



SPECIAL ISSUE: Flexible Intelligent Materials

# Organic crystal-based flexible smart materials

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**ABSTRACT** Although the famous brittle characteristics of molecular crystals are unfavorable when they are used as flexible smart materials (FSMs), an increasing number of organic crystal-based FSMs have been reported recently. This breaks the perception of their stiff and brittle properties and promises a bright future for basic research and practical applications. Crystalline smart materials present considerable advantages over polymer materials under certain circumstances, rendering them potential candidates for certain applications, such as rapidly responsive actuators, ON/OFF switching, and microrobots. In this review, we summarize the recent developments in the field of organic crystal-based FSMs, including the derivatives of azobenzene, diarylethene, anthracene, and olefin. These organic crystal-based FSMs can bend, curl, twist, deform, or respond otherwise to external stimuli, such as heat or light. The detailed mechanisms of their smart behaviors are discussed with their potential applications in exciting intelligent fields. We believe this review could provide guidelines toward future fabrication and developments for novel organic crystal-based FSMs and their advanced smart applications.

**Keywords:** organic crystal, smart, stimulus-responsive, flexible, mechanical motion

## INTRODUCTION

Inspired by natural stimuli-responsive phenomena [1,2], numerous novel smart materials (SMs), which can respond to environmental stimuli (chemicals, light, electricity, temperature, and mechanical stimuli) [3–10], have been developed in the last decade. The remarkable recent advancements in SMs have profoundly influenced many aspects of human life, and they can be used in actuators, sensors, switches, drug deliveries, and robots [11–15]. Among them, flexible SMs (FSMs) are of great importance as a media to transform energy into mechanical motion, which can perform macroscopic mechanical motion (variation in physical size and shape, locomotion, or self-actuation) as a result of external stimuli, e.g., heat, light, and chemical analytes [16–18]. This remarkable transduction of external energy into work has attracted special interest to materials science, and it renders FSMs promising candidates as

multifunctional SMs for actuators, sensors, optoelectronic devices, artificial muscles, and microrobots [19–23].

FSMs based on organic elastomers or liquid crystalline materials have been greatly developed and widely reported, owing to their excellent elasticity and facile fabrication [24,25]. However, the amount of research on molecular crystal-based FSMs is limited, owing to their stiffness and brittleness. In addition, the prerequisite of a mechanical response from a crystalline solid is nonrigidity, i.e., “flexibility”. In such crystalline materials, the local molecular perturbation exerts local stress in the crystalline lattice, and the effect is amplified in collective mechanical motion occurring at a large dimension [26]. Ultimately, the collective perturbation appears as macroscopic deformations in the bulk crystal. These mechanical effects are vital for the underlying dynamic crystal chemistry [27]. Moreover, single crystals present considerable advantages in terms of elasticity and other superior performances over polymer materials in certain circumstances [27]. Currently, an increasing number of unusually flexible crystalline SMs (organic crystal-based FSMs) have been reported, which breaks the narrative that single crystal is stiff and brittle and promises a bright future for basic research and practical application of these extraordinary materials [23]. For instance, these materials can be utilized to fabricate efficient actuators or energy-storage devices, including flexible electronic dynamic components in soft robotics, displays, switchable reflector units for projective displays, and monochromators in synchrotron facilities [14,28].

Herein, the progress, prospects, and current challenges of organic crystal-based FSMs are reviewed for the first time (hereinafter, “stimulus-responsive flexible” refers to “mechanically responsive” or “flexible smart”). First, the history and flexible mechanism of stimulus-responsive flexible organic crystals are discussed. Additionally, the representative examples for the discussion of the responsive behaviors of flexible organic crystals are distinguished by the types of molecular structures and stimuli. Furthermore, the potential applications of organic crystal-based FSMs in exciting fields are discussed. Finally, the prospects and current challenges are highlighted. We aim to present a brief overview of the representative flexible organic smart crystals and provide positive guidelines for future fabrication and developments in the field of flexible smart organic crystals and their advanced smart applications.

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## HISTORY AND BACKGROUND OF ORGANIC CRYSTAL-BASED FSMs

FSMs are emerging functional materials that can exhibit remarkable transduction of external energy (heat, light, electric field, and chemical analytes) into macroscopic mechanical motions, such as variation in physical size and shape, locomotion, or self-actuation [16,17]. Most reported FSMs generally comprise photoresponsive molecules and can exhibit mechanical motion upon photostimuli, in which the molecules undergo geometrical change as a result of photochemical reactions. Eventually, the synergy of each molecular motion leads to the mechanical motions of the FSMs.

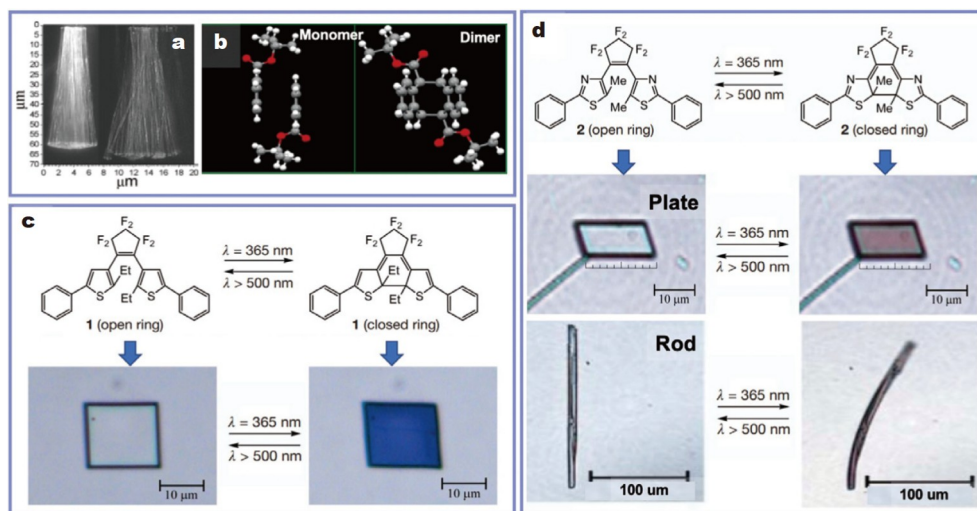
Apart from the intensively investigated polymer-based FSMs, studies on molecular crystal-based FSMs are limited, owing to their stiffness and brittleness. Molecular crystal-based FSMs were developed in the 1980s [29–31]. The first case was reported by Abakumov and Nevodchikov [29] in 1982, where a crystal comprising a semiquinone complex exhibited a photoresponsive bending by as much as 45° when irradiated under visible or near-infrared light. The radical-mediated formation of a Rh–Rh bond within the crystals led to the bending behavior. Unfortunately, this research did not attract considerable attention at that time and was not noted again until the early 2000s. For example, Bardeen's group [32] reported a crystalline nanorod comprising 9-tert-butyl anthroate, which exhibited a photoresponsive expansion behavior (Fig. 1a). Upon irradiation, the 9-tert-butyl anthroate underwent a rapid [4+4] photodimerization in the crystals, resulting in a 15% increase in rod length without fragmentation (Fig. 1b). Subsequently, Kobatake *et al.* [33] reported a diarylethene crystal exhibiting rapid and photo-reversible mechanical motions, e.g., shape variation, expansion, contraction, and bending (Fig. 1c, d). Thereafter, an increasing number of studies on molecular crystal-based FSMs emerged, in which various photoresponsive molecules were applied to fabricate mechanically responsive flexible crystals. Many kinds of mechanical motions have been reported, such as bending, expansion, contraction, rolling, coiling, and twisting, which will be detailed herein [16,33–46]. Among them, bending is the most

common mechanical behavior.

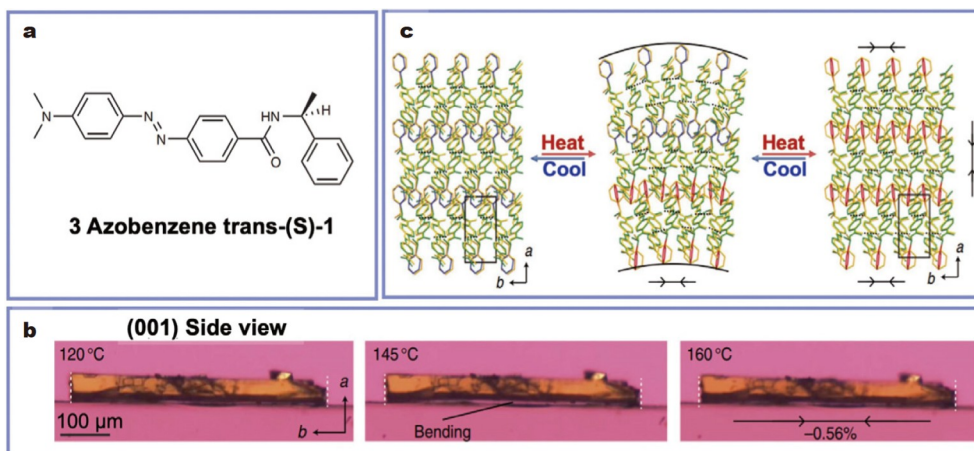
Recently, apart from the photoresponsive motions of molecular crystal-based FSMs, several thermoresponsive and solvent-responsive molecular crystal-based FSMs have been reported, where the responsive motions were attributed to the single-crystal-to-single-crystal (SCSC) phase transition [47–53]. For example, Koshima's group [50] reported thermoresponsive mechanical motions of azobenzene crystal triggered using thermo stimuli, which resulted from reversible SCSC phase transitions (Fig. 2a, b). The length of the crystal decreased above its transition temperature, indicating that the crystals will undergo bending when a temperature gradient is used along the thickness direction (Fig. 2c). Cases of solvent-responsive molecular crystal-based FSMs will be detailed subsequently. With further development in molecular crystal-based FSMs, this field breaks through the scope of single-component crystals, e.g., related studies on multicomponent cocrystals and molecular crystal-based hybrid materials have been reported [17,18,38,42,44,54,55], which will be detailed herein. The development of these new materials would undoubtedly provide opportunities for molecular crystal-based FSMs in programmable and intelligent fields.

## MECHANISMS OF MECHANICALLY FLEXIBLE ORGANIC CRYSTALS

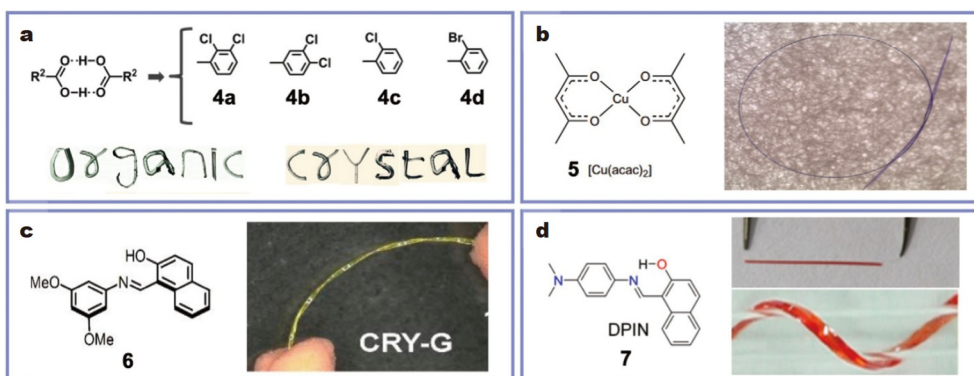
Initially, all crystals were thought to be rigid and brittle with a clear smooth face and straight edge. However, in 1962, it was discovered that many molecular crystals are soft [56], and the common apprehension of crystals may require reinterpretation. Presently, studies on flexibility or the mechanical response of organic single crystals have become the frontier research of crystal engineering, which opens up possibilities for applications of such highly ordered materials in smart devices, actuators, and sensors [57]. The flexible behaviors of the stiff and brittle crystals can be attributed to various noncovalent weak interactions within the crystals [58–69]. Although there are various mechanical deformations without losing crystallinity for flexible organic crystals (Fig. 3) [58,59,61–63], they are mainly divided



**Figure 1** (a) Images of a bundle of nanorods of 9-tert-butyl anthroate prior to and after being irradiated using 365 nm light. (b) X-ray crystal structure of monomer and dimer of 9-tert-butyl anthroate. Reprinted with permission from Ref. [32], Copyright 2006, American Chemical Society. (c, d) Photoreversible mechanical motions of diarylethene derivatives 1 and 2, including shape variation, expansion, contraction, and bending. Reprinted with permission from Ref. [33], Copyright 2007, Nature Publishing Group.



**Figure 2** (a) Molecular structure of *trans*-(S)-1 of azobenzene (3). (b) Shape changes in the crystal during heating and cooling in the (001) side view. During heating or cooling, a bending motion along the *b*-axis can be observed. (c) Changes in molecular arrangement during heating and cooling [50].



**Figure 3** (a) Flexible crystals of (a) 4a, 4b, 4c, and 4d fabricated to letters of “organic crystal”. Reprinted with permission from Ref. [59], Copyright 2016, American Chemical Society. (b) Chemical structure of [Cu(acetylacetonate)<sub>2</sub>] ([Cu(acac)<sub>2</sub>]) (left), and a [Cu(acac)<sub>2</sub>] crystal tied in an overhand knot (right). Reprinted with permission from Ref. [61], Copyright 2017, Nature Publishing Group. (c) Chemical structure of compound 6 (left) and the elastic bending of a twisted crystal of compound 6 (right). Reprinted with permission from Ref. [62], Copyright 2020, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (d) Chemical structure of compound 7 (left), images of the initial straight crystal (top right), and that screwed on a glass tube (down right). Reprinted with permission from Ref. [63], Copyright 2018, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

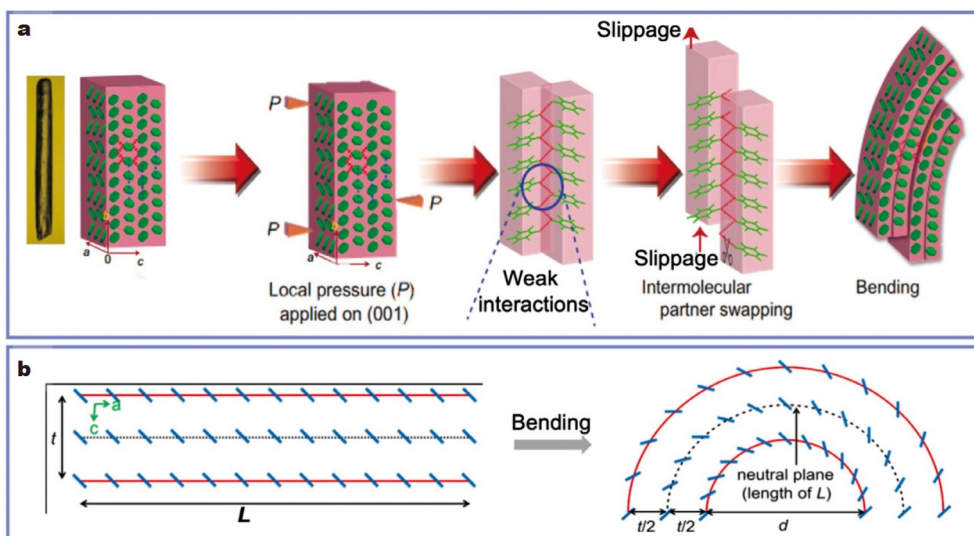
into two types: irreversible and reversible elastic deformations [59–63].

The plastic deformation (shearing, twisting, and bending) requires permanent crystallographic plane slippage/movement in the width and thickness directions of the crystals, accompanied by the destruction and rearrangement of weak intermolecular interactions that connect such planes, such as  $\pi\cdots\pi$  stacking, halogen bonding, hydrogen bond, or weak van der Waals interaction (Fig. 4a) [59,64–69]. It was concluded that the layers alleviated strain by slippage, and they facilitated different deformation of the lattices on both sides of the center plane, thereby alleviating the accumulation of long-range strain and preventing crystal cracking [70]. Breaking the translational symmetry of the lattices in the curved regions increases the mosaic diffusion, which leads to incomplete amorphization in the curved parts [70–72].

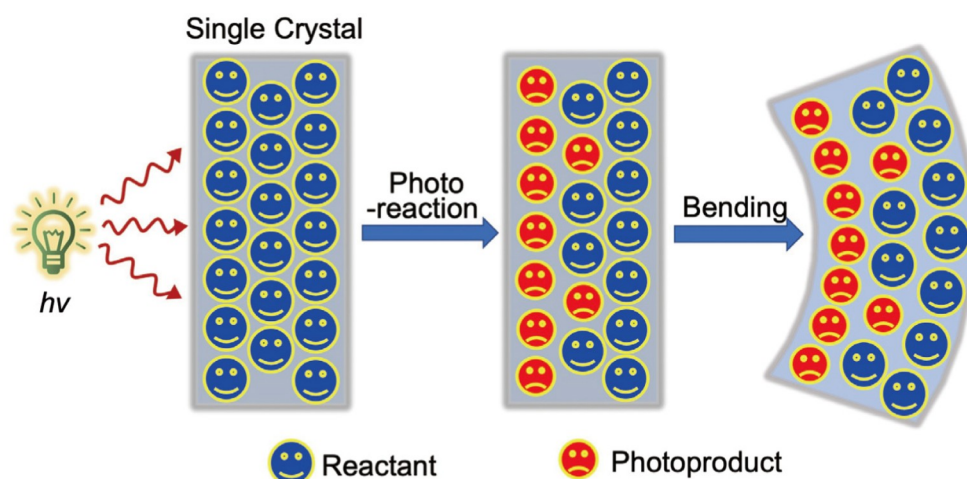
Conversely, elastic deformation, which is relatively common in the field of flexible smart crystals and limited to mechanical bending to date, results from slight and reversible self-variations in weak and dispersive intermolecular interactions and molecular packing modes during bending [62,73]. Additionally, corrugated packing patterns are essential, which would get

interlocked and prevent further relative slippage of neighboring chains [74]. During the elastic bending process of a crystal, the expansion and contraction of the exterior and interior arcs, respectively, are required (Fig. 4b). Therefore, the exterior arc will be long while the interior of the arc will be short, compared with the neutral position, which remains its length. Therefore, to realize expansion and compression when stress is adopted, reversible rearrangement of the molecules within the crystals is necessary [64,73,75,76]. Most  $\pi$ -conjugated molecules stack along the length directions of the crystal. The  $\pi$ - $\pi$  interaction acts as a “buffer” for expansion and compression and can reversibly respond to the expansion of the exterior arc by increasing the  $\pi$ - $\pi$  distance and respond to the compression of the interior arc by decreasing the  $\pi$ - $\pi$  distance [28,63]. In addition to the  $\pi$ - $\pi$  interaction, other weak interactions within molecular chains and the cross and close arrangement of the chain dimer can restrict the relative sliding of adjacent chains and chain dimers, respectively, during the bending process [63].

Every crystal could elastically deform when subjected to applied force, including diamond crystals [77]. In particular, organic crystals, which have relatively weaker bonds compared with inorganic crystals, typically take strains in the range of



**Figure 4** Mechanisms of plastic bending and elastic bending in single crystals. (a) Schematic diagrams of plastic bending under slip plane model. The green plates represent the  $\pi$ -conjugated molecules. Reprinted with permission from Ref. [67], Copyright 2014, Nature Publishing Group. (b) Schematic diagrams of the packing-structure changes during an elastic bending. The blue line represents the parallel stacked  $\pi$ -conjugated molecules. The dashed line represents the neutral plane.  $L$  and  $t$  are the length and thickness of the crystal, respectively, while  $d$  corresponds to the diameter of the inner arc. Reprinted with permission from Ref. [63], Copyright 2018, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.



**Figure 5** Schematic diagram of the mechanism of the photomechanical bending of organic crystals. The bimorph structure is formed by reactants and photoproducts [78].

~0.5%–1% and beyond. The elastic deformation in one-dimensional (1D) morphologies is easy to observe at a macroscopic scale, where the elasticity extent (% of strains) depends on the materials' internal structures and their abilities to prevent plastic fracture and flow. Moreover, when different (directions/types) external forces are applied to a crystal, rational molecular rearrangement may allow different deformations of the crystal, indicating that elastic and plastic deformations can be achieved in a crystal (Fig. 3c) [62].

### ORGANIC CRYSTAL-BASED FSMs

Flexible smart crystals can perform macroscopic mechanical motions as a result of external stimuli. The most common cases are photomechanical bending upon light irradiation, which are ascribed to the strain generated by the photoreaction within the crystals [78]. Therefore, the photomechanical bending of organic

crystals is considered as an example to illustrate the mechanism (Fig. 5). Typically, these photoresponsive crystals comprise photoresponsive molecules. Upon light irradiation on one side of the organic crystal, the photoresponsive molecules on this side will undergo various photoreactions, such as *cis-trans* isomerization, intramolecular ring-closing and ring-opening reactions, and intermolecular photodimerization. Thereafter, bimorph structures with asymmetry will be formed, which comprise reactants and photoproducts. The strain resulting from these bimorph structures leads to the mechanical bending of the crystal [79]. Therefore, photomechanical motions are attributed to the symmetry breaking of the molecular structures and arrangement in the crystal during the photoreaction [78].

### Photoresponsive flexible smart organic crystals

From a scientific or technological viewpoint, molecular crystals

need to demonstrate macroscopic mechanical motions resulting from changes in molecular geometry triggered by external stimuli. In particular, photomechanical crystals are attracting increasing research interest because of their great potential in actuators, molecular machines, light-harvesting, sensors, and smart switches [80]. Oppositely, it would provide an opportunity to understand their performance by analyzing the molecular arrangements *via* X-ray diffractions (XRDs) [51]. Organic crystals have many advantages, including fast response and recovery, less energy dissipation, and well-defined molecular stacking structures, compared with polymers and liquid crystals [14,81–83].

#### Classification of photoreactions in flexible smart organic crystals

The mechanical motion of a crystal is essentially driven by the structural transformation of the constituent molecules and changes in molecular arrangement upon external stimuli. After the remarkable findings prior to the early 2000s, many researchers joined this field, and various photoresponsive molecules associated with photomechanical behaviors have been reported, such as azobenzene, diarylethenes, olefins, and anthracene (Fig. 6) [16,36,42,44,51,55,84–89]. Light stimuli can remotely and wirelessly control the response magnitude with spatial selectivity and directly control it by changing its intensity and wavelength [90].

Different light-sensitive molecules have different photoresponsive mechanisms, such as *trans*–*cis* isomerization of azobenzene compounds (Fig. 7a) and anthracene-9-(1,3-butadiene) derivatives (Fig. 7b), enol-keto interconversion of salicylideneanilines (Fig. 7c), phototriggered ring-opening and ring-closing reactions (Fig. 7d) of diarylethene derivatives and furofulgide (Fig. 7e), [4+4] photodimerization and disassociation of anthracene molecules (Fig. 7f), and [2+2] cycloaddition of styryl benzoxazole derivatives and 1,2-bis(4-pyridyl)ethylene (4,4'-bpe) molecules (Fig. 7g–i). Examples associated with these reactions are detailed below.

#### Photoisomerization

When irradiated using ultraviolet (UV) light, the unit cell axis of molecular crystals of *trans*-azobenzene compounds, anthracene-9-(1,3-butadiene) derivatives, and salicylideneanilines will elongate, resulting from *cis*–*trans* isomerization (for azobenzenes and anthracene-9-(1,3-butadiene) derivatives) or keto-enol tautomerism (for salicylideneanilines). The number of photoproducts decreases with an increase in the penetration depth of the light, and the other nonirradiated sides of the crystals do not experience any photoreaction. The geometrical changes of these molecules result in accumulated strain in the crystals, eventually leading to macroscopic deformations, including bending, curling, and twisting of the crystals [45,46,84,91]. Compared with other stimuli, e.g., pH variation, heat, chemicals, humidity, and pressure, the light stimulus is ideal because of its ability for remote and noncontact manipulation as well as conveniently and precisely tuning the intensity, wavelength, and irradiation direction [92].

##### (1) *Trans*–*cis* isomerization of azobenzene

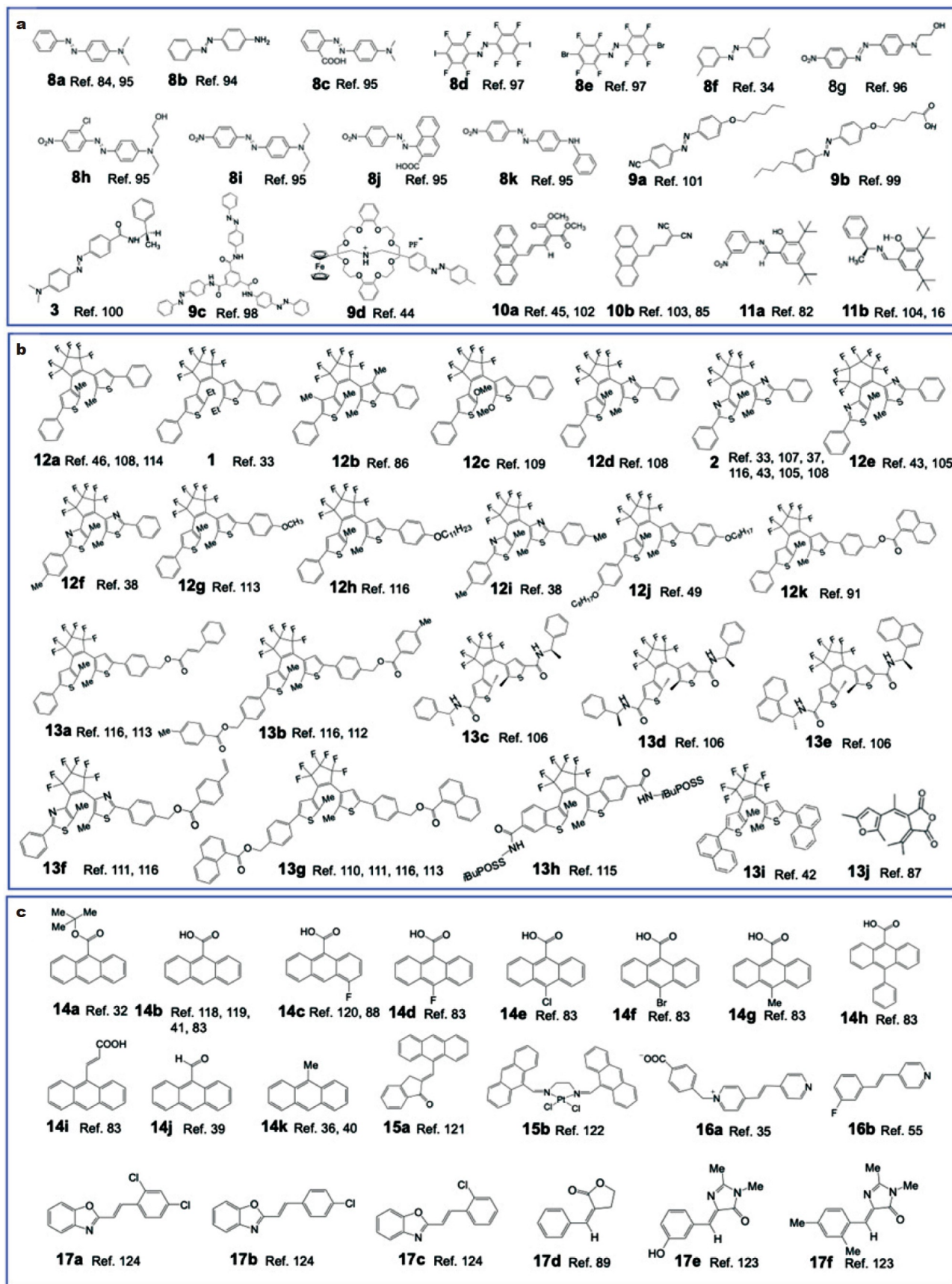
The most common strategy to fabricate photoresponsive materials is to introduce azobenzene regarding its typical photoisomerization between the metastable *cis* isomer and thermally stable *trans* isomer (Fig. 7a) [93]. In addition to the smart polymer materials, the development of azobenzene-based smart

crystals has recently flourished. Various mechanical motions have been reported by varying the substituent type of azobenzene and intermolecular interaction [34,44,84,94–101].

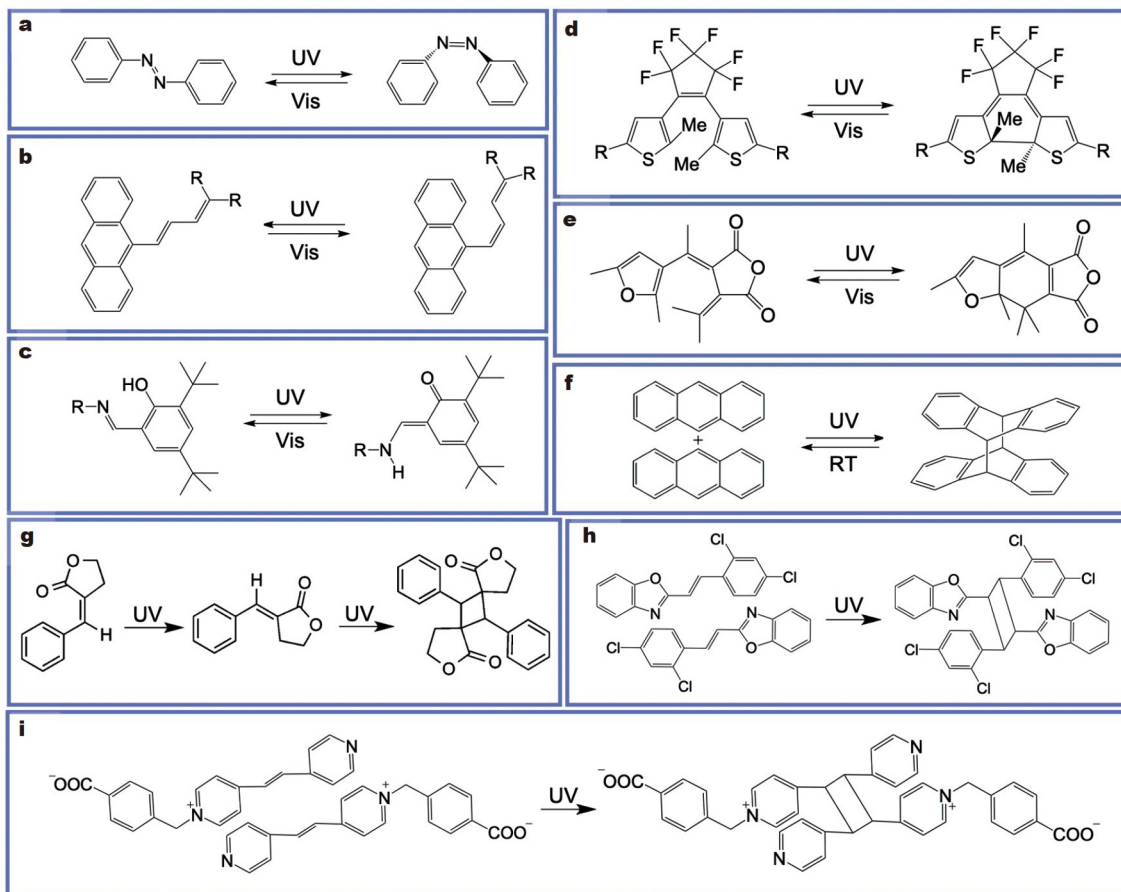
The photomechanical bending of the azobenzene crystals was first reported in 2009 [84]. The plate-like crystals of *trans*-4-(dimethylamino)azobenzene (*trans*-8a) exhibit reversible bending and straightening upon UV light irradiation on their (001) surface (Fig. 8a). The reversible bending and straightening can reach over 100 cycles with alternating UV irradiation and darkness. Subsequently, Koshima *et al.* [94] observed that the crystal of 4-aminoazobenzene (*trans*-8b) also bent reversibly when alternately irradiated using UV and visible light. Barrett's group [95] studied the effects of electronic structures, long-range molecular arrangement, molecular geometry, and macroscopic crystal orientation of photomechanical behaviors of azobenzene derivatives by choosing *trans*-8a, 8c, and 8h–k. The push-pull electronic structures of the substituents enhanced the photomechanical property of the single crystals by endowing them with sensitivity to visible light and rapid reverse motion of the crystal. Additionally, the low crystalline density and minimal thickness of crystals can significantly improve the high-magnitude phototriggered bending of the crystals.

Nath *et al.* [96] reported a slender photomechanical single crystal of *trans*-8g (Fig. 6a) and provided a mathematical model of the quasi-static and studied time-dependent photoresponsive bending of the macroscopic crystal. It was concluded that the crystal bending kinetics was dependent on the crystal size, excitation time, intensity, and direction. Barrett's group [97] demonstrated the first case of permanent photomechanical bending of azobenzene abbreviates, perhalogenated *cis*-8d and 8e (Fig. 8b). Upon irradiation with visible light, crystal *cis*-8e was transformed into a polycrystalline solid comprising the *trans*-isomer, and a significant and thermally irreversible photomechanical bending was observed. As the long thermal half-life of perhalogenated *cis*-azobenzene facilitated the characterization of its crystal structure (Fig. 8b, right), the evidence of crystal-to-crystal and azobenzene isomerization was first provided. In 2005, an interesting work, the continuous and directional motion of a crystal *trans*-8f induced by the simultaneous irradiation of two different wavelengths, was reported (Fig. 8c) [34]. The direction of the motion was well regulated by the irradiation position of the light source. Simultaneously, the plate-like crystal underwent a shape deformation, indicating its flexibility. The mechanism was analyzed; the phototriggered *trans*–*cis* isomerization of *trans*-8f induced melting and crystallization at the rear and front edges of the crystal, respectively, leading to motion and shape deformations. The UV and visible light were irradiated from the right and left sides, as shown in the image (Fig. 8c, bottom), respectively. Subsequently, the photomechanical nanowire actuator of azobenzene-containing 1,3,5-tricarboxamide derivative (compound 9c) was prepared [98]. It can reversibly bend controlled by light irradiation. The first example of limit-cycle self-oscillatory motions of the crystals coassembled from oleic acid and 9b was reported after a year (Fig. 8d) [99]. The crystal steadily flipped, irradiated with continuous blue light, owing to the alternating photoisomerization and phase transition processes, which provided a method toward the production of supramolecular motors based on molecule-based machines.

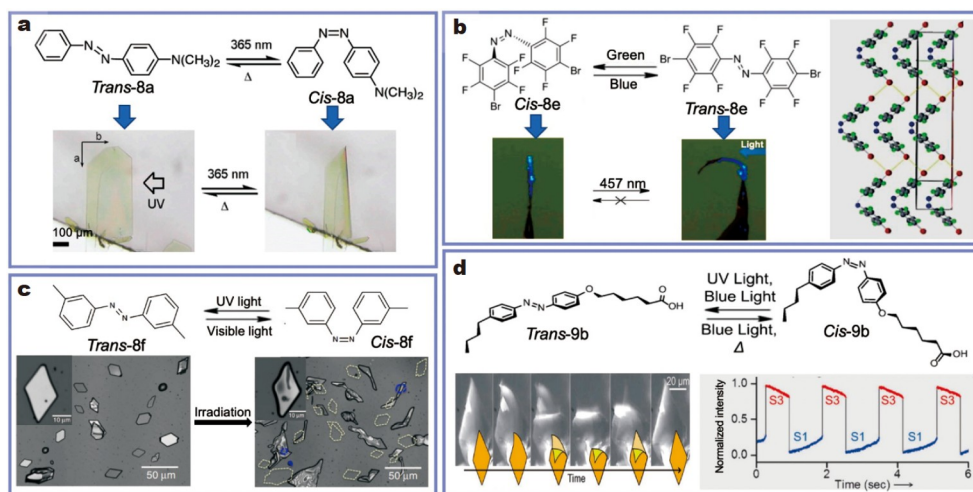
Recently, a new photoresponsive supramolecule, 9d, was prepared based on host-guest interaction between crown ether



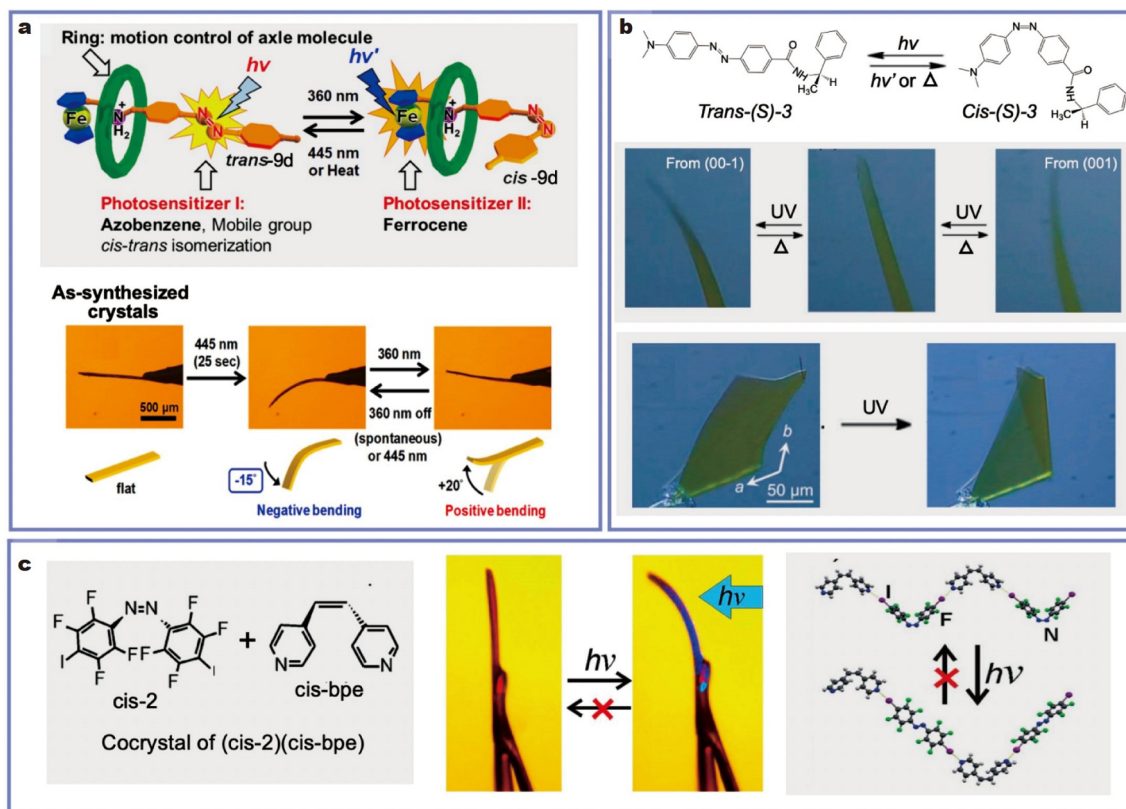
**Figure 6** Molecular structures of the reported photoresponsive flexible organic crystals, including molecules with *trans-cis* isomerization (a), phototriggered ring-opening and ring-closing reactions (b), and photodimerization (c).



**Figure 7** Common mechanisms of the photoreactions in the photoresponsive flexible organic crystals. *Trans*–*cis* isomerization of azobenzene compounds (a) and anthracene-9-(1,3-butadiene) derivatives (b); enol-keto interconversion of salicylideneanilines (c); phototriggered ring-opening and ring-closing reactions (d, e); [4+4] photodimerization and disassociation of anthracene molecules (f); [2+2] cycloaddition of styryl benzoxazole derivatives and 1,2-bis(4-pyridyl)ethylene (4,4'-bpe) molecules (g–i).



**Figure 8** *Trans*–*cis* isomerization of azobenzene compounds. (a) Top, photoreaction of molecule 8a during UV irradiation and heating. Bottom, images of the plate-like *trans*-8a crystal prior to and after being irradiated with UV light from the (001). Reprinted with permission from Ref. [84], Copyright 2009, American Chemical Society. (b) Left, irreversible bending of crystal *cis*-8e irradiated with 457 nm light. Right, crystal structure of *cis*-8e viewed from the crystallographic *ab*-plane perpendicular to the irradiation direction. Reprinted with permission from Ref. [97], Copyright 2013, American Chemical Society. (c) Top, photoisomerization of compound 8f. Bottom, microscopic images of crystals 8f prior to and after irradiation. The white dashed line represents the initial position of the crystals. (d) Top, photoreaction of molecule 9b. Bottom left, sequential micrographs of the crystal assembled from 9b and oleic acid in one cycle of self-oscillation during irradiation of 435 nm light. Bottom right, time profile of the self-oscillation of the crystal when irradiated with 435 nm light. Reprinted with permission from Ref. [99], Copyright 2016, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.



**Figure 9** (a) Top, schematic diagram of *cis-trans* isomerization of molecule 9d. Bottom, micrographs of photomechanical bending of the crystal irradiated by 360 and 445 nm wide-field laser. Reprinted with permission from Ref. [44], Copyright 2018, American Chemical Society. (b) Top, photoreaction of *trans*-(S)-3 during UV irradiation and heating. Middle, ribbon-like crystal of *trans*-(S)-3 prior to and after UV irradiation from the (00-1) and (001) faces, respectively. Bottom, square crystal of *trans*-(S)-3 prior to and after UV irradiation from the rear. Reprinted with permission from Ref. [100], Copyright 2016, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) Left, molecular structures of the cocrystal. Middle, permanent photoinduced bending of cocrystal (*cis*-2)(*cis*-bpe) induced by photochemical transformation into (*trans*-2)(*cis*-bpe). Right, cocrystal structure of the reactant and product phases in the photochemical reaction. Reprinted with permission from Ref. [54], Copyright 2010, Royal Society of Chemistry.

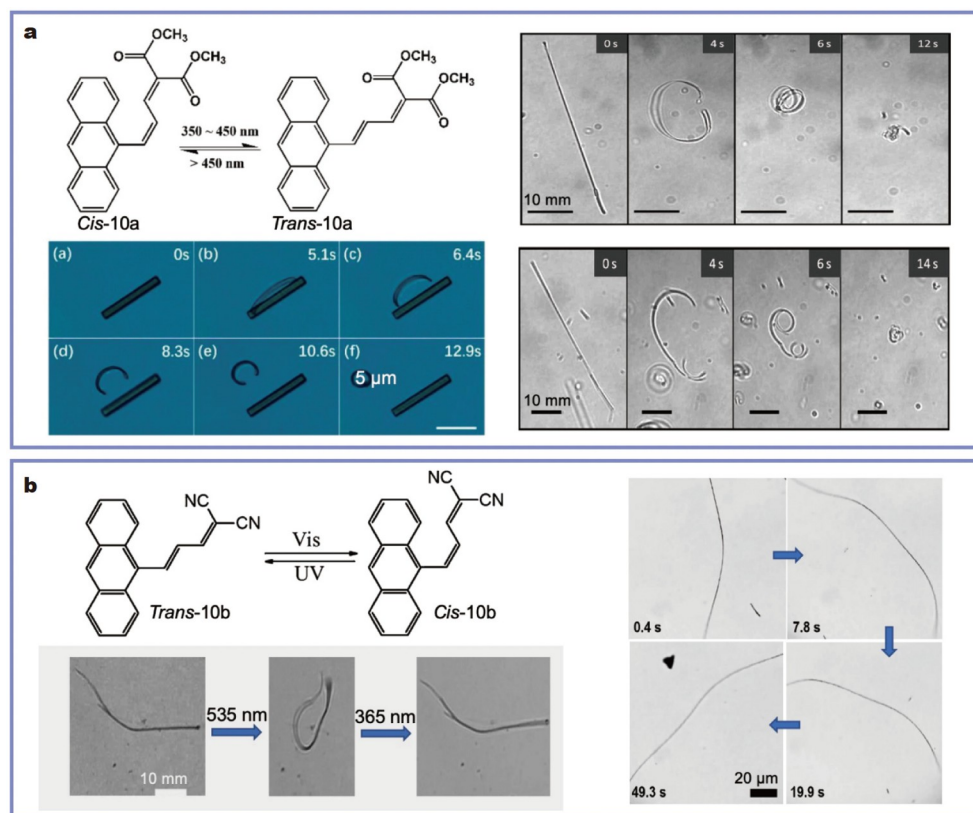
and a compound comprising dibenzo-[24]crown-8-ether and ferrocenylmethyl(4-methylphenyl)-ammonium [44]. The repeated alternating light irradiation of the 9d crystal at 360 and 445 nm resulted in bending in the range of 15°–30° in opposite directions (Fig. 9a). The rates of the photoinduced reversible and rapid bending of the crystal were dependent on the molecular structures. In another instance, the photomechanical motions of a chiral crystal of compound 3 with an (*R*)-phenylethyl-amide group were investigated [100]. Upon irradiation with UV light, the ribbon crystal of compound 3 bent away from the UV source along with twisting, and the square crystal bent toward the UV source with slight twisting (Fig. 9b). The twisting bending may be induced by shrinking along the *a*-axis and stretching along the *b*-axis. Recently, phototriggered multidirectional motions were first observed in organic crystals by choosing a plate-like crystal of molecule 9a [101]. Specifically, photoresponsive bending away from the UV source was observed below the melting point of 9a, and photoresponsive bending toward the UV source was achieved above the melting point. Below but near the melting point, a bidirectional motion was observed. Moreover, Frišćić's group [54] reported the first case of a new photomechanical azobenzene cocrystal. After cocrystallizing the azobenzene derivative (*cis*-2) with bis(4-pyridyl)ethylene (bpe), the structure of the as-prepared cocrystal of (*cis*-2)(*cis*-bpe) was confirmed by single-crystal XRD (SCXRD). Upon irradiation with UV light, (*cis*-2)(*cis*-bpe) was transformed into

(*trans*-2)(*cis*-bpe), leading to the bending of the cocrystals (Fig. 9c). The cocrystallization strategy opens up opportunities for the design and preparation of additional photomechanical crystals.

(2) *Trans-cis* isomerization of anthracene-9-(1,3-butadiene) derivatives

Except for the *trans-cis* isomerization of azobenzene derivatives, anthracene-9-(1,3-butadiene) derivatives can undergo *trans-cis* isomerization and exhibit photomechanical effects accordingly, which were developed by Bardeen and co-workers [45,85,102,103]. In 2012, Bardeen's group [102] first reported an example of a photomechanical crystal of *cis*-dimethyl-2-(3-(anthracen-9-yl)allylidene)malonate (10a), in which a curled amorphous layer was generated and peeled off from the parent crystal after irradiation with a pulse of 405 nm light (Fig. 10a). Subsequently, they reported an interesting phenomenon of straight nanowires of *cis*-10a and *trans*-10a rapidly curling and collapsing into tight bundles during the crystal-grown process; this was attributed to the photoisomerization of 10a (Fig. 10a) [45]. Afterward, Bardeen's group [103] prepared a photoresponsive anthracene derivative, 2-(3-(anthracen-9-yl)allylidene)-malononitrile (10b). The dimerization of the anthracene groups in the 10b crystal was prevented by the rapid non-radiative relaxation and high photoisomerization yield. The crystal demonstrated behaviors of reversible bending, straightening, and bending, under the irradiation of 535, 365, and





**Figure 10** Photoisomerization of anthracene-9-(1,3-butadiene) derivatives. (a) Top left, *cis-trans* isomerization of 10a. Reprinted with permission from Ref. [102], Copyright 1996, Royal Society of Chemistry. Bottom left, sequence of images of a *cis*-10a crystal undergoing phototriggered peeling processes during the irradiation of 405 nm light. Reprinted with permission from Ref. [45], Copyright 2013, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. Images of *trans*-10a nanowire (top right) and *cis*-10a nanowire (bottom right) after 1 s of light irradiation at a time of 0 s. (b) Top left, *cis-trans* isomerization of 10b. Reprinted with permission from Ref. [103], Copyright 2012, Royal Society of Chemistry. Bottom left, images of 10b nanowire irradiated with sequential visible and UV light. Reprinted with permission from Ref. [85], Copyright 2020, Wiley-VCH Verlag GmbH. A reversible bending behavior was observed. Right, sequential images of a *cis*-10b microwire during the combined irradiation of UV and visible light.

535 nm light, respectively (Fig. 10b). Recently, the first case of molecular crystals with complex oscillatory behavior induced by continuous irradiation was reported. It was shown that *cis*-10b microwires can be continuously actuated under combined irradiation of UV and visible light (Fig. 10b) [85], which mimicked the oscillatory behaviors of biological flagella and exhibited a photoinduced propagation through liquids or even across a surface. All the aforementioned contributions could provide a strategy to fabricate photoresponsive molecules that can undergo rapid isomerization in response to visible light.

#### Keto-enol tautomerism

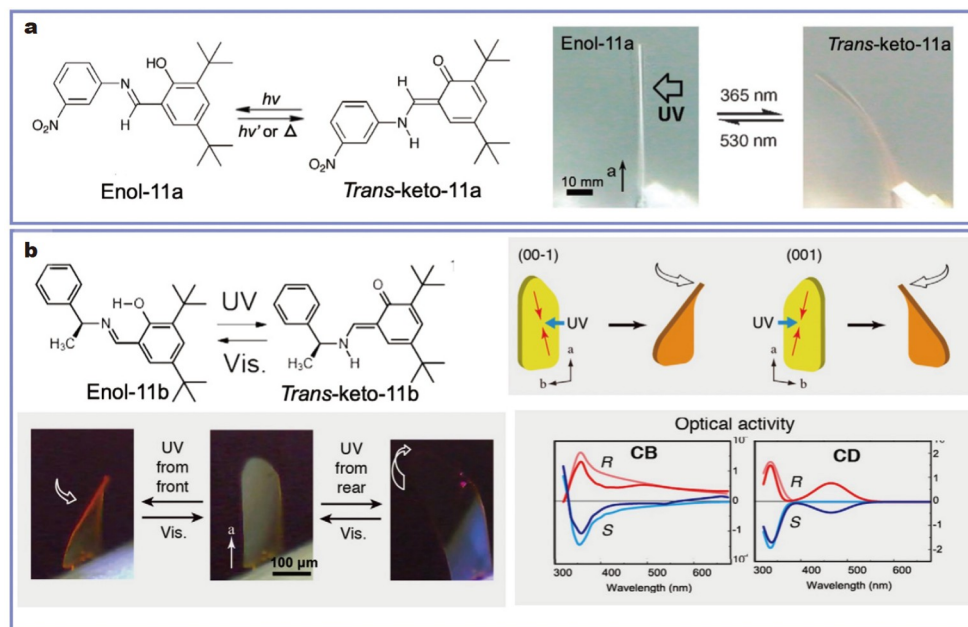
Koshima *et al.* [16,82,104] reported another kind of photoresponsive molecules (salicylideneanilines and their derivatives), which can undergo photoinduced reversible reactions through keto-enol tautomerism (proton transfer). For example, Koshima *et al.* [82] discovered that plate-like crystals of *N*-3,5-di-*tert*-butylsalicylidene-3-nitroaniline (11a) can repeatedly straighten and bend during irradiation with visible and UV light alternately (Fig. 11a). The reversible bending can be repeated up to 200 cycles. Afterward, Koshima *et al.* [104] reported the photoinduced bending of the chiral crystals of *R*- and *S*-enantiomers of *N*-3,5-di-*tert*-butylsalicylidene-1-phenylethylamine in an enol form (enol-(*R*)-11b and enol-(*S*)-11b). The achiral crystal of the racemic mixture [enol-(rac)-11b] of the *S*- and *R*-enantiomers

was taken as a contrast. The plate-like achiral and chiral crystals demonstrated similar photoinduced bending. The achiral crystal of enol-(rac)-11b was superior to the chiral crystal of enol-(*S*)-11b when used as a light-driven actuator.

Recently, new 2D crystals of enol-(*S*)-11b and enol-(*R*)-11b were prepared by Koshima *et al.* [16], which can undergo bending with twisting upon irradiation with UV light because of the shrinkage of the irradiated surfaces triggered by the photoisomerization of enol-(*R*)-11b to *trans*-keto-(*S*)-11b (Fig. 11b). The directions of bending with twisting can be well controlled by varying the irradiation face. Additionally, the optical chiroptical (circular birefringence, CB; circular dichroism, CD) properties of the enol-(*S*)-11b and enol-(*R*)-11b crystals were measured simultaneously prior to and after continuous irradiation with UV light. The CD spectra of the enol-(*S*)-11b and enol-(*R*)-11b crystals indicated negative and positive Cotton effects at 330 nm, respectively. The new peaks centered at 460 nm after irradiation with UV light were attributed to the photoisomerization of enol 11b into the *S* and *R* *trans*-keto 11b with approximately 10% conversion. The CB and CD spectra were contrary to those measured in solution and the simulated results.

#### Photocyclization

In addition to the photoisomerization reaction, photoinduced ring opening and closure of the component molecules can



**Figure 11** Keto-enol tautomerism. (a) Left, photochromic reaction of 11a. Right, a plate-like enol-11a crystal prior to and after being irradiated with UV light from the right side. Reprinted with permission from Ref. [84], Copyright 1996, Royal Society of Chemistry. (b) Top left, photochromic reaction of 11b. Bottom left, bending with twisting of a 2D enol-(S)-11b crystal prior to and after being irradiated with UV light from the front and rear, respectively. Top right, relationships between the irradiation face of the enol-(S)-11b crystals and twisting directions. Bottom right, CB and CD spectra of the S and R crystals. Reprinted with permission from Ref. [16], Copyright 2016, American Chemical Society.

endow a material with photomechanical motions [38,46,86,91,105].

#### (1) Ring opening and closure of diarylethenes

The most common molecules with photocyclization are diarylethenes, which exhibit photochromism attributed to their abilities to undergo reversible ring-opening and ring-closing reactions induced by light irradiation [42,46,86]. This “diarylethene” family can exhibit various photomechanical motions upon UV irradiation as reported. They are chosen as potential candidates for optical memory and molecular machines with high thermal stability [33,43,91,106].

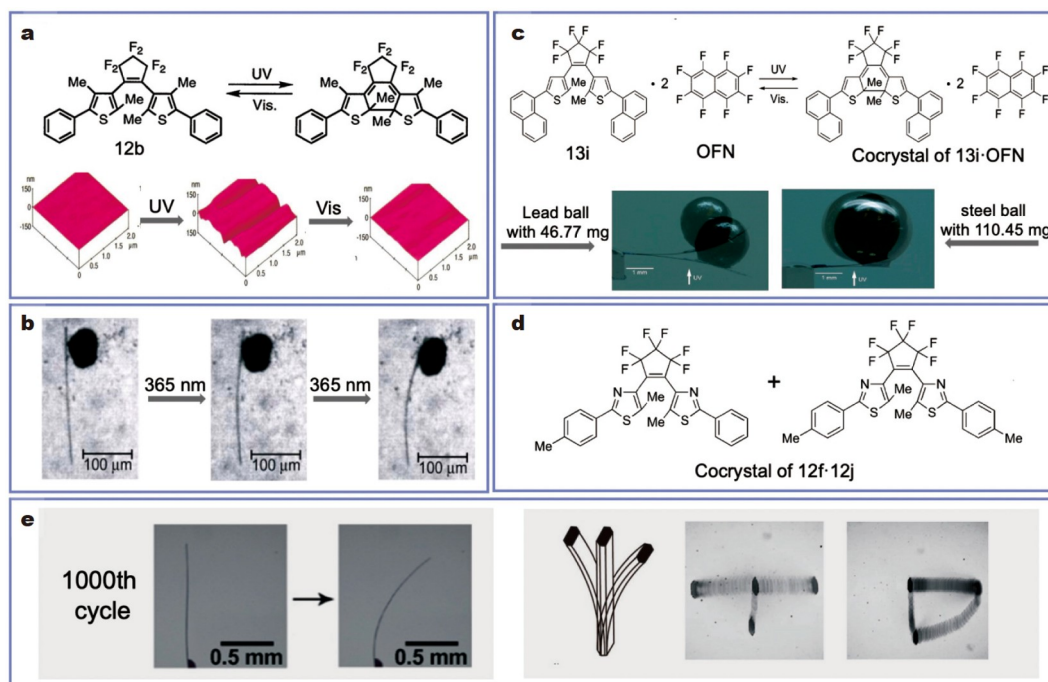
For instance, Irie and co-workers [33,38,86] reported several diarylethene crystals that exhibit photomechanical motions. In 2001, they reported the first case of photomechanical diarylethene single crystals with photoresponsive reversible deformation based on [1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)-perfluorocyclopentene] (12b) [86]. The crystal morphology underwent deformation when irradiated with 366 nm light, and new steps generated on the (100) surface that would disappear were induced by irradiation with a visible light (Fig. 12a). Six years later, Irie’s group [33] reported that the molecular crystals of diarylethene chromophores (compounds 1 and 2) exhibited rapid (~25 μs) and reversible macroscopic variations in size and shape induced by irradiation with UV and visible light, e.g., expansion, contraction, and bending (Fig. 1c, d). Interestingly, the rod-like crystals can move microscopic objects, rendering them promising candidates for possible photoactuators (Fig. 12b).

The aforementioned single-component crystal lacked durability and was deformed in less than 100 cycles, which should be improved for practical applications. Therefore, they fabricated a plate-like two-component cocrystal (13i-OFN) using 1,2-bis(2-methyl-5-(1-naphthyl)-3-thienyl)perfluorocyclopentene

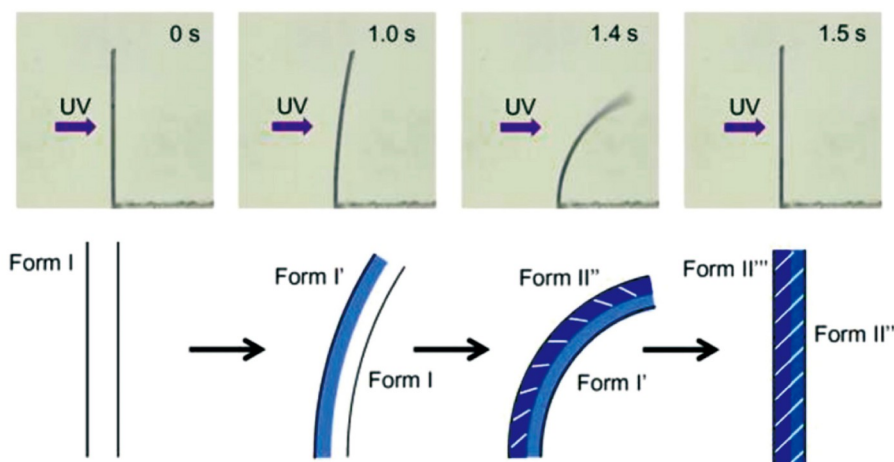
(compound 13i) and perfluoronaphthalene (OFN) [42]. The cocrystal exhibited reversible straightening and bending for up to 250 cycles upon alternate irradiation with visible and UV light (Fig. 12c). Remarkably, upon irradiation with UV light, the cantilever made of 13i-OFN crystals could lift a metal ball, whose weight was 200–600 times heavier than that of the crystals (Fig. 12c). During the aforementioned study on multicomponent crystals, Irie’s group [38] discovered that the durability can be further enhanced by the cocrystallization of two diarylethenes, 12f and 12j (Fig. 12d). The cocrystal can bend under light irradiation over 1000 times without any damage and can bend in any direction toward the light source within the temperature range of 4.6–370 K (Fig. 12e). The corresponding molecular-crystal actuator exhibited substantial mechanical properties compared with those of the piezoelectric crystal, rendering it a potential material for micromechanical applications.

In addition to the contributions by Irie *et al.*, the reversible phototriggered crystal bending of compounds 2 and 12j was studied by Kobatake and co-workers [37,49,107] and Uchida’s group [108]. In 2017, Kobatake’s group [49] reported an unusual photomechanical behavior of the crystal of compound 12j upon irradiation with UV light. After continuous UV irradiation from the left side of crystal 12j, it bent away from the light source first and returned to a straight shape (Fig. 13), which may have resulted from the combination of a reversible photochromic reaction and SCSC process. Recently, Uchida’s group [108] reported the first case of phototriggered bending for the thin crystals of compound 2.

Apart from the aforementioned diarylethenes, many other diarylethene derivatives with different morphologies and photomechanical behaviors have been developed by Uchida [43,105,106,108], Kobatake [46,91,107,109–114], and Shimojima [115]. For instance, in 2008, Uchida *et al.* [106] reported several



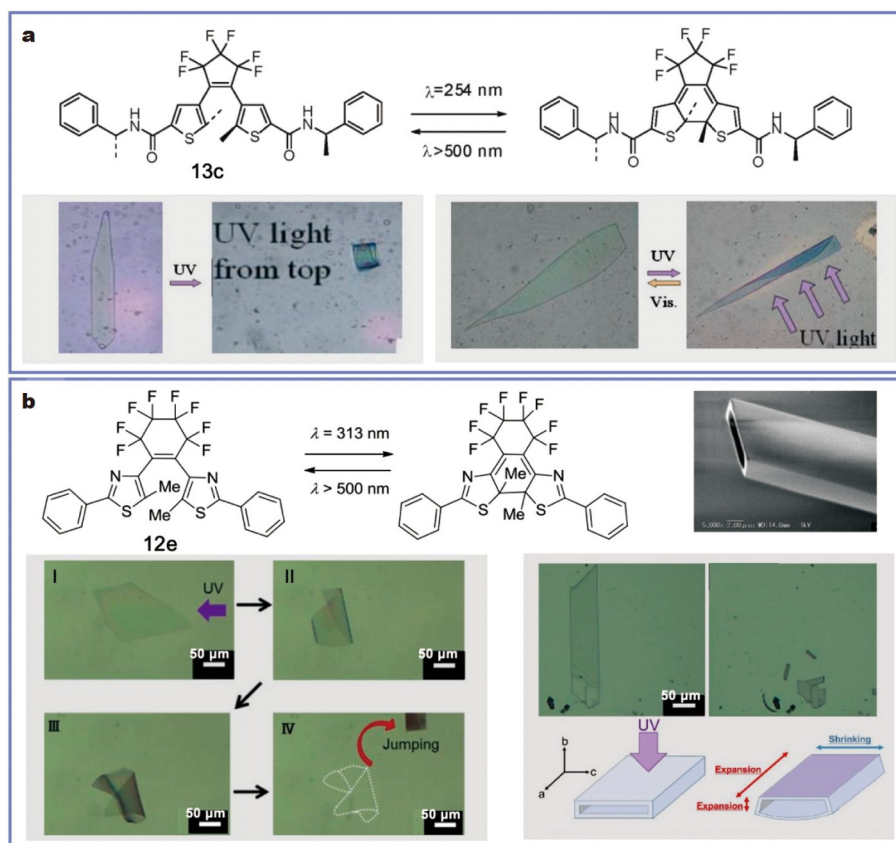
**Figure 12** (a) Top, photochromism of compound 12b. Bottom, atomic force microscopy (AFM) images of the (010) surface of the crystal prior to irradiation, after irradiation with 366 nm light, and after further irradiation with visible light. Reprinted with permission from Ref. [86], Copyright 2001, The American Association for the Advancement of Science. (b) Movement of a gold microparticle by the rod-like crystal of compound 2 when irradiated with 365 nm light, which can be moved to as far as 30 nm. Reprinted with permission from Ref. [33], Copyright 2007, Nature Publishing Group. (c) Top, photochromic reaction of 13i-OFN cocystal. Bottom, photomechanical motions of a cantilever made from 13i-OFN. The images prior to and after being irradiated with UV light are superimposed. Reprinted with permission from Ref. [42], Copyright 2010, American Chemical Society. (d) Molecular structure of the cocystal of 12f-12j (12f:12j = 63/37). (e) Left, pairs of images of the cocystal showing the 1000<sup>th</sup> cycle of reversible bending when alternately irradiated with UV and visible light. Right, bending of the rod-like cocystal in all directions. (d, e) Reprinted with permission from Ref. [38], Copyright 2012, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.



**Figure 13** An unusual photomechanical bending of crystal 12j and a proposed mechanism. Reprinted with permission from Ref. [49], Copyright 2017, American Chemical Society.

molecular crystals comprising a dithienylhexafluorocyclopentene with (*S*)- or (*R*)-*N*-phenylethylamide substituents, i.e., 13c, 13d, and 13e. Both 1D rod-like and 2D plate-like crystals were prepared through sublimation (Fig. 14a). After irradiation with UV light, the rod-like crystal exhibited reversible bending, and the 2D plate-like crystals exhibited irreversible width-wise rolling and reversible length-wise rolling. Recently, they reported the photoinduced bending of the 2D

plate-like crystals of compounds 12a, 12d, and 2 [108]. Additionally, photoinduced curling and jumping of the thin film crystal of a diarylethene with a perfluorocyclohexene ring (12e) were reported (Fig. 14b) [43]. The hollow crystals of 12e were prepared by sublimation, which exhibited a remarkable photosalient effect and scattered into small pieces when irradiated with UV light (Fig. 14b) [105]. Consequently, the scattering of a fluorescent bead inserted in the hollow of the crystal was trig-



**Figure 14** (a) Top, photochromism of compound 13c. Bottom left, irreversible width-wise rolling of the plate-like crystal induced by UV light irradiation. Bottom right, reversible length-wise rolling of the crystal. Reprinted with permission from Ref. [106], Copyright 1996, Royal Society of Chemistry. (b) Top left, photochromism of compound 12e. Bottom left, photoresponsive curling, followed by jumping of the thin film of 12e. Reprinted with permission from Ref. [43], Copyright 2012, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. Top right, scanning electron microscopy (SEM) image of a hollow crystal of 12e. Bottom right, optical microscopic image of the hollow crystal of 12e and that after photoinduced scattering as well as a proposed deformation mechanism of the hollow crystal upon UV irradiation. Reprinted with permission from Ref. [105], Copyright 2017, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

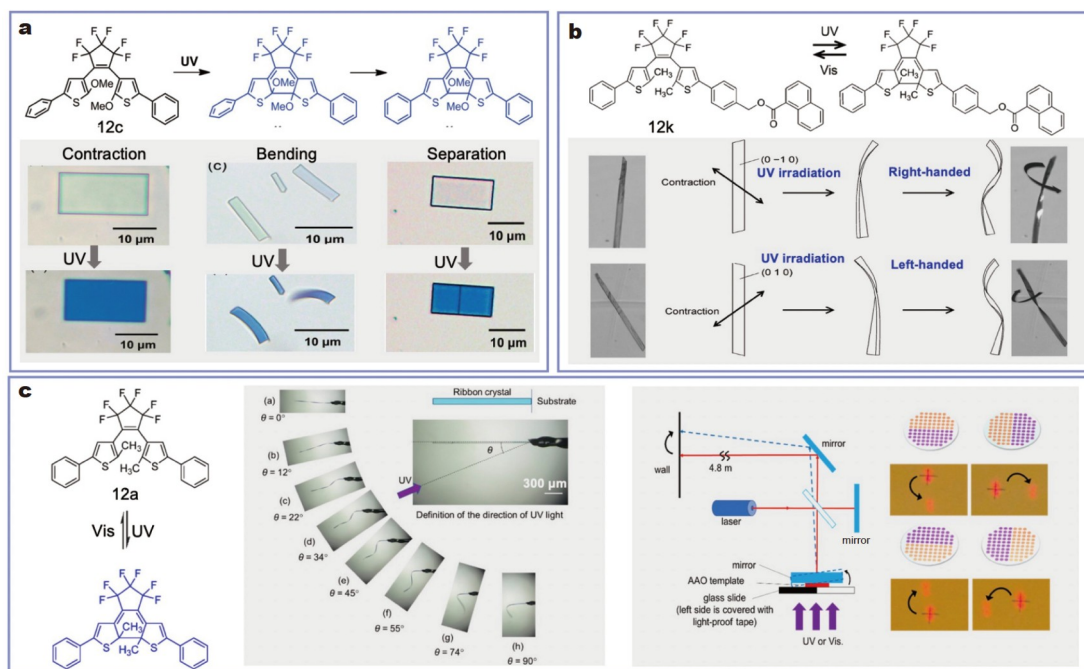
gered by UV irradiation because of the deformation and fracture of the hollow crystal.

In other studies [110–113,116], the reversible photoinduced bending behaviors of 1D crystals of compounds 2, 13a, 13b, 13f, and 13g were reported by Kobatake *et al.* [46,91,109,114]. Furthermore, they developed several photoresponsive motions of diarylethene derivatives. For example, they fabricated a thin crystal of 1,2-bis(2-methoxy-5-phenyl-3-thienyl)-perfluorocyclopentene (12c), which exhibited shape deformations, including bending, separation, and contraction, depending on the crystal thickness and irradiation methods (Fig. 15a) [109]. Afterward, the photoinduced reversible twisting of novel photochromic diarylethene crystals based on compound 12k was observed (Fig. 15b), which should be induced by the contraction of the crystals along the diagonal directions [91]. The twisting directions (left-handed and right-handed) can be well modulated by varying the irradiated faces of the rod-like crystals of 12k. Recently, they performed detailed studies on how the illumination directions affected the photomechanical twisting of a diarylethene crystal, 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (12a) crystal (Fig. 15c) [46]. The ribbon-like crystal prepared using the sublimation method can exhibit reversible photomechanical twisting when alternately irradiated by UV and visible light. Additionally, changing the UV irradiation directions with respect to the crystals will result in different twisting

modes, varying from helicoid to cylindrical helix, which provides a useful strategy to generate new photomechanical motions of single crystals (Fig. 15c). In another work, a photomechanical nanocrystal of 12a was organized on a macroscopic scale applying an inorganic alumina template and generating a hybrid organic-inorganic bending actuator (Fig. 15c, right) [114]. Importantly, when alternately irradiated with UV and visible light, the force generated by the 0.1 mg hybrid material can tilt a 1.28 g mirror and control a laser beam. In addition, Shimojima's group [115] reported the photoresponsive reversible bending of a new organic-inorganic hybrid molecule (13h) comprising a diarylethene backbone and polyhedral oligomeric silsesquioxane (POSS). The introduction of POSS increased the conversion ratio from open-ring to closed-ring isomers in solution when irradiated by UV light. The combination of the high fatigue resistance of the diarylethene moieties and improved thermal stability induced by the siloxane moieties render them promising materials for actuators and other smart devices.

#### (2) Ring opening and closure of other compounds

Another class of well-known photochromic compounds that can undergo photoinduced ring opening and closure reactions are fulgides (Fig. 7e). However, fulgide-based photomechanical crystals are rarely reported and require vigorous development. To date, only a plate-like microcrystal of furylfulgide, 13j, with photomechanical motion was reported in 2012 [87]. The crystal



**Figure 15** (a) Top, photochromic reaction in the crystal of 12c. Bottom, crystal deformations of contraction, bending, and separation of the 12c crystal irradiated with 365 nm light. Reprinted with permission from Ref. [109], Copyright 2011, American Chemical Society. (b) Top, photochromic reaction in the crystal of 12k. Bottom, relationships between the twisting directions and irradiated faces with UV light. Reprinted with permission from Ref. [91], Copyright 2013, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) Left, photochromic reaction in the crystal of 12a. Reprinted with permission from Ref. [46], Copyright 2018, American Chemical Society. Middle, different twisting motions modulated by the irradiation angle of the UV light, varying from helicoid to cylindrical helix. Right, schematic illustration and experiment demonstration of a laser deflection setup. Reprinted with permission from Ref. [114], Copyright 2019, American Chemical Society.

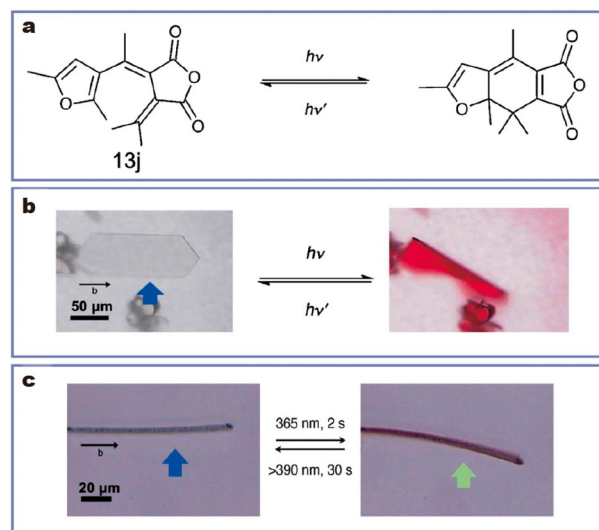
can be bent toward the UV source when irradiated and straightened when irradiated with visible light, which was observed for over 200 cycles during alternating irradiation with visible and UV light (Fig. 16).

#### Photocycloaddition reactions

Cycloaddition reactions, including [4+4] and [2+2] reactions in a solid, have attracted increasing interest since the rules of the topochemistry for cycloaddition reactions were established [117]. A photomechanical crystal requires a suitable molecular arrangement of light-sensitive molecules and an extremely strict packing distance of the cycloaddition-reactive groups. Similarly, the photomechanical crystals comprising cycloaddition-reactive molecules can exhibit various photomechanical motions, such as bending, curling, twisting, and jumping upon light irradiation, owing to the photocycloaddition reactions. Importantly, cycloaddition reactions are reversible and tend to depolymerize upon heating, which further facilitates the potential use of these materials as photoactuators.

#### (1) [4+4] photocycloaddition reactions

After UV light irradiation, the double bond at the 9,10 positions of an anthracene molecule can undergo a [4+4] photocycloaddition reaction, where the anthracene molecules are stacked in parallel, and the distance between two adjacent molecular planes should satisfy the Schmidt rule [117]. Several studies were performed on the photomechanical crystals of anthracene derivatives using this idea [32,36,39–41,83,88,118–122]. For instance, in 2006, a crystalline nanorod comprising 9-*tert*-butyl anthroate (14a) exhibited a photoresponsive expansion behavior (Fig. 1a) [32]. After irradiation, 9-*tert*-butyl anthroate

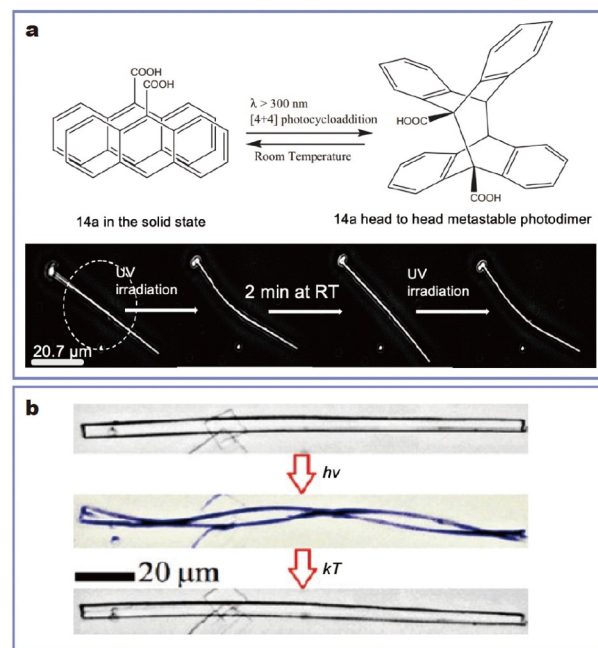


**Figure 16** (a) Photochromic reaction within the crystal of 13j. (b) The (101) face of the plate-like crystal of 13j prior to and after irradiation with UV light. (c) Bending of a 1D crystal of 13j prior to and after irradiation with UV light from the low side [87], Copyright 2012, The Chemical Society of Japan.

underwent a rapid [4+4] photodimerization in the crystals, resulting in a 15% increase in rod length without fragmentation. Thereafter, the research on photomechanical motions of anthracene derivatives increases. Additionally, they observed large shape changes in the crystalline nanorods of 9-anthracene-

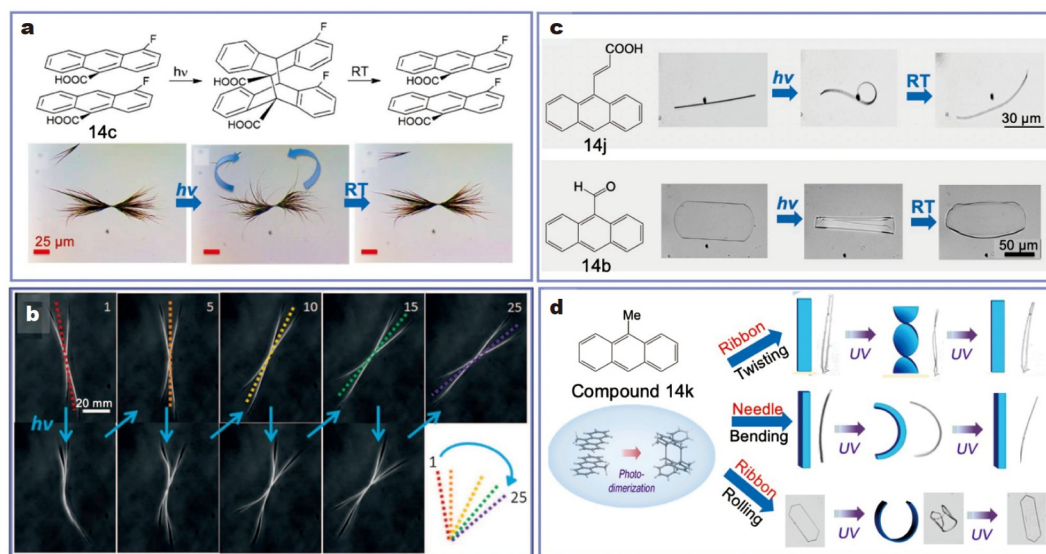
neocarboxylic acid (14b) (Fig. 17), which can be reversibly triggered by localized photoexcitation [41,83,118,119]. Bending was observed in the nanorods of 14b upon UV irradiation [83,118] or two-photon excitation [119] (Fig. 17a), and a translational motion of the rod was triggered by the sequential bending of the long parts. It was concluded that nanoscale molecular crystalline structures can alleviate the strain-induced disruption associated with photochemical reactions in large crystals. The reversible phototriggered twisting of the crystal microribbons of 14b was reported by Bardeen's group (Fig. 17b) [41]. When irradiated with spatially uniform light, the as-prepared photoreactive microribbons rapidly twisted. Several minutes after the irradiation, they relaxed to their original shapes.

The same group reported photoinduced bending and ratcheting rotary motions of a highly branched crystal of 4-fluoroanthracenecarboxylic acid (14c) [88,120]. When exposed to UV light, an intermolecular [4+4] photocycloaddition drove the bending and twisting of the branch (Fig. 18a) [120]. These motions made the overall crystal rotate, which can be repeated several times (Fig. 18b) [88]. Different crystal shapes will lead to a rotation with different magnitudes and directions. A typical branched crystal underwent a rotation of 50° net after 25 consecutive irradiations for 1 s. This ability to undergo ratchet-like rotation should be due to the chiral shape of the crystals. Moreover, more complex photoinduced motions, including coil, fold, curl, roll, and twist, have been observed for the crystals of anthracenes [36,39,40]. For instance, the microplates of 14j and microwires of (*E*)-3-(anthracen-9-yl)acrylic acid (14i) underwent photoinduced coiling-uncoiling and folding-unfolding transitions, respectively, after a 475-nm irradiation (Fig. 18c) [39]. Additionally, the photoinduced twisting in microribbons comprising 9-methylanthracene (14k) was reported [40]. Under different crystallization conditions, microribbons and micro-



**Figure 17** (a) Top, [4+4] photocycloaddition and dissociation of 14b. Bottom, images of a single nanorod of 14b in a 50% aqueous phosphoric acid solution. Reprinted with permission from Ref. [119], Copyright 2009, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) Optical microscopy images of microribbons of 14b with a reversible twisting. Top, prior to irradiation; middle, immediately after irradiation; bottom, microribbon recovered after 9 min in the dark. Reprinted with permission from Ref. [41], Copyright 2011, American Chemical Society.

needles were prepared. After irradiation, the microribbon twisted while the microneedle bent (Fig. 18d). The maximum



**Figure 18** (a) Top, [4+4] photocycloaddition and dissociation of 14c. Bottom, branched 14c microcrystal prior to irradiation with 365 nm light, during irradiation, and 10 s after the end of the irradiation. Reprinted with permission from Ref. [120], Copyright 1996, Royal Society of Chemistry. (b) After each irradiation cycle, a branched 14c crystal rotated clockwise. The cycle was repeated 25 times. Illustration of five cycles of the crystal prior to and after UV irradiation. Reprinted with permission from Ref. [88], Copyright 2016, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) Optical microscopy images of 14i microwire with coiling and uncoiling and 14j microplate with folding and unfolding, prior to light (475 nm) exposure, during and after light exposure, respectively. Reprinted with permission from Ref. [39], Copyright 1999, Royal Society of Chemistry. (d) Unbending and bending of 14k microneedle, untwisting and twisting of 14k microribbon, and curling and uncurling of 14k during 365 nm UV irradiation. Reprinted with permission from Refs [40] and [36], Copyright 2014 and 2018, American Chemical Society and Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, respectively.

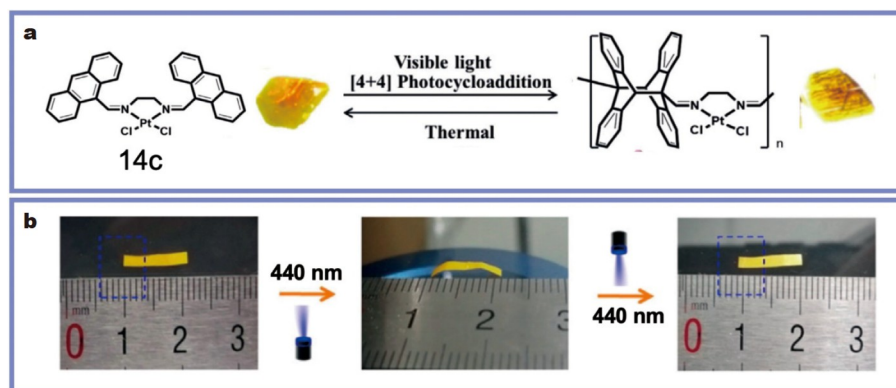
deformation of these crystals occurred approximately at the mid-point of the reaction, and further dimerization restored the crystals to their original shape. Recently, the newly fabricated elongated hexagonal platelet of compound 14c was observed to undergo a phototriggered rolling-up and unrolling (Fig. 18d) [36]. The rolled-up motion of the microribbons was masterly used to trap superparamagnetic nanoparticles, which can be carried along the direction of the magnetic field gradient.

There are extremely few cases reported for SMs based on “organic crystal-based hybrids”. For example, in 2019, Zhang’s group [122] obtained a large-sized Pt-based linear polymer crystal through a [4+4] cycloaddition of anthracene groups for the first time (Fig. 19a), which underwent a reversible contraction of their unit-cell volume upon irradiation or heating. The crystals were successfully hybridized with polyvinylidene fluoride (PVDF) to fabricate outstanding photoactuators, which can crawl by controlling light irradiation (Fig. 19b).

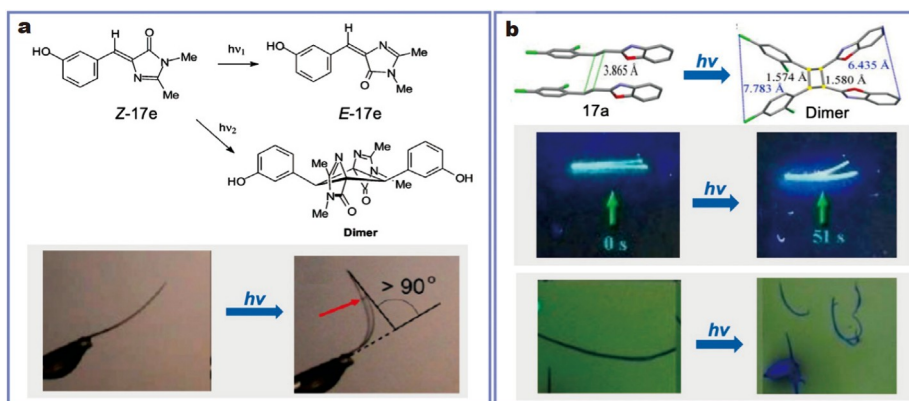
(2) [2+2] photocycloaddition reactions

Besides the [4+4] photocycloaddition of anthracene, [2+2] photocycloaddition of benzylidenedimethylimidazolinone, 4,4'-bpe derivative, 4-(3-fluorostyryl)-pyridine, 3-benzylidenedihydro-furan-2(3H)-one, and (*E*)-2-(2,4-dichlorostyryl)-benzo[*d*]-oxazole has been utilized to fabricate photomechanical crystals [35,55,89,123,124].

For instance, Naumov *et al.* [123] reported a meta-hydroxy chromophore (17e) with more than one stable polymorph in the pure state. One of the polymorphs (17e-A) with a multilayer structure underwent photodimerization after UV light irradiation, leading to photomechanical effects of unprecedented magnitude for a single crystal, where the single crystal bent to over 90° without a fracture (Fig. 20a). Afterward, they explored 3-benzylidenedihydrofuran-2(3H)-one (17d), which underwent *E* ↔ *Z* isomerization and [2+2] dimerization (Fig. 7g). Surface- and bulk-sensitive analysis techniques were employed to study a rare example of benzylidene-furanone crystals (crystal 17d), which exhibited several photomechanical effects, such as surface delamination and striation, phototriggered bending, and photosolvent effects (ballistic decomposition and motion). These results laid the foundation for the development of an overall theoretical model for the description of ordered solid-state photomechanics. Wang *et al.* [124] reported the bending, rolling, curling, and photosolvent effect of the molecular crystal of the styrylbenzoxazole derivative, (*E*)-2-(2,4-dichlorostyryl)benzo[*d*]-oxazole (17a and 17b), triggered by [2+2] photocycloaddition. The 17a microneedle exhibited reversible bending away from the UV light source, and the small slice exhibited photoinduced rolling (Fig. 20b). It was suggested that the rapid release in the generated strain during photocycloaddition resulted in the



**Figure 19** (a) Reversible [4+4] photocycloaddition and dissociation of 14c and optical microscopy images of the 14c crystal prior to and after irradiation. (b) Images of the 14c-PVDF photoactuator, which can crawl by controlling the light irradiation. Reprinted with permission from Ref. [122], Copyright 2019, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.



**Figure 20** (a) The isomerization and dimerization of 17e. Top, products of irradiating 17e. Bottom, photomechanical effect of the single crystal of 17e after unfocused weak UV irradiation. Reprinted with permission from Ref. [123], Copyright 2010, American Chemical Society. (b) Top, molecular configuration of 17a prior to and after irradiation with 365 nm light. Middle, images of the 17a microneedle prior to and after irradiation with 365 nm light (the irradiation direction is indicated by the arrows). Bottom, images of the 17a assembly prior to and after 365-nm irradiation. Reprinted with permission from Ref. [124], Copyright 2017, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

photosensitive effect, while the curling or bending occurred during a slow release in the strain. Remarkably, such never reported [2+2] cycloaddition occurred between two different conformational isomers of 17a.

Considering that 4,4'-bpe and its derivatives can undergo [2+2] cycloaddition, their photomechanical properties have been recently investigated [35]. For example, the crystal of a 1,2-bis(4-pyridyl)ethylene-based pyridinium salt (16a) can bend when triggered by [2+2] cycloaddition after UV irradiation (Fig. 21a). Importantly, the bending process with high fluorescence contrast renders them excellent candidates for the remote detection of photomechanical work. The cycloaddition caused a contraction of the plane parallel to the (001) faces, which resulted in a bending motion perpendicular to the *a*-axis of the crystals. Although photomechanical materials have been greatly explored for phototriggered actuators, metal-organic framework (MOF)-based actuators have been rarely reported [55]. Therefore, Lang *et al.* [55] observed that the incorporation of a photoreactive olefinic species (16b) into the MOF of [Zn(bdc)(3-F-spy)] (18) can generate photomechanical crystals, which underwent three types of photomechanical macroscopic motions upon UV light irradiation (Fig. 21b). To explore their practical potential, crystal 18 was included in a polyvinyl alcohol (PVA) composite membrane to amplify the mechanical stress, thereby generating a

macroscopic actuator.

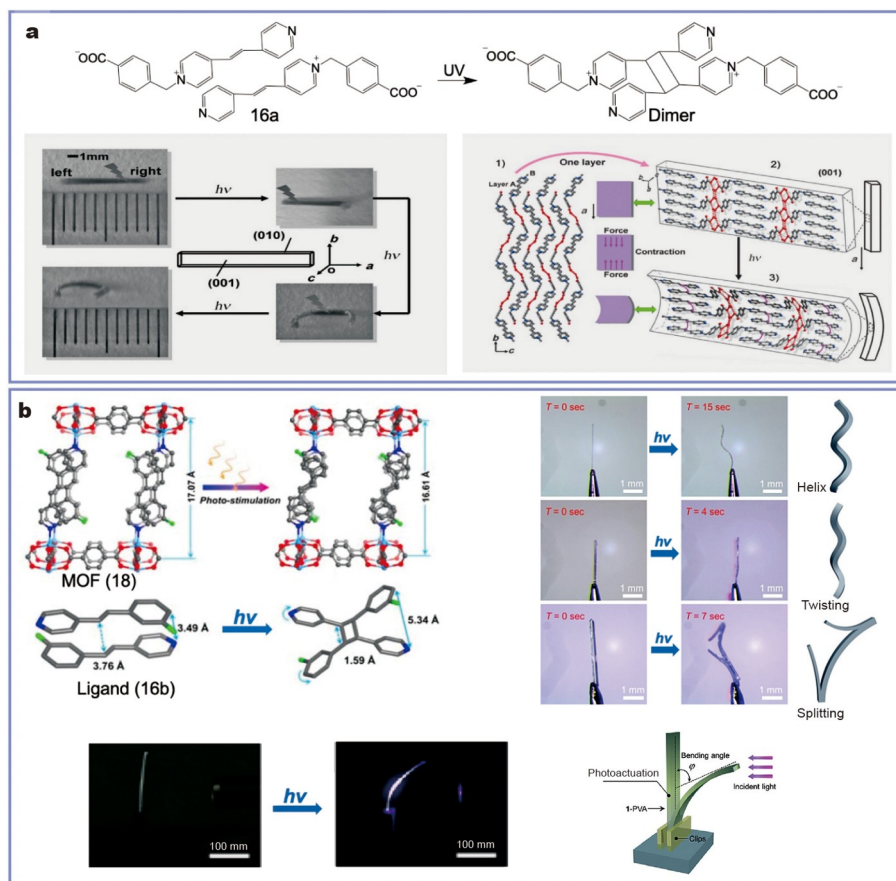
#### Other types of photomechanical crystals

With the development of photomechanical crystal-based SMs, other photoresponsive systems are required to broaden this field. Several rare examples of photomechanical crystals have been reported recently, including photoexcited intermolecular distortions of asymmetric perylene diimide (PDI) molecules (Fig. 22a) [125], topochemical polymerization reactions of diindene derivatives (Fig. 22b) [51], and photochromic reactions of dibenzobarrelene derivatives (Fig. 22c) [126]. These observations will facilitate the discovery of unique applications, owing to their characteristic mechanisms, which are not detailed herein.

#### Thermoresponsive flexible smart organic crystals

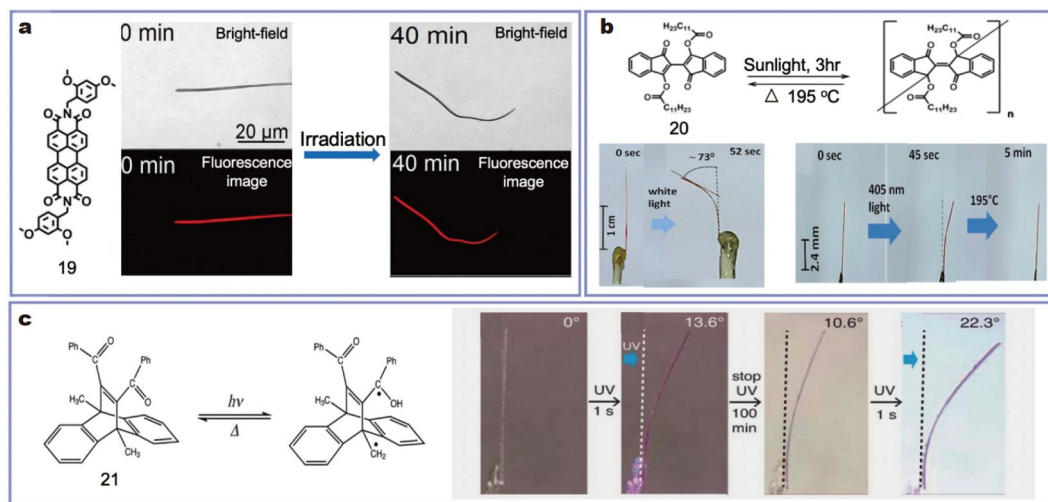
Exploring the temperature compatibility/response of flexible devices is essential for extending the applications of FSMs. Undoubtedly, heat-responsive mechanical molecular crystals, particularly organic crystals, are suitable candidates because of their effective conversion of heat to mechanical properties, such as burst, jump, bend, twist, or curl as well as a controllable preparation method.

Ghosh *et al.* [47] reported the elastic crystal of 2,6-dichlor-

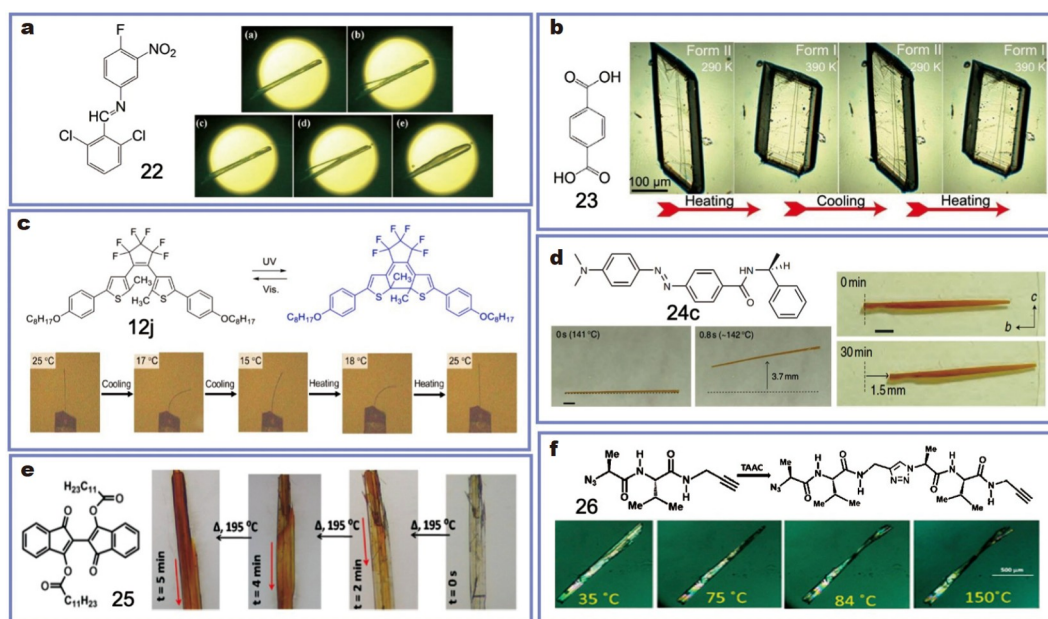


**Figure 21** (a) Top, [2+2] photocycloaddition of 16a. Bottom left, photoinduced rolling up of a crystal with controlled irradiation. Bottom right, illustrations of the proposed mechanism of bending and related crystal structures. Reprinted with permission from Ref. [35], Copyright 2013, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) Top left, structural representations of the phototriggered lattice contraction of MOF 18 and the photocycloaddition of the ligand (16b). Top right, images of photomechanical motions of crystal 18 with different sizes after UV light irradiation. Bottom, photomechanical bending of 18-PVA after 365 nm light irradiation and illustration of the experimental setup. Reprinted with permission from Ref. [55], Copyright 2019, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.





**Figure 22** (a) Photoinduced bending of a compound 19 microribbon. Top, images in a bright field; bottom, fluorescence images after irradiation using a laser (488 nm) in a dark field. Reprinted with permission from Ref. [125], Copyright 2016, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) Top, photopolymerization of orange monomer crystal (20) toward yellow polymer crystal after sunlight irradiation. Reverse depolymerization after heating (at 195°C). Photomechanical bending of crystal 20 by illumination (bottom left) and thermomechanical reversal using heat (bottom right). Reprinted with permission from Ref. [51], Copyright 2018, American Chemical Society. (c) Left, photochromism of compound 21 in the solid state. Right, photomechanical bending of compound 21 by UV irradiation [126].



**Figure 23** (a) Molecular structure of DFNA and its splitting across the phase transition. Reprinted with permission from Ref. [47], Copyright 2015, American Chemical Society. (b) Molecular structure of terephthalic acid and its form II crystal consecutively taken twice through the phase transition to form I. Reprinted with permission from Ref. [48], Copyright 2016, American Chemical Society. (c) Molecular structure of diarylethene and the bending behavior of their photoirradiated crystal by changing temperature. Reprinted with permission from Ref. [49], Copyright 2017, American Chemical Society. (d) Molecular structure of chiral azobenzene *trans*-(*S*)-1 and the inchworm that walks through repeated heating and cooling cycles of its long plate-like crystal (right), and rolling of a long thin plate-like crystal with a width gradient on heating (below). (e) Molecular structure of BIT-dodeca<sub>2</sub> and the images of a polymer-BIT-dodeca<sub>2</sub> crystal decomposing with time to a monomer at 195°C. Reprinted with permission from Ref. [51], Copyright 2018, American Chemical Society. (f) The SCSC oligomerization of dipeptide LL to a triazole-linked oligopeptide and microscopic images of crystals when heated from 35 to 150°C. Reprinted with permission from Ref. [52], Copyright 2018, American Chemical Society.

obenzylidene-4-fluoro-3-nitroaniline (DFNA), which exhibited a thermosalient effect (Fig. 23a). Crystals of the low-temperature ( $\beta$ ) form of DFNA were easily bent, while the high-temperature ( $\alpha$ ) form was stiff. According to the authors, this thermosalient effect originated from an anisotropic change within the three-

unit cell parameters during the phase transition, i.e., the *b*-axis parameter increased from 21.98 to 22.30 Å. Moreover, introducing two mechanical motions to the same single crystal afforded futuristic applications in devices that respond to two different external stimuli [47].

Karothu *et al.* [48] reported that the crystals of terephthalic acid exhibited extraordinarily compliant and reversible shape variations between two forms with different crystal habits (Fig. 23b). They suggested that a sudden release in the strain that was generated in the crystal of form I caused this mechanosensitive effect. This study provided additional evidence that the thermo/photo/mechanosensitive effects are macroscopic manifestations of martensitic transition in molecular crystals [48].

Kitagawa *et al.* [49] reported that a crystal comprising diarylethene (Fig. 23c), which had an octyl group at both sides, underwent unique mechanical motion caused by the combination of a photochromic reaction and reversible SCSC phase transition. This behavior could be attributed to the photoisomerization of diarylethene molecules from an open-ring isomer to a closed-ring isomer, as well as the reversible SCSC phase transition. The study provides a strategy for designing new materials that exhibit a mechanical response to the photoreaction conversion ratio [49]. Taniguchi *et al.* [50] reported the walking and rolling behaviors of chiral azobenzene crystals, which were driven by a reversible SCSC phase transition (Fig. 23d). The authors suggested that the possible mechanisms of the inchworm-like walk were the relaxation of the strain generated by the sudden finishing bending induced by a thermal phase transition, while the fast-rolling locomotion could be attributed to the loss of balance induced by the thermal phase transition tilt.

Samanta *et al.* [51] reported a novel diiodine compound, 1,1'-dioxo-1*H*-2,2'-biindene-3,3'-diyl didodecanoate (BIT-dodeca<sub>2</sub>), which exhibited photopolymerization in visible light in a monomer crystal SCSC process and thermal-induced reversible depolymerization (Fig. 23e). Although the precise mechanisms of such behaviors were not provided, the study demonstrated the possibility of utilizing highly ordered single crystalline polymeric materials for mechanical actuation with certain unique applications.

Rai *et al.* [52] reported the crystal of modified dipeptide LL (N<sub>3</sub>-L-Ala-L-Val-NHCH<sub>2</sub>C≡CH) that underwent spontaneous twisting to generate a right-handed twisted crystal at 25 and 0°C. This behavior could be attributed to a spontaneous topochemical azide-alkyne cycloaddition reaction at room temperature or lower (Fig. 23f). The authors suggested that this report could provide a tool to initiate mechanoresponse and chirality and design SMs. Liu *et al.* [53] reported that an organic crystal exhibited elasticity at an ultralow temperature (77 K), while at a higher temperature (>150°C), the organic crystal exhibited shapeability. The elasticity of this organic crystal at ultralow temperatures could be attributed to the strong  $\pi$ - $\pi$  interactions, hydrogen-bond network, and crosswise stacked molecular chain, while the loss of  $\pi$ -stacking defects in the crystals caused by the thermal phase transition could decrease the elasticity [53]. This contribution provided a strategy to achieve elasticity at an ultralow temperature based on organic molecules.

#### Other flexible smart organic crystals

In addition to the common single-component smart crystals, there is another kind of stimulus-responsive crystals, i.e., cocrystals, in which the stimulus-responsive behaviors depend on the variations in their crystal phases. Cocrystallization, an efficient but facile strategy to generate multifunctional high-performance organic materials, is a process to apply at least two molecules to form a cocrystal by tuning intermolecular inter-

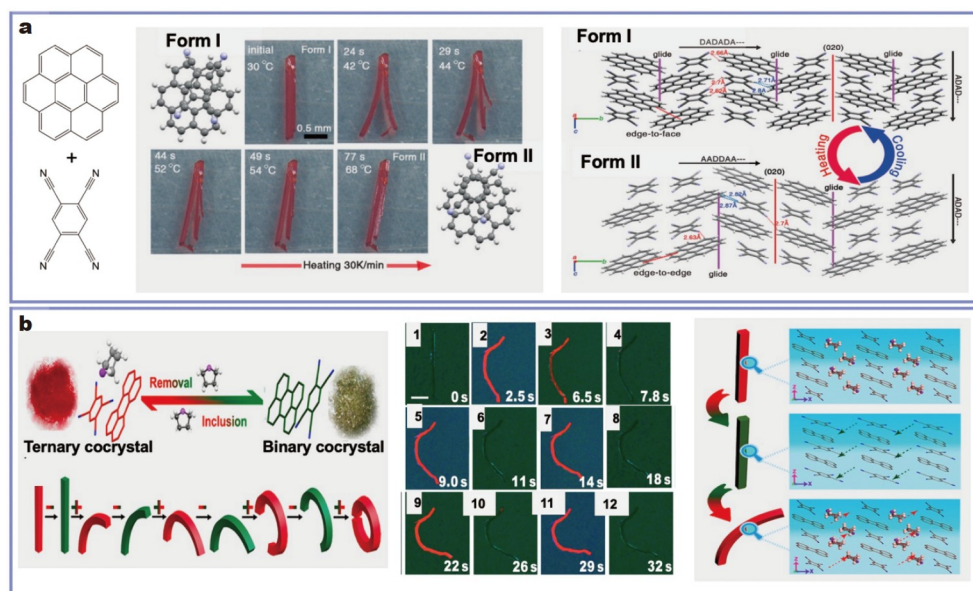
actions [127–129]. To generate suitable intermolecular interactions to successfully combine two components, such as  $\pi$ - $\pi$  stacking, hydrogen bonding, halogen bonding, and electrostatic interactions, it is crucial to choose one molecule as the donor and another as the acceptor. Recently, crystal engineering has attracted increasing attention because of its ability to easily modulate the solid-state performance of crystalline materials and introduce unpredicted and versatile properties. It has been widely studied in the field of optoelectronics and has gradually entered the field of SMs.

The photomechanical cocrystals containing photoresponsive molecules have previously been detailed [38,42,44,54]. Liu *et al.* [17] reported a thermomechanically responsive cocrystal comprising 1,2,4,5-tetracyanobenzene (TCNB) and coronene. The molecular-level motion of the coronene-based rotator was amplified to macroscopic motions by coassembling coronene with TCNB, generating a charge-transfer complex. The cocrystal exhibited excellent self-healing behaviors and thermomechanical bending as a result of a thermally induced reversible SCSC phase transition (Fig. 24a). The differential scanning calorimetry (DSC) experiment and crystal habit data further demonstrated the dynamic characteristics of the phase transitions. The molecular stacking mode of forms I and II can elucidate the structure-property relationship, i.e., the relationships between the crystal packing and macroscopic variations in the cocrystal.

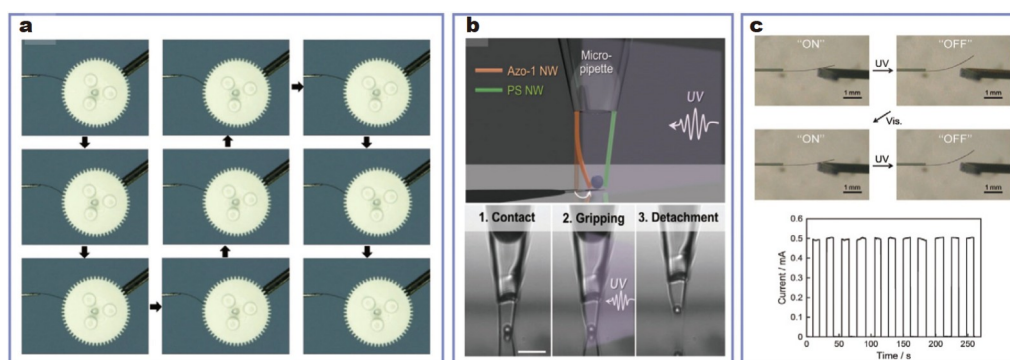
Similar molecular stacking modes and the rotatable character of TCNB and coronene molecules are conducive for the self-healing and thermomechanical bending of the cocrystal. Sun *et al.* [18] first reported another smart charge-transfer cocrystal with solvatomechanical bending behavior using tetrahydrofuran (THF) as the solvent. A ternary (perylene-TCNB)-2THF cocrystal was prepared, which can be transformed into a binary perylene-TCNB reversibly by successively incorporating or removing THF molecules. Macroscopic mechanical bending was achieved when stimulated using the THF vapor (Fig. 24b), which was caused by structural variations at a molecular scale. Although cocrystallization has been widely reported, the research on smart cocrystals is still in its infancy, and effort should be devoted to this area.

#### EMERGING APPLICATION OF FLEXIBLE SMART ORGANIC CRYSTALS

The smart actuators based on mechanically responsive crystals have attracted great interest from scientific and technological viewpoints and demonstrate great potential in various fields of actuators, photoswitches, artificial muscles, artificial robots, flexible devices, and aerospace devices [42]. For example, Kobatake *et al.* [33] observed that the phototriggered bending of the rod-like crystal of diarylethene chromophores can move a gold microparticle 90 times heavier than that of the crystal, and the crystal will straighten again upon visible light irradiation (Fig. 12b). Afterward, they fabricated a plate-like two-component cocrystal (13i-OFN) based on a diarylethene (compound 13i) and OFN [42]. When irradiated with UV light, the bending motion of the cantilever made of 13i-OFN crystal could lift a metal ball 200–600 times heavier than that of the cocrystal (Fig. 12c). The generated stress caused by the UV irradiation was estimated to be as high as 44 MPa, which was approximately 100 times higher than that of muscle (~0.3 MPa), and was comparable to a piezoelectric crystal (~50 MPa). Another instance of a molecular crystal used as an actuator was reported by Terao *et*



**Figure 24** (a) Left, molecular structures of the coronene-TCNB cocrystal. Middle, thermoinduced bending and self-healing behaviors of the cocrystal. Right, crystal packing in Forms I and II viewed from the  $a$ -axis. Reprinted with permission from Ref. [17], Copyright 2017, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) Left, reversible variations between the ternary (perylene-TCNB)-2THF and binary perylene-TCNB and the schematic diagram of the mechanical bending of the rod-like cocrystal (“+” and “-” indicate the inclusion and removal of THF, respectively). Middle, shape and color variations of a rod-like crystal when exposed to THF vapor (2, 5, 7, 9, and 11) and air (1, 3, 4, 6, 8, 10, and 12), respectively. Right, schematic diagrams of mechanical bending mechanisms on a molecular scale. Reprinted with permission from Ref. [18], Copyright 2018, American Chemical Society.



**Figure 25** (a) Gearwheel rotation operated using a light-induced cocrystal actuator fixed on the tip of a metal needle. The gear with a diameter of 3.2 mm can be rotated by the cocrystal upon alternate irradiation of visible and UV light. Reprinted with permission from Ref. [38], Copyright 2012, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) An azobenzene nanowire and PS nanowire arm was individually integrated at the tip of the microcapillary tube, and the as-fabricated tweezer successfully gripped a PS microparticle when irradiated with UV light: 1 (contact) → 2 (gripping) → 3 (detachment) [98]. (c) Photoreversible current switching caused by alternating irradiation by visible light and UV. The voltage was 1.0 V, and the external resistance was 2 k $\Omega$ . Reprinted with permission from Ref. [37], Copyright 1996, Royal Society of Chemistry.

*al.* [38]. Two diarylethenes, 12f and 12j (Fig. 12d), were cocrystallized, thereby generating a cocrystal that can bend under light irradiation over 1000 times without any damage. The rod-like cocrystal can trigger gearwheel rotation (Fig. 25a). When irradiated with UV light, the cocrystal bent and hit the gear, leading to a rotation of the gear. When irradiated with visible light, the cocrystal returned to its straight shape. Thereafter, the irradiation with UV light made the cocrystal bend again, which resulted in the rotation of the gearwheel. Moreover, when irradiated with UV light, the rod-like cocrystal acting as a cantilever arm can lift a metal as high as 0.10 mm, which is 908 times heavier than the cocrystal. The maximum stress (~56 MPa) was 180 times larger than that of muscle (~0.3 MPa), which is comparable to that of the piezoelectric crystal of lead

zirconate titanate (~50 MPa).

In addition, a nanowire comprising an azobenzene derivative was used to grip the micropipette (Fig. 25b) [98]. To construct the micropipette, the azobenzene nanowire was fixed to a polystyrene (PS) nanowire. When irradiated with UV light, the azobenzene nanowire bent toward the UV light source, while the PS nanowire underwent no photomechanical responses, leading to the grabbing of a small particle remotely. Kitagawa *et al.* [37] reported a gold-coated crystal of 1,2-bis-(5-methyl-2-phenyl-4-thiazolyl)perfluoro-cyclopentene, which demonstrated photo-triggered current ON/OFF switching behaviors (Fig. 25c). When irradiated with UV light from the upper position, the crystal bent toward the light source, resulting in a cutting off of the flowing current, i.e., the switch was in an OFF state. After

irradiation with visible light, the crystal contacted the electric wire, and the current flow and switch were in an ON state. This ON/OFF cycle can be repeated over ten times induced by light irradiation. These contributions provide a new way to develop photomechanical actuators and potential applications of photomechanical crystals.

## SUMMARY AND OUTLOOK

The dense and regularly arranged structures within organic crystal-based FSMs provide platforms for fast energy transfer with low energy dissipation. Therefore, these FSMs are promising candidates for multifunctional SMs required in actuators, sensors, flexible electronics, artificial muscles, and microrobots. In this review, we present a brief survey of recent notable examples of organic crystal-based FSMs, including derivatives of azobenzene, diarylethene, anthracene, and olefin, which can bend, roll, curl, twist, or respond otherwise to external stimuli, such as light or heat. Single-component crystals and multi-component cocrystals are summarized. In addition, the typical responsive mechanism and potential applications of stimulus-responsive flexible organic crystals are discussed. Although limited in progress over the polymer material, there is an increasing number of flexible smart organic crystals with remarkable mechanical responses. Importantly, the realization of crystals as flexible SMs has fueled related research fields, which are expected to usher in exciting developments in solid-state organic chemistry and physics. Although rapid development has been realized for flexible smart organic crystals, there are critical challenges for existing and potential opportunities. First, highly elastic reversible deformation is far less easy for crystals, owing to their stiffness and brittleness. This hinders the complete characterization of the crystalline materials after a smart response because of great structural variations and deterioration in the crystal quality. Second, although several possible mechanisms have been provided, the elucidation and substantial understanding of the exact mechanism of the bending behaviors of a single crystal remains a major challenge. Third, to realize the applications as an SM in the future, it is important to develop effective methods to satisfy the requirements for flexible smart crystals, such as reversibility, repeatability, rapid response rate, high sensitivity, and good fatigue resistance. Finally, the processes for transforming these mechanical motions into useful macroscopic work and rationally assembling these SMs into devices to perform significant work on a macroscopic scale are still in their infancy and require great effort. Although the aforementioned challenges exist, the outstanding performance of organic crystal responses to light or heat offers great potential for applications in photoactuators, sensors, flexible electronics, and soft robots. We believe that with the joint effort of the growing research groups that work on smart molecular crystals, organic crystal-based FSMs have an excellent and bright future.

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## 有机晶体基柔性智能材料

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**摘要** 虽然分子晶体显著的脆性特征不利于其在柔性智能材料中的应用, 但近些年越来越多的有机分子晶体基柔性智能材料(FSMs)被报道, 打破了人们对分子晶体刚性和脆性的认识, 这为分子晶体的基础研究和实际应用创造了发展契机. 在某些情况下, 晶体基智能材料相比于聚合物材料具有相当大的优势, 这使其成为某些应用的潜在候选材料, 例如快速响应制动器、开/关切换、微型机器人等. 在这篇综述中, 我们总结了有机晶体基FSMs的最新发展, 包括偶氮苯、二芳基乙烯、葱、烯炔等的衍生物. 这些有机晶体基FSMs可以发生弯曲、卷曲、扭曲、变形或以其他方式来响应外部刺激. 并讨论了此类材料的柔性智能行为的机理以及其在智能领域中的潜在应用. 我们相信这篇综述可以为新型有机晶体基FSMs的制备、发展及其先进的智能应用提供指导.