Abstract: It is generally believed that organic single crystals composed of a densely packed arrangement of anisotropic, organic small molecules are less useful as functional materials due to their mechanically inflexible and brittle nature, compared to polymers bearing flexible chains and thereby exhibiting viscoelasticity. Nevertheless, organic crystals have attracted much attention because of their tunable optoelectronic properties and a variety of elegant crystal habits and unique ordered or disordered molecular packings arising from the anisotropic molecular structures. However, the recent emergence of flexible organic crystal materials showing plasticity and elasticity has considerably changed the concept of organic single crystals. In this review, the author summarizes the state-of-the-art development of flexible organic crystal materials, especially functional elastic organic crystals which are expected to provide a foothold for the next generation of organic crystal materials.

Keywords: elastic organic crystals; mechanical deformation; π-conjugated molecules; photoluminescence; deformation-induced photoluminescence changes

1. Introduction

In general, organic molecular crystals have been believed to be inflexible and brittle (Figure 1a,b), because they have a densely packed, three-dimensional (3D), supramolecular structure and hence do not possess a mechanism for relaxation of the stress loaded. Meanwhile, it is known that several organic molecular crystals display plastic-like bending deformability, i.e., plasticity [1–7]. These crystals are plastically bended by photoirradiation or deformed by external stress (Figure 1a,c). Until 2016, various flexible organic crystal materials were discovered and reported [8–15].
which could lead to the development of flexible and wearable optoelectronic single-crystal devices (Figure 2). Furthermore, it was also anticipated to find out additional novel phenomena caused by the mechanical deformation of a dense supramolecular structure, despite anisotropic molecular orientation. In this review, the author summarizes the design (Section 2), potential structures (Section 3), detailed deformation (Section 4), and unique properties (Sections 5 and 6) of elastic organic crystals of π-conjugated molecules.

![Figure 1. Schematic illustration of three points stress for organic crystals. (a) Straight organic crystals. i: brittle breakage. ii: plastically bending deformation. iii: elastically bending deformation. (b) Brocken crystals. (c) Plastically deformed crystals. (d) Elastically deformed crystals.](image-url)

Recently, the examples of ferroelastic and superelastic crystals that can change their shape due to a crystal-to-crystal phase transition caused by the load of stress, and the examples of pseudo-elastic shape recovery of plastically deformed solids have been reported [8–10]. Since that time, we have been interested in elastic organic crystals, i.e., elastically deformable organic crystals that can realize bending deformation and spontaneous shape recovery in response to the load of stress (Figure 1a,d). By the way, the origin of elasticity observed for polymers can be classified into two thermodynamical factors, namely enthalpy and entropy effects [11,12]. In the case of organic molecular crystals, the elasticity should be related to the change of the molecular arrangement in the crystal during deformation. If the entropic elasticity operated in the crystals at the nanoscopic level, by applying an external force, the regularly arranged molecular packing were forced to change to an irregular state and could not return to the original packing according to the second law of thermodynamics. This assumption was not correct. The elastic organic crystals showed enthalpic deformation by applying an external force and returned to the original molecular packing owing to the restoring force.

In this context, we have realized the combination of the elastic flexibility and unique ‘optical and electronic functions’ of organic molecular crystals [16–24], which is most likely to open up a new field of organic crystal materials chemistry (Figure 2). π-conjugated molecules were reported to demonstrate various optoelectronic functions, such as light absorption and emission, semiconductor performance and so forth, because of the π-electron systems [25–42]. Accordingly, it was expected that endowing a flexible and tough elastic crystal with this π-functionality would enable to develop a new research field which could lead to the development of flexible and wearable optoelectronic single-crystal devices (Figure 2). Furthermore, it was also anticipated to find out additional novel phenomena caused by the mechanical deformation of a dense supramolecular structure, despite anisotropic molecular orientation. In this review, the author summarizes the design (Section 2), potential structures (Section 3), detailed deformation (Section 4), and unique properties (Sections 5 and 6) of elastic organic crystals of π-conjugated molecules.
Therefore, if close attention is paid to the molecular structure that forms these wire bundles, and if the crystal structure accompanying the change in the “metastable structure” would cause deformation and relaxation of the crystal (Figure 3c). To construct a structure that allows expansion and contraction of organic crystals, a method that causes molecular slipping by face-to-face slip-stacking must be devised (Figure 3c,d). It is envisioned that molecular sliding between π-molecular plains affects the microscopic stretchability (Figure 3e).

Figure 2. Schematic illustration of the concept on “elastic organic crystals of π-conjugated molecules”. Flexible organic crystals with π-functionality.

2. Design of Elastic Organic Crystals Composed of π-Conjugated Molecules

Here the definite guidelines for the molecular design to afford elastic organic crystals with specific functions are discussed. To endow organic crystals with flexibility, they must have an intermolecular packing so as to relax the stress loaded (Figure 3a) [14,15]. Wire bundles, such as the fibril lamella structure, can exhibit high flexibility, as seen in the macrostructure of muscle fibers (Figure 3b). Therefore, if close attention is paid to the molecular structure that forms these wire bundles, and if the constituent molecules form a slip-stack structure with “rigid and highly planar π-conjugated molecules”, the “stable structure” due to molecular sliding accompanies stress loading. The change in the crystal structure accompanying the change in the “metastable structure” would cause deformation and relaxation of the crystal (Figure 3c). To construct a structure that allows expansion and contraction of organic crystals, a method that causes molecular slipping by face-to-face slip-stacking must be devised (Figure 3c,d). It is envisioned that molecular sliding between π-molecular plains affects the microscopic stretchability (Figure 3e).

Predicting and designing the crystal structure of any compound is extremely difficult. However, the skillful design of molecular structures and realization of intended packing structures based on functional group interactions and molecular shapes have been receiving attention in recent years. In recent years, based on the structure concept shown in Figure 4, the author has designed, synthesized, and crystallized π-conjugated molecules to achieve intended crystal structures and create functional elastic crystals.
years. This methodology is called noncovalent synthesis, as opposed to organic synthesis based on covalent bond conversion. The structural unit is called a supramolecular synthon, like a synthon in organic synthesis [14,43,44]. In recent years, based on the structure concept shown in Figure 4, the author has designed, synthesized, and crystallized \( \pi \)-conjugated molecules to achieve intended crystal structures and create functional elastic crystals.

![Chemical structures for light-emitting elastic organic crystals reported by Hayashi so far.](image)

Figure 4. Chemical structures for light-emitting elastic organic crystals reported by Hayashi so far. 1 [15], 2 [16], 3 [20], 4 [20], 5 [19], 6 [21].

To form rigid and planar \( \pi \)-conjugated molecules and their slip stack-structures, we have focused on oligothiophenes containing fluoroarene structures 1–4 (Figure 4) [34,37,45,46]. The fluorine atom of the fluoroarene interacts with the sulfur atom of thiophene and forms hydrogen bonds with the adjacent aromatic hydrogen to improve the rigidity (suppression of free rotation) and planarity by multiple intramolecular interactions, and it is expected that face-to-face slip-stacking can be effectively formed by the thiophene-tetrafluorophenylene-thiophene alternating structures 1–4 (Figure 4).

The crystallization of molecules 1–4 crystallized on a millimeter or centimeter scale. From the crystal structure of each molecule, an interatomic distance shorter than the sum of the van der Waals radii of sulfur and fluorine or that of hydrogen and fluorine was observed in the molecule. Therefore, high rigidity and flatness based on the intramolecular S\( \cdot \cdot \cdot \)F interaction and H\( \cdot \cdot \cdot \)F hydrogen bond were suggested. In addition, the molecules pack by the face-to-face slip-stacking structure, and it can be considered that a single crystal with a target crystal structure based on the molecular design is obtained.

Owing to the stress applied to each crystal, it was found that the crystals of 1–4 showed elasticity, whereas the crystal of bis(5-methylthien-2-yl)-2,3,5,6-tetrafluorobenzene was brittle like a normal organic crystal. For example, the crystal of 1 bent when stress was applied, and it quickly returned to its original shape when the stress was released (Figure 5). That is to say, the crystal exhibiting elastic properties was obtained by the proposed design of a molecular crystal structure. In addition, this crystal showed efficient emission characteristics (sky blue emission, \( \lambda_{PL} = 500 \text{ nm, } \varphi_{PL} = 24\% \)), and possessed functions unique to the \( \pi \)-electron system [15,16].

![Photograph of elastic bending of the light-emitting elastic organic crystal of 1.](image)

Figure 5. Photograph of elastic bending of the light-emitting elastic organic crystal of 1. Reproduced from [15] with permission of Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, copyright 2016.
The intramolecular H···F hydrogen bond in the crystal structure is stronger than the S···F interaction [34,37,45,46]. Therefore, when the core is difluorophenylene, the intramolecular H···F hydrogen bond with thiophene takes precedence, and the planarity increases. However, increasing the molecular hardness (suppression of free rotation) by four interactions by using a tetrafluorophenylene skeleton as the core is considered to afford the ultimate elasticity. In addition, owing to the face-to-face slip-stacking structure, which is another key to develop elasticity, the π-conjugated molecules form a through-space type of conjugated system, different from roughly isolated solution in solution. The absorption and photoluminescence (PL) bands undergo a large red-shift [15,16,37]. Therefore, it can be considered that such a crystal structure design exerts not only the mechanical properties of the crystal, but also a favorable effect on the optical properties.

3. Potential Structures of Elastic Organic Crystals

The author believes that there are some specific methods for developing such elastically deformable properties of organic crystals (Figure 6a) [47–53]. One method is to form a crystal structure by slip-stacking of planar π-conjugated molecules, as described above (Figure 6b) [15–18]. Conversely, as reported by Desiraju and co-workers [14], a method to make the crystal structure easy to move by halogen–halogen interactions can be used (Figure 6c). Because of this interaction, plastically deformable organic crystals have also been discovered. In addition, supramolecular host crystals including guests are likely to develop elasticity (Figure 6d). Ghosh and Reddy [13] reported elastic organic cocrystals formed from caffeine and 4-chloro-3-nitrobenzoic acid in methanol [13]. The guest methanol molecules in the cocrystal contribute to the elastic bending flexibility, which is lost upon desorption of methanol. This result indicates the importance of guest solvent molecules to evolve the elasticity. From this point of view, the supramolecular crystals developed by Ono et al. [54] are likely to periodically contain various solvents, resulting in various properties.

![Figure 6. (a) Schematic illustration of applied stress for the elastic organic crystals. (b) Illustration of face-to-face slip-stacking of planar conjugated molecules. (c) Illustration of zig-zag packing with intermolecular halogen-halogen interactions. (d) Illustration of supramolecular host crystal including solvents.](image)

4. Detailed Deformation of Elastic Organic Crystals

Elongation and contraction are commonly observed with elastic bending deformation of elastic organic crystals. From observation of the crystal tip, it was found that the outer side elongated and the inner side contracted (Figure 7a). The elongation and contraction in the bent form are the same as the deformation caused by bending of rubber (Figure 7b). This is common deformation behavior for elastomers, and the elongation and contraction ratio of crystals can be calculated from this curvature.
The bending deformation of a plastic material results in a different crystal tip compared with the case of elastic materials (Figure 7c). Elongation and contraction do not occur in plastically deformable organic crystals because of slipping between the crystal layers. Thus, the strain of the elastic organic crystals ($\varepsilon$) is calculated by the following formula:

$$\varepsilon = 2dr,$$

Figure 7. (a) Schematic illustration of bending-relaxation of elastic organic crystals. (b) Photograph of straight and bent rubber. (c) Illustration of the difference between elastic and plastic bent materials. Reproduced from [19] with permission of American Chemical Society, copyright 2017.

Because such crystal deformation causes a change in the crystal structure, it is considered to affect the results of structural analysis and physical property measurement. With the development of light-emitting elastic organic crystals, the author first discussed the effect of deformation on the physical properties from the PL spectrum. This will be described later. Conversely, Worthy et al. [55] found that there is a qualitative difference in the crystal structure by investigating from elongation at the outside to contraction at the inside by focusing the beam in X-ray structural analysis of the bent copper acetylacetonate, Cu(acac)$_2$, crystal. The author proposed a facile method for investigating nanostructure changes of flexible organic crystals by using readily accessible X-ray equipment [56]. X-ray diffraction (XRD) with a curved jig, which applied macroscopic stress–strain (%), revealed reversible and quantitative crystal structure changes under bending stress and relaxation. Importantly, the method provides a way to quantitatively measure reversible structural changes without synchrotron X-ray analysis. In addition, Kenny et al. [57] discussed the relation between the magnetic properties and the bending deformation of this crystal. That is to say, elastic deformation is capable of producing a difference in the crystal structure and physical properties.

Because various mechanical deformations are attractive, it is possible to discover various applications by realizing not only flexibility, but also wearability. The crystals mechanically deform from symmetrical natural form to unnatural non-symmetrical shapes. For the first time, the author discovered not only bending, but also coiling and twisting of elastic organic crystals (Figure 8). Although this crystal showed various deformation behaviors, the deformable behavior differed depending on the crystal structure. This is because the molecular orientation differs for each crystal,
but it is very interesting that the mechanical deformation behavior can be controlled by the arrangement. In addition, this deformation behavior is observed macroscopically, but in the future it is desirable that the change is microscopic.

Figure 7. (a) Schematic illustration of bending-relaxation of elastic organic crystals. (b) Photograph of elastically bending. (c) Photograph of elastically coiling. Reproduced from [15] with permission of Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, copyright 2016.

Poisson’s effect is the ratio of the strain generated in the direction perpendicular to the stress to the strain generated in the stress direction when stress is applied to the body within the elastic limit [21]. In addition, when the crystals are stretched with a jig, changes due to such deformation occur. Poisson’s effect of organic crystals is derived from deformation of the crystal lattice. Unlike general elastomers, it is expected that the amount of change differs depending on the direction based on the anisotropic arrangement of the molecules (Figure 9). Therefore, a unique Poisson’s effect with a densely arranged molecular arrangement is shown. The calculated Poisson’s ratio ($\nu$) is defined as the ratio of the change in the width per unit width of the material (e.g., plastic or metal) to the change in its length per unit length as a result of strain. For common materials, $\nu = 0.2–0.5$ because of the wide contraction as the material stretches. The Poisson’s ratio is calculated by the following formula:

$$ v_b = \frac{\varepsilon_b}{\varepsilon_a}, \quad v_c = \frac{\varepsilon_c}{\varepsilon_a}, $$

Figure 8. (a) Photograph of elastically bending. (b) Photograph of elastically coiling. (c) Photograph of elastically twisting. Reproduced from [15] with permission of Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, copyright 2016.

Figure 9. Schematic illustration of stretching stress for the elastic organic crystals. Relationships between strain and Poisson’s ratio. Reproduced from [21] with permission of Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, copyright 2020.

The $\nu$ values of the (011)- and (001)-faces of the crystal of 9,10-dibromoanthracence 6 induced by elongation of the long axis ($\Delta\varepsilon_a$) were determined to be 0.243 and 0.057, respectively (Figure 10a) [21]. Thus, the (011)-face direction is more easily changed than the (001)-face
direction. Therefore, the macroscopic anisotropic deformation of an elastic organic crystal can be observed. Conversely, density functional theory (DFT) simulation of the crystal structure suggested that the width lengths of the $b$ and $c$ axes decreased upon elongation of the $a$ axis. DFT simulations supported these results. The lengths of the $b$ and $c$ axes were predicted to increase upon contraction of the $a$ axis. The change of the $c$ axis was larger than that of the $b$ axis, which is consistent with the experimental results. Thus, the change in Poisson's ratio of the $c$ axis is larger than that of the $b$ axis. Simulations of the crystal not only supported this result, but also revealed changes in the intermolecular packing (Figure 10b). Interestingly, this structural change can be investigated experimentally. 1D X-ray diffraction (XRD) measurements of the crystal under applied elongation stress with a (011)-face-up setup geometry gave microscopic insight into the contraction of the short axis of the crystal (Figure 10c). Under the original straight-shape state, two strong diffraction peaks at $2\theta = 5.577^\circ$ and $11.197^\circ$ were observed (Figure 10d,e). These are correspond to $d$ spacings of 15.8465 and 7.9023 Å arising from the (001) and (002) planes of the single crystal. The observed values of the $d$ spacings were consistent with those calculated from the single crystal data of 6. Under the application of elongation stress, the diffraction peaks shifted to the larger $2\theta$ region (Figure 10d,e), which suggested that the lengths of the layer spacings of the (001) and (002) planes decreased owing to contraction of the $c$ axis upon elongation of the $a$ axis, which was also observed in macroscopic deformation. The diffraction peak from the (001) plane of $5.613^\circ$ ($d = 15.7449$ Å) under elongation stress. The contraction ratio was 0.64\%. When the elongation stress was released, the XRD peaks almost returned to their original positions, which indicated that the shape of the crystal lattice was also recovered (Figure 10d,e). This result suggests that reversible macroscopic crystal shape deformation induced microscopic crystal lattice deformation.

Figure 10. (a) Anisotropic Poisson’s effect. Schematic illustration based on the results of macroscopic observation of the elastic crystal of 9,10-dibromoanthracence (6) crystal. (b) Illustration of the simulation calculation results. Simulation of crystal structure under stretching deformation. (c-e) 1D X-ray diffraction patterns of original (black), elongated (red), and relaxed (blue) elastic 9,10-dibromoanthracence crystals. Reproduced from [21] with permission of Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, copyright 2020.
5. Unique Properties of Elastic Organic Crystals: Mechanically Induced Shaping into Perfect Crystal Fibers

Crystals of π-conjugated molecules have attracted much attention owing to their potential applications in organic optoelectronic devices [58–61]. The macroscopic shapes of the materials are important for various organic device applications and depend on bottom-up fabrication processes [58–61]. Consequently, it is difficult to control their shapes. Top-down shaping is a practical method for crystal shape control (i.e., forming small fine crystals from larger crystals), but it is only feasible for flexible materials. Typical flexible materials, such as polymers, are of great interest because their flexibility allows various shapes to be formed by facile mechanical shaping. However, unlike flexible polymer materials, applying stress to common less flexible organic crystals generally causes them to disintegrate into powders and cracked small crystals.

Thermal- or photochemical-stimulus-triggered splitting deformations of organic crystals into small or fine crystals (e.g., salient effect) are very interested in crystal engineering [62–64]. However, these deformations randomly occur at crystal defects and are thus not suitable for top-down-controlled crystal shaping method. Laser fabrication of microcrystals into nanoparticles is a common top-down shaping approach. However, this method can only produce nanoscale crystals. Mechanical shaping is one of the ideal process for fabricating organic devices, but the brittleness of organic crystals makes it difficult to produce the exact shapes that are required for use in organic devices. However, if large-scale organic crystals (i.e., greater than micrometer scale) could be endowed with elastic bending flexibility and toughness, the bulk crystals could be easily processed into various fine shapes, such as fibers and films, by mechanical shaping.

Mechanically induced shaping of organic single crystals is one of an undeveloped area of research [17,18]. The author has described the mechanical splitting of the elastic organic crystal of 1, which shows fibril lamella crystal morphology (Figure 3), and a facile shaping method for centimeter-scale of elastic organic crystals into various fine crystalline fibers (~50 μm thickness, ~150 μm width, and ~25 mm length) (Figure 11a) [17,18]. The produced fibers maintained their original crystal structure and optical properties (i.e., quantum efficiency and elastic flexibility). Thus, these long, fine and flexible photoluminescent organic crystal fibers would show potential for optoelectronic applications. Moreover, crystalline films (2D crystal) could be fabricated using the Scotch tape method like a synthesis of graphene. Elastic organic crystals based on fibril lamella structure (Figure 3) provide a new approach for fabrication of crystal fibers and films (top-down synthesis of supramolecular one-dimensional and two-dimensional materials). In addition, mechanically induced shaping of elastic organic crystals with similar crystal morphologies to 1 and other elastic crystals (1,4-bis(2-thienyl)-2,3,5,6-tetrafluorobenzene 2 and copper acetylacetonate) which also show fibril lamella crystal morphologies can be performed.

![Figure 11. Cont.](image-url)
was observed (Figure 11e). In other words, a perfect crystal fiber in which the original crystal properties (Figure 11b). More interestingly, the (010) and (001) faces of the crystal before shaping showed sky (\(\lambda = 502\) nm) of the (001) face were observed because the (010) and (001) faces of the crystal have different directional molecular alignment orientation (Figure 11b). More interestingly, the (010) and (001) faces of the crystal before shaping showed sky blue and green PL, respectively (Figure 11c). A green PL line was observed when the crystal of 1 was cut along its length using a knife (Figure 11c). The shaped crystal showed green PL of the (001) face in the cross-section (Figure 11c).

Spectroscopic measurements and 1D X-ray analysis have been performed to understand the crystal structural features before and after mechanically induced shaping of the crystals. From absorption and PL spectral measurements, it was found that there was no remarkable change in the optical properties of the crystal and the fiber. However, grinding caused a change in the spectrum [37]. In addition, a comparison of the obtained fiber and the crystal before shape processing by XRD measurement showed that there was no change in the structural pattern. From this result, the physical properties and structure were maintained after machining. When the crystal fiber (Figure 11d) changed its direction on the substrate and a powder XRD pattern was recorded, a pattern derived from each lamella interval was observed (Figure 11e). In other words, a perfect crystal fiber in which the original crystal properties were transferred by crystal processing was obtained.

The phenomenon whereby an organic crystal mechanically breaks into a specific shape has been observed [62–65]. However, there has been no research on processing such an organic crystal to obtain a single crystal with a desired shape. Therefore, it can be considered that a very new phenomenon has been revealed from the aspect of crystal engineering. In addition, from the viewpoint of the fiber materials, it is noteworthy that a completely new material was produced. Therefore, there have been several examples of low molecular weight fiber growth. Because it is more difficult to adjust low molecular weight fiber material than high molecular weight fiber, the former fiber has attracted attention. However, it is difficult to grow a crystal without branching, and there is no example of a fiber that can be considered to be a perfect crystal. Therefore, I believe that fibers obtained by processing organic crystals are expected to become new fiber materials.

6. Unique Properties of Elastic Organic Crystals: Mechanically Induced Photoluminescence Change

The most interesting character of the light-emitting organic crystals is the deformation-induced photophysical property changes (called mechanochromism and mechanofluorochromism) [19–21]. The molecular packing and intermolecular interactions in light-emitting crystals are perturbed or...
changed by external mechanical forces (e.g., shearing, grinding, tension, and hydrostatic pressure), which can cause a change in the light-emission of the crystals. There have been few reports of reversible color and PL changes under application and release of mechanical stress (or pressure) [66–68]. Consequently, flexible and tough crystals of π-conjugated molecules are candidate materials for reversible mechanoochemical sensors (Figure 12).

The author has also investigated the crystal of readily available 4,7-dibromo-2,1,3-benzothiadiazole 5 [19]. The centimeter-scale of needle-shaped single crystal of 5 bent under applied stress and rapidly reverted to its original crystal shape upon relaxation. Moreover, the crystal showed greenish blue PL, while under application of bending stress near its elastic bending limit (about 30°) the PL color changed to sky blue. The unique mechanical and light-emitting properties of the crystal referred to as mechanofluorochromism are based on the mechanical bending–relaxation. The change in the PL is probably due to a change of the center-to-center separation length in the face-to-face slip-stacked molecular packing, similar to the packing change in the crystal of 9,10-dibromoanthracence (6) (Figure 10) [21]. The molecular packing of 5 shifts from stable to metastable under application of mechanical bending stress, resulting in a blue-shifted PL band. Relaxation of the bent crystal of 5 allows for the recovery of the stable crystal packing.

To estimate the change in the structure and physical properties due to bending in detail, it is necessary to focus on a very small region of the crystal. For example, μ-focused X-ray analysis using a synchrotron can analyze the deformed part of the crystal in detail (Figure 13). In addition, the changes outside and inside the bent crystal can be observed [55]. Thus, it is possible to confirm the changes in the physical properties due to deformation of the crystal by performing μ-focused spectroscopic analysis of the outside and inside of the bent crystal.

Figure 12. (a) Schematic illustration of elastically bending deformation-induced photoluminescence change. (b) Schematic illustration of elastically stretching deformation-induced photoluminescence change.

Figure 13. Schematic illustration of μ-focused X-ray analysis.
The stress-induced changes in the photophysical properties, that is, the deformation-induced PL changes of the crystal, have been successfully observed by spatially resolved µ-PL (µPL) measurement (Figure 14a) [21]. The PL spectra of the original crystal without stress are shown in Figure 14c,e, and the PL maximum wavelength ($\lambda$) was 500 nm. When bending stress was applied to the crystal, elongation and contraction simultaneously occur at both the outside and inside position sides of the curvature. On the other hand, no strain occurred at the center position. PL measurement of the microscopic areas—inside, center, and outside positions—of the bent crystal was performed using a spatially resolved µ-photoluminescent measurement system, µPL (Figure 14b–g). The PL spectra of the inside, center, and outside positions of the straight crystal revealed that $\lambda = 500$ nm (Figure 14b,c). However, a red-shift ($\lambda = 506$ nm) and a blue-shift ($\lambda = 497$ nm) of the PL bands, respectively, compared with that of the center position ($\lambda = 505$ nm) were clearly observed under bending strain of $\varepsilon = 1.3\%$ (Figure 14d,e). These observations suggested that an elongation deformation-induced red-shift and a contraction deformation-induced blue-shift indeed occurred at the outside and inside positions of the bent crystal, respectively. The bending strain induces slipping of the $\pi$-plane of face-to-face slip-stacked structure to increase the J-aggregate character at the outside of the crystal and H-aggregate character at the inside of the crystal, which would lead to the red-shift and blue-shift, respectively. In bending–relaxation, PL spectrum changes similar to the outside of the bent crystals were observed by crystal elongation (Figure 14f). Upon elongation along the $a$ axis with $\varepsilon_a = 1.0\%$, a clear red-shift of the PL band ($\lambda = 505$ nm) was observed (Figure 14g, red line). The PL band returned to the original crystal shape when the elongation stress was released (Figure 14g, blue line). A larger red-shift ($\lambda = 511$ nm) was also observed upon elongation along the $a$ axis with $\varepsilon_a = 2.0\%$ (Figure 14g, green line). The spectral changes were reversible due to elastically changes in the crystal structure. This deformation-induced PL change probably resulted from the molecular sliding in the molecular packing.

**Figure 14.** (a) Schematic illustration of specially resolved µ-photoluminescent measurement system. (b) Illustration of straight crystal. (c) PL spectra of the straight 9,10-dibromoanthracence crystal at outside, center, and inside. (d) Illustration of bent crystal. (e) PL spectra of the bent 9,10-dibromoanthracence crystal at outside, center, and inside. (f) Illustration of crystal stretching. (g) Reversible change of PL band of the 9,10-dibromoanthracence crystal. Reproduced from [21] with permission of Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, copyright 2020.
Twisted elastic organic crystals are thought to be able to give chirality to the crystal structure. The measurement of circular dichroism (CD), circular PL dichroism (CPL), and second harmonic generation (SHG) for the mechanically deformed elastic organic crystal will enable an investigation regarding the creation of chiral organic crystals.

7. Unique Properties of Elastic Organic Crystals: Flexible Optical Waveguide

The optical waveguide (OWG) has been investigated as a tool for capturing light and transmitting the light, but there is no flexible and highly efficient material because of the trade-off relationship of each material. The characteristics of the materials that have been applied as OWGs are summarized in Table 1 [69]. The refractive index, which is important for this tool, is one of the most important parameters for optical materials. Essentially, the refractive index values are large for high density materials. Inorganic crystals have less flexibility and tunability of optical properties, but often exhibit sufficient characteristics for OWGs [69]. In polymer chemistry, attention is often paid to the sizes of the atomic and molecular units to control or improve the refractive index. For π-conjugated polymer fiber, a flexible fiber can be prepared by the electrospray method or a similar method [70]. There has been no report containing a flexible waveguide using a π-conjugated polymer fiber, but because there are many defects inside and outside the material, in addition to low performance, the little phenomenon is observed [70]. In addition, organic-inorganic hybrids such as fluorescent lanthanoid metal-organic frameworks and a mixture of fluorescent lanthanoid coordination polymers and other polymers are known as new waveguiding materials [71]. Such new crystal and amorphous polymer materials show potentials for high-performance that differ from the summary in Table 1. Therefore, it can be considered that an organic crystal with a close-packed structure of organic molecules has a very high refractive index and thereby is a suitable material. In addition, most of the reported optical waveguides in organic materials chemistry are organic crystals because they have the advantage that there are few molecular defects, such as amorphous domains, inside and outside the material [69]. However, as mentioned above, since many organic crystals are inflexible, flexible OWGs cannot be made.

Table 1. Comparison of inorganic crystals, polymer solids, and organic crystals in terms of photoluminescent waveguide applications.

| Materials                  | Inorganic Crystals | Polymer Solids | Organic Crystals   |
|----------------------------|--------------------|----------------|--------------------|
| Preparation methods        | Vapor-phase deposition | Template polymerization, Electro-spinning | Vapor-phase deposition, Self-assembly |
| Crystallinity              | Single crystal     | Amorphous, Less-crystalline | Single crystal |
| Surface defects            | Less of defects    | Unavoidable defects | Less of defects |
| Interactions               | Covalent bond, Ionic bond | Weak interactions ¹ | Weak interactions ¹ |
| Photo-stability            | Relative stable    | Decomposition   | Bleaching          |
| Optical properties         | Excellent but not easy tunable | Tunable ² | Tunable ³ |
| Refractive index, n        | >2                 | 1.5–2.0         | >1.5               |
| Flexibilities              | Less flexible      | Flexible (viscoelastic) or brittle | No flexibility |
| Waveguide types            | Passive and active | Passive and active | Active |

¹ van der Waals force, π-π interactions, hydrogen bonds; ² by modification of the substituents; ³ by design and synthesis of molecules and crystal structure.

The waveguide characteristics differ depending on the shape and molecular orientation of the luminescent organic crystals (Figure 15a,b). To investigate this, it is necessary to focus on a very small area of the crystal, irradiate the laser, and detect the light emitted from the edge of the organic crystal. For example, the needle-shaped crystal of 2,5-dimethoxybenzene-1,4-dicarbardehyde show waveguide ability (Figure 15c) [72]. To measure the waveguide performance of the organic crystal, the loss
The optical loss coefficient of the waveguides was determined by measuring the spatially resolved PL spectra through local excitation of the crystal. When excited by a focused laser at different positions along its length, the green colored emission was observed from the edge and both ends of the crystal, irrespective of the laser-focused position. This is a typical characteristic of OWG. The spectral intensity and band profiles of the laser light excitation did not substantially change with the position along the crystal. However, the PL intensity at the end of the crystal almost exponentially decreased with increasing distance between excited site and emitting tip (Figure 15d). The optical loss coefficient, $\alpha$, by single exponential fitting ($I_{in}/I_{out} = A \exp(-\alpha X)$) where $X$ is the distance between the excited site and the emitting tip were calculated by recorded PL intensities at the excited site ($I_{in}$) and emitting tip ($I_{out}$). The $\alpha$ value was thus calculated to be 0.00120 dB/µm (Figure 15e). It should be noted that the $\alpha$ value is relatively high for this reported material. The $\alpha$ value and red-shifted feature are mainly affected by reabsorption during propagation of the light along the crystal. In the short wavelength region, the PL band overlaps with the absorption band in the solid state and the excitation spectrum of the crystal, resulting in a high $\alpha$ value. In the long wavelength region, the PL and absorption spectra of the crystal are well separated, which is beneficial for propagating light in the crystal, resulting in a low loss coefficient. This result gave a red-shift of the band and a very narrow full width at half-maximum (FWHM) (Figure 15d).

The organic crystals exhibited unique OWG characteristics (Figure 16) [20]. The refractive index are very important factors for the performance and a small amount of surface defects is negative factor against the OWG [69–77]. Organic crystals of light-emitting $\pi$-conjugated molecules are suitable OWG materials compared with flexible light-emitting $\pi$-conjugated polymer fibers, but their crystals are generally less flexible. Thus, light-emitting elastic organic crystals are considered to be suitable or...
new for high performance and flexible OWG materials (Table 1). By excitation of the straight original crystal of 3 with a focused laser (405 nm) at different positions, reddish orange colored emission was detected from the end of the straight crystal of 3, irrespective of the excitation position (Figure 16a). This is a typical result of OWG materials [69]. The elastic strain ($\varepsilon$) value for the crystal of 3 was calculated to be 1.9% (Figure 16b). The PL spectra of the straight and bent crystals at the illuminated position (black dotted line) and end of the crystal (solid line) are shown in Figure 16c,d. The PL band at the end of the crystal showed a peak at 597 nm with a narrower FWHM (34 nm) than at the illuminated position (573 nm, FWHM = 56 nm). The spectral profile did not substantially change with the illumination position, although the PL intensity at the end very slightly decreased with increasing distance (Figure 16c,d). The PL intensities at the illuminated position ($I_{in}$) and end of the crystal ($I_{out}$) were measured to calculate the optical loss coefficient $\alpha$ values by measuring the spatially resolved PL spectra and fitting by a single exponential curve. The $\alpha$ values were calculated to be 0.043 (the straight crystal) and 0.047 dB/mm (bent crystals), respectively (Figure 16e). It is noteworthy that OWG applications with various physical properties have been reported for various light-emitting elastic organic crystals by Zhang and co-workers [75–77]. These are good showcases for the great potential of such crystals. The author expects that more diverse applications will be developed in the future.

8. Conclusions

Here, the author described the deformation-induced structures and changes to the physical properties of organic crystals that behave with enthalpy elasticity. The structural features and material possibilities of flexible and functional organic crystals, especially elastic organic crystals of $\pi$-conjugated...
molecules, have been discussed. Recently, flexible organic crystals have become one of the active areas in crystal engineering. Therefore, various challenges have been proposed to discover these crystals and methods for their investigation. A design of the organic molecules for such materials (supramolecular synthon) and its applications (e.g., deformation-induced photoluminescence changes, conductivity, optical waveguides, and organic devices) would be accepted. I think that more detailed information of regarding the structure and deformation-induced changes in the physical properties remain. The promotion of mechanical property measurement methods, including nanoindentation [78], calculation simulation such as energy frameworks [79], and other effective crystal investigation methods will provide more information in this area. In the future, more accurate analysis and the application of new ideas and technological innovation will be required. In addition, flexible and functional organic crystals have not been utilized yet functioned as flexible organic devices. Verifying the combination of flexible organic crystals with various substrates will also be an important issue.

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