Spatially resolved structure and spectroscopic analysis of a plastically bent molecular crystal

The general perception of organic crystals being fragile and brittle has been disclaimed by the recent observation of exceptional malleability and flexibility in certain organic crystals that bend similar to polymers upon the application of external pressure [1,2]. This bending is rooted in the sliding of the slip planes in the crystal lattice, which are held together by weak intermolecular interactions such as halogen-halogen interactions or halogen-heteroatom interactions [2,3]. The rapid elastic response from the crystal under external stress can be utilized as a physical platform for energy transducing materials to develop shape-adaptive and self-actuating devices [4]. Herein with a simple organic crystal of hexachlorobenzene (HCB), we demonstrate the bending mechanism and the molecular level structural consequences of plastic deformation of a crystal under externally applied local pressure [5].

Crystals of HCB can sustain mechanical force when local pressure is applied on the (001) face and bend up to 360° without fracturing or cracking, but they crack and splinter easily when pressure is applied on the (100) face. As observed by scanning electron microscopy (SEM), unlike the smooth monolithic appearance of the straight part (Figs. 1(a,b)), the bent part of the crystal is striated and features distinctive layers, which are separated from each other with an average distance of 3.16 μm (Fig. 1(c)). AFM images of the (001) face reveal a staircase-like topography, while the (100) face is undulated and ridged, where each ridge has a fine structure (Fig. 1(d)), supporting the delamination mechanism. Upon bending, the crystal retains its macroscopic integrity by increasing the mosaic spread by sliding its layers atop each other, which becomes possible through regenerative Cl···Cl bond (interaction) breaking and reformation.

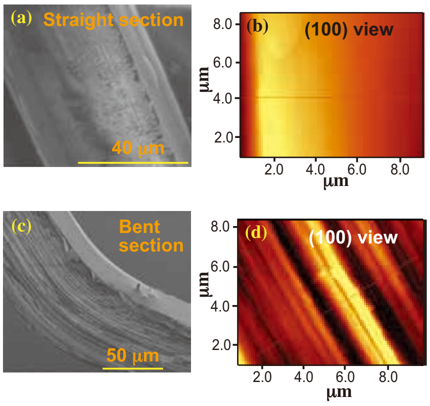

Fig. 1. Surface morphology of the (001) face of a bent HCB crystal at the straight and bent sections, observed by SEM and AFM. Note that the layers appearing in the bent location are absent in the straight location.

To provide insight into the changes that occur during delamination at the molecular and supramolecular levels, we carried out non-polarized and linearly polarized μ-focus IR spectroscopy (**BL43IR**) and μ-focus X-ray analysis (**BL40XU**) with synchrotron radiation available at SPring-8. The IR spectra of a mechanically bent HCB crystal were recorded at a resolution of 2 cm^{-1} on the concave (cc) and convex (cx) sides in the bent region. These spectra were compared to the straight sections of the crystal (Figs. 2(a,c)). The straight part of the crystal reproduced the spectra of an unbent crystal, but, the bands in the bent region were considerably broader. Shifts and splitting were also observed, supporting the increased mosaic spread in the bent region.

We presumed that if bending is due to sliding of the layers which causes the interlayer Cl···Cl bond (interaction) rupture and reformation, then it should be reflected in the stretching frequency of the C—Cl bonds (at $\nu_{C-Cl}\sim700$ cm^{-1}), as well as in the C=C bonds along the bent region. In fact, both polarized and non-polarized spectra on the convex (cx) side exhibited a blue-shifted ν_{C-Cl} band compared to the concave (cc) side, indicating strengthening of the C—Cl bonds and weakening of the Cl···Cl interactions in the cx region. The broadening and splitting of the intrinsic $\nu_{C=C}$ modes at 1345 and 1295 cm^{-1}, which are expected to be less sensitive to the intermolecular interactions relative to the ν_{C-Cl} modes, indicate a reduced symmetry of the HCB molecules upon bending (Fig. 2(c)). The decreased intensities of the Raman bands at 332 cm^{-1} (in-plane δ(C—Cl)) and 229 cm^{-1} (out-of-plane δ(C—Cl)) are in line with the weakening of the Cl···Cl interactions at the cx side of the bent crystal.

To understand the structural mechanism for bending the HCB crystal, we performed spatially resolved X-ray diffraction analysis with a microfocus X-ray setup using synchrotron radiation. A moderately bent crystal was scanned across the bent locations at ten equidistant points (Fig. 2(b)). Small but significant perturbations of the unit cell parameters were observed, supporting the fact that the slippage of layers is associated with expansion or contraction of the crystal lattice. As shown in Figs. 2(d-g), the cell axes (*a*, *b*, and *c*) of the lattice are slightly expanded on both the cx and cc sides, while the angle β increases from the cx to cc side. A closer look at the packing structure of HCB indicates that the Cl···Cl intermolecular interactions are roughly oriented on the *ac* plane while the $\pi\cdots\pi$-stacking interactions are oriented along the *b* axis. Thus, elongations of the *a* and *c* axes in both the cx and cc regions are related to the

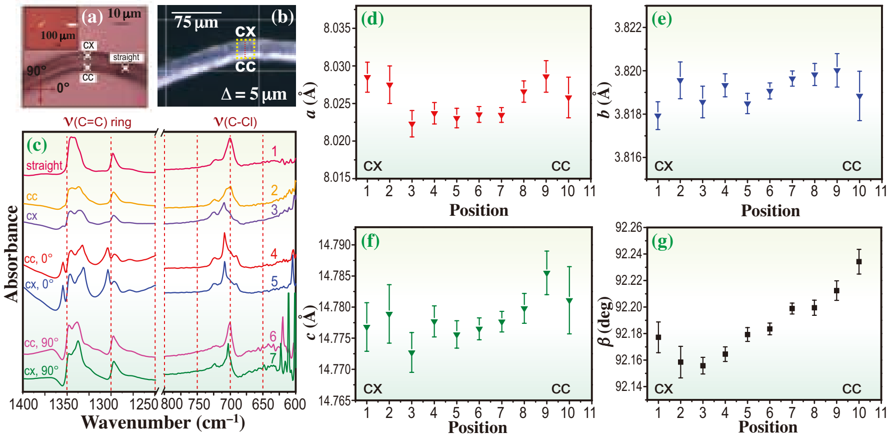

Fig. 2. Unpolarized and polarized IR spectra **(a, c)** and perturbed unit cell parameters **(d-g)** of a moderately bent HCB crystal measured across the crystal kink **(b)**.

increased mosaicity mediated by reorganization of the Cl···Cl interactions and splaying of the molecules in the layers, leading to changes in the *b* axis. This structural adaptation of the crystal lattice under external force prevents the crystal from rupturing.

We postulated that the sliding of layers due to the applied tensile force leads to changes in the crystal density as well as the mechanical response along the bent and unbent locations of the crystal. In fact, our hot-stage experiment reveals that the bent part of the crystal melts earlier than the straight part, which is consistent with a lower density at the bent location of the crystal. In order to study the nanomechanical properties of a bent slender crystal of HCB, exhaustive nanoindentation measurements were performed by profiling the crystal across different faces in the bent and unbent sectors. A clear trend of decreasing elastic modulus (*E*) and hardness (*H*) is observed when going from the straight to the bent location, which is a signature of the softer and more ductile nature of the bent part due to increased the mosaic spread upon sliding of the layers.

Based on the above analysis, we present a model (Fig. 3) for the mechanism of plastic bending of HCB crystals. Applying three-point local pressure on the (001) face results in the formation of ridged layers, which glide atop each other by bond breaking and reformation of the interlayer Cl···Cl bonds (interactions) accompanied with unit cell perturbation, where the cell axes are stretched on the cx side and the cc side. The overall crystal integrity is preserved due to this structural adaptation at the molecular level as well as at the supramolecular level. We postulate that the mechanism proposed here for HCB may be used to explain the extraordinary plasticity of other bendable crystals.

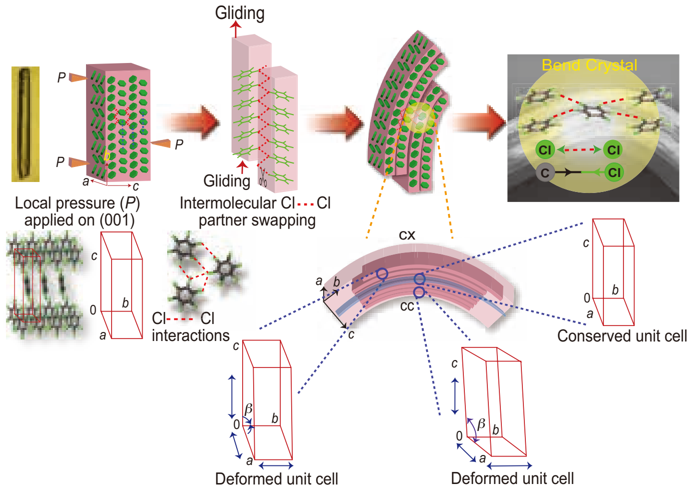

Fig. 3. Model for the mechanism of plastic bending of HCB crystal. Applying external pressure (*P*) on the (001) face causes gliding of the slip layers by weakening of the interlayer Cl···Cl interaction followed by regenerative partner swapping of the Cl···Cl interaction, which makes bending possible without losing the crystal integrity. Unit cell at convex (cx) and concave (cc) positions appear to be deformed due to stretching and gliding of the layers.

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