

Review

# Symmetry Breaking and Photomechanical Behavior of Photochromic Organic Crystals

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**Abstract:** Photomechanical materials exhibit mechanical motion in response to light as an external stimulus. They have attracted much attention because they can convert light energy directly to mechanical energy, and their motions can be controlled without any physical contact. This review paper introduces the photomechanical motions of photoresponsive molecular crystals, especially bending and twisting behaviors, from the viewpoint of symmetry breaking. The bending (right–left symmetry breaking) and twisting (chiral symmetry breaking) of photomechanical crystals are based on both intrinsic and extrinsic factors like molecular orientation in the crystal and illumination conditions. The ability to design and control this symmetry breaking will be vital for generating new science and new technological applications for organic crystalline materials.

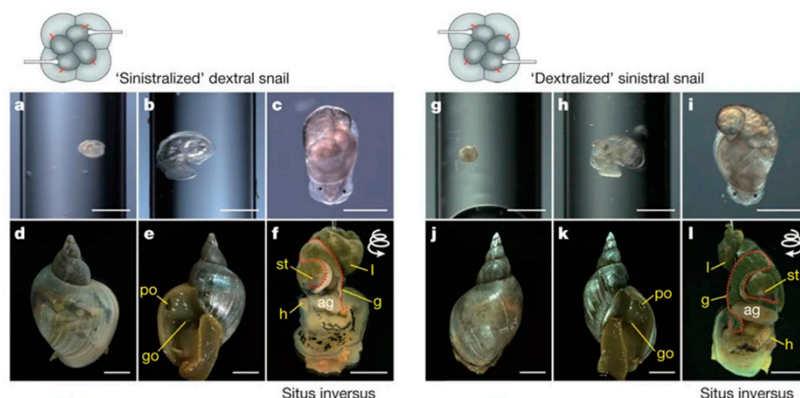
**Keywords:** photomechanical; crystal; right–left symmetry breaking; chiral symmetry breaking

## 1. Introduction

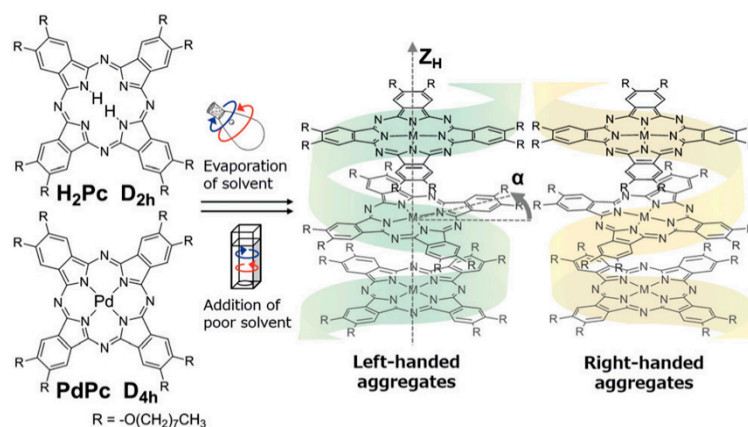
Symmetry is a very important concept in various fields, from natural sciences like mathematics, physics, chemistry, biology, geology, and astronomy to engineering fields such as architecture and urban design. For instance, the 1979 and 2008 Nobel Prizes in Physics were awarded to research on symmetry, specifically a unified symmetry description of electromagnetic and weak interactions and the discovery of the mechanism of spontaneous breaking of symmetry [1–5]. The well-known Woodward–Hoffmann rules in chemistry that rationalize pericyclic reactions rely on the fact that the symmetry of the molecular orbitals of the electrons involved in the reaction must be preserved during the reaction [6]. The 1981 Nobel Prize in Chemistry was awarded to the Woodward–Hoffmann rules and the frontier molecular orbital theory reported by Kenichi Fukui [7]. In biology, the homochirality of amino acids that almost always exist in the left-handed form (L-amino acids) is well known. The origin of this homochirality is not known but may be related to symmetry breaking. Moreover, in architecture, symmetry also plays an important role. In Islamic architecture, the elegance of the mosque is due to its symmetry and golden ratio. Thus, our life is closely related to symmetry.

The concept of symmetry is also important in biological and materials science research. For example, Kuroda et al. reported that the zygotic left–right asymmetry pathway in snails is dictated by its chiral blastomere arrangement [8]. Briefly, they physically twisted the blastomere and showed that the right-handed and left-handed conch was determined by the difference in the shape of the blastomere (Figure 1). Ishii et al. also reported on the control of chiral supramolecular nanoarchitectures by macroscopic mechanical rotations [9]. They revealed that the macroscopic mechanical rotation of a rotary evaporator could induce enantioselective H-aggregation of achiral phthalocyanines: counterclockwise rotation resulted in right-handed aggregation, but clockwise rotation gave left-handed aggregation

(Figure 2). These results indicate that the chirality of physical outputs can be controlled by applying external mechanical stimuli that break the symmetry. In this paper, we introduce photomechanical molecular crystals that respond to light as an external stimulus and show that this perturbation can generate chiral mechanical motion as an output.



**Figure 1.** Generation of right-handed and left-handed snails, depending on the physical twist of the blastomere. After the third-cleavage manipulations, both sinistralized dextral embryos (a) and dextralized sinistral embryos (g) were raised to adult snails. Development was observed at trochophore (a,g), veliger (b,h) and juvenile snail (c,i) stages. Adult snails were pictured dorsally (d,j) and ventrally (e,k). The shell was removed to observe the position of internal organs (f,l, dorsal view). ag, albumen gland; g with dotted red line, gut; go, female genital opening; h, heart; l with white coil, liver; st, stomach; po, pulmonary sac opening. Scale bars: a–c, g–i, 0.5 mm; d–f, j–l, 5 mm. Reproduced from [8] with permission of Springer Nature, copyright 2009.



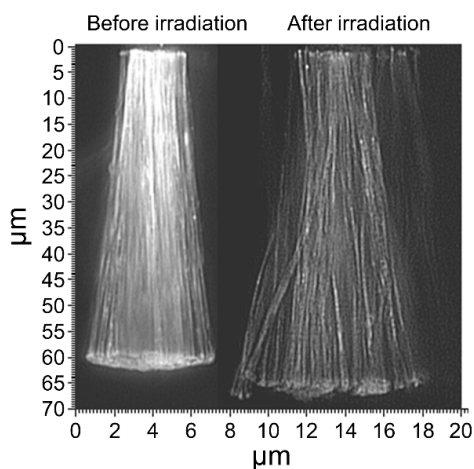
**Figure 2.** Control of chiral supramolecular nanoarchitectures by macroscopic mechanical rotations. Reproduced from [9] with permission of Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, copyright 2013.

## 2. History and Background of Photomechanical Molecular Crystals

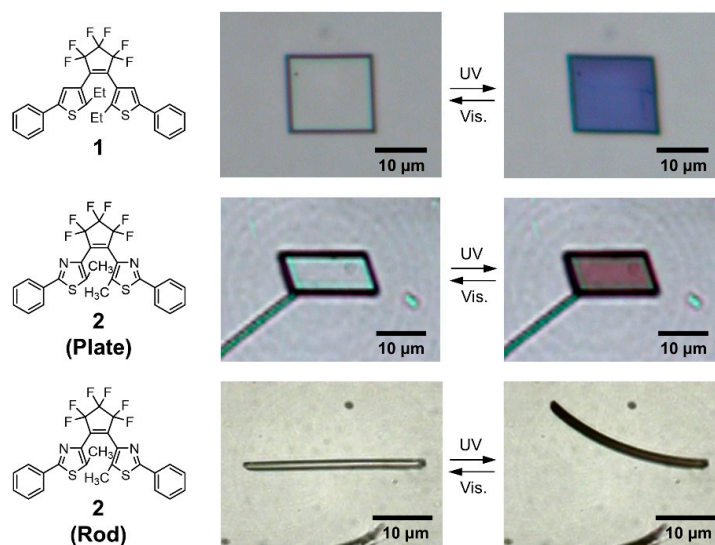
Photomechanical materials exhibiting mechanical motions upon photoirradiation generally consist of photoresponsive molecules. When photoresponsive molecules undergo geometrical changes due to photochemical reactions, the individual molecular motions act in concert, resulting in the mechanical motion of the material itself. Liquid crystalline polymers and molecular crystals made from photoresponsive molecules are well known and have been intensively investigated so far.

The history of photomechanical molecular crystals starts from research in 1982, reported by Abakumov and Nevodchikov et al. [10]. The crystals, composed of a semiquinone complex of platinum group metals, exhibited a photomechanical bending of the crystal by as much as  $45^\circ$  upon irradiation with visible or near-infrared light. The crystal reverted to its original shape within 0.1 s when the

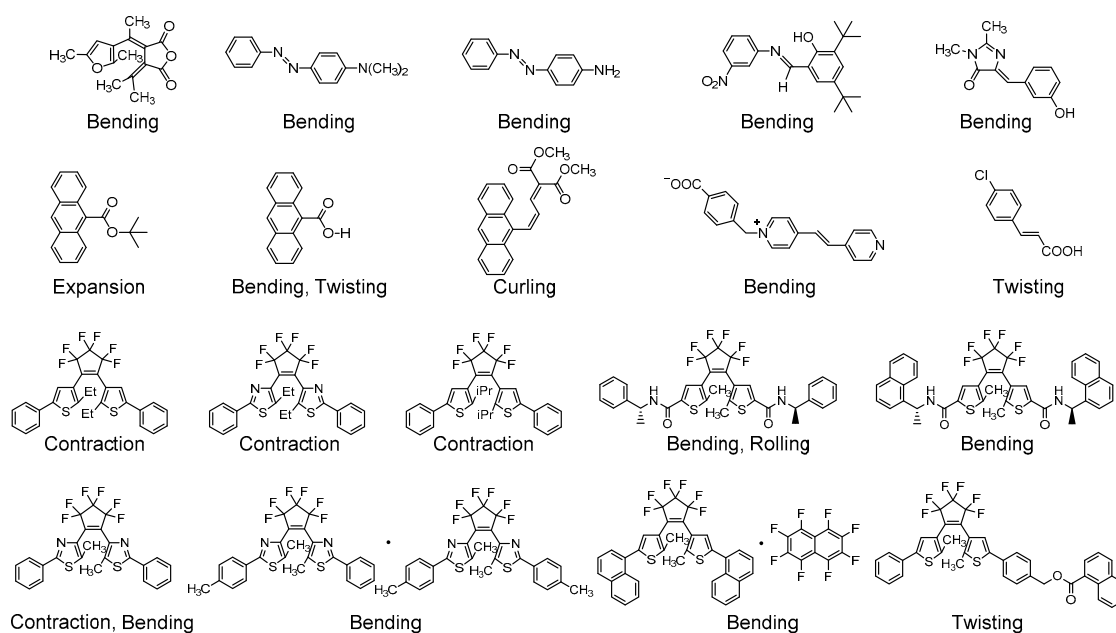
light exposure was stopped. The bending behavior was due to the radical-mediated formation of dimerized Rh-Rh bonds in the crystal. However, at that time, this photomechanical behavior did not attract much attention. After a while, in the early 2000s, it was noted again. Bardeen et al. reported on the photochemically driven expansion of crystalline nanorods composed of an anthracene derivative, 9-tert-butyl anthroate (9-TBAE) (Figure 3) [11]. 9-TBAE undergoes a [4 + 4] photodimerization in the crystalline state, which results in a 15% increase in rod length without fragmentation. Kobatake and Irie et al. reported on the rapid and photoreversible shape changes of photochromic diarylethene crystals, including transforming from a square shape to a lozenge shape, expansion and contraction, and bending (Figure 4) [12]. After these remarkable findings, many researchers joined this research field, and it has been revealed that crystals of various photoresponsive molecules can exhibit photomechanical behavior such as expansion and contraction, bending, twisting, coiling, rolling, and so on (Figure 5) [13–43]. As can be seen, bending is an especially common motion.



**Figure 3.** Fluorescence image of a bundle of nanorods, consisting of 9-tert-butyl anthroate (9-TBAE), before and after irradiation with a 365 nm light. The rods lengthen by an average of 15% as measured along a single rod. Reproduced from [11] with permission of the American Chemical Society, copyright 2006.



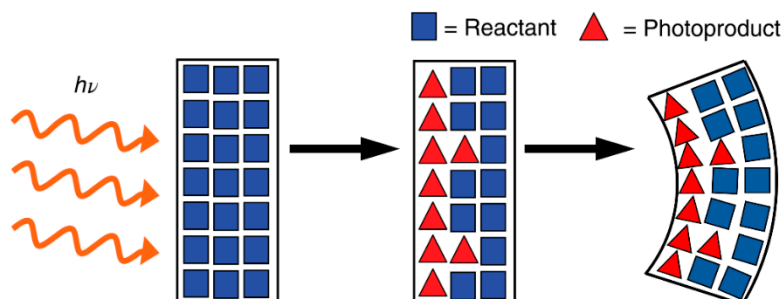
**Figure 4.** Photoreversible crystal shape changes of diarylethene derivatives 1 and 2. Adapted from [12] with permission of Springer Nature, copyright 2007.



**Figure 5.** Photochromic compounds exhibiting photomechanical behaviors in crystals.

### 3. Photomechanical Bending Motion of Molecular Crystals: Right–Left Symmetry Breaking

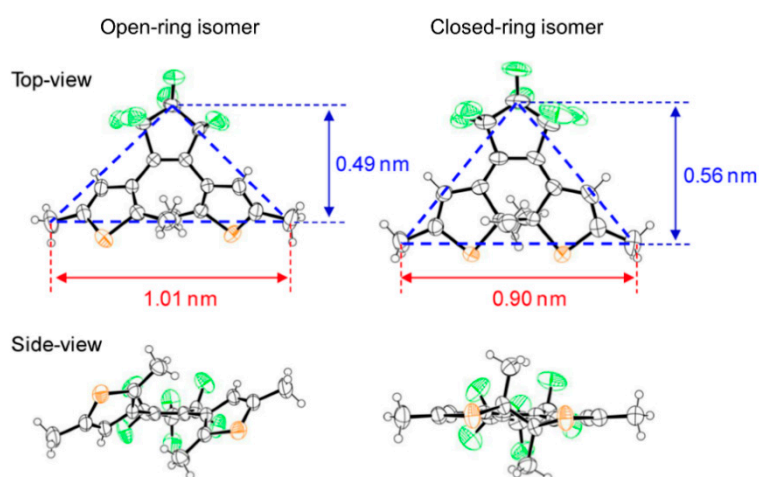
Photomechanical motion of photoresponsive organic crystals is ascribed to the strain generated by the photoreactions in the crystal. The mechanism can be explained with the example of photomechanical crystal bending as follows. Upon ultraviolet (UV) light irradiation from one side of the crystal, photoresponsive molecules undergo various reactions such as intramolecular ring-closing and opening reactions, cis–trans isomerization, intermolecular [2 + 2] photodimerization, [4 + 4] photodimerization, and so on, which results in the formation of a bimorph or bimetal structure between reactants and photoproducts. This asymmetry arises because the photoreactions proceed more on the side where light is irradiated. The strain induced by this bimorph or bimetal structure leads to the bending deformation of the crystal itself (Figure 6) [44]. From the viewpoint of symmetry, photomechanical behavior is induced by the breaking of symmetry of the molecular structure and arrangement in the crystal due to the progress of the photoreaction. Moreover, the bending direction can be controlled by moving the illumination source. Most bending crystals based on the bimorph or bimetal mechanism exhibit this control of symmetry breaking by an extrinsic factor. Thus, it can be said that the symmetry breaking plays an important role even in the simplest photomechanical behavior.



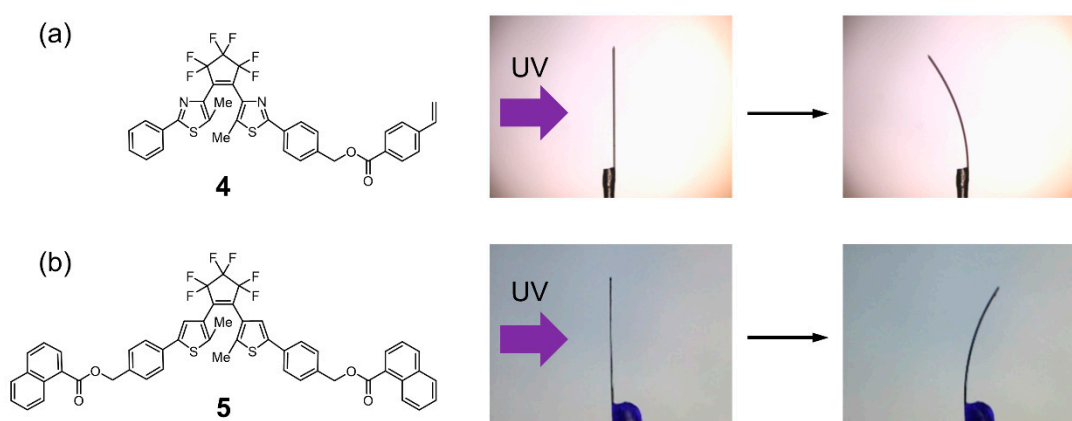
**Figure 6.** Schematic illustration of a bimorph or bimetal structure composed of reactants and photoproducts. Adapted from [44] with permission of John Wiley & Sons, Ltd., copyright 2017.

As mentioned in the previous section, bending is the most common photomechanical motion. In addition to illumination direction, the bending behavior is influenced by the molecular crystal structure itself. A good illustration of this can be seen by taking diarylethene molecular crystals as

examples. Diarylethene molecules undergo a  $6\pi$  ring-closing and ring-opening reaction between the colorless open-ring isomer and the colored closed-ring isomer. During this photoisomerization reaction, the long axis of the molecule shrinks, the short axis of the molecule extends, and the thickness of the molecule decreases, as shown in Figure 7 [45]. This small but apparent molecular structural change results in photomechanical motion. When a rod-shaped crystal of a diarylethene derivative, 1-(5-methyl-2-(4-(*p*-vinylbenzoyloxymethyl)phenyl)-4-thiazolyl)-2-(5-methyl-2-phenyl-4-thiazolyl)perfluorocyclopentene (4), is irradiated with UV light, the crystal bends toward the light source and straightens out after irradiation with visible light (Figure 8a) [23]. On the other hand, the crystal of a diarylethene derivative, 1,2-bis(2-methyl-5-(4-(1-naphthoyloxymethyl)phenyl)-3-thienyl)perfluorocyclopentene (5), shows different behavior. Upon irradiation with UV light, the crystal bends away from the light source and returns to its initial shape by visible light irradiation (Figure 8b) [21]. The different bending directions are ascribed to different molecular packings in the crystals. Therefore, molecular packing also plays an important role as an intrinsic factor in determining the bending direction.

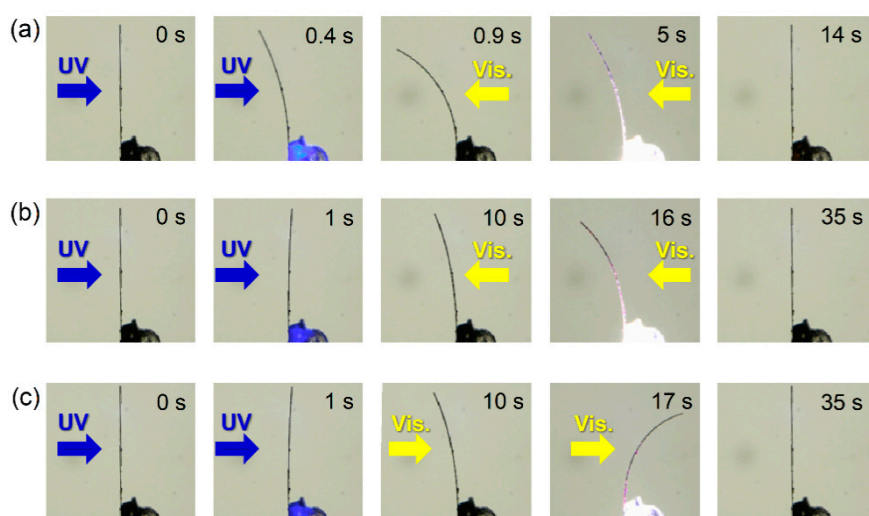


**Figure 7.** Molecular structural change of a diarylethene derivative, 1,2-bis(2,5-dimethyl-3-thienyl)-perfluorocyclopentene (3), accompanied with the photochromic reaction. Reproduced from [45] with permission of the American Chemical Society, copyright 2014.



**Figure 8.** Photomechanical crystal bending behaviors of diarylethene derivatives 4 and 5 (a) bending toward the UV light source (adapted from [23] with permission of the European Society for Photobiology, the European Photochemistry Association, and The Royal Society of Chemistry, copyright 2014) and (b) bending away from the UV light source at 365 nm (adapted from [21] with permission of the American Chemical Society, copyright 2013).

One question is whether such bending behavior can be observed for crystals of any size. It is a long-known fact for chemists that when the size of a crystal is large, the crystal usually disintegrates as the photoreaction proceeds. To gain insight into the size dependence of the photomechanical bending behavior, the dependence of the bending velocity on the crystal thickness was investigated [21,23]. The initial bending velocity ( $V_{\text{init}}$ ) increases as the crystal thickness decreases, and the relationship between the  $V_{\text{init}}$  and the crystal thickness was well explained by Timoshenko's bimetal model. Based on this analysis, it was found that a crystal with a thickness of a few micrometers bent well. In larger crystals, the strain generated by the photoisomerization reaction cannot be relaxed by deformation of the crystal, and the crystal tends to fracture. Furthermore, it was found that  $V_{\text{init}}$  increased in proportion to the light irradiation intensity, suggesting that the photomechanical bending was directly proportional to the amount of molecular reactions that have occurred [46]. This finding inspired us to examine the effect of illumination conditions on photomechanical behavior. When the crystal of a diarylethene derivative, 1,2-bis(5-methyl-2-phenyl-4-thiazolyl)perfluorocyclopentene (**2**), was irradiated with a 365 nm light, it bent toward the incident light. However, upon irradiation with a 380 nm light, the crystal bent away from the light source at first, then bent back toward the incident light after prolonged irradiation (Figure 9) [47]. This result is related to the difference in depth of the photochromic reaction from the crystal surface for different illumination wavelengths. Similar results could be observed when polarized UV light was used as the incident light [48]. Thus, the photomechanical bending direction (i.e., right-left symmetry breaking) can be controlled by both intrinsic and extrinsic factors, such as the molecular packing in the crystal and the illumination conditions (source direction and wavelength).

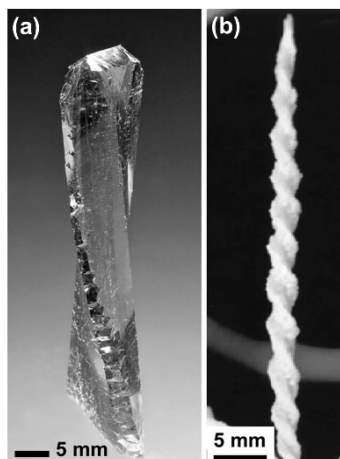


**Figure 9.** Different photomechanical bending behavior of a diarylethene **2** crystal depending on the illumination wavelength. (a) The crystal was irradiated with a 365 nm light from the left side and then irradiated with visible light from the right side. (b) The crystal was irradiated with a 380 nm light from the left side and then irradiated with visible light from the right side. (c) The crystal was irradiated with a 380 nm light from the left side and then irradiated with visible light from the left side. Reproduced from [47] with permission of the PCCP Owner Societies.

#### 4. Crystal Twisting: Chiral Symmetry Breaking by Intrinsic Factors

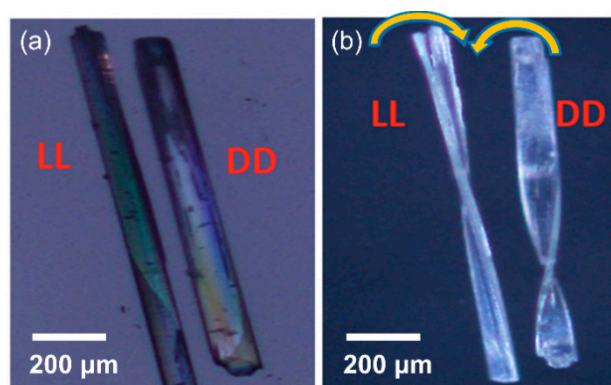
In the research field of crystal growth, twisted crystal growth is an interesting topic. Twisted crystal growth has been observed in crystals of a variety of substances including elements, minerals, simple salts, organic molecules, and polymers. Figure 10 shows the photographs of the twisted crystals of natural quartz and  $\text{K}_2\text{Cr}_2\text{O}_7$  as examples of twisted crystal growth. Shtukenberg and Kahr et al. have written a review paper on the mechanism of growth-actuated twisting of single crystals [49]. Since various factors can play a role in growth-actuated twisting, such as chemical composition, size, shape, and growth conditions, there is no universal mechanism for the twisting. However, in all cases,

it can be concluded that the crystal twists as a result of the chiral symmetry breaking due to various factors such as surface charge, electrostatics, piezoelectricity, screw dislocation, twinning, surface stress, and so on. These are all examples of symmetry breaking due to intrinsic environmental factors in the absence of a chemical reaction.

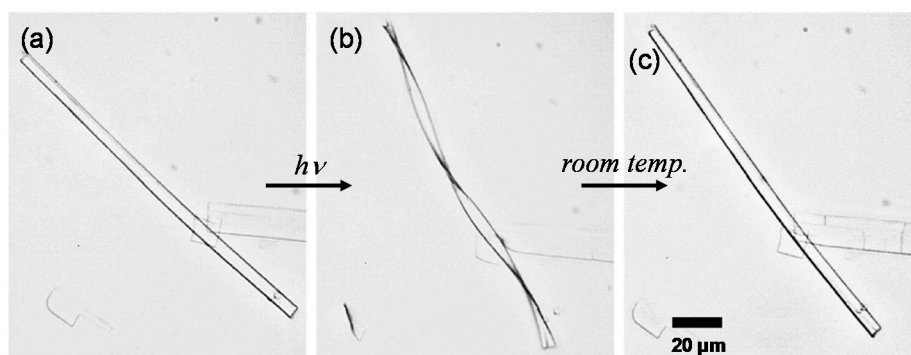


**Figure 10.** Photographs of a representative twisted crystal growth of (a) natural quartz and (b)  $K_2Cr_2O_7$ . Reproduced from [49] with permission of Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, copyright 2014.

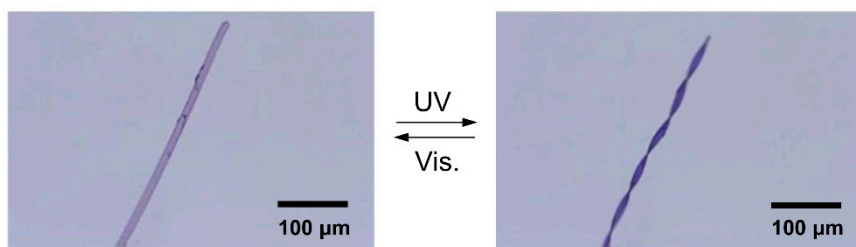
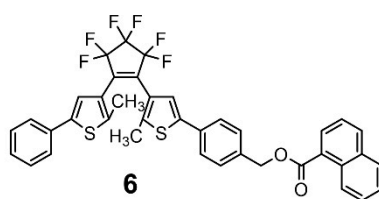
Recently, Sureshan et al. reported on chirality-controlled twisting of dipeptide crystals by a thermal topochemical reaction [50]. The presence of chiral reactants could induce crystal twisting during the reaction under heating, and the direction of the twisting (i.e., right-handed or left-handed) depended on the chirality of the precursor dipeptide (Figure 11). This is an example of stimuli-responsive twisting. The heating acts as a stimulus and leads to chiral symmetry breaking, resulting in twisting. A twisting motion due to photochemical reactions has also been reported. Bardeen et al. reported that microribbon crystals composed of 9-anthracenecarboxylic acid (9AC) exhibited twisting upon UV irradiation [26]. After the light was turned off, they relaxed back to their original shapes over the course of minutes (Figure 12). This is T-type (thermally reversible) photomechanical twisting. Kitagawa and Kobatake et al. reported that microribbon crystals made from a diarylethene derivative also exhibited reversible photomechanical crystal twisting [22]. In this case, the crystal could be reversibly switched back and forth between twisted and straight with alternating irradiation with UV and visible light (Figure 13). This is P-type (photochemically reversible) photomechanical twisting. These photomechanical crystal twisting behaviors were observed under spatially uniform light irradiation. The twisting motion is induced by strain in the diagonal direction relative to the crystal's long axis, which depends on the molecular orientation with respect to the long axis of the plate. Al-Kaysi and Bardeen et al. elucidated that controlling crystal morphology resulted in different photomechanical behaviors [51]. When crystals of 9-methylanthracene (9MA) were prepared by seeded growth using a surfactant, hexagonal microplates were obtained that exhibited photomechanical curling behavior (Figure 14a). On the other hand, rectangular microribbons prepared by a floating drop method (i.e., dropping the organic solvent containing 9MA into water) showed helical twisting behavior upon UV irradiation (Figure 14b). The hexagonal microplates and rectangular microribbons of 9MA are the same polymorph, but have different internal molecular orientations (i.e., the crystal growth directions of the hexagonal microplates and rectangular microribbons are different).



**Figure 11.** Twisting of crystals consisting of chiral dipeptides ( $N_3$ -L-Ala-L-Val-NHCH<sub>2</sub>C≡CH) upon heating as an external stimulus (a) before heating and (b) after heating at 85 °C for 1 day. Adapted from [50] with permission of National Academy of Sciences, copyright 2018.

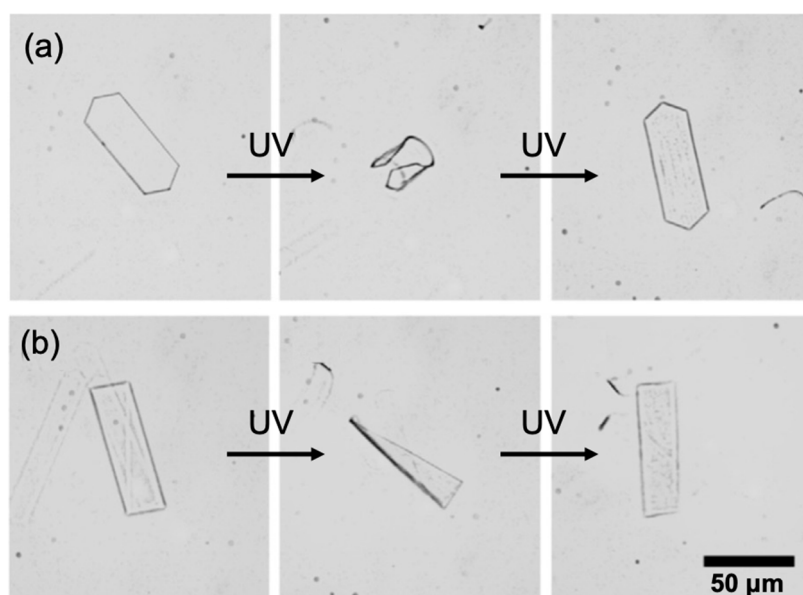


**Figure 12.** Photomechanical twisting behavior of a 9AC crystal upon UV irradiation (a) before photoirradiation and (b) immediately after irradiation. The twisted crystal returns to the original shape over the course of minutes by removing the incident light. (c) Nine minutes after removing the light. Adapted from [26] with permission of the American Chemical Society, copyright 2011.



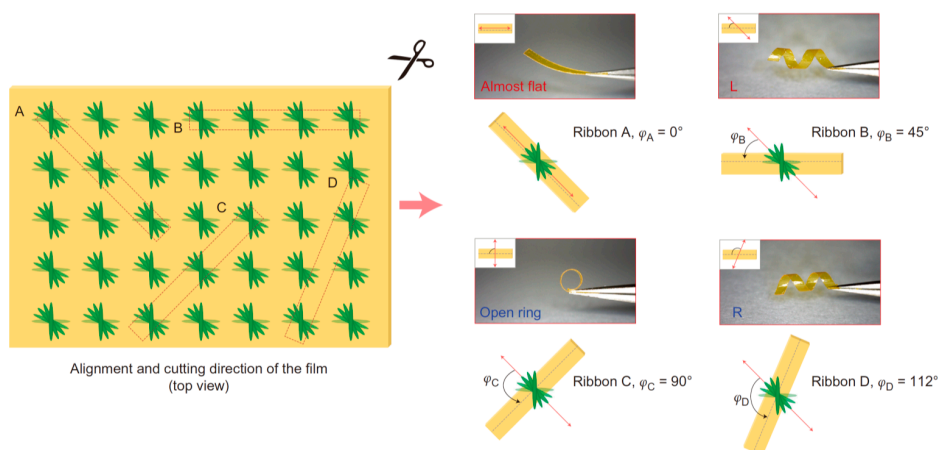
**Figure 13.** Photoreversible photomechanical twisting of a diarylethene **6** crystal upon alternating irradiation with UV and visible light. Adapted from [22] with permission of Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, copyright 2013.



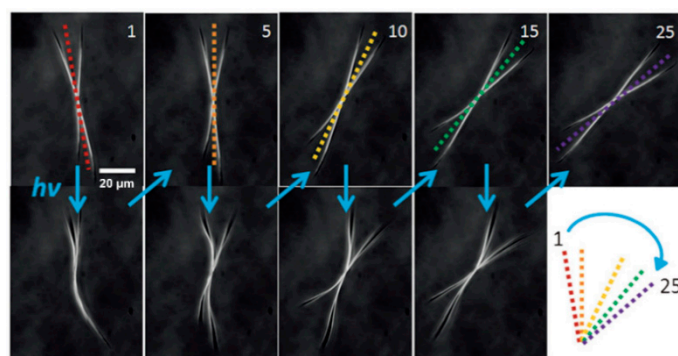


**Figure 14.** Photomechanical curling and twisting of 9-methylanthracene (9MA) crystals, depending on the crystal morphology. (a) A 9MA hexagonal microplate and (b) a 9MA rectangle microplate. Adapted from [51] with permission of Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, copyright 2018.

By controlling the molecular orientation within a crystal, it is possible to generate different photomechanical behaviors (Figure 14). On larger scales, the shape of the crystal itself can lead to symmetry breaking and directional motion. Katsonis et al. reported that ribbons made from a liquid crystalline polymer with an azobenzene derivative could exhibit curling, right-handed or left-handed helical twisting, depending on the direction in which they were cut (Figure 15) [52]. This is because the direction of the shrinkage and expansion in the plane of the material can be tuned by the direction of the cutting. This is an excellent study on controlling the photomechanical twisting by controlling the macroscopic structure. Al-Kaysi and Bardeen et al. reported that branched crystals composed of 4-fluoroanthracene-9-carboxylic acid (4F-9AC) could be prepared by a pH-driven reprecipitation method [53]. A branched crystal will rotate in one direction like a ratchet under sequential illumination (Figure 16). This is due to symmetry breaking by the crystal branching. The rotation direction depends on the chirality of the branched crystal shape. In all the cases in this section, the twisting was intrinsic in the sense that some internal structural factor led to twisting. Changing the external perturbation, i.e., the light field, was not used to influence the twisting motion.



**Figure 15.** Photomechanical behaviors of liquid crystalline azobenzene polymer, depending on the cutting direction. Reproduced from [52] with permission of Springer Nature, copyright 2014.

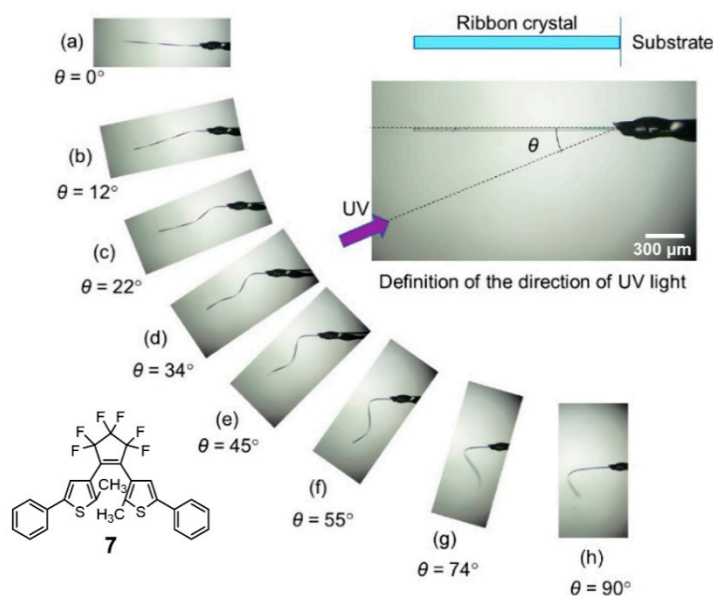


**Figure 16.** Photomechanical ratchet-like motion of X-shaped 4F-9AC crystals upon UV irradiation. Adapted from [53] with permission of Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, copyright 2016.

### 5. Control of Chiral Crystal Twisting by Control of Light Illumination as an Extrinsic Factor

The control of chiral symmetry breaking by external factors is an important research topic, and many scientists have made efforts in this field [54]. For example, in the introduction, we described how a dynamic external perturbation (rotovap spinning direction) could change the chiral structure of supramolecular aggregates. In photomechanical materials, control of chirality by extrinsic factors (that is, control of photomechanical twisting) has also been investigated.

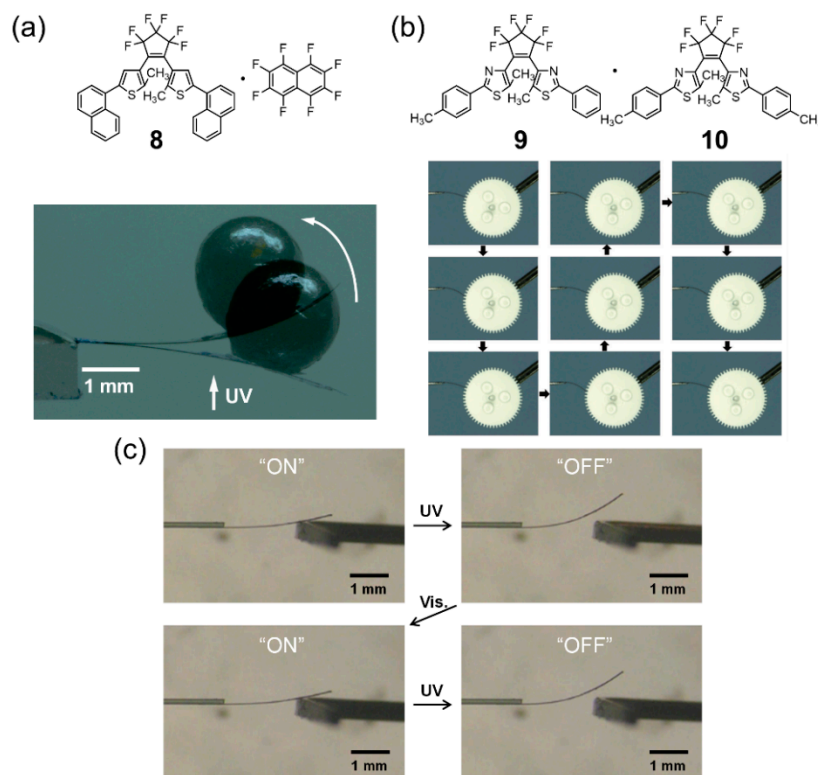
Light is the main extrinsic perturbation that can be used in the case of molecular crystals. Chirality control can be realized by changing the illumination direction. We demonstrated that ribbon crystals that consist of a diarylethene derivative could exhibit different twisting motions, ranging from a helicoid to a cylindrical helix, depending on the angle of the incident light (Figure 17) [55]. This was ascribed to the preferential excitation of differently oriented molecules within the crystal by different light directions. In other words, by exciting differently oriented molecules, the photoinduced strain tensor in the crystal (and thus the mode of photomechanical deformation) can be controlled by the direction of the UV light irradiation. Note that this control is only possible for crystals where all the molecules have a precise orientation with respect to the lab frame. The detailed mechanism is still under investigation, but this is a unique example of controlling chiral photomechanical twisting by an extrinsic factor.



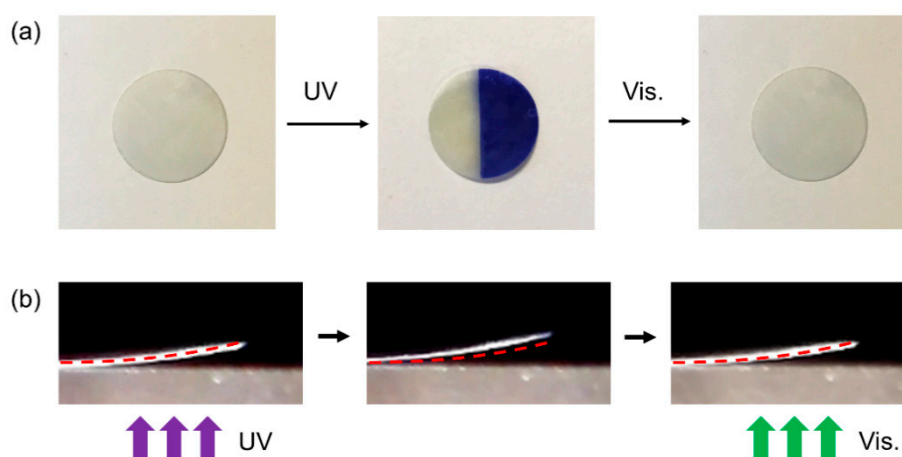
**Figure 17.** Control of photomechanical twisting of a ribbon crystal consisting of diarylethene **7** by illumination direction. Reproduced from [55] with permission of the American Chemical Society, copyright 2018.

## 6. Future Directions

There is now a large body of work showing that photoreactive crystals can generate mechanical motion. However, one major challenge is incorporating these crystals into actuator structures that can do useful work. As examples of applications, molecular crystal devices that give rise to cantilever motion [18], gearwheel rotation [19], and current switching [56] have been demonstrated, as shown in Figure 18. However, nano- and micro-sized crystals can only generate small amounts of work in isolation. It is still challenging to sum up the work of many individual crystals into one large output. As one of the strategies to overcome this issue, embedding crystals in polymer hosts has been demonstrated [57–60]. However, it is still difficult to order the crystals regularly in polymer hosts, and a large output has not been obtained. Recently, we reported that hybrid organic–inorganic materials consisting of a diarylethene derivative and anodic aluminum oxide (AAO) porous template can exhibit photomechanical actuation (Figure 19) [61,62]. These ordered composites combine the photoresponsive properties of the organic with the high elastic modulus of the ceramic, making them a photon-powered analog to piezoelectric actuators.

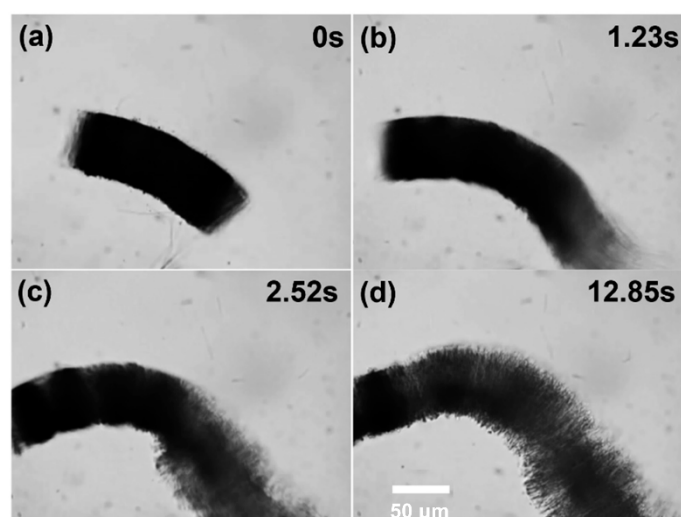


**Figure 18.** Examples of application of photomechanical bending behaviors of diarylethene crystals. (a) Molecular crystal cantilever, consisting of **8** and a perfluoronaphthalene co-crystal (reproduced from [18] with permission of the American Chemical Society, copyright 2010); (b) gearwheel rotation, working by complicated motions of a diarylethene derivatives **9** and **10** mixed crystal (reproduced from [19] with permission of Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, copyright 2012); and (c) current switching caused by photoreversible bending of a gold-coated diarylethene **2** crystal (reproduced from [56] with permission of The Royal Society of Chemistry).



**Figure 19.** (a) Photographs of the hybrid organic–inorganic materials, consisting of a diarylethene derivative **7** and anodic aluminum oxide (AAO) porous template, and (b) its photomechanical actuation. Reproduced from [61] with permission of the American Chemical Society, copyright 2019.

A second challenge for organic photomechanical crystals is to improve their energy conversion and power efficiency. For example, in most cases, only a few percent of the photochromic molecules react and contribute to the photomechanical response. To increase conversion, negative photochromic compounds are the best candidates. The absorption spectra of negative photochromes undergo a shift to higher energies after photoisomerization, allowing the excitation light to penetrate through the crystal. Bardeen et al. recently reported on the photomechanical behavior of a phenylbutadiene derivative, (*E*)-4-fluorocinnamaldehyde malononitrile ((*E*)-4FCM), that undergoes a negative photochromic reaction based on a [2+2] photocycloaddition in the crystal form [63]. The nanowire bundles composed of (*E*)-4FCM exhibited a rapid expansion and spread by as much as 300% (Figure 20). AAO membranes containing this molecule were capable of lifting approximately four times as much weight as membranes containing a positive photochrome based on diarylethene. Thus, varying and optimizing the molecular photochrome is still one of the essential topics.



**Figure 20.** Spreading of nanowire bundles consisting of (*E*)-4-fluorocinnamaldehyde malononitrile ((*E*)-4FCM) upon UV irradiation. Reproduced from [63] with permission of The Royal Society of Chemistry.

## 7. Conclusions

In this paper, we introduced various photomechanical motions of photochromic molecular crystals from the viewpoint of symmetry breaking, such as right–left symmetry breaking and chiral symmetry breaking, by both intrinsic and extrinsic factors. Photomechanical molecular crystals have great potential as materials that convert light energy directly to mechanical energy, with large elastic moduli, high energy densities, and fast response times. This is an advantage compared with liquid crystalline polymers. In addition to the challenges described in the previous section, it is necessary to develop a quantitative understanding of how molecular-level structure changes and photochemical reaction kinetics give rise to a macroscopic photomechanical response. Such a predictive understanding will allow us to design photomechanical crystals with properties optimized for different applications. While there are still problems to be addressed, it is clear that this research field is rapidly developing and attracting many researchers. The ability of these high-symmetry structures to undergo symmetry breaking motion in response to light will continue to generate new science and new technological applications for organic crystalline materials.

**Author Contributions:** Conceptualization, D.K. and C.J.B.; writing—original draft preparation, D.K.; writing—review and editing, C.J.B and S.K.; project administration, S.K.; All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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