On the elasticity of Copper(II)acetylacetonate crystals

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Structure-property correlations in a wide variety of elastic molecular crystals indicate that (a) corrugated structures that can interlock readily (prevent plastic deformation either through geometrical or energetic considerations) and (b) a multitude of weak and dispersive intermolecular interactions that would act as structural buffers through easy rupture and reformation during deformation, are structural features that impart a crystal the ability to accommodate large elastic strains.¹⁻⁵ Based on their studies on copper(II)acetylacetonate crystals (**1**, hereafter), Worthy *et al.* claimed that these criteria are “incorrect”.⁶ In order to examine their claim critically, we conducted detailed experiments on crystals of **1**. Our flexure experiments show that they indeed readily undergo plastic deformation when bent on the (101) face, which contradicts Worthy *et al.*’s assertion that the (101) face is highly elastic. Therefore, the crystal **1** is not an ideal model system for rejecting the prevailing—and widely accepted—molecular mechanisms for exceptional elastic flexibility of organic crystals.

Upon stressing, all solids deform elastically first, before the onset of either plastic deformation or brittle failure. Depending on the extent to which a molecular crystal exhibits these characteristics, it is broadly termed elastic, plastic, or brittle.¹ In particular, elastic crystals are those that can accommodate extraordinarily large elastic strains.

Figure 1. Morphology and qualitative mechanical behaviour of crystal **1**. (a) Schematic representation of as-grown crystals' morphology and exfoliation of slices. (b), (c) and (d) Plastic deformation on (101) in thick crystals. Notice the delamination at the strained regions. (e-g) Crystals showing plastic bending and (h) a pellet made using bulk microcrystalline powder sample of **1**. Face dependent bending behaviours, elastic on $(10\bar{1})$ (i) and plastic on (101) (j) on a same exfoliated crystal. Sliced crystals showing elastic deformation on $(10\bar{1})$, resulting a crystal knot (k), half circle (l) and another half circle with indicated elastic strain limit (m). Note that panels (b-d, i-m) are optical images and (e-h) are scanning electron micrographs (SEMs).

We obtained 1-3 cm long needle type crystals of **1**, grown along b -axis (Fig. 1a), with morphologies consistent with those of Worthy *et al.* Our qualitative mechanical tests, with forceps and a metal pin, revealed that the as-grown crystals of **1** undergo plastic deformation readily when bent on the major (101) face with the flexural strain exceeds $\sim 1\%$ (see Figs. 1b-g and Figs. S1, S2 in SI). Plasticity is accompanied by delamination parallel to (101) (Figs. 1b-g and Figs. S1c). The irreversible morphological changes are similar to those observed in other well-known plastically bent crystals, such as C_6Cl_6 .⁷⁻⁹ These crystals of **1** can be easily exfoliated parallel to $(10\bar{1})$ by stressing with a needle, producing thin, long, ribbon-like crystals (Fig. 1a).² Crystals bent on $(10\bar{1})$, particularly the thin ribbons obtained by slicing the pristine crystals, showed remarkable elastic flexibility (Figs. 1k-m and Figs. S1e-g,i), unlike the (101) face studied by Worthy *et al.* for deducing the bending mechanism. The $(10\bar{1})$ of crystals accommodated significant strains (larger than 4 %) (Fig. S3) and could be tied into knots having a small radius, confirming its superior elastic nature as compared to (101) (Figs. 1k, S1i). Beyond the elastic limit, the crystals undergo fracture on $(10\bar{1})$ face without any appreciable plastic deformation (Fig. S1).

Worthy *et al.* overlooked these distinct mechanical responses of the two faces. They stated that the (101) face is more elastic than (10-1) face and that these observations are in agreement with the lower elastic moduli of (101) face (4.8 – 6.9 GPa) than (10-1) face (11.3 – 13.8 GPa). Indeed, the relatively lower elastic modulus of (101) confirms its compliant nature, but not necessarily higher elasticity, contrary to what is stated by Worthy *et al.* Careful three point bending tests on crystals with different orientations would have allowed the quantitative assessment of the two faces. But, Worthy *et al.* failed to mark the faces of bent crystals used for several experiments, leading to ambiguity in their analysis. For instance, their crystal-knot (Fig. 1b in their paper) resembles our exfoliated crystal of **1** bent on (10 $\bar{1}$) (Fig. 1k).⁶ In contrast, when bending the as grown crystals on their (101) face, we could not form an elastic knot as they readily underwent plastic deformation. Since the micro focused X-ray diffraction studies by Worthy *et al.* were performed on crystals of **1** bent on the predominantly plastic (101) face (Figs. 1c and 3b in their paper), but not on the elastic (10 $\bar{1}$) face, the validity of their proposed mechanism and conclusions are in question.⁶

Additionally, we ascertained the plastic nature of crystals **1** by measuring the stress transmission ratio (STR, axial compression stress to radial die wall stress) of its bulk powder during die compression. STR is a widely used measure in the pharmaceutical industry for assessing the tabletability of the active pharmaceutical ingredients. A more plastic material can transmit stress from the axial direction to the radial direction effectively, exhibiting a higher STR.¹⁰ The observed stress transmission behaviour of **1** resembles that of the well-known highly plastic microcrystalline cellulose,¹¹ confirming the predominantly plastic nature of crystals of **1** during die compression (see SI, Fig. S4).

Worthy *et al.* performed their structural investigations only within a small elastic strain. On that basis, they proposed a molecular rotation mechanism, which was used to rationalize elongation (outer arc) and compression (inner arc) of the bent crystals. However, their assertion that the observed structural changes in **1** can be applied to explain exceptionally high elastic strain in some molecular crystals is *incorrect*. Especially, the molecular rotation features in **1**, cannot form a basis for rejecting the other structural requirements postulated for highly elastic molecular crystals.^{1-5,12-14} We further contend that the rotation model is applicable *only* to crystals formed by non-spherical species. For instance, rotations by nearly spherical molecules do not result in any expansion or compression of crystals. Hence, any elasticity observed in such systems cannot be explained by the “rotation” based mechanisms. Instead, small linear displacements of constituents are sufficient to rationalize their elastic compression and expansion, for instance, as seen in single crystals of elemental metals.¹⁵

Thus, interlocking between adjacent molecular layers, either mechanically or energetically, remains a necessary condition for a molecular crystal to exhibit a high elastic limit. It follows that increasing the strength of interactions that operate at longer distances between adjacent molecular planes facilitates larger elastic strain limits in crystals. Such molecular crystals exhibit both higher rigidity, by more effectively hindering plastic deformation, and greater elastic flexibility, by accommodating more changes in molecule positions that can recover after withdrawal of the external stress.¹⁶

In summary, although the study by Worthy *et al.* sheds light on the molecular level response of crystals of **1** to external stresses within a small elastic strain, it fails to emphatically provide a valid basis for casting aspersions on the validity of the earlier postulated structural features for molecular crystals to exhibit high elastic flexibility. This clarification is important for the following two important reasons: (i) design of exceptionally elastic molecular materials for potential technological applications, and (ii) set the record straight for this exciting area of scientific research.

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Author contributions

Material synthesis, crystallization and all mechanical manipulation of crystals was done by SD. Face dependent behaviour and face indexing on pristine crystals was further independently checked by GV. Die compression studies on powders were done by GV under the supervision of CCS. CMR, CCS and UR analysed all the results and co-wrote the manuscript taking inputs from all the authors.

Competing interests

The authors declare no competing interests.

Additional information

All additional data is available in the supplementary materials.

Supplementary Information

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References

Supplementary note 1: Crystal growth, mechanical response of as-grown and exfoliated crystals.

Crystal Growth. The copper(II)acetylacetonate complex was prepared by following the known method.¹⁷ Blue long needle shaped crystals were obtained from warm chloroform solution by using slow evaporation crystallization technique.

Mechanical response of as-grown and exfoliated crystals. Blue long needle-like as grown single crystals of $\text{Cu}(\text{acac})_2$, **1**, mainly consist of two faces, wide (101) and thin ($10\bar{1}$) faces [Fig. S1a-(i)]. As-grown crystals tend to fracture when stressed locally on ($10\bar{1}$) face [Figs. S1a-(ii-iii)], but undergo facile plastic deformation when stressed on (101) face [Figs. S1a-(iv)&(v), S1b]. The pristine crystals, upon poking on (101) face by a needle, exfoliate parallel to ($10\bar{1}$) planes, resulting in thin, long ribbon-like slices (Fig. 1a, main draft). Such exfoliation reduces the area of (101), hence the ($10\bar{1}$) appears larger (Fig. 1a, main draft). The exfoliated crystals of **1** show plastic deformation on (101) (Figs. S1c,d), similar to the pristine crystals, whereas upon bending on ($10\bar{1}$) face, they display large elastic flexibility (Figs. S1e-g). The crystals also can be twisted plastically around the growth axis (Fig. S1h). Knots could be readily formed from thin, long ribbon type crystals obtained from exfoliating pristine crystals (Fig. S1i).

Supplementary note 2: Plasticity assessment. The bulk powders of **1** transmits axial stress to radial die wall more effectively than the highly plastic microcrystalline cellulose (MCC)¹¹ (Fig. S4a). For a liquid, the stress transmission ratio (STR, i.e., the slope of the linear portion of the curve) is unity. A solid with a STR value closer to unity is more plastic. By the measure of STR, the plasticity of **1** is comparable to that of the highly plastic MCC. Additionally, **1** exhibits a high propensity of punch sticking during compression, which is also indicative of high plasticity.¹⁸

Figure S1. Face-dependent mechanical responses of as-grown and exfoliated crystals of **1**. (a) Identification of (101) and (10 $\bar{1}$) faces of an as-grown crystal (i); qualitative three-point bending tests illustrate fracture on (10 $\bar{1}$) face (ii-iii), and facile plastic deformation on (101) faces (iv-v). (b) A thick version of an as-grown crystal with facile plastic bending. (c,d) Irreversible bending deformation with change in interfacial angle at the top edge of an exfoliated crystal, comparable to many well-known plastically deformable crystals. (e) Elastic loop formed using an exfoliated crystal. (f) Elastic deformation of an exfoliated ribbon separated from an as-grown crystal. (g) Exceptional elastic bending in a very thin exfoliated crystal. (h) Crystal with an irreversible twisting around the needle axis. (i) Comparison of a mother/ as-grown crystal and an exfoliated or sliced crystal (parallel to (10 $\bar{1}$) face), which is capable of being deformed into a *Crystal Knot*.

Figure S2. Different mechanical behaviours observed from different faces, (a) $(10\bar{1})$ and (b) (101) and the crystallographic packing diagrams marked with corresponding crystallographic planes, (c) and (d), respectively. (e) A crystal packing viewed down the b -axis with crystallographic planes (101) and $(10\bar{1})$.

Figure S3. Calculation of strain in exfoliated crystals of **1** on different faces. (a-c) Elastic bending strain on (101) of the crystals with varied thickness before fracture. (d,e) Elastic bending strain on (101) of crystals before plastic deformation sets in. (f) Calculation method used following the *Euler-Bernoulli beam-bending theory* of strain on perturbed crystals.

Figure S4. Plasticity of **1** quantified by radial die wall stress transmission in comparison to common materials, including lactose monohydrate (LM), microcrystalline cellulose (MCC), and dibasic calcium phosphate (DCPA). (a) Radial pressure as a function of axial pressure during the course of compression. The dashed line represents 100 % transmission of axial stress to the die wall. (b) Stress transmission ratios ($n = 3$).

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