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An Organic Crystal with High Elasticity at an Ultra-Low Temperature (77 K) and Shapeability at High Temperatures

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Abstract: Organic single crystals with the elastic bending capability have been known recently, and potential applications of this type of unusual crystals in flexible devices and sensors have been elucidated. Exploring the temperature compatibility of elasticity is essential for defining application boundaries of elastic materials. However, related studies have rarely been reported for elastic organic crystals. Here, we show an organic crystal which displays elasticity even in liquid nitrogen (77 K). The elasticity can be maintained below *ca.* 150 °C. At higher temperatures, the heat setting property enables us to make various shapes of crystalline fibres based on this single kind of crystal. Through detailed crystallographic analyses and contrast experiments, the mechanisms behind the unusual low-temperature elasticity and high-temperature heat setting are disclosed.

Introduction

Organic single crystals have attracted a great deal of research interest as functional materials, including the active materials for optoelectronic applications (e.g. organic light-emitting diodes,^[1,2] field-effect transistors^[3,4] and optical waveguides^[5,6]), as well as light,^[7,8] heat,^[9,10] the responsive materials for pressure/grounding^[11,12]and solvent vapors^[13,14] Recently, organic crystals with elasticity, which break the traditional thinking that organic crystals are hard and brittle, have been known, and more and more elastic organic single crystals (EOSCs) have been reported.^[15-22] Besides the interesting elastic phenomenon itself, potential applications of EOSCs in flexible devices and sensors were the driving force for related studies.^[23-29]

Regarding the application of an elastic material, the influence of temperature on elasticity is nonnegligible. Take rubbers (natural and synthetic) as an example, they only show elasticity and are applicable at the temperatures between the brittle (T_b) and the viscous flow (T_f) temperatures, and such applicable temperatures are typically within -60 to 300 °C for the most commonly used rubbers.^[30] Expanding the applicable temperature range of elastic materials is essential for extending application boundaries. Specially, good elasticity at low temperatures is fairly important as there are a number of lowtemperature circumstances to meet, but the elastic materials tend to get harder and display significantly reduced elasticity at the deactivated low temperatures due to atom bonding/molecular motion of elastic materials.^[30] Although the EOSCs are a potential class of useful elastic materials, their

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elasticity is usually examined at room temperature (r.t.). To the best of our knowledge, only one organic crystal has been observed to maintain elasticity at -100 °C and lose elasticity at 60 °C (due to the loss of co-crystallized solvents).^[15] In-depth investigations of the elastic properties of EOSCs at low and high temperatures is a step forward for applications.

In line with our studies on EOSCs and their applications,^[31–35] we have developed a new EOSC based on a π -conjugated molecule, (*Z*)-2-(4-(((*E*)-2-hydroxy-5-methylbenzylidene)amino)phenyl)-3-phenylacrylonitrile

(HMBPPA) (Figure 1a). The crystal was found to show elasticity not only at r.t. but also even in liquid nitrogen (LN2). We note that some low-density and porous aerogels/foams based on inorganic boron nitride^[36] or carbon materials^[30,37–39], e.g. graphene, carbon nanotubes, have recently been reported to show elasticity in LN2. However, purely organic materials (including polymers) that display elasticity at such extreme circumstances are not known. It is amazing for the high-density materials formed with organic small molecules, especially those in the highly crystalline state, to show elasticity at ultra-low temperatures. Properties of the crystal at high temperatures have also been tested. The elasticity was maintained before 150 °C. Higher temperatures result in the interesting heat-setting property induced by phase transition, which enables us to make different shapes of inelastic crystalline fibers with this single kind of elastic crystal. This property provides a potential method for the free shaping of crystalline materials.

Results and Discussion

HMBPPA was synthesized in a good yield by three steps of reactions (Supporting Information, Scheme S1). Needle-shaped crystals of the compound were easily obtained by diffusing hexane to the saturated CH2Cl2 solution. The crystals are orange in color and emit orange light under UV irradiation. Under microscope, the crystal body shows two pairs of parallel faces, with one pair being much wider (Figure 1b). The lengths of the crystals are in centimeters scale, and widths/thicknesses are tens to hundreds of micrometers. At r.t., the wider pair of faces can be bent to the thickness direction under external forces applied at the ends of the crystal and recover immediately its straight shape after the release of external forces (Supporting Information, Movie 1). Thus, the crystal is elastically bendable. The good elasticity is indicated by the feasibility to form a loop (Figure 1c) and the integrity of the crystal after multiple bendingrelaxation processes. Amazingly, even in LN2 (77 K), the bending-relaxation process can still be performed and repeated (Figure 1d and Supporting Information, Movie 2). The wellmaintained elasticity in LN2 conflicts with the common sense that elastic materials tend to get hard and lose elasticity at a too low temperature. An intuitive comparison is the irreversible deformation of an elastic isobutylene isoprene rubber bar in LN2 (Figure 1e). Considering that the crystal is composed of highly

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ordered organic small molecules, having not even the factors contributing to the elasticity of rubbers, *e.g.* low crystallinity, compressible and stretchable polymer segments, and various additives, the high elasticity at 77 K is fantastic.



Figure 1. Elastic bending of the needle-shaped HMBPPA crystal at r.t. and 77 K. a) chemical structure of HMBPPA. b) microscopic image of the crystal body showing the wider and narrower faces. c) a crystal bent to form a knot shape at r.t. d) bending experiments of a crystal in LN2: the edges of two pieces of cover glass were stuck together through Scotch tapes, and one end of a crystal was stuck on one of the cover glass through glue, while the other end was free; thus, when folding the two pieces of cover glass, the crystal was bent. e) the loss of elasticity of the isobutylene isoprene rubber after frozen in LN2 for comparison.

For EOSCs, elasticity is basically determined by molecular arrangements and intermolecular interactions.^[16,19] Thus, singlecrystal X-ray diffraction (SCXRD) was performed at r.t. to resolve the crystal structure and get insight into the factors related to elasticity. By face indexing, the wider and bendable crystal faces were confirmed to coincide with the crystallographic (100) plane (Figure 2a). The length direction of the crystal corresponds to the crystallographic b axis, and the thickness direction is along the crystallographic a axis. There is one molecule in the asymmetric unit of the crystal. The molecular skeleton shows high planarity. The phenolyl group and the central benzene ring are almost coplanar, and the terminal phenyl group is only slightly twisted out of the plane defined by the central benzene ring with an angle of 12.12° (Figure 2b). Along the crystal-length direction (b axis), molecules are packed to form a chain structure through intermolecular $\pi \cdots \pi$ interactions (Figure 2c). The π-stacked molecules are perfectly parallel and exhibit a quite large overlapping area and a short interaction distance (ca. 3.37 Å). Thus, strong $\pi \cdots \pi$ interactions can be concluded (Figure 2d). As-formed molecular chains are dimerized along the crystallographic c axis (width direction) through C-H···N interactions (Figure 2e). Each chain dimer is crosswise packed with neighboring chain dimers through C–H···O hydrogen bonds to form a layered structure (Figure 2e and f). There are no obvious intermolecular interactions between molecular layers. Notably, each molecule in a molecular chain is linked with two molecules in the adjacent chain of the same chain dimer, as well as two molecules in a neighboring chain dimer (Figure 2e). This feature makes all the molecules in a layered structure included in a hydrogen-bond network.



Figure 2. Molecular and packing features of the needle-shaped HMBPPA crystal at r.t. a) schematic presentation of the crystal showing the face indexes. b) molecular conformation with high planarity. c) one-dimensional molecular chains formed along the crystallographic *b* axis through π -··· π stacking (double-headed arrows). d) overlapping area and vertical distance of the π ··· π interaction (view perpendicular and along the mean plane of the non-hydrogen atoms of a molecule). e) hydrogen-bond network connecting the molecules: blue and green dashed lines represent two types of C–H···N hydrogen bonds within a chain dimer; red and gray dashed lines represent two types of C–H···O hydrogen bonds between chain dimers. f) the crosswise packed chain dimers in molecular layers (the units labelled with red and yellow represent respectively a chain dimer), and the expansion and contraction directions of outer and inner arcs formed in the bending process, respectively.

Various intermolecular non-covalent interactions, including hydrogen bonding, $^{[21]}$ halogen-halogen, $^{[16]}\pi \cdots \pi ^{[23]}$ and van der Waals^[32] interactions, have been proposed to contribute to the elasticity of EOSCs. These interactions are generally weak and adjustable so that, in the bending process, they cannot only enhance the linkage between molecules to enhance the resistance of a crystal towards external forces, but also allow the crystal deformation through slight self-changes. Among these interactions, the $\pi \cdots \pi$ interactions are guite often detected in EOSCs,^[15,16,20] and some of the EOSCs,^[23,26] including the present one, are designed based on relevant considerations. In this crystal, the π -stacked molecules can turn intermolecular horizontal distance to fit the length requirement of a compressed/shortened inner arc and a stretched/elongated outer arc formed in the bending process (Figure 2f).^[15] A slight relative slippage between adjacently stacked m-systems along

Crystals	а	b	С	α	β	Y	V
HMBPPA (r.t.)	14.7884(12)	4.6170(4)	25.987(2)	90.0	100.057(3)	90.0	1747.1(2)
HMBPPA (100 K)	14.7445(18)	4.5978(5)	25.854(3)	90.0	99.538(6)	90.0	1728.5(3)
	(0.296%) ^[a]	(0.416%) ^[a]	(0.511%) ^[a]		(0.519%) ^[a]		(1.060%) ^[a]
DPIN (r.t.)	5.1980(3)	9.9584(6)	29.0475(17)	90.0	93.243(2)	90.0	1501.20(15)
DPIN (100 K)	5.2089(3)	9.8280(6)	28.5562(16)	90.0	92.709(2)	90.0	1460.25(15)
	(-0.210%) ^[a]	(1.309%) ^[a]	(1.691%) ^[a]		(0.573%) ^[a]		(2.728%) ^[a]

Table 1. Crystallographic information of the HMBPPA and DPIN crystals at r.t. and 100 K.

[a] Values in parentheses are the contraction ratios from r.t. to 100 K.

the length direction of the π -skeleton, accompanied by the formation of a small angle between the parallel π -systems, can also occur to fit the curvature of the bent faces in the bending process.^[20] These factors ensure a prerequisite for elastic bending. The hydrogen-bond network in a molecular layer makes intra-layer π -systems become an integer and prefer synergic movements, which should reduce the cracking risk of the crystal in the bending process because higher uniformity and less defects of the crystal body can be expected. Moreover, the hydrogen-bond network, together with the strong π --- π interactions, should enhance the tolerance of the molecular chains to tensile forces/pressure. These factors contribute to the good elasticity of the crystal.

To further understand the elasticity at 77 K, a known roomtemperature elastic crystal (DPIN crystal) reported by us has also been subjected to low-temperature experiments because this crystal is a good example with the elasticity closely related to $\pi \cdots \pi$ interactions.^[31] Actually, the π -skeletons in DPIN crystal are also one-dimensionally stacked along the length direction of the crystal, similar to the case in the needle-shaped crystal of HMBPPA (see ref. 31 and Supporting Information, Figure S1). However, molecules of DPIN are more twisted, and the π skeletons possess a reduced overlapping degree and a longer vertical distance. In addition, there are no obvious intermolecular interactions in the width direction of the crystal to link molecules, unlike the well-linked network observed in the crystal of HMBPPA. The DPIN crystal was found to break immediately when bent in LN2 regardless of thicknesses and lengths (Supporting Information, Movie 3), although the crystal still possessed smooth surfaces after it was put into LN2 in the straight shape (Supporting Information, Figure S2). This result indicates that the one-dimensional $\pi \cdots \pi$ stacking, the common feature of the two crystals, is not simply the reason for elasticity at 77 K. To analyse the factors potentially leading to the distinct low-temperature properties, the cell parameters and molecular and packing structures of the crystals measured at 100 K were compared with corresponding results obtained at r.t. To get a reliable comparison, the diffraction experiments at these temperatures were performed using a single sample of HMBPPA/DPIN crystal settled in the diffractometer. Only the temperatures were changed in the experiments. The three axes of the HMBPPA crystal were contracted by 0.296-0.511% from r.t. to 100 K, and the cell volume was contracted by 1.060% (Table 1). The molecules of HMBPPA at 100 K maintained basically the geometry observed at r.t., with the key intramolecular torsion angles changed within 1.16° (Supporting Information, Figure S3). The contraction of the b axis was accompanied by the slight shortening of not only the horizontal distance but also the vertical (0.594%) distance between parallel π -skeletons. Overall, slightly stronger π ··· π interactions were observed. A slight rotation of the π -skeleton towards a smaller dihedral angle (0.318% less) relative to the (100) plane (i.e. bending faces) was also observed, which is likely the response to the contraction of the a axis (Supporting Information, Figure S3). As for the DPIN crystal, the cell volume was contracted more seriously (2.728%) at 100 K, which was accompanied by the large contraction of the b (1.309%) and c (1.691%) axes and, interestingly, the expansion of the a axis (0.210%) along which the π -skeletons are stacked one-dimensionally (Table 1). The expansion of the a axis at 100 K was accompanied by the lengthening of the horizontal distance between π -skeletons, as well as a more twisted molecular conformation that was indicated by the increases of 2.67 and 7.98° for two of the key torsion angles within the molecular skeleton (Supporting Information, Figure S4). The more twisted conformation made the π ... π interactions become poorer at 100 K. Based on above results, the distinct low-temperature properties of the two crystals can be understood. For the HMBPPA crystal, the cold contraction is weaker and relatively isotropic, and thus the molecular conformation and packing features are well maintained. Therefore, the ease of bending at ultra-low temperatures is similar to that at r.t. Moreover, the slightly strengthened $\pi \cdots \pi$ interactions at low temperatures further enhance the tolerance of the molecular chains to tensile forces/pressure. These two factors contribute to the good elasticity of the HMBPPA crystal at low temperatures. The difficulty in the changes of molecular conformations and packing structures at low temperatures benefit from the hydrogen-bond network, because it makes the change/movement of a molecule restricted seriously by a number of other molecules. In particular, the crosswise arrangement of chain dimers in the hydrogenbond network strongly restricts the crystal contraction along the a axis (thickness direction), because the contraction prefers the rotation of π -skeletons towards a smaller dihedral angle relative to the (100) plane but such rotation is harder due to the mutual restriction of crosswise packed chain dimers through hydrogen bonds. As for the DPIN crystal, the severer and anisotropic response to cooling makes the molecular conformation and packing structure changed to a larger extent, and thus the bending property under external forces is significantly changed. The nature of the loss of elasticity could be related to the increased difficulty in the relative slippage of neighboring π skeletons as they are more twisted, as well as the weaker ability of molecular chains to confront with tensile forces as the π ... π interactions are poorer. In addition, the larger change of

molecular conformation and packing structure may lead to large internal stresses after cooling, which may increase the cracking risk of the crystal.



Figure 3. Stress-strain curves of the HMBPPA (a) and DPIN (b) crystals, as well as the elastic modulus (EM) and fracture strength (FS) values, obtained from the tensile tests of three samples of each crystal.

To explore the influence of molecular packing structures on their stretchability that is closely related to the extension of the outer arc in the bending process, the tensile test of the HMBPPA crystal was performed at r.t. through the tension at the two ends of the crystal. Contrast experiments were also performed on the DPIN crystal. For both crystals, only the elastic deformation occurred before breaking as indicated by the linear correlation between tensile stresses and strains. The elastic modulus (EM, slopes of the stress-strain curves) of the HMBPPA crystal is large (4000-4900 MPa), being much higher than that of the DPIN crystal (560-730 MPa) (Figure 3). This result indicates that, under the same external force, a HMBPPA crystal can be stretched to a much less degree compared with a DPIN crystal with the same transversal area. However, the HMBPPA crystal can endure much larger stress at a unit transversal area as indicated by its much larger fracture strength (FS: 47-65 MPa for the HMBPPA crystal vs. 11-19 MPa for the DPIN crystal). The larger fracture strength clearly indicates the advantage of strong $\pi \cdots \pi$ interactions and molecular synergic movement for the tolerance to external forces for stretch. It means that larger maximum external forces can be applied for stretching the HMBPPA crystal to overcome the difficulty in stretch caused by a larger elastic modulus, so that an appreciable maximum strain can be insured for the HMBPPA crystal (*ca.* 1-1.5% determined by experiments), although the strain is still smaller than corresponding value of the DPIN crystal (*ca.* 2-3%) (Figure 3). The tolerance of the molecular packing structure to large forces for compression is also reasonably expected.

The outstanding bending properties of the HMBPPA crystal at low temperatures inspired us to test the high-temperature properties. At the temperatures below 150 °C, the elasticity of the crystal was well maintained. Interestingly, the crystal was found to lose elasticity and become brittle at higher temperatures, and the disappearance of elasticity was accompanied by the changes of crystal color and emitting light (Figure 4a). When the crystal was cooled to r.t., the changes were not reversed. The changing process is caused by an endothermic crystalline-phase transition as confirmed by the differential scanning calorimetry (DSC) analyses (Figure 4a). Interestingly, based on such a property of the HMBPPA crystal, heat setting of the crystal enables us to prepare various shapes of crystals. The preparation process includes: 1) bending the crystal at r.t. to form a desired shape; 2) heating the crystal to the temperature of ca. 170 °C; and 3) cooling the crystal to r.t. As an example, a long crystal with a helical shape was prepared (Figure 4b). Our results provide a new thinking for shaping crystalline materials, which is the construction and utilization of EOSCs with the phase transition property.



Figure 4. Heat-setting property of the needle-shaped HMBPPA crystal. a) the DSC curve of the HMBPPA crystal showing the phase transition process leading to the heat setting (insets show the changes of crystal color in the process). b) the preparation of an inelastic helical-shaped crystal through using the heat-setting property (the crystal was initially screwed on a glass tube to form a helical shape, and the two ends of the crystal were stuck on the tube with glues).

To get insight into the molecular packing features of the new crystalline form generated after phase transition, SCXRD was performed. However, the diffraction data of the new form was poor for resolving detailed structures. The poor data is likely due to the formation of many defects in the crystal, which is implied by the loss of transparency of the crystal after phase transition. After various attempts, crystals with a crystalline phase same as

that obtained after phase transition (determined by X-ray powder diffraction and DSC) have finally been achieved by vacuum sublimation (Supporting Information, Figure S5). These crystals are block-shaped without the possibility of being bent. Compared with the molecules in the needle-shaped crystals obtained from solvent diffusion, the molecules in the blockshaped crystals are much more twisted as indicated by the larger torsion angles formed within the molecular skeleton (Figure 5a). In the block-shaped crystals, molecules also form molecular chains through $\pi \cdots \pi$ interactions (Figure 5b). However, the $\pi \cdots \pi$ interactions between the twisted molecules are weak, as indicated by a crosswise and nonparallel arrangement of neighboring molecules and the resulting limited overlapping degree, as well as a large interaction distance (Figure 5c). The poor π -stacking and the defects in the crystal, caused by the phase transition process, could be the reason for the loss of elasticity.



Figure 5. Molecular and packing features of the block-shaped HMBPPA crystal. a) molecular conformation with the key torsion angles being shown. b) one-dimensional molecular chains formed through $\pi \cdots \pi$ stacking (double-headed arrows). c) overlapping area and vertical distance of the $\pi \cdots \pi$ interactions (view perpendicular and along the plane defined by the central benzene ring).

Conclusion

In summary, the elasticity in liquid nitrogen, an unusual property for elastic materials, has been discovered for an organic single crystal. The strong $\pi \cdots \pi$ interactions, a hydrogen-bond network connecting the m-systems, as well as crosswise packed molecular chains, are crucial for the elasticity at ultra-low temperatures. Another unusual and interesting property, i.e. heat setting caused by phase transition, has also been found for the same crystal. This study provides a method for achieving elasticity at ultra-low temperatures based on materials with organic components, which is the highly crystalline and rational packing of organic small molecules rather than the mobility enhancement of polymer fragments. It may give birth to new organic materials applicable in extreme circumstances, such as the outer space. Although more and more factionalized single crystals have been developed, the free shaping of crystals is challenging. The heat-setting strategy of elastic crystals shown in this paper is a potentially useful shaping method for achieving functional crystals with various shapes for diverse applications.

Experimental Section

Single-crystal growth. Saturated dichloromethane solution of HMBPPA was added in test tubes, and then triple volume of cyclohexane was added along the tube-wall without destroying the previous solution surface. The test tubes were sealed with a cover. After standing at r.t. for 3–7 days, the needle-shaped crystals of HMBPPA were obtained. Block-shaped crystals of HMBPPA were grown by vacuum sublimation. HMBPPA solid was heated at 180 °C under vacuum (*ca.* 3 Pa) in a sublimator and the crystals were generated at the deposition area with a setting temperature of 100 °C. The crystals of DPIN were regrown through the method described in our previous paper.^[31]

X-ray diffraction analyses. Single-crystal X-ray diffraction data were collected on a Bruker D8 Venture diffractometer using the ω -scan mode with graphite-monochromator Mo•K α radiation. The structures were solved with direct methods using the Olex2 programs and refined with full-matrix least-squares on F^2 . Non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated and refined isotropically. The crystallographic information has been deposited at the Cambridge Crystallographic Data Centre (CCDC). CCDC numbers: 1917965, 1917964, 1917953, 1917952 and 1917951 for the needle-shaped crystal of HMBPPA measured at r.t. and 100 K, block-shaped crystal of HMBPPA, and the crystal of DPIN measured at r.t and 100 K, respectively.

Tensile tests. Tensile stress was measured using an Instron 5944 Universal Testing System. The static load cell is Instron 2530 load cell with capacities of 10 N. The sample was fixed on one surface of the mechanical grip by 502 glue to avoid slippage during testing. Raw data were obtained in displacement controlled mode at a rate of 1 mm/min. During the mechanical testing, load and displacement were recorded in real time. The stress, strain and elastic modulus were calculated by the equations below.^[20]

$$Elastic modulus = \frac{Stress}{Strain}$$

$$Stress (MPa) = \frac{F}{A} = \frac{Apllied force}{Cross - section area}$$

$$Strain = \frac{\Delta L}{L} = \frac{Chang in length}{Inital length}$$

The elastic modulus of a sample was determined from the slope of the stress-strain curve. The fracture strength corresponds to the maximum stress value of the stress-strain curve.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: organic crystal • elastic bending • 77 K • low-temperature crystal structure • heat setting

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RESEARCH ARTICLE

Here, we report an organic crystal which displays elasticity even in liquid nitrogen (77 K). It may give birth to new organic materials applicable in extreme circumstances, such as the outer space. Another unusual and interesting property, *i.e.* heat setting caused by phase transition, has also been found for the same crystal. At higher temperatures, the heat setting property enables us to make various shapes of crystalline fibres based on this single kind of crystal.



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An Organic Crystal with High Elasticity at an Ultra-Low Temperature (77 K) and Shapeability at High Temperatures