application field for flexible organic single crystals has been developed, namely, the polarization rotation.

5.3. Luminescence Regulation

Mechanical force is a reliable and environmentally friendly energy source that can provide exciting luminescent properties for materials.[168] In recent years, as various flexible crystalline materials have been reported, it has been found that the optical properties of some crystals can be adjusted by changing the
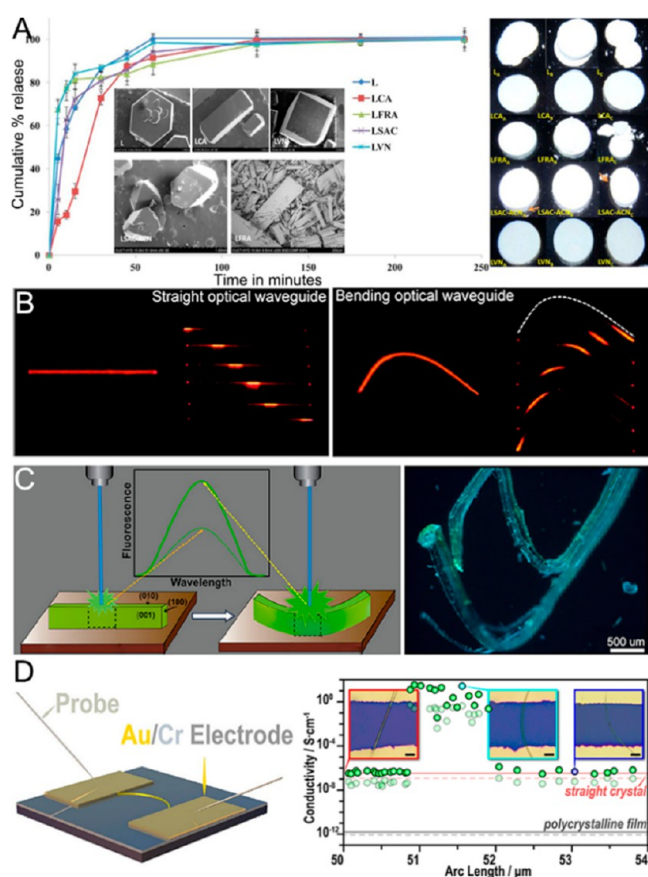
Figure 14. Typical applications of flexible molecular crystals. (A) Application of crystal flexibility in the pharmaceutical industry. Changes in drug tablet properties by preparing the flexible crystals blend. Reproduced from ref 154. Copyright 2015 American Chemical Society. (B) Flexible optical waveguides based on single-component organic bulk crystals. Reproduced from ref 149. Copyright 2019 American Chemical Society. (C) Bending promotes the fluorescence enhancement of crystals. Reproduced with permission from ref 169. Copyright 2020 Wiley-VCH GmbH. (D) Bending promotes electrical performance of crystal. Reproduced with permission from ref 19. Copyright 2021 Wiley-VCH GmbH.

degree of bending. Bhattacharya et al. reported a plastic crystal that exhibits an unusual fluorescence enhancement during its irreversible mechanical bending (Figure 14C).[169] The crystal, ethyl[(4Z)-2-methyl-5-oxo-4-(2,3,4-trimethoxybenzylidene)-4,5-dihydro-1H-imidazol-1-yl] acetate, demonstrates significant plastic bending properties, and the application of bending strain can result in a 3-fold enhancement of fluorescence. The crystal possesses the potential to be engineered as a mechanically adjustable, pliable, luminescent material and demonstrates promising prospects in the field of mechanical sensors and flexible optoelectronic devices. The mechanism of such an enhanced fluorescence was ascribed to the accumulation of strained molecules in the perturbed region.

The fluorescence alterations can also be caused by elastic deformation of functional elastic organic crystals. Hayashi, S et al. demonstrated the attainability of reversible changes in morphology and fluorescence within elastic π-conjugated crystals during the mechanical bent-relaxation process.[63] They have further discovered that crystals of 9,10-dibromoanthracene demonstrated an extension-induced bathochromic shift and a contraction-induced hypochromatic shift.[93]

5.4. Flexible Electronic Devices

The inherent lack of flexibility of molecular crystals often imposes limitations on their utilization in electronic devices.[170] The lower density and higher performance of flexible nano crystals with and conductivity make them promising alternatives for future applications in optoelectronics. Using the physical vapor transport manufacturing technique, Briseno et al. prepared and demonstrated high-performance organic single crystal transistors.[78] Its electrical properties were comparable to those of amorphous silicon and superior to those of previously reported flexible organic thin film transistors. The authors believed that flexible transistors based on thin, conformable organic single crystals might give rise to alternative applications that could have a profound influence on consumer electronics. Hu et al. constructed organic single crystal transistors and hybrid circuits by combining organic single crystal nanowires of CuPc (copper phthalocyanine, p-type) and F16CuPc (copper hexadecafluorophthalocyanine, n-type) with inorganic antimony-doped tin dioxide (SnO_2:Sb) nanowires.[141] These devices exhibited low operating voltage, high mobility, and good stability, demonstrating potential application prospects in more complex logic circuits. The studies on the relationship between mechanical properties and the performance of organic single crystal devices indicated that organic nanowires were more flexible and suitable for the field of portable flexible electronics, compared with inorganic nanowires.[171] In addition, the average mobility of bending crystals could be higher than that of straight crystals, which showed that the intrinsic bending of organic crystals could improve the performance of their electronic devices. The increased mobility of bent crystals was ascribed to enhanced intermolecular interactions in the compressed molecularlayer.

Gong et al. reported an example of deformation-induced functional enhancement in crystalline materials.[19] Taking inspiration from the magic angle twisted bilayer graphene, the author utilized halobenzene as a model to uncover the unexplored correlation between mechanical deformation and crystal function. Compared to the straight ones, the device based on the bending crystal exhibited a significant increase in conductivity (Figure 14D).[19] It demonstrates that a single crystal can be tailored into intelligent and flexible electronics to adapt complex circuits and perform diverse functions.

6. CONCLUSION AND OUTLOOK

After two decades of development, significant advancements have been made in the field of flexible crystals, which is expanding toward functionalization, integration, and intelligence. From the applications in the pharmaceutical industry to applications in flexible optical waveguides, wearable materials, and electronic devices, the potential applications of flexible crystals are vast and promising. Moreover, although the mechanism of the mechanical deformation of nanowire crystals is still unclear, flexible nanocrystals have exhibited promising application potential in the field of flexible electronic materials. However, fundamentally addressing potential obstacles such as the scalability, manufactuability, and stability of flexible crystals in various applications requires a full understanding of the flexibility mechanism.

The importance of intermolecular interactions and crystal stacking arrangements cannot be overstated in determining the mechanical properties of a crystal. Understanding the role of intermolecular interactions in the mechanical flexibility of molecular crystals is helpful to establish a universal design strategy for creating mechanically flexible crystals. It is evident that flexible crystals enable the rearrangement of their constituent molecules, thereby satisfying both internal compression along the crystal structure and external expansion. However, the design strategies of flexible crystals mainly rely on empirical knowledge and currently lack a comprehensive summary of flexible design strategies. Although the relationship between the microstructure and macroscopic mechanical properties of flexible crystals has been preliminarily established, further studies concentrating on the investigations of atomic-scale rearrangement are still needed to provide more robust shreds of evidence for flexibility mechanisms. Moreover, it is urgent to investigate deeper mechanisms and strategies to provide general guidance in this field due to the limited number of reported flexible molecular crystals and the lack of systematic exploration.

The combination of experimental and computational tools has proven helpful in advancing the understanding of the relationship between molecular stacking and mechanical properties, and there is still ample space for further exploration and development in this aspect. New insights are being put into this interdisciplinary field with advances in instrumentation, such as micro-Raman, microinfrared, and micro-X-ray diffraction techniques. The widespread use of advanced precision instruments, such as synchrotron radiation, has significantly contributed to the understanding of the response behaviors of flexible molecular crystals at the molecular level. These tools allow for more precise measurements and analysis of the connection of structure and mechanical properties, enabling further understanding of the flexible crystals and expanding their potential applications.

To establish a general design strategy for flexible crystals, it is necessary for crystal engineers to work together to build a more comprehensive database of flexible crystal structures and properties. It will enable researchers to draw upon a wider range of databases and insights when designing new flexible molecular crystals with specific mechanical and structural properties. Collaboration in this realm will also accelerate the development of standardized research methods and facilitate the sharing of information and results within the scientific

community. It is expected that in the near future, as technical means continue to advance and theoretical understanding grows increasingly mature, a more precise and effective design strategy for flexible molecular crystals will be abled. With the development of new experimental techniques and the continued refinement of computational tools, crystal engineers will be better equipped to explore the structural and mechanical properties of flexible molecular crystals and design materials with specific properties and applications. This will, in turn, contribute to the development of new technologies in fields such as electronics, photonics, and energy storage.

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Notes

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■ REFERENCES

(1) Naumov, P.; Chizhik, S.; Panda, M. K.; Nath, N. K.; Boldyreva, E. Mechanically responsive molecular crystals. *Chem. Rev.* **2015**, *115* (22), 12440−12490.

(2) Das, S.; Mondal, A.; Reddy, C. M. Harnessing molecular rotations in plastic crystals: a holistic view for crystal engineering of adaptive soft materials. *Chem. Soc. Rev.* **2020**, *49* (24), 8878−8896.

(3) Naumov, P.; Karothu, D. P.; Ahmed, E.; Catalano, L.; Commins, P.; Mahmoud Halabi, J.; Al-Handawi, M. B.; Li, L. The rise of the dynamic crystals. *J. Am. Chem. Soc.* **2020**, *142* (31), 13256−13272.

(4) Xu, W.; Sanchez, D. M.; Raucci, U.; Zhou, H.; Dong, X.; Hu, M.; Bardeen, C. J.; Martinez, T. J.; Hayward, R. C. Photo-actuators via epitaxial growth of microcrystal arrays in polymer membranes. *Nat. Mater.* **2023**, *22* (9), 1152−1159.

(5) Zheng, Y.; Jia, X.; Li, K.; Xu, J.; Bu, X. H. Energy Conversion in Single-Crystal-to-Single-Crystal Phase Transition Materials. *Adv. Energy Mater.* **2022**, *12* (4), 2100324.

(6) Sato, O. Dynamic molecular crystals with switchable physical properties. *Nat. Chem.* **2016**, *8* (7), 644−656.

(7) Zhao, C.; Hou, J.; Hill, M.; Freeman, B.; Wang, H.; Zhang, H. Enhanced Gating Effects in Responsive Sub-nanofluidic Ion Channels. *Acc. Chem. Res.* **2023**, *4* (9), 786−797.

(8) Panda, M. K.; Runčevski, T. e.; Husain, A.; Dinnebier, R. E.; Naumov, P. e. Perpetually self-propelling chiral single crystals. *J. Am. Chem. Soc.* **2015**, *137* (5), 1895−1902.

(9) Duan, Y. L.; Semin, S.; Tinnemans, P.; Cuppen, H.; Xu, J. L.; Rasing, T. Robust thermoelastic microactuator based on an organic molecular crystal. *Nat. commun.* **2019**, *10* (1), 4573.

(10) Yao, Z. Q.; Wang, K.; Liu, R.; Yuan, Y. J.; Pang, J. J.; Li, Q. W.; Shao, T. Y.; Li, Z. G.; Feng, R.; Zou, B.; et al. Dynamic Full-Color Tuning of Organic Chromophore in a Multi-Stimuli-Responsive 2D Flexible MOF. *Angew. Chem., Int. Ed.* **2022**, *61* (17), No. e202202073.

(11) Deng, W.-F.; Li, Y.-X.; Zhao, Y.-X.; Hu, J.-S.; Yao, Z.-S.; Tao, J. Inversion of Molecular Chirality Associated with Ferroelectric Switching in a High-Temperature Two-Dimensional Perovskite Ferroelectric. *J. Am. Chem. Soc.* **2023**, *145* (9), 5545−5552.

(12) Duan, Y.; Semin, S.; Tinnemans, P.; Xu, J.; Rasing, T. Fully controllable structural phase transition in thermomechanical molecular crystals with a very small thermal hysteresis. *Small* **2021**, *17* (14), 2006757.

(13) Chen, J.; Leung, F. K.-C.; Stuart, M. C.; Kajitani, T.; Fukushima, T.; van der Giessen, E.; Feringa, B. L. Artificial muscle-like function from hierarchical supramolecular assembly of photo-responsive molecular motors. *Nat. Chem.* **2018**, *10* (2), 132−138.

(14) Iamsaard, S.; Aßhoff, S. J.; Matt, B.; Kudernac, T.; Cornelissen, J. J.; Fletcher, S. P.; Katsonis, N. Conversion of light into macroscopic helical motion. *Nat. Chem.* **2014**, *6* (3), 229−235.

(15) Browne, W. R.; Feringa, B. L. Making molecular machines work. *Nat. Nanotechnol.* **2006**, *1* (1), 25−35.

(16) Shi, R.; Zhao, S.; Luo, R.; Cheng, P.; Liu, C.; Han, X.; Qi, S.; Zhang, Y.; Zhu, J.; Xu, J.; Bu, X.-H. Controllable shape deformation of an organic single crystal actuated by anisotropic thermal expansion. *Cell Rep. Phys. Sci.* **2023**, *4* (6), 101451.

(17) Ito, S. Mechanochromic luminescence of soft crystals: Recent systematic studies in controlling the molecular packing and mechanoresponsive properties. *J. Photoch. Photobio. C* **2022**, *51*, 100481.

(18) Sagara, Y.; Yamane, S.; Mitani, M.; Weder, C.; Kato, T. Mechanoresponsive luminescent molecular assemblies: an emerging class of materials. *Adv. Mater.* **2016**, *28* (6), 1073−1095.

(19) Chen, Y.; Chang, Z.; Zhang, J.; Gong, J. Bending for Better: Flexible Organic Single Crystals with Controllable Curvature and Curvature-Related Conductivity for Customized Electronic Devices. *Angew. Chem., Int. Ed.* **2021**, *60* (41), 22424−22431.

(20) Kusumoto, S.; Kim, Y.; Hayami, S. Flexible metal complex crystals in response to external mechanical stimuli. *Coord. Chem. Rev.* **2023**, *475*, 214890.

(21) Szafranski, M.; Katrusiak, A. Mechanism of pressure-induced phase transitions, amorphization, and absorption-edge shift in photovoltaic methylammonium lead iodide. *J. Phys. Chem. Lett.* **2016**, *7* (17), 3458−3466.

(22) Weder, C. Mechanoresponsive materials. *J. Mater. Chem.* **2011**, *21* (23), 8235−8236.

(23) Chang, Z.; Yang, D. H.; Xu, J.; Hu, T. L.; Bu, X. H. Flexible metal-organic frameworks: recent advances and potential applications. *Adv. Mater.* **2015**, *27* (36), 5432−5441.

(24) Gao, F. F.; Song, H. P.; Li, Z. G.; Qin, Y.; Li, X.; Yao, Z. Q.; Fan, J. H.; Wu, X.; Li, W.; Bu, X. H. Pressure-Tuned Multicolor Emission of 2D Lead Halide Perovskites with Ultrahigh Color Purity. *Angew. Chem., Int. Ed.* **2023**, *62* (12), No. e202218675.

(25) Reddy, C. M.; Gundakaram, R. C.; Basavoju, S.; Kirchner, M. T.; Padmanabhan, K. A.; Desiraju, G. R. Structural basis for bending of organic crystals. *Chem. Commun.* **2005**, No. 31, 3945−3947.

(26) Reddy, C. M.; Padmanabhan, K. A.; Desiraju, G. R. Structure-property correlations in bending and brittle organic crystals. *Cryst. Growth Des.* **2006**, *6* (12), 2720−2731.

(27) Ghosh, S.; Reddy, C. M. Elastic and bendable caffeine cocrystals: implications for the design of flexible organic materials. *Angew. Chem., Int. Ed.* **2012**, *51* (41), 10319−10323.

(28) Ghosh, S.; Mishra, M. K.; Kadambi, S. B.; Ramamurty, U.; Desiraju, G. R. Designing Elastic Organic Crystals: Highly Flexible Polyhalogenated N-Benzylideneanilines. *Angew. Chem., Int. Ed.* **2015**, *54* (9), 2674−2678.

(29) Fang, K.; Wang, R.; Zhang, H.; Zhou, L.; Xu, T.; Xiao, Y.; Zhou, Y.; Gao, G.; Chen, J.; Liu, D.; et al. Mechano-responsive, tough, and antibacterial zwitterionic hydrogels with controllable drug release for wound healing applications. *ACS Appl. Mater. Interfaces* **2020**, *12* (47), 52307−52318.

(30) Thompson, A. J.; Orué, A. I. C.; Nair, A. J.; Price, J. R.; McMurtrie, J.; Clegg, J. K. Elastically flexible molecular crystals. *Chem. Soc. Rev.* **2021**, *50* (21), 11725−11740.

(31) Park, S.; Wang, G.; Cho, B.; Kim, Y.; Song, S.; Ji, Y.; Yoon, M.-H.; Lee, T. Flexible molecular-scale electronic devices. *Nat. Nanotechnol.* **2012**, *7* (7), 438−442.

(32) Hassan, M.; Abbas, G.; Li, N.; Afzal, A.; Haider, Z.; Ahmed, S.; Xu, X.; Pan, C.; Peng, Z. Significance of flexible substrates for wearable and implantable devices: Recent advances and perspectives. *Adv. Mater. Technol.* **2022**, *7* (3), 2100773.

(33) Stoddart, J. F. Mechanically interlocked molecules (MIMs)—molecular shuttles, switches, and machines (Nobel Lecture). *Angew. Chem., Int. Ed.* **2017**, *56* (37), 11094−11125.

(34) Seki, T.; Hoshino, N.; Suzuki, Y.; Hayashi, S. Functional flexible molecular crystals: intrinsic and mechanoresponsive properties. *CrystEngComm* **2021**, *23* (34), 5686−5696.

(35) Caruso, M. M.; Davis, D. A.; Shen, Q.; Odom, S. A.; Sottos, N. R.; White, S. R.; Moore, J. S. Mechanically-induced chemical changes in polymeric materials. *Chem. Rev.* **2009**, *109* (11), 5755−5798.

(36) Sagara, Y.; Kato, T. Mechanically induced luminescence changes in molecular assemblies. *Nat. Chem.* **2009**, *1* (8), 605−610.

(37) Delogu, F.; Mulas, G.; Schiffini, L.; Cocco, G. Mechanical work and conversion degree in mechanically induced processes. *Mater. Sci. Eng., A* **2004**, *382* (1−2), 280−287.

(38) Wang, K.; Mishra, M. K.; Sun, C. C. Exceptionally elastic single-component pharmaceutical crystals. *Chem. Mater.* **2019**, *31* (5), 1794−1799.

(39) Panda, M. K.; Ghosh, S.; Yasuda, N.; Moriwaki, T.; Mukherjee, G. D.; Reddy, C. M.; Naumov, P. Spatially resolved analysis of short-range structure perturbations in a plastically bent molecular crystal. *Nat. Chem.* **2015**, *7* (1), 65−72.

(40) Worthy, A.; Grosjean, A.; Pfrunder, M. C.; Xu, Y.; Yan, C.; Edwards, G.; Clegg, J. K.; McMurtrie, J. C. Atomic resolution of structural changes in elastic crystals of copper (II) acetylacetonate. *Nat. Chem.* **2018**, *10* (1), 65−69.

(41) Bhattacharya, B.; Michalchuk, A. A.; Silbernagl, D.; Rautenberg, M.; Schmid, T.; Feiler, T.; Reimann, K.; Ghalgaoui, A.; Sturm, H.; Paulus, B.; et al. A mechanistic perspective on plastically flexible coordination polymers. *Angew. Chem., Int. Ed.* **2020**, *59* (14), 5557−5561.

(42) An, L.-C.; Li, X.; Li, Z.-G.; Li, Q.; Beldon, P. J.; Gao, F.-F.; Li, Z.-Y.; Zhu, S.; Di, L.; Zhao, S.; et al. Plastic bending in a semiconducting coordination polymer crystal enabled by delamination. *Nat. Commun.* **2022**, *13* (1), 6645.

(43) Commins, P.; Karothu, D. P.; Naumov, P. Is a Bent Crystal Still a Single Crystal? *Angew. Chem., Int. Ed.* **2019**, *58* (30), 10052−10060.

(44) Raut, D.; Kiran, M. S.; Mishra, M. K.; Asiri, A. M.; Ramamurty, U. On the loading rate sensitivity of plastic deformation in molecular crystals. *CrystEngComm* **2016**, *18* (20), 3551−3555.

(45) Reddy, C. M.; Kirchner, M. T.; Gundakaram, R. C.; Padmanabhan, K. A.; Desiraju, G. R. Isostructurality, polymorphism and mechanical properties of some hexahalogenated benzenes: the nature of halogen···halogen interactions. *Chem. - Eur. J.* **2006**, *12* (8), 2222−2234.

(46) Li, J.; Li, J.; Liu, H.; Zhang, L.; Lu, Y.; Zhou, Z. Structural landscape investigations on bendable plastic crystals of isonicotinamide polymorphs. *Chin. Chem. Lett.* **2022**, *33* (8), 4069−4073.

(47) Liu, Y.; Yang, P.; Zhang, K.; Xu, J.; Wu, S.; Gong, J. Bendable and Twistable Crystals of Flufenamic Acid Form III with Bending Mechanofluorochromism Behavior. *Cryst. Growth Des.* **2022**, *22* (2), 1312−1318.

(48) Krishna, G. R.; Devarapalli, R.; Lal, G.; Reddy, C. M. Mechanically flexible organic crystals achieved by introducing weak interactions in structure: supramolecular shape synthons. *J. Am. Chem. Soc.* **2016**, *138* (41), 13561−13567.

(49) Saha, S.; Desiraju, G. R. Crystal engineering of hand-twisted helical crystals. *J. Am. Chem. Soc.* **2017**, *139* (5), 1975−1983.

(50) Thomas, S. P.; Shi, M. W.; Koutsantonis, G. A.; Jayatilaka, D.; Edwards, A. J.; Spackman, M. A. The elusive structural origin of plastic bending in dimethyl sulfone crystals with quasi-isotropic crystal packing. *Angew. Chem., Int. Ed.* **2017**, *56* (29), 8468−8472.

(51) Owczarek, M.; Hujsak, K. A.; Ferris, D. P.; Prokofjevs, A.; Majerz, I.; Szklarz, P.; Zhang, H.; Sarjeant, A. A.; Stern, C. L.; Jakubas, R.; et al. Flexible ferroelectric organic crystals. *Nat. Commun.* **2016**, *7* (1), 13108.

(52) Turner, M. J.; Thomas, S. P.; Shi, M. W.; Jayatilaka, D.; Spackman, M. A. Energy frameworks: insights into interaction anisotropy and the mechanical properties of molecular crystals. *Chem. Commun.* **2015**, *51* (18), 3735−3738.

(53) Devarapalli, R.; Kadambi, S. B.; Chen, C.-T.; Krishna, G. R.; Kammari, B. R.; Buehler, M. J.; Ramamurty, U.; Reddy, C. M. Remarkably distinct mechanical flexibility in three structurally similar semiconducting organic crystals studied by nanoindentation and molecular dynamics. *Chem. Mater.* **2019**, *31* (4), 1391−1402.

(54) Pisacic, M.; Biljan, I.; Kodrin, I.; Popov, N.; Soldin, Z.; Đaković, M. Elucidating the origins of a range of diverse flexible responses in crystalline coordination polymers. *Chem. Mater.* **2021**, *33* (10), 3660−3668.

(55) Pisačić, M.; Kodrin, I.; Biljan, I.; Đaković, M. Exploring the diversity of elastic responses of crystalline cadmium (II) coordination polymers: from elastic towards plastic and brittle responses. *CrystEngComm* **2021**, *23* (40), 7072−7080.

(56) Pisačić, M.; Kodrin, I.; Trninić, A.; Đaković, M. Two-dimensional anisotropic flexibility of mechanically responsive crystalline cadmium (II) coordination polymers. *Chem. Mater.* **2022**, *34* (5), 2439−2448.

(57) Tang, Z.; Sun, X.-P.; Wang, S.-D.; Ji, X.-Y.; Li, Y.; Yao, Z.-S.; Tao, J. Altering elastic-plastic mechanical response of a series of isostructural metal-organic complex crystals. *Sci. China Chem.* **2022**, *65* (4), 710−718.

(58) Chinnasamy, R.; Munjal, B.; Suryanarayanan, R.; Peedikakkal, A. M. P.; Mishra, M. K.; Ghosh, S. Pressure and Temperature Induced Dual Responsive Molecular Crystals: Effect of Polymorphism. *Cryst. Growth Des.* **2022**, *22* (1), 615−624.

(59) Saini, A. K.; Natarajan, K.; Mobin, S. M. A new multitalented azine ligand: elastic bending, single-crystal-to-single-crystal transformation and a fluorescence turn-on Al (III) sensor. *Chem. Commun.* **2017**, *53* (71), 9870−9873.

(60) Gupta, P.; Karothu, D. P.; Ahmed, E.; Naumov, P.; Nath, N. K. Thermally twistable, photobendable, elastically deformable, and self-healable soft crystals. *Angew. Chem., Int. Ed.* **2018**, *130* (28), 8634−8638.

(61) Đaković, M.; Borovina, M.; Pisačić, M.; Aakeröy, C. B.; Soldin, Ž.; Kukovec, B. M.; Kodrin, I. Mechanically responsive crystalline coordination polymers with controllable elasticity. *Angew. Chem., Int. Ed.* **2018**, *57* (45), 14801−14805.

(62) Liu, H.; Lu, Z.; Zhang, Z.; Wang, Y.; Zhang, H. Highly elastic organic crystals for flexible optical waveguides. *Angew. Chem., Int. Ed.* **2018**, *57* (28), 8448−8452.

(63) Hayashi, S.; Koizumi, T. Elastic Organic Crystals of a Fluorescent π-Conjugated Molecule. *Angew. Chem., Int. Ed.* **2016**, *55* (8), 2701−2704.

(64) Liu, H.; Ye, K.; Zhang, Z.; Zhang, H. An Organic Crystal with High Elasticity at an Ultra-Low Temperature (77 K) and Shapeability at High Temperatures. *Angew. Chem., Int. Ed.* **2019**, *58*, 19081.

(65) Chu, X.; Lu, Z.; Tang, B.; Liu, B.; Ye, K.; Zhang, H. Engineering mechanical compliance of an organic compound toward flexible crystal lasing media. *J. Phys. Chem. Lett.* **2020**, *11* (14), 5433−5438.

(66) Hayashi, S.; Yamamoto, S. y.; Takeuchi, D.; Ie, Y.; Takagi, K. Creating elastic organic crystals of π-conjugated molecules with bending mechanofluorochromism and flexible optical waveguide. *Angew. Chem., Int. Ed.* **2018**, *57* (52), 17002−17008.

(67) Wei, C.; Bai, L.; An, X.; Xu, M.; Liu, W.; Zhang, W.; Singh, M.; Shen, K.; Han, Y.; Sun, L.; et al. Atomic-resolved hierarchical structure of elastic π-conjugated molecular crystal for flexible organic photonics. *Chem.* **2022**, *8* (5), 1427−1441.

(68) Takamizawa, S.; Miyamoto, Y. Superelastic Organic Crystals. *Angew. Chem., Int. Ed.* **2014**, *53* (27), 6970−6973.

(69) Liu, G.; Liu, J.; Liu, Y.; Tao, X. Oriented single-crystal-to-single-crystal phase transition with dramatic changes in the dimensions of crystals. *J. Am. Chem. Soc.* **2014**, *136* (2), 590−593.

(70) Commins, P.; Hara, H.; Naumov, P. Self-Healing Molecular Crystals. *Angew. Chem., Int. Ed.* **2016**, *55* (42), 13028−13032.

(71) Commins, P.; Al-Handawi, M. B.; Karothu, D. P.; Raj, G.; Naumov, P. Efficiently self-healing boronic ester crystals. *Chem. Sci.* **2020**, *11* (10), 2606−2613.

(72) Tang, S.; Ye, K.; Zhang, H. Integrating Low-Temperature-Resistant Two-Dimensional Elastic-Bending and Reconfigurable Plastic-Twisting Deformations into an Organic Crystal. *Angew. Chem., Int. Ed.* **2022**, *61* (42), No. e202210128.

(73) Liu, H.; Lu, Z.; Tang, B.; Qu, C.; Zhang, Z.; Zhang, H. A Flexible Organic Single Crystal with Plastic-Twisting and Elastic-Bending Capabilities and Polarization-Rotation Function. *Angew. Chem., Int. Ed.* **2020**, *59* (31), 12944−12950.

(74) Di, Q.; Li, J.; Zhang, Z.; Yu, X.; Tang, B.; Zhang, H.; Zhang, H. Quantifiable stretching-induced fluorescence shifts of an elastically bendable and plastically twistable organic crystal. *Chem. Sci.* **2021**, *12* (46), 15423−15428.

(75) Chen, K.; Wang, J.; Wu, W.; Shan, H.; Zhao, H.; Wang, N.; Wang, T.; Huang, X.; Hao, H. Multi-flexible organic crystal

responding to different mechanical forces for flexible optical waveguides. *Dyes Pigm.* **2023**, *219*, 111536.

(76) Hasija, A.; Chopra, D. Potential and challenges of engineering mechanically flexible molecular crystals. *CrystEngComm* **2021**, *23* (34), 5711−5730.

(77) Reddy, C. M.; Krishna, G. R.; Ghosh, S. Mechanical properties of molecular crystals—applications to crystal engineering. *CrystEngComm* **2010**, *12* (8), 2296−2314.

(78) Briseno, A. L.; Tseng, R. J.; Ling, M. M.; Falcao, E. H.; Yang, Y.; Wudl, F.; Bao, Z. High-performance organic single-crystal transistors on flexible substrates. *Adv. Mater.* **2006**, *18* (17), 2320−2324.

(79) Liu, X.; Michalchuk, A. A.; Bhattacharya, B.; Yasuda, N.; Emmerling, F.; Pulham, C. R. High-pressure reversibility in a plastically flexible coordination polymer crystal. *Nat. Commun.* **2021**, *12* (1), 3871.

(80) Ghosh, S.; Mishra, M. K. Elastic molecular crystals: From serendipity to design to applications. *Cryst. Growth Des.* **2021**, *21* (4), 2566−2580.

(81) Saha, S.; Mishra, M. K.; Reddy, C. M.; Desiraju, G. R. From molecules to interactions to crystal engineering: mechanical properties of organic solids. *Acc. Chem. Res.* **2018**, *51* (11), 2957−2967.

(82) Lakshmipathi, M.; Emmerling, F.; Bhattacharya, B.; Ghosh, S. Structure-mechanical property correlation of a series of 4-(1-Napthylvinyl) pyridine based cocrystals. *J. Mol. Struct.* **2022**, *1268*, 133670.

(83) Rajagopal, S. K.; Philip, A. M.; Nagarajan, K.; Hariharan, M. Progressive acylation of pyrene engineers solid state packing and colour via C-H⋯ H-C, C-H⋯ O and π-π interactions. *Chem. Commun.* **2014**, *50* (63), 8644−8647.

(84) Chinnasamy, R.; Arul, A.; AlMousa, A.; Kiran, M. S.; Das, P.; Jalilov, A. S.; Peedikakkal, A. M. P.; Ghosh, S. Structure property correlation of a series of halogenated schiff base crystals and understanding of the molecular basis through nanoindentation. *Cryst. Growth Des.* **2019**, *19* (11), 6698−6707.

(85) Ahmed, E.; Karothu, D. P.; Naumov, P. Crystal Adaptronics: Mechanically Reconfigurable Elastic and Superelastic Molecular Crystals. *Angew. Chem., Int. Ed.* **2018**, *57* (29), 8837−8846.

(86) Horstman, E. M.; Keswani, R. K.; Frey, B. A.; Rzeczycki, P. M.; LaLone, V.; Bertke, J. A.; Kenis, P. J.; Rosania, G. R. Elasticity in macrophage-synthesized biocrystals. *Angew. Chem., Int. Ed.* **2017**, *56* (7), 1815−1819.

(87) Thekkeppat, N. P.; Lakshmipathi, M.; Jalilov, A. S.; Das, P.; Peedikakkal, A. M. P.; Ghosh, S. Combining optical properties with flexibility in halogen-substituted benzothiazole crystals. *Cryst. Growth Des.* **2020**, *20* (6), 3937−3943.

(88) Rath, B. B.; Vittal, J. J. Mechanical bending and modulation of photoactuation properties in a one-dimensional Pb (II) coordination polymer. *Chem. Mater.* **2021**, *33* (12), 4621−4627.

(89) Hayashi, S.; Koizumi, T. Mechanically induced shaping of organic single crystals: Facile fabrication of fluorescent and elastic crystal fibers. *Chem. - Eur. J.* **2018**, *24* (34), 8507−8512.

(90) Brock, A. J.; Whittaker, J. J.; Powell, J. A.; Pfrunder, M. C.; Grosjean, A.; Parsons, S.; McMurtrie, J. C.; Clegg, J. K. Elastically flexible crystals have disparate mechanisms of molecular movement induced by strain and heat. *Angew. Chem., Int. Ed.* **2018**, *57* (35), 11325−11328.

(91) Kusumoto, S.; Sugimoto, A.; Zhang, Y.; Kim, Y.; Nakamura, M.; Hayami, S. Elastic Crystalline Fibers Composed of a Nickel (II) Complex. *Inorg. Chem.* **2021**, *60* (3), 1294−1298.

(92) Thompson, A. J.; Price, J. R.; McMurtrie, J. C.; Clegg, J. K. The mechanism of bending in co-crystals of caffeine and 4-chloro-3-nitrobenzoic acid. *Nat. Commun.* **2021**, *12* (1), 5983.

(93) Hayashi, S.; Ishiwari, F.; Fukushima, T.; Mikage, S.; Imamura, Y.; Tashiro, M.; Katouda, M. Anisotropic Poisson Effect and Deformation-Induced Fluorescence Change of Elastic 9, 10-Dibromoanthracene Single Crystals. *Angew. Chem., Int. Ed.* **2020**, *59* (37), 16195−16201.

(94) Panda, M. K.; Bhaskar Pal, K.; Raj, G.; Jana, R.; Moriwaki, T.; Mukherjee, G. D.; Mukhopadhyay, B.; Naumov, P. e. Flexibility in a molecular crystal accomplished by structural modulation of carbohydrate epimers. *Cryst. Growth Des.* 2017, 17 (4), 1759–1765.

(95) Zhang, X.; Dong, H.; Hu, W. Organic semiconductor single crystals for electronics and photonics. *Adv. Mater.* 2018, 30 (44), 1801048.

(96) Hayashi, S. Elastic organic crystals of π-conjugated molecules: anisotropic densely packed supramolecular 3D polymers exhibit mechanical flexibility and shape tunability. *Polym. J.* 2019, 51 (9), 813–823.

(97) Das, S.; Saha, S.; Sahu, M.; Mondal, A.; Reddy, C. M. Temperature-Reliant Dynamic Properties and Elasto-Plastic to Plastic Crystal (Rotator) Phase Transition in a Metal Oxyacid Salt. *Angew. Chem., Int. Ed.* 2022, 61 (8), No. e202115359.

(98) Liu, H.; Bian, Z.; Cheng, Q.; Lan, L.; Wang, Y.; Zhang, H. Controllably realizing elastic/plastic bending based on a room-temperature phosphorescent waveguiding organic crystal. *Chem. Sci.* 2019, 10 (1), 227–232.

(99) Wang, J.-R.; Li, M.; Yu, Q.; Zhang, Z.; Zhu, B.; Qin, W.; Mei, X. Anisotropic elasticity and plasticity of an organic crystal. *Chem. Commun.* 2019, 55 (59), 8532–8535.

(100) Wang, C.; Sun, C. C. Computational techniques for predicting mechanical properties of organic crystals: a systematic evaluation. *Mol. Pharmaceutics* 2019, 16 (4), 1732–1741.

(101) Gupta, P.; Rather, S. A.; Saha, B. K.; Panda, T.; Karothu, D. P.; Nath, N. K. Mechanical flexibility of molecular crystals achieved by exchanging hydrogen bonding synthons. *Cryst. Growth Des.* 2020, 20 (5), 2847–2852.

(102) Huang, K.; Song, L.; Liu, K.; Lv, A.; Singh, M.; Shen, K.; Shen, J.; Wang, J.; Wang, H.; Shi, H.; et al. Elastic organic crystals with ultralong phosphorescence for flexible anti-counterfeiting. *npj Flexible Electron.* 2021, 5 (1), 21.

(103) Thompson, J. O. Hooke's law. *Science* 1926, 64 (1656), 298–299.

(104) Varughese, S.; Kiran, M.; Ramamurty, U.; Desiraju, G. R. Nanoindentation in Crystal Engineering: Quantifying Mechanical Properties of Molecular Crystals. *Angew. Chem., Int. Ed.* 2013, 52 (10), 2701–2712.

(105) Zhuo, Z.; Lin, J.; Li, J.; Wu, S.; Hu, W.; Gong, J. Research progress of mechanically flexible molecular crystals: From bending mechanisms to applications. *Chem. Eng. J.* 2022, 450, 138333.

(106) Thompson, A. J.; Worthy, A.; Grosjean, A.; Price, J. R.; McMurtrie, J. C.; Clegg, J. K. Determining the mechanisms of deformation in flexible crystals using micro-focus X-ray diffraction. *CrystEngComm* 2021, 23 (34), 5731–5737.

(107) Aragão, D.; Aishima, J.; Cherukuvada, H.; Clarken, R.; Clift, M.; Cowieson, N. P.; Ericsson, D. J.; Gee, C. L.; Macedo, S.; Mudie, N.; et al. MX2: a high-flux undulator microfocus beamline serving both the chemical and macromolecular crystallography communities at the Australian Synchrotron. *J. Synchrotron Radiat.* 2018, 25 (3), 885–891.

(108) Holland, T.; Redfern, S. Unit cell refinement from powder diffraction data; the use of regression diagnostics. *Mineral. Mag.* 1997, 61 (1), 65–77.

(109) Zhao, Y.; Matsuba, G.; Moriwaki, T.; Ikemoto, Y.; Ito, H. Shear-induced conformational fluctuations of polystyrene probed by 2D infrared microspectroscopy. *Polymer* 2012, 53 (21), 4855–4860.

(110) Moriwaki, T.; Ikemoto, Y. BL43IR at SPring-8 redirected. *Infrared Phys. Technol.* 2008, 51 (5), 400–403.

(111) Suzuki, Y.; Koga, S.; Kitaura, K.; Kawamata, J.; Yano, K.; Hoshino, N.; Akutagawa, T.; Hayashi, S. Noninvasive Three-dimensional Assessment of Single Molecular Crystals Using Multi-photon Microscopic Observation and Their Deformation-induced Emission Characteristics. *Langmuir* 2023, 39 (33), 11646–11652.

(112) Denk, W.; Strickler, J. H.; Webb, W. W. Two-Photon Laser Scanning Fluorescence Microscopy. *Science* 1990, 248 (4951), 73–76.

(113) Helmchen, F.; Denk, W. Deep tissue two-photon microscopy. *Nat. methods* 2005, 2 (12), 932–940.

(114) Takezaki, M.; Kawakami, R.; Onishi, S.; Suzuki, Y.; Kawamata, J.; Imamura, T.; Hadano, S.; Watanabe, S.; Niko, Y. Integrated Fluorescent Nanoprobe Design for High-Speed In Vivo Two-Photon Microscopic Imaging of Deep-Brain Vasculature in Mice. *Adv. Funct. Mater.* 2021, 31 (20), 2010698.

(115) Desiraju, G. R. Supramolecular synthons in crystal engineering—a new organic synthesis. *Angew. Chem., Int. Ed. Engl.* 1995, 34 (21), 2311–2327.

(116) Spackman, M. A.; Jayatilaka, D. Hirshfeld surface analysis. *CrystEngComm* 2009, 11 (1), 19–32.

(117) Spackman, M. A.; Byrom, P. G. A novel definition of a molecule in a crystal. *Chem. Phys. Lett.* 1997, 267 (3–4), 215–220.

(118) Panini, P.; Chopra, D. Experimental and theoretical characterization of short H-bonds with organic fluorine in molecular crystals. *Cryst. Growth Des.* 2014, 14 (7), 3155–3168.

(119) Spackman, M. A.; McKinnon, J. J.; Jayatilaka, D. Electrostatic potentials mapped on Hirshfeld surfaces provide direct insight into intermolecular interactions in crystals. *CrystEngComm* 2008, 10 (4), 377–388.

(120) Maahs, A. C.; Ignacio, M. G.; Ghazzali, M.; Soldatov, D. V.; Preuss, K. E. Chiral crystals of an achiral molecule exhibit plastic bending and a crystal-to-crystal phase transition. *Cryst. Growth Des.* 2017, 17 (3), 1390–1395.

(121) McKinnon, J. J.; Spackman, M. A.; Mitchell, A. S. Novel tools for visualizing and exploring intermolecular interactions in molecular crystals. *Acta Crystallogr. Sect. B: Struct. Sci.* 2004, 60 (6), 627–668.

(122) McKinnon, J. J.; Mitchell, A. S.; Spackman, M. A. Hirshfeld surfaces: a new tool for visualising and exploring molecular crystals. *Chem.—Eur. J.* 1998, 4 (11), 2136–2141.

(123) Sheldrick, G. M. SHELXT-Integrated space-group and crystal-structure determination. *Acta Crystallogr., Sect. A: Found. Adv.* 2015, 71 (1), 3–8.

(124) Liu, Y.; Zhang, C.; Liu, Z.; Truhlar, D. G.; Wang, Y.; He, X. Supervised learning of a chemistry functional with damped dispersion. *Nat. Comput. Sci.* 2023, 3 (1), 48–58.

(125) Civalleri, B.; Zicovich-Wilson, C. M.; Valenzano, L.; Ugliengo, P. B3LYP augmented with an empirical dispersion term (B3LYP-D*) as applied to molecular crystals. *CrystEngComm* 2008, 10 (4), 405–410.

(126) Gavezzotti, A. Computational contributions to crystal engineering. *CrystEngComm* 2008, 10 (4), 367–367.

(127) Carter, D. J.; Rohl, A. L. Noncovalent interactions in SIESTA using the vdW-DF functional: S22 benchmark and macrocyclic structures. *J. Chem. Theory Comput.* 2012, 8 (1), 281–289.

(128) Moellmann, J.; Grimme, S. DFT-D3 study of some molecular crystals. *J. Phys. Chem. C* 2014, 118 (14), 7615–7621.

(129) Brandenburg, J. G.; Grimme, S. Accurate modeling of organic molecular crystals by dispersion-corrected density functional tight binding (DFTB). *J. Phys. Chem. Lett.* 2014, 5 (11), 1785–1789.

(130) Carter, D. J.; Rohl, A. L. Benchmarking calculated lattice parameters and energies of molecular crystals using van der Waals density functionals. *J. Chem. Theory Comput.* 2014, 10 (8), 3423–3437.

(131) Grimme, S. Supramolecular binding thermodynamics by dispersion-corrected density functional theory. *Chem. - Eur. J.* 2012, 18 (32), 9955–9964.

(132) Yang, M.; Wang, W.; Su, K.; Yuan, D. Dimeric Calix [4] resorcinarene-based Porous Organic Cages for CO2/CH4 Separation. *Chem. Res. Chin. Univ.* 2022, 38 (2), 428–432.

(133) Yu, H. S.; He, X.; Li, S. L.; Truhlar, D. G. MN15: A Kohn-Sham global-hybrid exchange-correlation density functional with broad accuracy for multi-reference and single-reference systems and noncovalent interactions. *Chem. Sci.* 2016, 7 (8), 5032–5051.

(134) Turner, M. J.; Grabowsky, S.; Jayatilaka, D.; Spackman, M. A. Accurate and efficient model energies for exploring intermolecular interactions in molecular crystals. *J. Phys. Chem. Lett.* 2014, 5 (24), 4249–4255.

(135) Yang, X.; Lan, L.; Pan, X.; Di, Q.; Liu, X.; Li, L.; Naumov, P.; Zhang, H. Bioinspired soft robots based on organic polymer-crystal

hybrid materials with response to temperature and humidity. *Nat. commun.* **2023**, *14* (1), 2287.

(136) Karothu, D. P.; Mahmoud Halabi, J.; Ahmed, E.; Ferreira, R.; Spackman, P. R.; Spackman, M. A.; Naumov, P. Global analysis of the mechanical properties of organic crystals. *Angew. Chem., Int. Ed.* **2022**, *61* (10), No. e202113988.

(137) Rus, D.; Tolley, M. T. Design, fabrication and control of soft robots. *Nature* **2015**, *521* (7553), 467–475.

(138) Feiler, T.; Bhattacharya, B.; Michalchuk, A. A.; Rhim, S.-Y.; Schröder, V.; List-Kratochvil, E.; Emmerling, F. Tuning the mechanical flexibility of organic molecular crystals by polymorphism for flexible optical waveguides. *CrystEngComm* **2021**, *23* (34), 5815–5825.

(139) Wang, L.; Yue, X.; Sun, Q.; Zhang, L.; Ren, G.; Lu, G.; Yu, H.-D.; Huang, W. Flexible organic electrochemical transistors for chemical and biological sensing. *Nano Res.* **2022**, *15* (3), 2433–2464.

(140) Zhao, Z.; Liu, K.; Liu, Y.; Guo, Y.; Liu, Y. Intrinsically flexible displays: key materials and devices. *Natl. Sci. Rev.* **2022**, *9* (6), nwac090.

(141) Jiang, L.; Hu, W.; Wei, Z.; Xu, W.; Meng, H. High-performance organic single-crystal transistors and digital inverters of an anthracene derivative. *Adv. Mater.* **2009**, *21* (36), 3649–3653.

(142) Zhao, S.; Yamagishi, H.; Oki, O.; Ihara, Y.; Ichiji, N.; Kubo, A.; Hayashi, S.; Yamamoto, Y. Mechanically flexible and optically tunable organic crystal resonator. *Adv. Opt. Mater.* **2022**, *10* (2), 2101808.

(143) Duggirala, N. K.; Perry, M. L.; Almarsson, Ö.; Zaworotko, M. J. Pharmaceutical cocrystals: along the path to improved medicines. *Chem. Commun.* **2016**, *52* (4), 640–655.

(144) Li, X.; Liu, Y.; Zhang, J.; Wu, F.; Hu, M.; Yang, H. Flexible artificial synapses based on field effect transistors: from materials, mechanics towards applications. *Adv. Intell. Syst.* **2022**, *4* (9), 2200015.

(145) Sang, M.; Kim, K.; Shin, J.; Yu, K. J. Ultra-Thin Flexible Encapsulating Materials for Soft Bio-Integrated Electronics. *Adv. Sci.* **2022**, *9* (30), 2202980.

(146) Wang, H.; Li, S.; Lu, H.; Zhu, M.; Liang, H.; Wu, X.; Zhang, Y. Carbon-Based Flexible Devices for Comprehensive Health Monitoring. *Small Methods* **2023**, *7*, 2201340.

(147) Huang, L.-F.; Tong, W.-Q. T. Impact of solid state properties on developability assessment of drug candidates. *Adv. Drug Delivery Rev.* **2004**, *56* (3), 321–334.

(148) Yang, X.; Lan, L.; Li, L.; Liu, X.; Naumov, P.; Zhang, H. Remote and precise control over morphology and motion of organic crystals by using magnetic field. *Nat. Commun.* **2022**, *13* (1), 2322.

(149) Liu, B.; Di, Q.; Liu, W.; Wang, C.; Wang, Y.; Zhang, H. Red-Emissive Organic Crystals of a Single-Benzene Molecule: Elastically Bendable and Flexible Optical Waveguide. *J. Phys. Chem. Lett.* **2019**, *10* (7), 1437–1442.

(150) Di, Q.; Li, L.; Miao, X.; Lan, L.; Yu, X.; Liu, B.; Yi, Y.; Naumov, P.; Zhang, H. Fluorescence-based thermal sensing with elastic organic crystals. *Nat. Commun.* **2022**, *13* (1), 5280.

(151) Chen, Z.; Hu, Y.; Shi, G.; Zhuo, H.; Ali, M. A.; Jamróz, E.; Zhang, H.; Zhong, L.; Peng, X. Advanced Flexible Materials from Nanocellulose. *Adv. Funct. Mater.* **2023**, *33*, 2214245.

(152) Bolla, G.; Nangia, A. Pharmaceutical cocrystals: walking the talk. *Chem. Commun.* **2016**, *52* (54), 8342–8360.

(153) Sanphui, P.; Tothadi, S.; Ganguly, S.; Desiraju, G. R. Salt and cocrystals of sildenafil with dicarboxylic acids: solubility and pharmacokinetic advantage of the glutarate salt. *Mol. Pharmaceutics* **2013**, *10* (12), 4687–4697.

(154) Thipparaboina, R.; Kumar, D.; Mittapalli, S.; Balasubramanian, S.; Nangia, A.; Shastri, N. R. Ionic, Neutral, and Hybrid Acid-Base Crystalline Adducts of Lamotrigine with Improved Pharmaceutical Performance. *Cryst. Growth Des.* **2015**, *15* (12), 5816–5826.

(155) Sanphui, P.; Mishra, M. K.; Ramamurty, U.; Desiraju, G. R. Tuning mechanical properties of pharmaceutical crystals with

multicomponent crystals: voriconazole as a case study. *Mol. Pharmaceutics* **2015**, *12* (3), 889–897.

(156) Blagden, N.; de Matas, M.; Gavan, P. T.; York, P. Crystal engineering of active pharmaceutical ingredients to improve solubility and dissolution rates. *Adv. Drug Delivery Rev.* **2007**, *59* (7), 617–630.

(157) McNamara, D. P.; Childs, S. L.; Giordano, J.; Iarriccio, A.; Cassidy, J.; Shet, M. S.; Mannion, R.; O'Donnell, E.; Park, A. Use of a glutaric acid cocrystal to improve oral bioavailability of a low solubility API. *Pharm. Res.* **2006**, *23*, 1888–1897.

(158) Smith, A. J.; Kavuru, P.; Wojtas, L.; Zaworotko, M. J.; Shytle, R. D. Cocrystals of quercetin with improved solubility and oral bioavailability. *Mol. Pharmaceutics* **2011**, *8* (5), 1867–1876.

(159) Bag, P. P.; Chen, M.; Sun, C. C.; Reddy, C. M. Direct correlation among crystal structure, mechanical behaviour and tabletability in a trimorphic molecular compound. *CrystEngComm* **2012**, *14* (11), 3865–3867.

(160) Duggirala, N. K.; Perry, M. L.; Almarsson, Ö.; Zaworotko, M. J. Pharmaceutical cocrystals: along the path to improved medicines. *Chem. Commun.* **2016**, *52*, 640–655.

(161) Joshi, T. V.; Singaraju, A. B.; Shah, H. S.; Morris, K. R.; Stevens, L. L.; Haware, R. V. Structure-mechanics and compressibility profile study of flufenamic acid: nicotinamide cocrystal. *Cryst. Growth Des.* **2018**, *18* (10), 5853–5865.

(162) Kuehne, A. J.; Gather, M. C. Organic lasers: recent developments on materials, device geometries, and fabrication techniques. *Chem. Rev.* **2016**, *116* (21), 12823–12864.

(163) Ye, Y.; Bai, Y.; Qi, L.; Li, T.; Yan, L.; Yin, Q.; Zhang, Y.; Xie, C. Flexible Optical Waveguides in Heterocyclic Schiff Base Self-Assembled Hydrogen-Bonded Solvates. *Cryst. Growth Des.* **2023**, *23* (3), 1403–1411.

(164) Peng, J.; Han, C.; Bai, J.; Wang, J.; Cao, X.; Jia, J.; Wang, Y.; Wu, J. Organic Single Crystal/Polymer Hybrid Actuator with Waveguide, Low Temperature, and Humidity Actuation Properties. *Cryst. Growth Des.* **2022**, *22* (12), 7187–7194.

(165) Lan, L.; Di, Q.; Li, L.; Liu, B.; Yu, X.; Naumov, P. e.; Zhang, H. Packing-Dependent Mechanical Properties of Schiff Base Crystals. *Cryst. Growth Des.* **2022**, *22* (5), 3435–3441.

(166) Peng, J.; Bai, J.; Cao, X.; He, J.; Xu, W.; Jia, J. Elastic Organic Crystals Based on Barbituric Derivative: Multi-faceted Bending and Flexible Optical Waveguide. *Chem. - Eur. J.* **2021**, *27* (64), 16036–16042.

(167) Liu, B.; Liu, H.; Zhang, H.; Di, Q.; Zhang, H. Crystal engineering of a hydrazone molecule toward high elasticity and bright luminescence. *J. Phys. Chem. Lett.* **2020**, *11* (21), 9178–9183.

(168) Li, Y.; Ma, Z.; Li, A.; Xu, W.; Wang, Y.; Jiang, H.; Wang, K.; Zhao, Y.; Jia, X. A single crystal with multiple functions of optical waveguide, aggregation-induced emission, and mechanochromism. *ACS Appl. Mater. Interfaces* **2017**, *9* (10), 8910–8918.

(169) Bhattacharya, B.; Roy, D.; Dey, S.; Puthuvakkal, A.; Bhunia, S.; Mondal, S.; Chowdhury, R.; Bhattacharya, M.; Mandal, M.; Manoj, K.; et al. Mechanical-Bending-Induced Fluorescence Enhancement in Plastically Flexible Crystals of a GFP Chromophore Analogue. *Angew. Chem., Int. Ed.* **2020**, *59* (45), 19878–19883.

(170) Dong, G.; Li, S.; Yao, M.; Zhou, Z.; Zhang, Y.-Q.; Han, X.; Luo, Z.; Yao, J.; Peng, B.; Hu, Z.; et al. Super-elastic ferroelectric single-crystal membrane with continuous electric dipole rotation. *Science* **2019**, *366* (6464), 475–479.

(171) Tang, Q.; Tong, Y.; Zheng, Y.; He, Y.; Zhang, Y.; Dong, H.; Hu, W.; Hassenkam, T.; Bjørnholm, T. Organic nanowire crystals combine excellent device performance and mechanical flexibility. *Small* **2011**, *7* (2), 189–193.