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Highly Elastic Organic Crystals for Flexible Optical Waveguides

Huapeng Liu, Zhuoqun Lu, Zuolun Zhang,* Yue Wang, and Hongyu Zhang*

Abstract: The study of elastic organic single crystals (EOSCs) has emerged as a cutting-edge research of crystal engineering. Although a few EOSCs have been reported recently, those suitable for optical/optoelectronic applications have not been realized. Here, we report an elastic crystal of a Schiff base, (*E*)-1-(4-(dimethylamino)phenyl)iminomethyl-2-hydroxyl-naphthalene. The crystal is highly bendable under external stress and able to regain immediately its original straight shape when the stress is released. It displays bright orange-red emission with a high fluorescence quantum yield of 0.43. Intriguingly, it can serve as a low-loss optical waveguide even at the highly bent state. Our result highlights the feature and utility of "elasticity" of organic crystals.

As a class of organic solid materials, organic single crystals have attracted increased attention in optical/optoelectronic applications, such as optical waveguides,^[1] solid lasers,^[2] fieldeffect transistors^[3] and light-emitting diodes.^[4] One of the current developing trends of optical/optoelectronic technology is the realization of flexibility. However, organic crystals are generally brittle, leading to a serious problem for their application in flexible devices. To make single-crystal materials applicable in flexible devices, the exploration of crystals with both elastic (reversible) bending ability and optical/optoelectronic functions is essential. Although being a challenging target, elastic organic single crystals (EOSCs) have been realized in recent years.^[5] Ghosh and Reddy gave a pioneer contribution to the EOSCs. They reported that needle-like cocrystals comprising of three components display elastic bending under applied stress,^[6] rather than plastic (irreversible) deformation.^[7] Subsequently, based on the study of a series of N-benzylideneanilines, Ghosh et. al. proposed a structural feature of EOSCs: interlocked packing with weak and dispersive interactions in crystal.^[8] Hayashi et. al. reported an elastic crystal of 1,4-bis[2-(4methylthienyl)]-2,3,5,6-tetrafluorobenzene with fluorescence property.^[9] Very recently, the elasticity was observed in macrophage-synthesized biocrystals by Rosania et. al.^[10] All of these works significantly advanced the study of EOSCs. However, the number of known EOSCs is still very limited. Especially, the EOSCs with functions for use in the fast developing optical/optoelectronic technology have not been achieved.

To realize EOSCs with optical/optoelectronic functions, π conjugated molecules with a relatively planar donor-acceptor structure would be a good choice. Such structure on one hand facilitates efficient solid-state emission. On the other hand, it allows the intermolecular π -stacking, which can be

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expanded/compressed to a certain degree and thus serve as a somewhat designable packing feature contributing to the bending property of single crystals.^[10,11] In addition, the π -stacking is usually observed to associate with some fascinating functions of crystalline materials, such as the high carrier mobility and waveguiding capability.^[12]

In our exploration of functionalized EOSCs, we attempted the use of а Shiff base (E)-1-(4-(dimethylamino)phenyl)iminomethyl-2-hydroxyl-naphthalen (DPIN in Figure 1a). The formation of intramolecular hydrogen bond between the OH and CH=N groups is expected because similar interactions have been commonly observed in the crystal structures of analogs compounds.^[13] The hydrogen bond should result in a relatively planar conjugated skeleton for π -stacking. It was found that brightly fluorescent ultra-long EOSCs which are highly bendable under external stress can be prepared using DPIN (Figures 1b and c). Intriguingly, taking advantage of the good elasticity and bright luminescence, the crystal works as a flexible optical waveguide which indicate the possibility of realizing flexible optoelectronics based on bulk singlecomponent organic single crystals.

By layering hexane on the top of a CH₂Cl₂ solution (0.1 M) of DPIN and subsequent solvent diffusion, ultra-long rod-like single crystals were easily obtained. The typical lengths of the crystals were 15–25 mm, and the widths and thicknesses were in the range of 40–200 μ m. Under microscope, a prismatic body of the DPIN crystal with three pairs of parallel prism faces was observed (Figure 1d). Two faces in each pair had nearly identical widths. One pair of the faces was wider than the other two pairs.



Figure 1. Molecular structure of DPIN (a), photographs of the rod-like single crystals of DPIN taken under room light (b) and 365 nm UV light (c), the prismatic crystal body observed under microscope (top: view perpendicular to the widest face, which is white due to the light reflection; bottom: view alone the widest face) and schematic elucidation of the cross-section shape of the crystal (d), and absorption and emission spectra of the DPIN crystal (e).

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Figure 2. Elastic bending under mechanical stress applied through a pair of tweezers: (a) the initial straight crystal with a length of about 11 mm; (b–f) the bending process; (g) the recovery of crystal shape upon removing the stress, and the photographs taken under room light (h) and UV light (i) for a crystal screwed on a glass tube.

Upon applying stress at the two tips of a straight crystal with a pair of tweezers, the widest faces of the crystal were easily bent (Figures 2a–f and S1). A half loop could be formed, without cracking or breaking the crystal. Once the stress was released, the original straight shape was recovered immediately (Figure 2g). The bending-relaxing process could be repeated many times. These results indicate the highly elastic nature of the crystal. The high elasticity is also reflected by the feasibility of screwing the crystal on a glass tube with a diameter of 1.20 mm (Figures 2h and i). Overbending led to the direct cracking of crystal, but not the plastic (irreversible) deformation.

Single-crystal X-ray diffraction analysis indicates that the crystal belongs to the monoclinic space group P2₁/c. One DPIN molecule exists in the asymmetric unit, and there are no solvent molecules within the crystal lattice. As expected, O–H···N hydrogen bond (H···N: 1.77 Å, O–H···N: 148.26°) is formed between the OH and CH=N groups, resulting in a nearly coplanar arrangement of the naphthalene, CH=N and OH moieties (Figure 3a). The C₆H₄ group is twisted out of the CH=N plane by a small angle of 23.07°. Above structural features indicate a relatively planar molecular skeleton, which facilitates the intermolecular π -stacking.

To understand the elasticity, the index of the highly bendable crystal faces was firstly determined through calculating the morphology of DPIN crystal by the software of Materials Studio 8.0 with the crystallographic data as the input information. Based on the crystalline-plane attachment energies, which determine the growth rates of crystalline planes, the crystallization morphology as well as the indexes of the side faces was The calculated morphology reproduced obtained. the experimentally observed prismatic shape of the crystal body (Figure S2). According to the calculation, the two widest faces of the crystal correspond to the (002) plane, and the length direction of the crystal is along the a axis. Therefore, the bending process observed in Figure 2 is the bending of (002) plane along the perpendicular (010) plane.

Figure 3b shows the molecular packing structure viewed down the (010) plane. Infinite $\pi \cdots \pi$ interactions are formed along the *a* axis (red arrows), with an overlapping area between neighboring molecules being about two third of a molecule and a $\pi \cdots \pi$ vertical distance of about 3.44 Å. These $\pi \cdots \pi$ interactions, together with the intermolecular C-H··· π interactions formed between the CH₃ and C₆H₄ groups (dashed green line; H··· π : 2.88 Å), result in the formation of a molecular chain along the *a* axis. Two adjacent molecular chains interact through C-H···O hydrogen bonds between the CH₃ and OH groups (dashed yellow line; H···O: 2.61 Å, C-H···O: 160.78°) to form a chain dimer along the *c* axis. The cross arrangement of chain dimers with the closest inter-dimer distance of about 3.0 Å can be observed.

The elastic bending of the crystal requires the expansion and contraction of the outer and inner arcs, respectively (Figure 3b). As the molecular chains are formed along the crystal length direction (*a* axis), the $\pi \cdots \pi$ interactions within the chains can respond to the expansion of the outer arc by enlarging the $\pi \cdots \pi$ distance and to the contraction of the inter arc by decreasing the $\pi \cdots \pi$ distance. Therefore, these interactions are a key factor for the realization of crystal elasticity. A tiny relative slippage of the adjacent and parallel π -systems along the bending direction, accompanied by the formation of a small angle between these π -systems, should also occur in the bending process to fit the



Figure 3. (a) Structure of DPIN in the single crystal (the dashed pink line represents the intramolecular hydrogen bond); (b) molecular packing structure viewed down the (010) plane along the *b* axis (the red arrows and green dashed line represent the $\pi \cdots \pi$ and C–H $\cdots \pi$ interactions within a molecular chain, respectively; the dashed yellow lines show the C–H \cdots O hydrogen bonds between molecular chains).

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Figure 4. Graphical presentation of the packing-structure variation when the crystal is bent to form a half loop. The short blue lines represent the parallel stacked π -systems within molecular chains. The dashed lines represent the neutral plane. *t* and *L* correspond to the thickness and length of the crystal, respectively, while *d* is the diameter of the inner arc.

curvature of the bent faces (Figure 4). In addition to the infinite π -stacking, the C–H··· π interactions within molecular chains could also serve as a factor that suppress the breaking trend of molecular chains towards expansion and thus benefit the bending resistance of the crystal. Moreover, C–H···O hydrogen bonds within the chain dimers and the cross and close arrangement of chain dimers restrict, respectively, the relative slippage of neighboring chains and chain dimers in the bending process. Therefore, plastic (irreversible) deformation of the crystal which might be caused by such relative slippage^[14] can be avoided during bending. Consequently, the C–H···O hydrogen bonds and the cross and close packing feature also contribute to the high elasticity.

As the expansion and contraction of $\pi \cdots \pi$ distance are closely related to the bending process, one question is if the overexpansion of $\pi \cdots \pi$ interaction directly caused the creaking of the crystal upon overbending. To investigate the question, the expansion and contraction limits of the π ... π distance in our crystal was studied. During the elastic bending process, the expansion ratio of the outer arc and the contraction ratio of the inner arc, relative to the neutral plane with a constant length during the bending process (Figure 4), are equal to each other.^[6] When the crystal is bent to form a half loop, the molecular chains can be expanded/contracted uniformly and the bendingcaused angle between originally parallel and adjacent π systems should be fairly small because of the existence of a huge number of molecules in a molecular chain. In this case, the $\pi \cdots \pi$ distance at the outer/inner arc is approximately expanded/contracted to a degree same as that of the outer/inner arc itself. The extension/contraction ratio (ϵ) of the outer/inner arc can be estimated by the equation of $\varepsilon = t/(d+t)$, where *t* is the thickness of the crystal and d is the diameter of the inner arc (Figure 4 and the Supporting Information).^[8] According to the

equation, the thickest crystal able to form a half loop with a fixed inner-arc diameter corresponds to the largest expansion/contraction ratio of the outer/inner arc. By winding the crystals with different thicknesses on a ballpoint pen refill (external diameter: 4.46 mm) to form a half loop, the largest applicable thickness was determined to be around 103 µm (Figure S3). Correspondingly, the largest extension/contraction ratio of the outer/inner arc of our crystal is estimated to be 2.26% according to the above-mentioned equation. Accordingly, the π ··· π distance is approximately expanded from 3.44 to 3.52 Å at the outer arc and contracted from 3.44 to 3.36 Å at the inner arc when the bending limit is reached. Notably, 3.52 and 3.36 Å are just in the middle of the distance range of normally observed π ··· π interactions (ca. 3.2–3.7 Å).^[15] Therefore, the cracking of the crystal upon overbending seems to be not directly caused by the over-expansion of $\pi \cdots \pi$ interaction.

Due to the relatively small extension/contraction ratio of $\pi \cdots \pi$ distance and the synergic movement of molecules caused by the cooperation of multiple factors, i.e. $\pi \cdots \pi$ interactions, hydrogen bonds and the cross and close stacking of chain dimers, relative arrangement of molecules in the bending process only alter slightly from that of the original straight crystal. This is supported by the existence and elongation of diffraction spots for a bent crystal in the single-crystal X-ray diffraction experiment (Figure S4).^[6] When the external stress applied on the crystal is released, the original packing structure is recovered, as confirmed by the nearly identical cell parameters of the straight crystal and the crystal recovered from the bending experiment. Thus, the morphology of the crystal is restored. The easy recovery of the packing structure in turn supports the slight variation of molecular arrangements in the bending process.

Under UV light, the crystal emits bright orange-red emission. The emission spectrum shows the maximum at 607 nm and a shoulder peak at 563 nm (Figure 1e). A high absolute fluorescence quantum yield of 0.43 was determined for the crystal despite the self-absorption suggested by the overlap between the emission and absorption spectra. Interestingly, the crystal possesses optical waveguiding property, which was initially detected from the brighter emission of the crystal tips than the body when the straight crystal was irradiated with a UV lamp. Further examination indicated that the waveguiding behavior could be realized not only by the straight crystal, but also by the highly bent crystal (Figure 5b). To examine the influence of elastic bending on waveguiding performance, optical loss coefficients (OLCs) of a single DPIN crystal (length: 5 mm) at both the straight and the highly bent (close to a half loop) states were studied. By irradiating different positions of the crystal using the same excitation light of 355 nm laser and collecting the emission spectrum corresponding to each irradiation position at one tip of the crystal, distance-dependent emission spectra were firstly obtained (Figure 5c and d). The emission intensity at the tip decreases gradually when the distance between the tip and the irradiated position is increased, due to the loss of more emitted light for a longer propagation distance. In addition, with increased propagation distance, the emission spectra show a slight redshift because of heavier reabsorption in the overlapping range of the emission and absorption spectra (ca. 530-620 nm; Figure 1e). By fitting the data of Figure 5c and d, respectively, according to literature

procedures,^[16] the OLCs at 615 nm are estimated to be 0.270 dB mm⁻¹ for the straight state and 0.274 dB mm⁻¹ for the bent state (Figure S5). These values are among the smallest OLCs ever reported for organic crystals and comparable to or even better than those of some polymers (Table S3), suggesting the good waveguiding performance for both states of the crystal. Notably, the OLC of the bent state is only slightly higher than that of the straight state. The retaining of a low OLC at the highly bent state is intriguing considering that the optical loss of waveguides is usually serious in the bent state.^[17]

In order to further demonstrate the potential utility of elastic DPIN crystal as flexible materials, a crystal was repeatedly bended and recovered, and multiple measurements of optical waveguide were conducted. The optical waveguiding property of the crystal, in terms of emission maximum and intensity, did not change upon repeatedly bending and recovering (Figure S6), highlighting the good elasticity of DPIN crystal as well as its potential application in flexible optical/optoelectronic devices.



Figure 5. Fluorescence photographs of straight (a) and bent (b) crystals excited with a UV lamp (uppermost line) and with 355 nm laser focused at different positions, and fluorescence spectra collected at a tip of a single DPIN crystal in either the straight (c) or the bent (d) state, with the distance between this tip and the excitation site of the laser changed gradually.

In addition, we also tested the crystal elasticity of some analogs of DPIN (Table S4). Several strategies, e.g. π -extension and introduction of hydrogen bonds, have been adopted to tune the intermolecular interactions in crystal, and thus change the mechanical property. We found that only a small part of analogs

could form elastically bendable crystals. Among these kinds of elastic crystals, the DPIN crystal is the only choice which further exhibits optical waveguiding property.

In conclusion, a π -conjugated molecule with a relatively planar donor-acceptor structure has been applied to develop functionalized elastic organic bulk crystals. The structural feature of the compound endows its single crystal with not only bright emission, but also infinite π ··· π interactions that serve as a key factor for the high elasticity of the crystal. Taking advantages of the high elasticity and bright luminescence, a flexible optical waveguide based on single-component organic bulk crystals has been achieved. The structural feature of the untilized compound is of guiding significance for the design of organic compounds for EOSCs with optical/optoelectronic functions. The easier preparation of centimeters-long EOSCs and their use in low-loss flexible optical waveguides shown in this study suggest the application potential of the single-crystal materials in flexible optical/optoelectronic devices.

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Keywords: fluorophore • organic crystal • optical waveguide • elastic bending• crystal structure

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Organic Crystal

Functionalized elastic organic

crystals: centimeters-long elastic organic crystals of a Schiff base have been facilely prepared and display bright orange-red emission with a high fluorescence quantum yield of 0.43. These elastic crystals show waveguiding property with low optical loss coefficient not only in the straight state, but also in the highly bended state, demonstrating the usability of "elasticity".



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