Shape-memory effects in molecular crystals

E. Ahmed[1], D. P. Karothu[1], M. Warren[2], P. Naumov[1]

[1]New York University Abu Dhabi, PO Box 129188, Abu Dhabi, UAE
[2]Diamond Light Source, Didcot, Oxfordshire, OX11 0DE, UK

ea79@nyu.edu

Molecular crystals can be bent elastically by simultaneous expansion and contraction or plastically by delamination into slabs that glide along slip planes [1,2]. Here we describe a hitherto unreported mechanism of crystal bending in terephthalic acid crystal which undergoes pressure-induced phase transition upon bending where the two phases (form II and form I) coexist at ambient conditions. Scanning electron microscopy and microfocus XRD using synchrotron radiation provided direct evidence that upon bending, terephthalic acid crystals can undergo a mechanically induced phase transition without delamination and their overall crystal integrity is retained [3]. We report a distinctly different mechanism of plastic bending of molecular single crystals which have two phases and we provide the crystal structure of the bent section of such plastically bent crystal as direct evidence of the proposed mechanism. We also establish that this plastic deformation which effectively results in coexistence of two phases in the bent section of the crystal is the origin of unconventional properties such as shape-memory and self-restorative effects. Such plastically bent crystals act as bimorphs and their phase uniformity can be recovered thermally by taking the crystal over the phase transition temperature. This recovers the original straight shape and the crystal can be bent by a reverse thermal treatment, resulting in shape memory effects akin of those observed with some metal alloys and polymers. We anticipate that similar memory and restorative effects are common for other molecular crystals having metastable polymorphs.

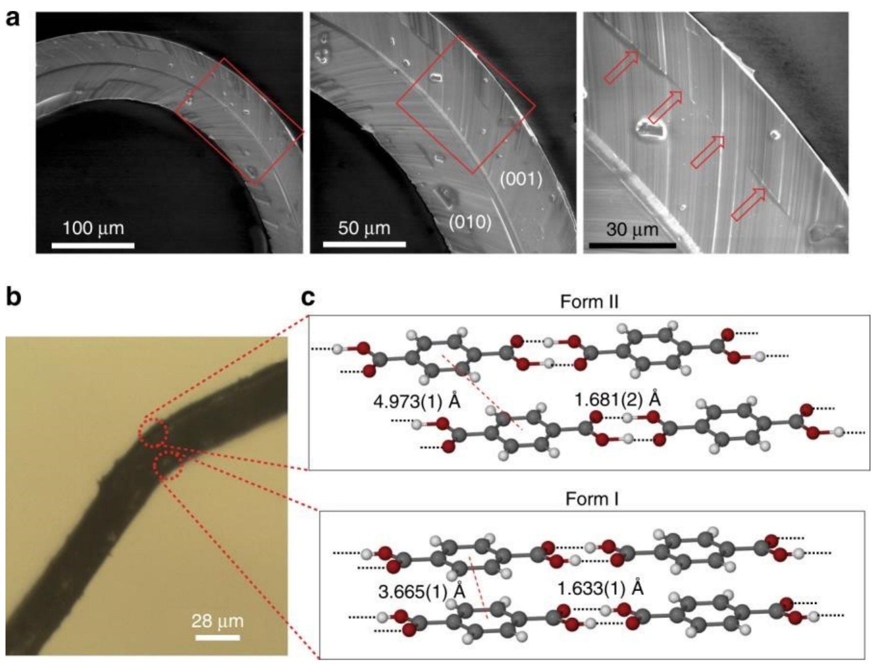

Figure 1. Scanning electron microscopy (SEM) imaging and structure analysis of a bent TA crystal. **a** SEM images of the crystal after bending with striations from the grain boundaries visible on the surface. The line that runs across the center of the crystal (marked with red arrows) corresponds to the habit plane (inter-phase boundary) between the two phases. **b** Optical image of a bent crystal of TA analyzed by microfocus X-ray diffraction. The approximate locations where the structure was determined are marked with circles. **c** Crystal structures determined in the circled regions of the bent crystal shown in panel (**b**).

1. Ahmed, E., Karothu, D. P. & Naumov, P. (2018). *Angew. Chem. Int. Ed.* **57**, 8837.