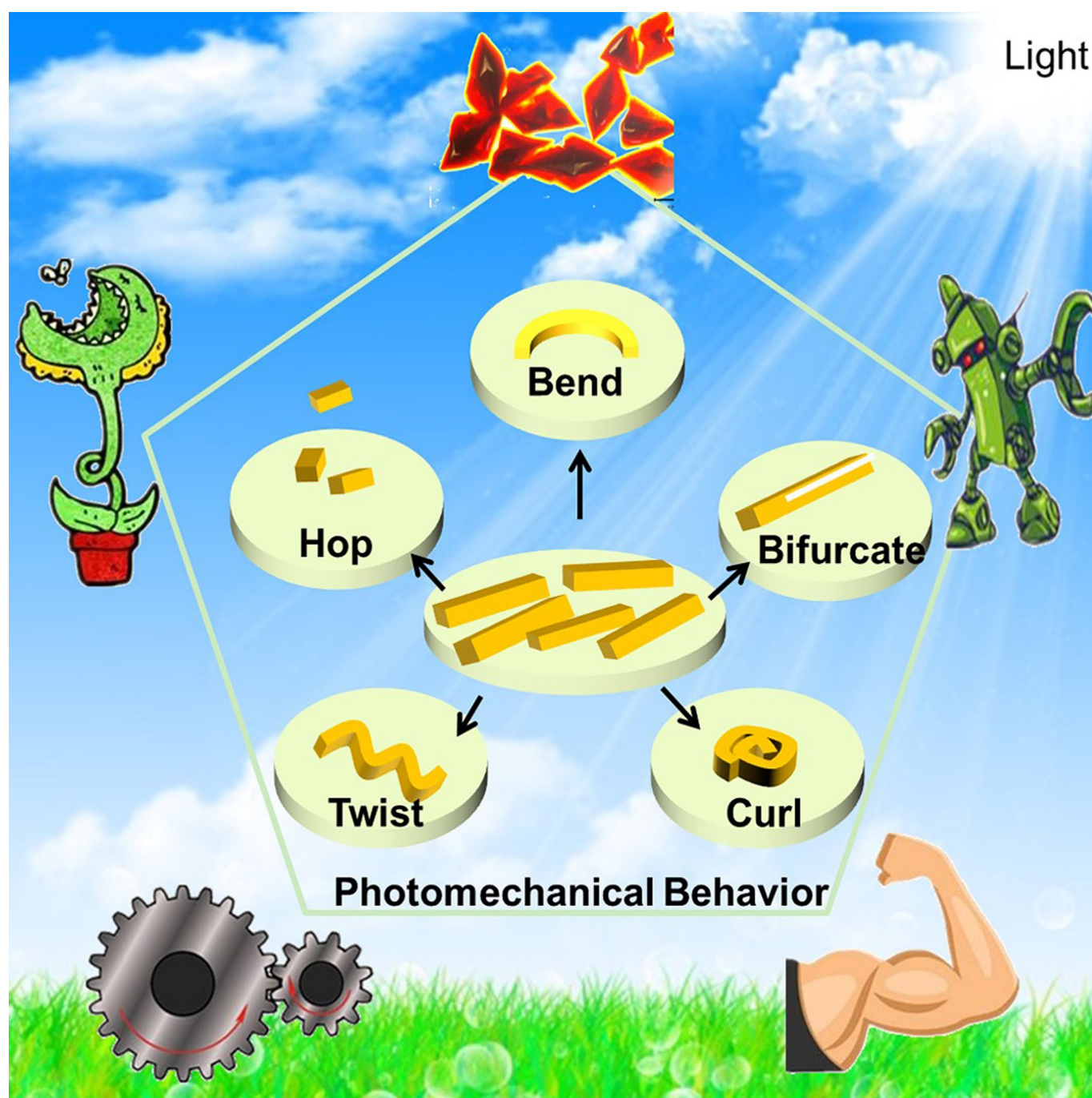**CHEMISTRY**
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Minireview

█ **Photochemistry** | *Reviews Showcase* |

Photomechanical Organic Crystals as Smart Materials for Advanced Applications

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Abstract: Photomechanical molecular crystals are receiving much attention due to their efficient conversion of light into mechanical work and advantages including faster response time; higher Young's modulus; and ordered structure, as measured by single-crystal X-ray diffraction. Recently, various photomechanical crystals with different motions (contraction, expansion, bending, fragmentation, hopping, curling, and twisting) are appearing at the forefront of smart materials research. The photomechanical motions of these single crystals during irradiation are triggered by solid-state photochemical reactions and accompanied by phase transformation. This Minireview summarizes recent developments in growing research into photoresponsive molecular crystals. The basic mechanisms of different kinds of photomechanical materials are described in detail; recent advances in photomechanical crystals for promising applications as smart materials are also highlighted.

1. Introduction

The conversion of external energy into macro-, micro-, or nanoscopic mechanical motion by stimuli-responsive materials is of great interest from both fundamental and technological standpoints. Stimuli-responsive materials can present dramatic mechanical motions under the stimuli such as light irradiation,[1] heating,[2] external force,[3] solvent,[4] electrical fields,[5] and so on.[6] Among these stimuli, light is currently attracting increasing interest due to its superior advantages, including noncontact control, easy to obtain, cost-effectiveness, and various manipulating methods.[7] Various photomechanical materials, such as polymers,[8] elastomers,[9] liquid-crystalline materials,[10, 11] and molecular crystals,[12] have been reported, to date. In particular, photomechanical crystals have attracted increasing attention because they not only have great potential for applications in light harvesting, mechanical actuators, molecular machines, optical sensors, and smart switches,[13] but also provide the opportunity to understand their performance through XRD methods by solving ordered molecular structures.[14] Compared with polymers, elastomers, and liquid-crystalline materials, molecular crystals possess many advantages, such as faster response times,[12] shorter recovery times, a higher Young's modulus,[15] and a well-defined crystal structure.[16, 17] In addition, light and mechanical energy transfer rapidly occurs in ordered molecular single crystals with less energy dissipation.

Various types of photomechanical motions have been observed in photomechanical crystals, including jumping, expanding, bending, twisting, crawling, rolling, and even walking, upon irradiation with UV or visible light. The mechanical motion of crystals is usually directly driven by the transformation of their molecular structure and molecular packing upon exposure to stimuli. Dramatic crystal shape changes always originate from strain accumulation in the crystal interior caused by crystal structural transformations. Therefore, different light-sensitive chromophores associate with different photoresponsive mechanisms, including *trans–cis* isomerization of azobenzene, photocyclization of diarylethenes, [2+2] cycloaddition of olefins, [4+4] photodimerization of anthracene, and other *cis–trans* isomerism transformations. Commonly, photomechanical molecular crystals can be classified into two types, according to the recovery conditions from photogenerated products to original phases, namely, T type (thermally reversible) and P type (thermally irreversible, but photochemically reversible).[15] Most photomechanical molecular crystals are of T type, which require heating to recover their photomechanical ability, such as azobenzene, olefins, and anthracene. Only a few families of molecular crystals can undergo photochemically reversible reactions, such as diarylethenes.

To date, photomechanical behavior has been observed in molecular crystals of organic compounds, coordination complexes, and organometallic compounds. It should be noted that most studies related to photomechanical crystals focus on organic crystals due to their modular design nature and convenient synthesis. Herein, recent progress and development in photomechanical organic crystals are summarized, and remarks on existing challenges and possible future directions in this field are given.

2. Classification of Photomechanical Organic Crystals Based on Photoreactions

2.1 Photomechanical organic crystals induced by *trans–cis* isomerization

2.1.1 The trans–cis isomerization of azobenzene

Azobenzene, a diazene (HN=NH) derivative in which both hydrogen atoms are replaced by phenyl groups, is a prominent family of photomechanical molecules based on *trans–cis* isomerization.[18] The *trans–cis* isomerization phase transition is usually driven by UV-light irradiation, which causes large-scale

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deformation of the crystal shape and size. The reverse reaction of *cis* to *trans* isomerization occurs spontaneously at room temperature in the dark due to the thermodynamic stability of the *trans* isomer relative to that of the *cis* isomer. Geometry changes to azobenzene result in crystal motion, owing to strain accumulated in the crystals. Azobenzene and its derivatives exhibit remarkable photostability and faster responses under light irradiation (Figure 1). Photoinduced bending of the azobenzene crystal under UV-light irradiation was first reported in 2009.[19] The development of azobenzene photomechanical crystals has boomed in the past few years. Through modulating the substituent sites of azobenzene and interactions between molecules, various mechanical motions are exhibited.
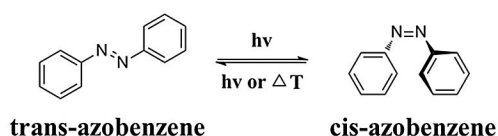

Figure 1. Isomerization of azobenzene.

Norikane and co-workers reported an azobenzene derivative, the 3,3-dimethylazobenzene (DMAB) crystal, which exhibited directional and continuous motion on a glass surface during simultaneous irradiation at two different wavelengths ($\lambda = 365$ and 465 nm; Figure 2).[20] Moreover, crystals can climb on vertical surfaces at room temperature. This *trans–cis* conversion induced liquefaction of the crystals; in other words, caused the crystalline phase to transform into a liquid. This finding makes
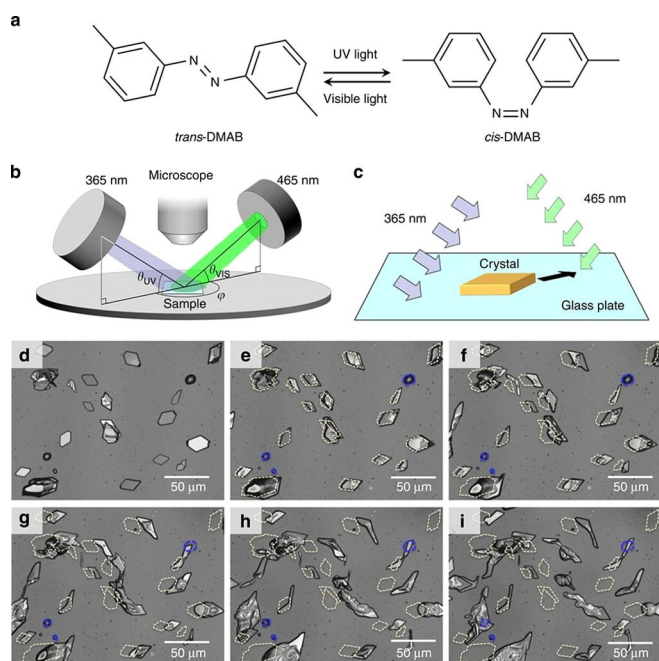
it possible for applications in remote-controlled microsized valves on solid substrates.

The photoinduced bending behavior of azobenzene derivate crystals has been widely studied. Under continuous UV excitation, crystals bend continuously with a range of curvatures; this provides a basis to study effects of deformation. Upon kinematic analysis, the authors disentangled the relationship between intrinsic factors (the size and initial shape of the crystal) and external factors (excitation power, direction, and time) in detail.[21] The *trans–cis* isomerization of azobenzene crystals was usually stimulated by UV irradiation, which greatly limited their practical applications due to the inconvenience and potential dangers of UV light. Thus, the preparation of azobenzene crystals photoresponsive to visible light is of great significance. Barrett et al. reported a series of azobenzene compounds that responded to visible-light irradiation through modifying a strong electron-withdrawing "pull" group and a strong "push" donor in molecules of azobenzene.[22] This class

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Figure 2. a) Molecular structure of DMAB; b) schematic illustration of the experimental setup and motion; c) microscopy images of the motion of DMAB crystals after irradiation for 0 (d), 3 (e), 6 (f), 10 (g), 15 (h), and 20 min (i). (Copyright, 2014, Springer Nature.)

of photomechanical crystals not only responded to visible light, but also demonstrated spontaneous and rapid reverse motion.

In addition to exploring new compounds with chromophore groups, the cocrystal strategy, under the guidance of crystal engineering, has proven to be an efficient approach to prepare an increasing number of photomechanical crystals. Crystal engineering is an efficient method to allow modification of the solid-state properties through the formation of cocrystals, including multicomponent crystals. The formation of azobenzene cocrystals was explored through forming weak interactions between different components, including π–π stacking, electrostatic interactions, and hydrogen-bonding interactions. Friščić and Barrett et al. demonstrated the first example of generating new photomechanical azobenzene cocrystals.[23] After combining azobenzene derivatives and bis(4-pyridyl)ethylene (bpe) together in a crystal, the structure of (*cis*-**2**)(*cis*-bpe) was determined through single-crystal X-ray diffraction (SCXRD; Figure 3). Under light irradiation, the cocrystal of (*cis*-**2**)(*cis*-bpe) transformed into the (*trans*-**2**)(*cis*-bpe) phase, which induced the bending behavior. Unfortunately, the diffraction intensity of the (*trans*-**2**)(*cis*-bpe) cocrystal decreased after light irradiation. These results revealed that the cocrystal synthetic method opened up a new opportunity to design more photomechanical materials. Obtaining the crystal structure of the *cis* isomer of azobenzene is also helpful to demonstrate the *trans–cis* phase transformation.[24]
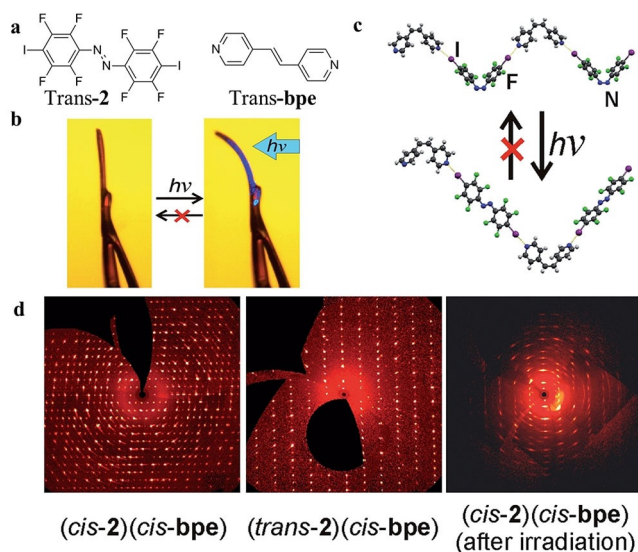
Figure 3. a) Structures of the *trans* isomers of **2** and bpe. b) Photomechanical bending of the (*cis*-**2**)(*cis*-bpe) cocrystal after irradiation. c) Single-crystal structural changes during the transformation of (*cis*-**2**)(*cis*-bpe) into (*trans*-**2**)(*cis*-bpe). d) Composite diffraction images of the *h*0*l* plane for different processes. (Copyright, 2014, The Royal Society of Chemistry.)

2.1.2 The trans–cis isomerization of vinyl compounds

Apart from *trans–cis* isomerization of azobenzene, *trans–cis* isomerization of vinyl groups also exhibited photomechanical effects. The group of Lu reported an example of a naphthylvinyl-

benzoxazole (NBO) crystal, in which molecules packed in a parallel fashion to form a herringbone-like shape.[25] The distance between C=C bonds was 6.107 Å, which was too great to allow a normal [2+2] cycloaddition reaction. However, the large distance provided enough space for *trans–cis* photoisomerization. Notably, the needlelike crystals can bend backwards away from the UV light source. If the irradiation direction was reversed, the crystals bent back to the original positions. This process could be repeated many times without fatigue (Figure 4).

Bardeen and Al-Kays and co-workers reported a dimethyl-2-(3-anthracen-9-yl)allylidenemalonate (DMAAM) divinylanthracene derivative.[26] The DMAAM crystal could undergo slight bending upon exposure to visible light ($\lambda = 450$–500 nm) for 1 min in water due to the *E–Z* isomerization of the vinyl group (Figure 5). However, if crystals were dispersed in CTAB, the crystals almost lost their crystallinity and dissolved in CTAB after irradiation. The authors found that the crystals in surfactants (CTAB) could help to accelerate the photochemical reaction rate by at least a factor of 10 compared with that in water. CTAB provided a surface environment that facilitated molecular motion on the surface. The photochemical reaction rates can be accelerated and expose new regions of the crystals to further catalyze the reaction.

2.2 Photomechanical organic crystals induced by photocyclization of diarylethenes

Although various molecules with photomechanical properties have been reported, to date, only limited numbers of them can undergo photoreversible processes (most of them with thermoreversible processes) after irradiation with light of different wavelengths. A "diarylethene" family (P-type), derivatives of stilbene, appears to a potential and indispensable candidate for use in optical memory and molecular machines with good thermal stability. After irradiation and measurement by SCXRD, the crystalline phase revealed that the diarylethene molecule could undergo a photoreaction process from ring-opening isomers to ring-closing isomers.[27] The geometry of the diarylethene derivatives remained almost the same after irradiation, which permitted the occurrence of photochromism in a crystalline phase. After irradiation with UV light, the ring in the diarylethene isomers closes and returns to the ring-opened state upon exposure to visible light. Because molecules pack densely in a lattice, deformation of the crystal on the macroscopic scale is anticipated following the photochromic process of diarylethene molecules.

In 2007, Irie et al. reported a molecular crystal composed of a diarylethene compound (Figure 6a).[28] This molecular crystal exhibited rapid and reversible macroscopic changes in shape and size induced by UV and visible light. After irradiation with UV light ($\lambda = 365$ nm), the single crystal of **1** changed from a colorless square microcrystal to a blue lozenge-shaped one. The angle of crystal **1** decreased by as much as 5–6° (Figure 6b). The deformed crystals can easily return to their original status upon exposure to visible light ($\lambda > 500$ nm).
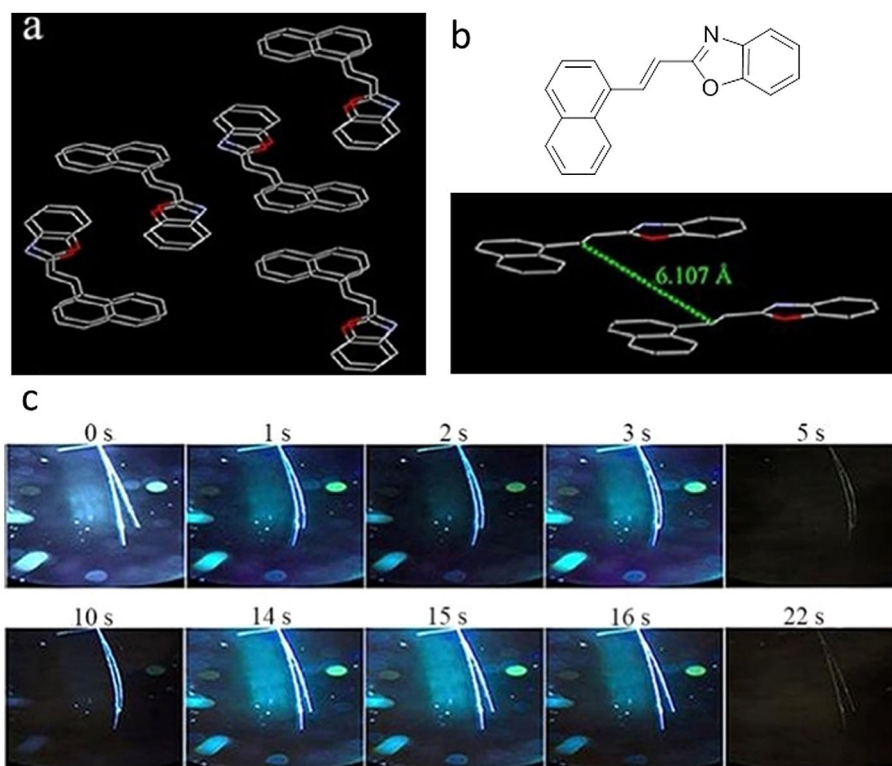
Figure 4. a) Crystal and b) chemical structure of NBO and the packing distance. c) Photomechanical bending of NBO after increasing irradiation times, from right (top line) to left (bottom line). (Copyright, 2013, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)
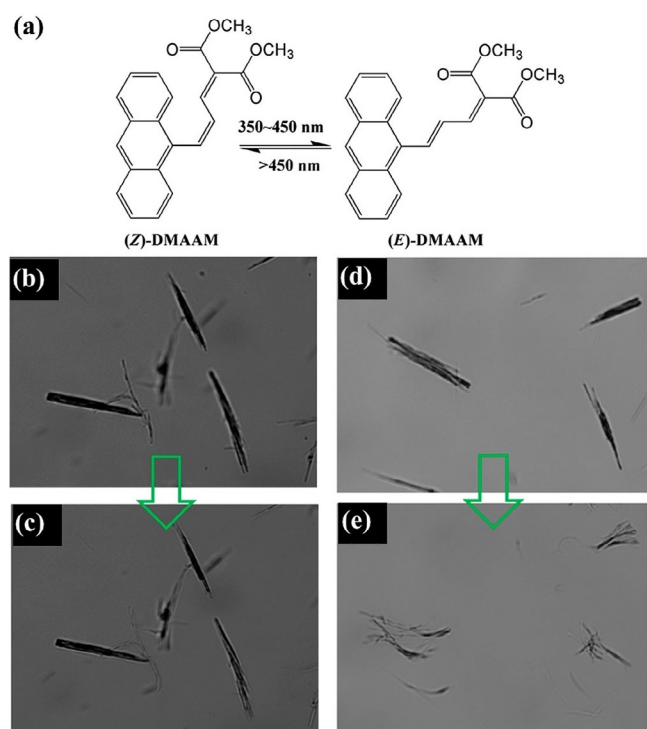

Figure 5. a) Photoisomerization of the DMAAM molecule. Optical microscopy images of (*E*)-DMAAM nanowires (NWs) in pure water before (b) and after (c) irradiation for 1 min. Photomechanical bending in 2 mм cetyltrimethylammonium bromide (CTAB) before (d) and after (e) irradiation for 5 s. (Copyright, 2017, American Chemical Society.)

Another cocrystal containing two-component diarylethene can endure bending motions of more than 1000 cycles without any cracking or flaws emerging; thus revealing outstanding fatigue resistance. The response speed of the photochromic crystal can be enhanced to 5 µs, which is superior to that of existing polymer muscles. Photoresponsive crystals of diarylethene are promising functional materials in manufacturing light-driven actuators after they can overcome the imperfections of structural fatigue.[29]

Recently, Kobatake and Bardeen et al. found unique behavior of a reversible photomechanical twisting motion upon irradiation with a light source.[30] Apart from the photomechanical properties being influenced by light wavelength, the irradiation direction also induced different photomechanical behavior. If the ribbonlike crystal was irradiated from the top of the crystal (incident light angle $\theta = 0°$), the crystal twisted into a helicoid shape (Figure 7a). As the irradiation angle increased, the crystal gradually transformed into a cylindrical helix shape (Figure 7b–g). If the incident light angle was about 90° (Figure 7h), the crystal exhibited bending behavior rather than twisting. These results indicated that the stress tensor on the crystal surface could be tuned by the direction of light irradiation.

Changes in the initial shape of the crystals will lead to different photomechanical behavior. Uchida and Morimoto et al. reported a hollow crystal of diarylethene (Figure 8a, b, and e) that displayed a remarkable photosalient phenomenon.[31] Interestingly, it was observed that the flying debris released from
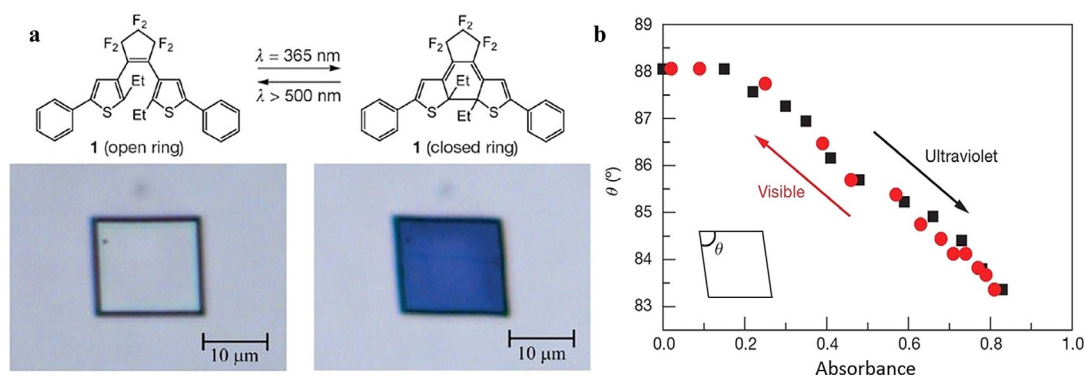
Figure 6. a) Chemical structure and deformation of a crystal of 1,2-bis(2-ethyl-5-phenyl-3-thienyl)perfluorocyclopentene (**1**). b) Relationship between the angle of the single crystal and absorbance of the crystal. (Copyright, 2007, Springer Nature.)
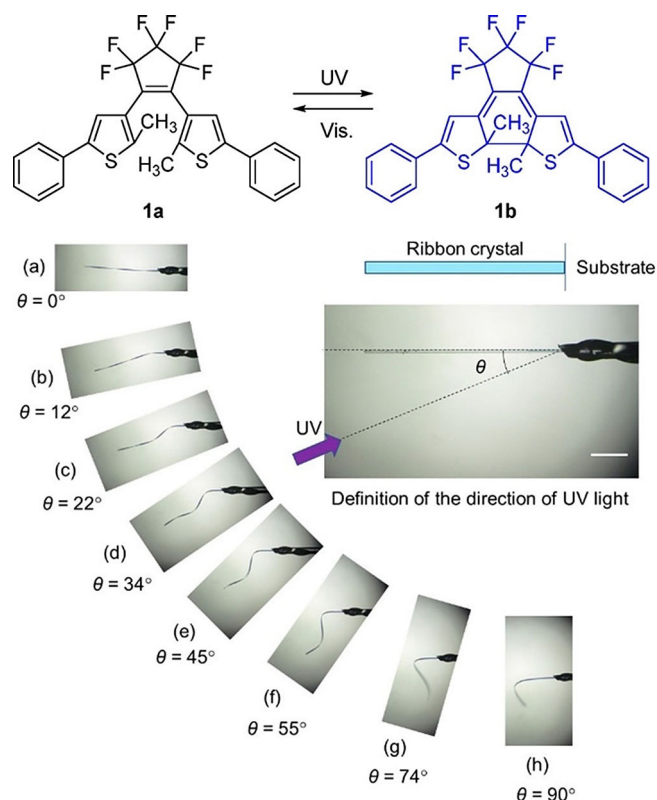
Figure 7. a–h) Different twisting motions depending on the angle of the incident light. (Copyright, 2018, American Chemical Society.)

the crystal exceeded several meters per second upon UV irradiation. In addition, the hollow crystal first elongated along the photoirradiated surface (Figure 8 f) upon light irradiation and cracked perpendicular to the *a* axis on the surface as the irradiation time extended (Figure 8 c and d). The four corners of the hollow crystals were fixed in the hollow structure, which resulted in breaking of the hollow structure instead of bending.

2.3 Photomechanical organic crystals induced by photocycloaddition reactions

Solid-state cycloaddition reactions, which include [2+2] and [4+4] reactions, have attracted increasing interest since the groups of Schmidt and MacGillivray established rules of the topo-photochemical reaction for cycloaddition reactions.[32–34] According to their rules, the challenge of obtaining a photomechanical crystal not only lies in suitable stacking arrangements of light-sensitive chromophores, but also in a very strict requirement for packing distances of chromophores. Photomechanical crystals demonstrated various photomechanical motions, including bending, jumping, curling, and twisting, if the photocycloaddition reaction occurred upon light irradiation. Notably, cycloaddition reactions are reversible and inclined to shift towards depolymerization under heating, which provides a pathway from photomechanical motion to photoactuators.

2.3.1 Photocycloaddition of olefins

It is an advantage of photocycloaddition reactions that the reaction process can be tracked through SCXRD due to the reaction nature of photocycloaddition. The group of Naumov found that multiple mechanical responses could be elicited in the same material, and they reported on how to tune the photochemical response through surface modification, deformation, and disintegration of crystals.[35] Under UV-light irradiation, 3-benzylidenedihydrofuran-2(3H)-one (Z-BDHF) first transformed into E-BDHF through an isomerization reaction (Figure 9a). Continuous irradiation would induce the [2+2] photocycloaddition reactions, as evidenced by single-crystal structural changes to the E-BDHF structure (Figure 9b). The crystals exhibited various mechanical response motions due to different effects. For example, 1) the crystals cracked, while remaining still (Figure 9c); 2) they moved through displacement by hopping off the stage (Figure 9d); 3) some crystals split into pieces and flew off in opposite directions (Figure 9e); and 4) some crystals would bend first and move or split into pieces subsequently (Figure 9f). Cracks appeared in response to the
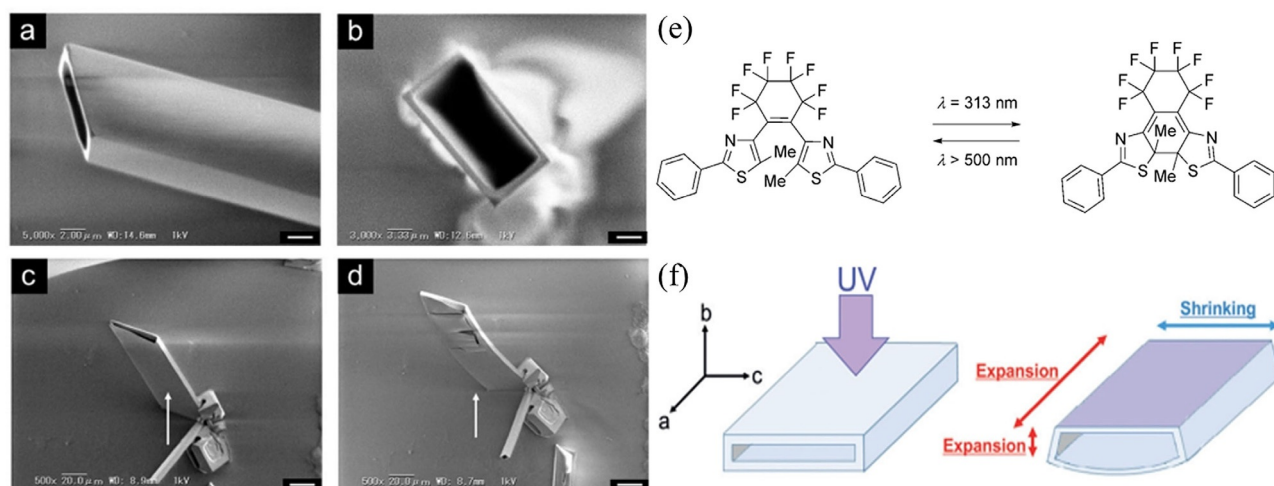
Figure 8. SEM images of a hollow crystal of diarylethene: a) side view; b) top view; c) standing hollow crystal, and d) upon exposure to $\lambda = 313$ nm light for 1 min. e) Molecular structures of ring-opening and ring-closing isomers. f) Schematic illustration of the hollow crystal upon UV irradiation. (Copyright, 2017, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)
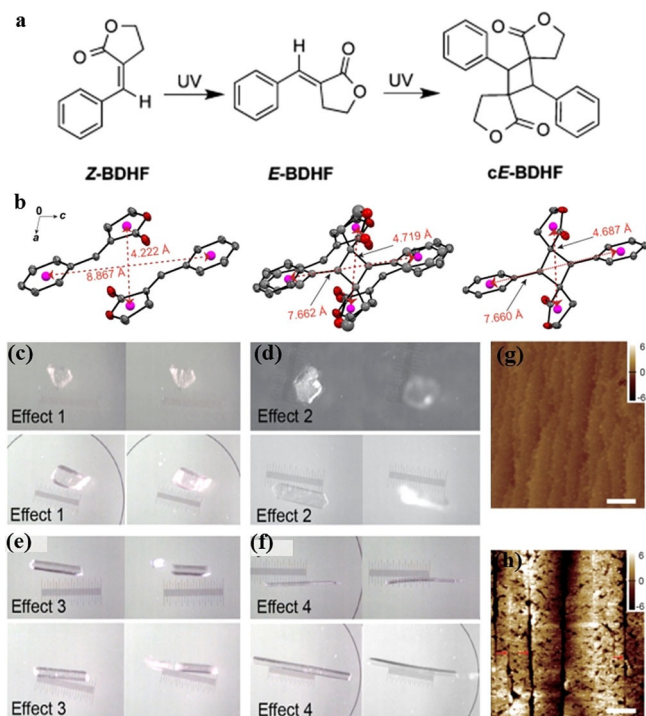
Figure 9. a) Scheme of the reaction process. b) Changes to the crystal structure of *E*-BDHF. c–f) Different photomechanical motions under UV-light irradiation. AFM images of the surface of the crystals before (g) and after (h) light irradiation. (Copyright, 2015, American Chemical Society.)

tendency of the crystal to relax differential anisotropy between the surface and inner layers (Figure 9 g and h).

The group of Lu discovered a photosalient effect of the olefin crystal driven by the photocycloaddition reaction.[36] Upon irradiation with UV light from below, the thinner crystal bent upward clearly, whereas the thicker one bent upward slightly. The two bending needlelike crystals could straighten after irradiation from opposite directions (Figure 10 a). If the

crystals were soaked in methanol organogel for irradiation, the nanofibers curled drastically, even into a circle. Meanwhile, a small slice rolled in the organogel under UV light (Figure 10 b). After UV-light irradiation, the C···C length changed from 3.865 Å to 1.580 and 1.574 Å in the single-crystal structure of photodimers (Figure 10 c–e). This structural change followed an accumulation of strain in crystals that would be released through mechanical motion.

2.3.2 Photocycloaddition of anthracenes

Apart from [2+2] photocycloaddition of olefins, double bonds at the 9,10-positions of anthracene molecules are also photo-active and can undergo [4+4] photocycloaddition reactions if anthracene molecules pack in parallel and the distance between two anthracene planes satisfies the Schmidt rules. The photoresponsive behavior of crystals through the [4+4] reaction is always different from that of [2+2] cycloaddition.

Bardeen et al. synthesized branched microcrystals of 4-fluoroanthracenecarboxylic acid (Figure 11 a) through a pH-driven precipitation method.[37] If the branched microcrystals were illuminated with light of $\lambda = 405$ nm, the individual branched crystals underwent a combination of twisting and bending. These deformations drove the rotation of branched crystals clockwise after each irradiation period (Figure 11 b). If the light was off, the bending arms relaxed and returned to the original shape within 30 s. The authors claimed that the ability of this crystal to undergo ratchetlike rotation was attributed to the chiral shape. 9-*tert*-Butylanthracenecarboxylate nanorods were synthesized in Al_2O_3 templates. The nanocrystals expanded by as much as 15% along the long axis under UV-light irradiation.[38] The same group also studied a series of 9-anthroate esters as photomechanically responsive crystalline nanorods (200 nm in diameter).[39]

Recently, we designed and synthesized a series of novel anthracene derivatives (BA*n*DA; $n = 2$–8). These crystals can har-
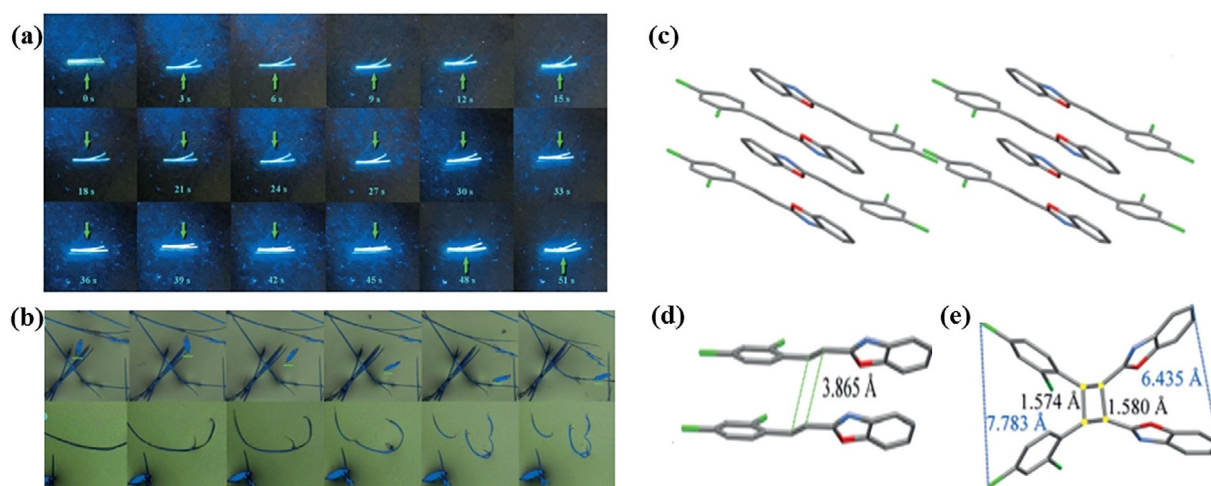
Figure 10. a) Images of needlelike crystals before and after irradiation; b) rolling and curling of the crystals in a methanol organogel; c) single-crystal structure viewed along the *b* axis; d) the distance between two adjacent parallel molecules; and e) structure of the photodimer formed. (Copyright, 2017, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)
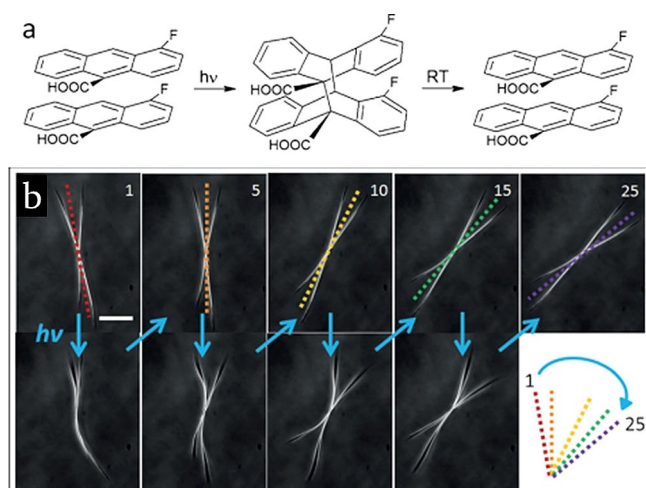

Figure 11. a) Reaction sequence and b) optical microscopy images of the clockwise rotation of X-shaped crystals. (Copyright, 2016, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

vest the energy of visible light and transform it into various motions, including bending, curling, jumping, and wriggling.[40] The crystal also exhibited high elasticity and flexibility, even under mechanical force (Figure 12). These results provided a new avenue to design and synthesize new photomechanical crystals based on anthracene derivatives.

2.4 Other types of photomechanical crystals

In addition to the abovementioned photomechanical crystals, there are also some photomechanical crystals based on relatively less studied functional groups. For example, Asahi and Koshima et al. reported platelike crystals of *S* and *R* enantiomers of photochromic *N*-3,5-di-*tert*-butylsalicylidene-1-phenylethylamine.[41] The transformation between enol-(*S*)-**1** and enol-(*R*)-**2** caused bending behavior along with a twisting motion upon UV-light irradiation (Figure 13a and b). Koshima
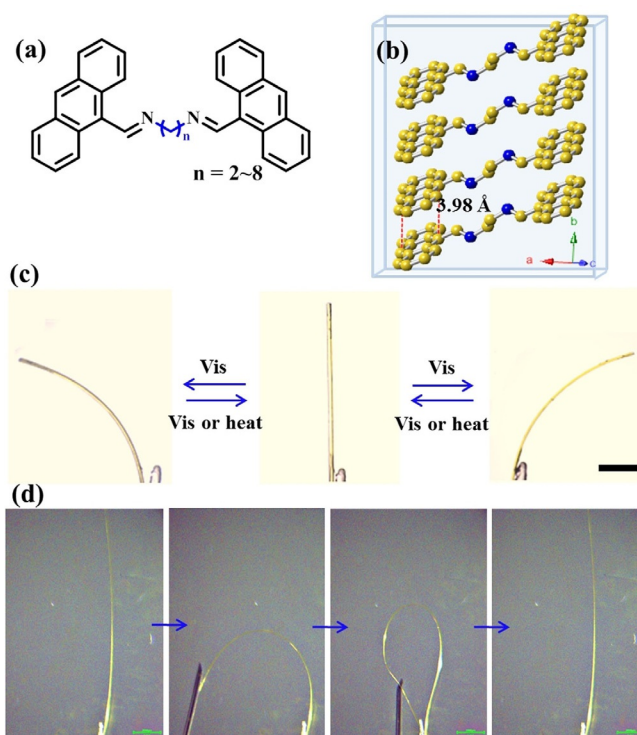
Figure 12. a) Chemical and b) crystal structures of the BA2DA molecule. c) The bending behavior of the crystal under white-light irradiation. d) Elasticity under mechanical force. (Copyright, 2018, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

and co-workers reported a platelike crystal with reversible bending behavior upon alternating irradiation with UV and visible light (Figure 13c).[42] If the microcrystal was irradiated from the diagonal underside with UV light for 1 s, the crystal curled from the upper-right corner toward the light and reached a maximum twisted curl after irradiation for 2 s. The phase transformation was always accompanied by a color change from pale yellow to red (Figure 13d).
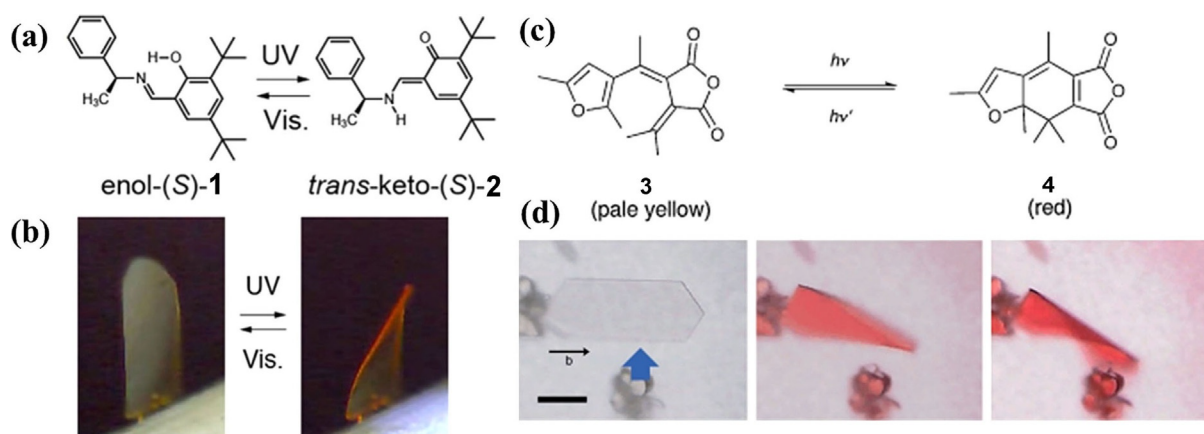
Figure 13. a) Photoinduced hydrogen-transfer reaction of salicylidenephenylethylamines enol-(*S*)-**1** and enol-(*R*)-**2**. b) Bending with a twisting motion of a wide and thin platelike crystal. (Copyright, 2016, American Chemical Society.) c) Photochromic reaction of furylfulgide **4**. d) The (101) face of a platelike micro-crystal before and after UV irradiation for 1 and 2 s. (Copyright, 2011, The Chemical Society of Japan.)

## 3. Potential Applications of Photomechanical Crystals

It is of great importance to study mechanical motion based on changes to the geometrical structure of molecular crystals induced by light stimuli from scientific and technological points of view. The crucial function to convert chemical energy into mechanical work has attracted increasing attention. Various types of molecular crystals for potential applications in actuators, artificial muscles, photoswitches, and artificial robots have been studied. For instance, Kobatake and Kitagawa reported a crystal of 1,2-bis-(5-methyl-2-phenyl-4-thiazolyl)perfluorocyclopentene covered with gold, which exhibited photoreversible current ON/OFF switching behavior (Figure 14).[43] If the gold-coated diarylethene crystal was irradiated with UV light from above, the crystal bent towards the light and the flow current was cutoff. Thereafter, the switch was in the OFF state. Once irradiated with visible light, the crystal started to have contact with the electrical wire and the current flowed, so the switch

was in the ON state. This ON and OFF process can undergo more than 10 cycles of light irradiation. These findings not only provide a new strategy to design photomechanical actuators, but also reveal a potential practical use of photomechanical crystals.

Another example of molecular crystals acting as actuators was reported by Irie et al.[29] The rodlike crystal of diarylethene bent towards the direction of the incident light. The bending crystal moved a gold macroparticle with a weight 90 times greater than that of the crystal over a distance of 30 μm; thus the crystal proved itself a promising material for possible light-driven actuator applications. The rodlike crystal can bring about gearwheel rotation. Upon irradiation with UV light, the crystal bent and hit the gear to rotate the gearwheel (Figure 15). This is actual photomechanical work by molecular crystals. The rodlike crystal was also able to lift a metal weight (2.2710 mg) 908 times heavier than that of the crystal; this can be ascribed to a high Young's modulus of the crystalline material.
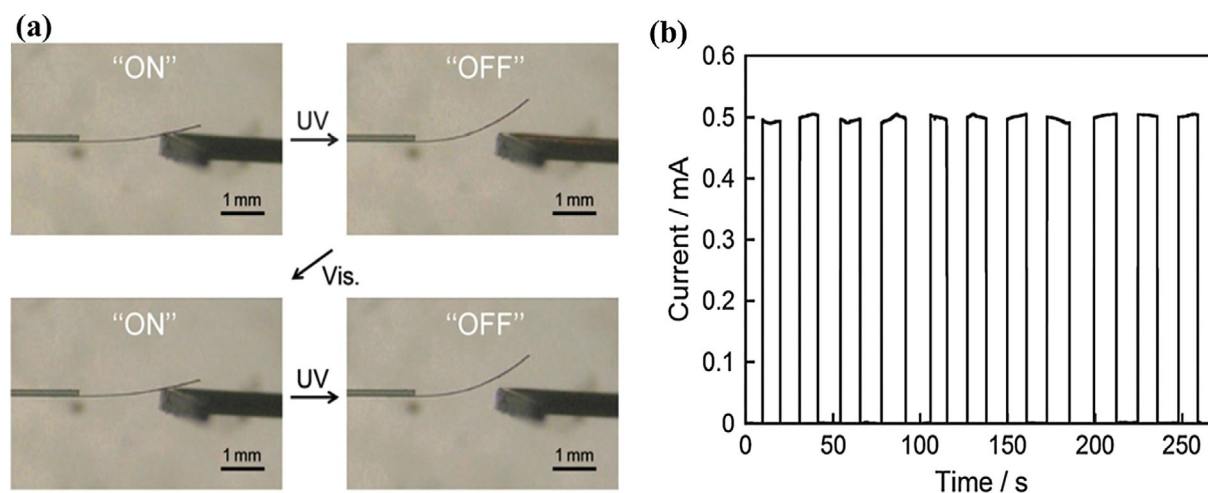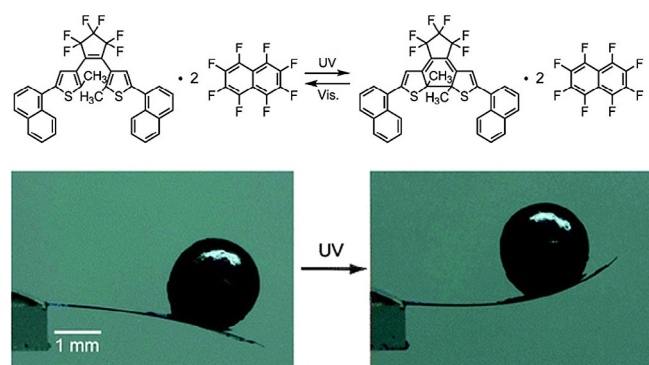

Figure 14. Images (a) and photoreversible current switching (b) upon alternating irradiation with UV and visible light of a crystal of 1,2-bis-(5-methyl-2-phenyl-4-thiazolyl)perfluorocyclopentene covered with gold. (Copyright, 2015, The Royal Society of Chemistry.)
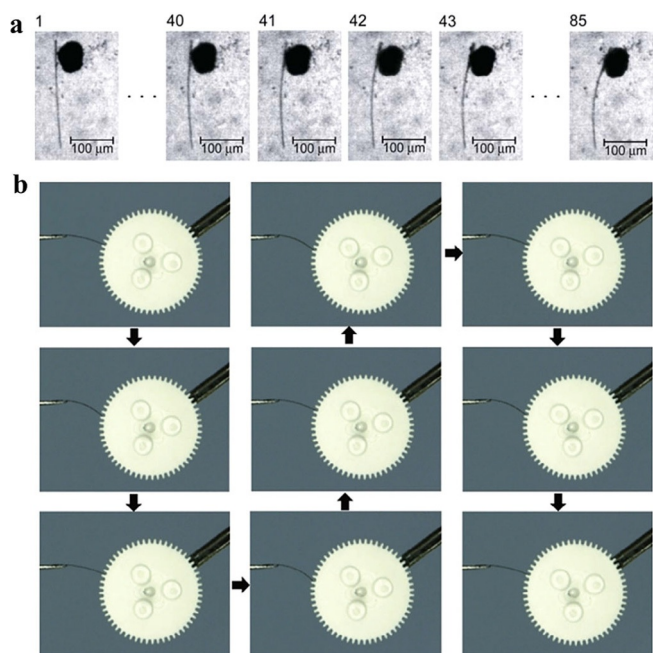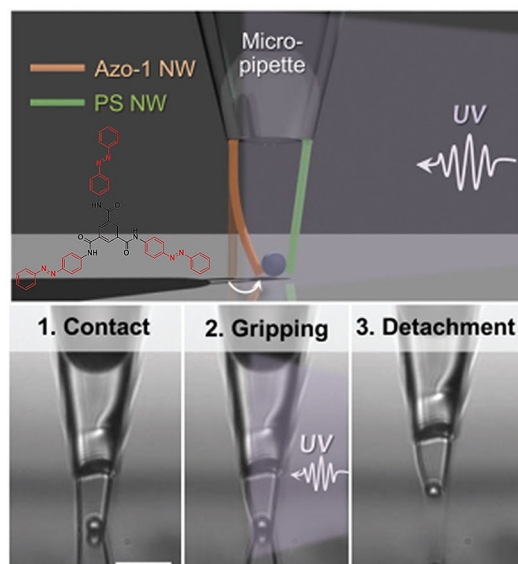
Figure 15. a) Movement of a gold macroparticle by a crystal upon irradiation with UV light. b) Gearwheel rotation operated by a light-driven molecular crystal actuator. (Copyright, 2012, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

Figure 17. Tris{4-[(*E*)-phenyldiazenyl]phenyl}benzene-1,3,5-tricarboxamide (Azo-1) and a polystyrene (PS) NW arms select, lift, and move a microparticle on a silicon substrate. (Copyright, 2015, The Royal Society of Chemistry.)

Irie and Morimoto reported a diarylethene cocrystal with perfluoronaphthalene. The crystal exhibited reversible bending motion upon alternate irradiation with UV and visible light.[44] The molecular crystal could lift a metal ball that was 200–600 times heavier than itself upon UV irradiation (Figure 16). The maximum generated stress was estimated to be 44 MPa after UV irradiation. The stress was about 100 times larger than that of muscles (0.3 MPa) and comparable to that of piezoelectric crystals (50 MPa).

A single NW with an azobenzene crystal derivative was synthesized by employing a direct writing method.[45] This NW exhibited reversible omnidirectional bending and unbending with large displacements (≤ 1.7 μm) upon irradiation with UV and visible light (Figure 17). The Azo-1 NW (yellow) was used together with a PS NW arm (Figure 17, black). After irradiation with UV light, the azobenzene NW bent towards the UV light
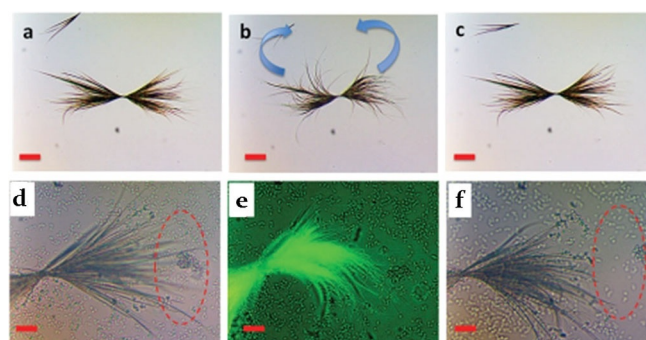
and the PS NW experienced no photomechanical response, which allowed the device to grip a micro-object remotely. The light-driven NW actuators for manipulation of micro-/nano-objects have general utility in biomedical science and engineering.

In 2017, the group of Bardeen and Al-Kaysi[46] synthesized branched crystals of 4-fluoroanthracene-9-carboxylic acid through a slow-release method with a specific combination of temperature (35 °C) and solution (phosphoric acid/sodium dodecyl sulfate (SDS)/1-dodecanol) conditions. Upon exposure to UV light, the sheaflike microcrystals tended to partially twist and bend in a collective manner toward the center (Figure 18 a–c). This photomechanical motion generated a sweeplike behavior. After UV irradiation, about 75 % of the silica microspheres were swept out of the region to stir microenvironments and returned to the original shape in seconds (Figure 18 d–f). This result provided a good demonstration of the use of photomechanical crystals for novel applications.

Figure 16. A diarylethene cocrystal lifting a heavy metal ball. (Copyright, 2010, American Chemical Society.)

Figure 18. A branched microcrystal before (a) and after (b) exposure to UV light; c) 10 s after the UV light is switched off; and d)–f) the sweeping action of branched crystals. (Copyright, 2017, The Royal Society of Chemistry.)
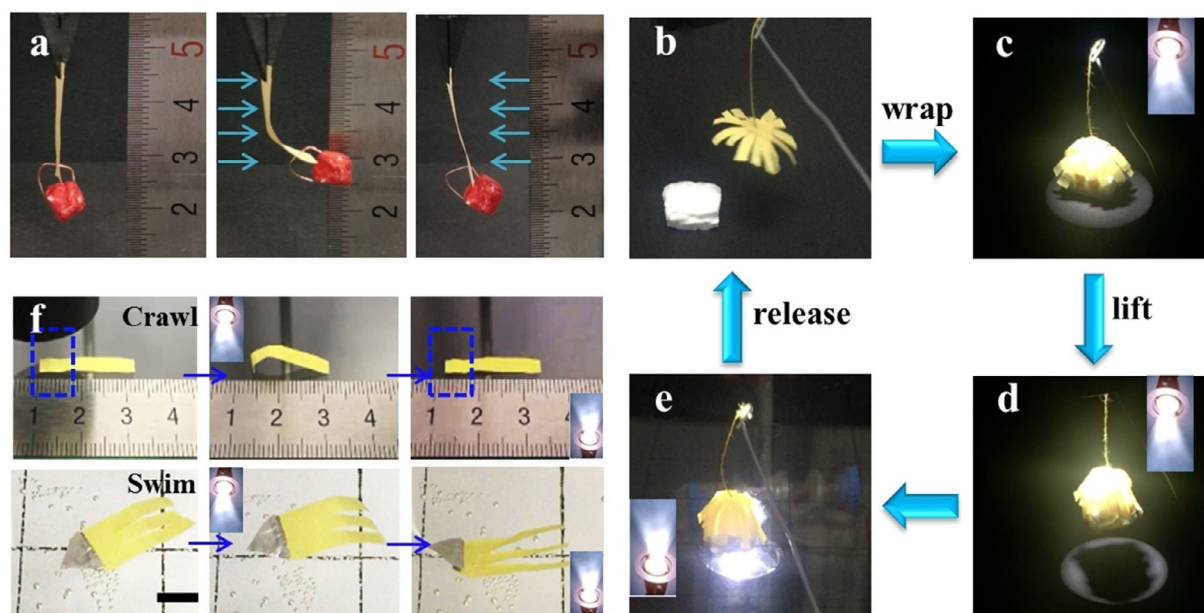
Figure 19. a) Optical images of crystal–polymer hybrid materials hanging a red object from an arm; b–e) grasping objects with multiple arms; and f) crawling and swimming behavior. (Copyright, 2012, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)

For the first time, we successfully employed a mixed-matrix membrane (MMM) method to combine the motions of mechanical crystals through connective polymers. The crystals were mixed with polyvinylidene fluoride (PVDF) polymer. The formed hybrid materials can be controllably actuated by light on the macroscale and exhibit rapid, reversible, and fatigueless mechanical actuation to mimic the motility of artificial muscles. Benefiting from the features of photomechanical crystals and connective polymers, the hybrid materials were deemed to be artificial muscles with extended elasticity and motility. The hybrid materials demonstrated exceptionally controllable mobility, and were able to reversibly lift objects (Figure 19 a), grasp objects (Figure 19 b–e), and crawl and swim (Figure 19 f); all movements were triggered by visible-light irradiation. Our work thus not only opened up a new strategy to combine photomechanical crystals with polymers as artificial muscles, but also provided a new approach to the design of thermo-/photomechanical artificial muscles.

4. Summary and Outlook

We discussed current progress in the synthesis and application of photomechanical organic crystals, including derivatives of azobenzene, vinyl, diarylethene, olefins, and anthracene. Although molecular crystals with photomechanical motions are in the process of rapid development, there are still some unsolved challenges and potential opportunities. First, developing new materials or strategies to prepare macroscale photoresponsive devices based on photomechanical crystals is essential. Second, it is of great urgency to design and prepare photoresponsive molecular crystals toward efficient, rapid, controllable, and fatigueless mechanical responses that are essential for optical molecular actuators. Third, prior to realizing application as smart materials in the future, some requirements for mechanical crystals must be satisfied, including reversibility, rapid response rate, repeatability, high sensitivity, and good fatigue resistance. The photomechanical organic crystals presented herein illustrate growing interest in solid-state chemistry and their various mechanical effects. Transforming light energy into mechanical work with organic crystals is important in the developing area of mechanical actuators, artificial muscles, optical sensors, and switches. However, the question remains on how to transform this mechanical work into useful work on a macroscopic scale. The increasing number of reported photomechanical crystals promises a bright future in the field of crystal engineering as smart materials. The outstanding performance of molecular crystals responding to light sources offers great potential for applications in photoelectric materials, biological science, and photoactuators.

Conflict of interest

The authors declare no conflict of interest.

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