SHORT COMMUNICATION

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Flexible Organic Single Crystal with Elastic Bending and Plastic Twisting Capabilities

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n INTRODUCTION

Organic single crystals have found wide-spread applications in smart materials,[1] optical waveguide devices,[2] photonic applications,[3] lasers,[4] OLED materials, and so on. Because of the strong interaction of molecules inside the crystal, it tends to be hard and brittle. A slight pressure can destroy the crystal, rendering it useless. In recent years, the emergence of flexible crystals (elasticity and plasticity) has brought new light to the application and development of crystalline materials.[5] Extensive studies have revealed that isotropic molecular packing (existing a large number of weak and dispersed interactions) is the essential reason for the elasticity of crystals. On the contrary, anisotropic molecular stacking and low-energy slip planes dominated the plasticity of the crystals.[6] With the development of flexible crystals, researchers have achieved the fusion of elastic and luminescent properties of crystalline materials, opening up their applications in flexible luminescent materials. For example, Zhang's team has developed waveguide applications for flexible crystals for the first time, triggering extensive research on optical waveguides for flexible crystals.[7] Hayashi group has explored the bending-induced fluorochrome property of flexible crystals, again opening new windows for flexible crystal applications.[8] However, the above-mentioned flexible crystals exhibit only a single elastic or plastic property because the elasticity and plasticity of crystals often do not coexist. To the best of our knowledge, few reports have combined elastic and plastic properties in the same crystal. Zhang and his collaborators have obtained single flexible organic crystals based on (E)-1-(((3,5-dimethoxyphenyl)imino)methyl)-naphthalen-2-ol, which exhibited elastic bending and plastic twisting properties. Then, the potential of the crystals for application in polarized rotators was explored.[9] Hao et al. have reported organic crystals based on 9-anthraldehyde with plastic twisting, two-dimensional elastic bending, and light-induced bending properties.[10] The design of molecules and the acquisition of organic crystals with elasticity (and) plasticity remain an urgent problem to be explored and solved. It is well known that the degree of anisotropy/isotropy can essentially be fine-tuned by regulating interactions such as halogen bonding, hydrogen bonding, C-H···π and π···π interactions.[11] Benzil contains two carbonyl groups, which easily form intermolecular C-H···O hydrogen bonds. Therefore, the introduction of oxygen atoms contributes to the elastic nature of the crystal. C-H···Br has a long hydrogen bonding distance and a low interaction energy. When the molecule contains bromine atoms, it is easy to form a low-energy slip plane. Therefore, in this article, we combined the above advantages and selected 1,2-bis(3-bromophenyl)-ethane-1,2-dione (**BBPED**) for study. Fortunately, needle-shaped crystals based on it have two-dimensional elastic bending and 3-dimensional plastic twisting properties (Figure 1). We hope that **BBPED** can become a typical model and provide new ideas for the design of elastoplastic molecular crystals.

n RESULTS AND DISCUSSION

Crystal Elasticity and Plasticity Testing. The absorption peaks of **BBPED** in cyclohexane at 262 nm (HOMO-5 → LUMO) and 301 nm (HOMO-3 → LUMO) were derived from the molecular π···π transition (Table S1 and S2). In the meantime, the corresponding emission peaks were located at 473 and 502 nm (Table S1, Figure S1). Cyclic voltammetry measurements and quantum chemical calculations were performed to further understand the molecular properties (Table S1, Figure S2). As depicted in Figure S2, the LUMO electron density of **BBPED** was distributed in the benzil portion, indicating that the benzil part is more electron deficient than the bromine atom. Furthermore, due to the *J*-aggregation of the molecules, both the absorption and emission spectra in the microcrystals were significantly redshifted compared to the solution (Figure S3).[2] By slow volatilization, we prepared the centimeter-scale needle-shaped crystals from a mixed solution of dichloromethane/petroleum ether (*V*/*V* = 4/8, mL). As shown in Figure 1b-c and Figure S4, the average lifetime of the crystal at 545 nm was 0.476 ms, indicating that it exhibited room-temperature green phosphorescence emission. Using the three-point bending test method, we applied mechanical force to the front face ((002) face) of the crystal which could undergo reversible elastic bending (Figure 1d, Figures S5-S6, Video S1). Subsequently, we further applied downward pressure to both ends of the crystal (002) face using a tweezer. With the tip of a needle, a backward pulling force was applied to the side ((200) side) of the crystal that underwent a three-dimensional plastic twisting (Figure 1d, Figures S5-S6, Video S1). Interestingly, the twisted crystal also had excellent elastic bending properties (Figure 1d, Figures S5-S6, Video S1). A crystal with a size of 5.5mm × 0.13mm × 0.03mm was selected for the torsion experiment. Owing to the small size, we could only complete three twist points. Subsequently, we performed a three-point bending experiment on the torsioned crystal. Even after 45 times of bending, the crystals did not break, indicating excellent elasticity (video S2). High-definition microscope photos of the twisted crystal showed no obvious fracture in the deformed position, which means the twisting had not damaged the crystal (Figure S7). Figure S5d shows the SEM pictures of the crystal, the

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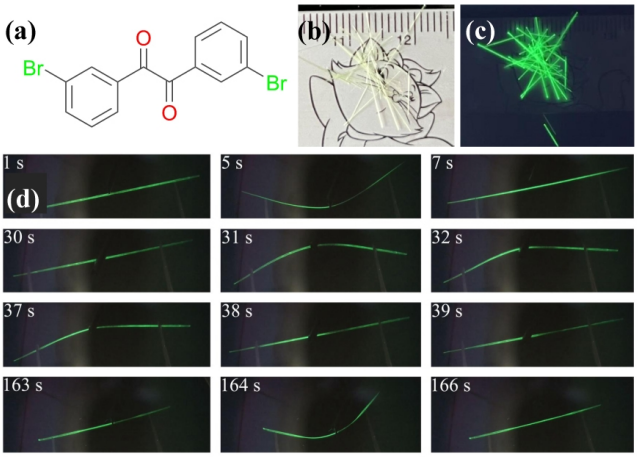

Figure 1. Molecular structure of **BBPED** (a); Images of **BBPED** under visible light (b) and 365 nm light (c); The crystal elastic bending (1s-7s), plastic twisting (30s-39s) and elastic bending after twisting (163s-166s) pictures (d, the time in the picture corresponds to that in **video S1**).

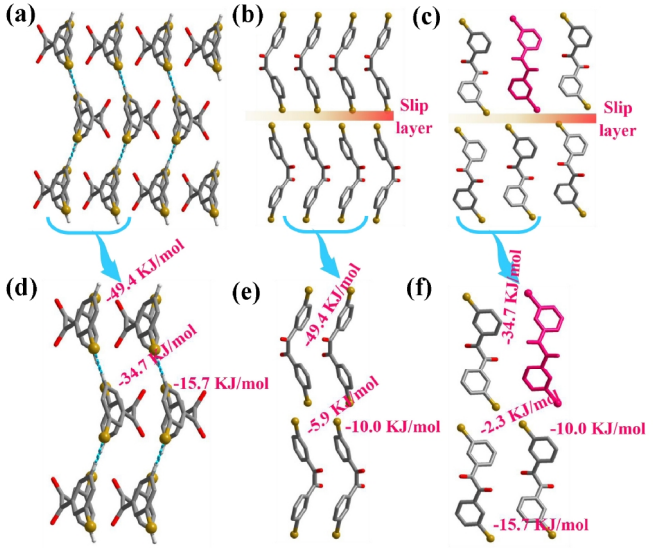

Figure 2. The total energy frame of the interaction and the corresponding energy data of the **BBPED** crystal in (002) (a), (200) (b) and (020) (c) planes; energy framework and energy of the interactions (d-f). Color code: C, gray; O, red; H, white; Br, yellow. Some hydrogen atoms have been removed for clarity.

BFDH morphology of which was simulated using the CSD-particle feature of mercury software based on the CIF file (CCDC deposit 2194270). By comparing the SEM images with the BFDH morphology (Figures S5a-S5c), we could see that the front and side faces of the crystal are (002) and (200) surfaces, respectively. The PXRD data of the crystal clearly show the diffraction peak of the (002) plane (Figure S8). Among them, (002) face elastic modulus/hardness (nanoindentation test) are 5.58±0.54 GPa and 0.16±0.02 GPa, respectively, suggesting the crystals have good elasticity (Figure S9, Table S3).[2] The (200) face of the crystal is too narrow to obtain accurate indentation data.

Single-Crystal Data Analysis. To explore the nature of elastic bending and plastic twisting of **BBPED** crystals, we analyzed the molecular structure and stacking inside the crystals using single-crystal data, energy frameworks, and Hirshfeld surface maps. Figures S10a and S10d show the intermolecular interactions and molecular stacking on the (002) face, respectively. There are C-H···π (3.613 Å) and weak π···π (4.099 Å) intermolecular interactions between the molecular planes. Also, intermolecular forces C-H···O (2.898 Å), C-H···π (3.205 Å) and C-H···Br (3.395 Å) are observed. The above interactions promote intermolecular interconnections that dominate the elastic properties of the (002) face. As shown in Figures S10b and S10e, there are C-H···O (3.671, 3.015 Å), C-H···π (3.499 Å) and π···π (4.099 Å) interactions between the molecular planes. The existence of C-H···Br (3.320, 3.571 Å) interactions between the upper and lower molecules promotes the plasticity of the crystal. Similarly, by observing the (020) face of the crystal, C-H···O (2.538 Å, 2.560 Å) intramolecular hydrogen bonds and C-H···Br (3.437 Å, 3.320 Å), C-H···π (3.477 Å, 3.078 Å, 3.205 Å, 3.607 Å), C-H···O (2.637 Å) and Br···Br (3.731 Å) intermolecular interaction (Figure S10c, Figure S10f) are found. Analysis of the 2D fingerprint plot and the Hirshfeld surface showed that the H-Br, O-H, C-H, C-C and Br-Br interactions account for 71.3% of all interactions in the crystal (Figures S11-S12). Although the percentage of H-H reaches 22.1%, its contribution to the elastic and plastic properties of the crystal is small.[2] Therefore, the introduction of bromine and oxygen atoms facilitates the formation of crystal elasticity and plasticity.

It could be seen that the energies of the intermolecular interaction on the crystal (002) face are -15.7, -34.7 and -49.4 kJ/mol (Figure 2a and 2d). These intermolecular interactions could buffer the mechanical pressure and thus produce elasticity. On the crystal (200) and (020) faces, the intermolecular interaction energies between the upper and lower layers are -5.9, -10.0 and -2.3 kJ/mol (Figures 2b-c, Figures 2e-f). These energies are significantly lower than those in the (002) plane, so that the molecular layers could slip significantly under the action of mechanical forces.

Therefore, we speculated that the mechanism of elastic and plastic crystal bending is as follows.[12] 1) When mechanical forces are applied, the C-H···π, π···π, C-H···O and C-H···Br interactions in the crystal (002) plane could buffer the forces and produce elastic deformation. 2) In the crystal (200) plane, there is only C-H···Br interaction between the upper and lower molecular layers and the corresponding energy is too low. When the direction of the force is appropriate, the molecular layer could slip, resulting in plastic deformation. After slipping, the original intermolecular interactions are not completely destroyed. At the same time, new intermolecular interactions might be formed, and therefore, the crystal still exhibited excellent elasticity.

The crystals had good elastoplastic, luminescent and thermal stability properties (Figure S13). Therefore, it has a broad application prospect in light-wave transmission. For this, we chose a suitable crystal and twisted it. Under 365 nm light excitation, there are obvious bright spots on both ends of the crystal, indicating good light transmission characteristics (Figure S14 and Video S3). Effective transmission of light waves from one-dimension to three-

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dimension could be achieved. In the meantime, upon excitation, the torsion point of the crystal had no prominent bright spot (light leakage), which also showed that the twisting crystal had not broken, further indicating the excellent plasticity of the crystal. The crystal has excellent elasticity, plasticity and light transmission properties. These results indicate that the crystals have potential applications in optical waveguide devices, waveguiding biomaterials, fiber-optic transducers, semiconductors, etc.[2,13-15]

n CONCLUSION

In summary, we obtained **BBPED**-based needle-shaped crystals. Luckily, the crystal (002) face could undergo significant elastic bending under mechanical force. Subsequently, the crystal underwent plastic twisting by applying appropriate pressure to the (200) face. Fortunately, the twisted crystals could still undergo elastic deformation, indicating the mutual compatibility of elasticity and plasticity. The elastic modulus/hardness of the (002) face are 5.58 ±0.54 and 0.16±0.02 GPa, respectively, indicating good elasticity for the crystals. Single-crystal data and energy framework analysis indicated that isotropic molecular packing and low-energy slip planes between the molecular layers were essentially responsible for the elasticity and plasticity of the crystal. Meanwhile, the crystal has good light transmission characteristics, and thus it could achieve effective light transmission from one- to three-dimension. Our findings suggested that elastic and plastic properties could be combined in the same crystal through effective molecular design, providing new ideas for subsequent studies.

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n COMPETING INTERESTS

The authors declare no competing interests.

n ADDITIONAL INFORMATION

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