

Locating dislocations in organic crystals

Oliver Lin, Zhichu Tang & Qian Chen

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The formation of dislocations upon slip–slide events in organic crystals has been revealed by advanced electron microscopy and data-mining techniques.

In the eighteenth century, French mineralogist René-Just Haüy accidentally dropped his friend's collection of prismatic calcite crystals. The sharp cleavage of the crystal, which retained the same angular shapes as the original crystal, sparked his 'Eureka' moment. This experience led Haüy to dedicate his life's work to relating the physical appearance of crystals to their internal structure. These geometric rules established him as the father of crystallography, a field that has endured for centuries and continues to play an essential role in modern materials design and bioengineering. New trends in the field include the investigation of not only the lattice structure but also disruptions of order due to defects – whether they occur naturally during growth or are induced by external mechanical impact. The range of systems studied has also expanded, from traditional metals and ceramics that can withstand high-energy and high-resolution probes of X-ray or electron beams, to organic molecules that are sensitive to these probes and exhibit extensive structural flexibility.

Organic semiconductor molecules are an exciting class of electronic materials due to their low-cost production, light weight and solution processability. The presence of defects can lead to complex atom displacement fields throughout the crystal structures, due to the flexible nature of molecular packing originating from physical interactions such as hydrogen bonding and π – π stacking¹. These structural changes impact their charge carrier transport properties but have remained challenging to characterize. In 1975, Jones and co-workers took great efforts to study dislocations in an organic semiconductor crystal, *p*-terphenyl, using bright-field transmission electron microscopy (TEM)². Along with the labour-intensive data collection requiring many sample tilts, the authors had to compromise the quality of structural analysis by using images of samples that distorted and changed within minutes due to electron damage. This electron damage posed a challenge for later studies aimed at imaging defects in organic crystals using electron microscopy.

Now, writing in *Nature Materials*, Collins and co-workers report a strategy to minimize beam damage in the characterization of dislocation networks in a series of crystals of organic molecules, including *p*-terphenyl, anthracene, theophylline and a paraffin *n*-hentriacontane³. For all these samples, high-quality structural analysis from one single data collection is consistently achieved. They image and analyse dislocations in deformed organic crystals by scanning electron diffraction (SED), a sub-type of a recently emergent electron microscopy technique called four-dimensional scanning TEM (4D-STEM), as shown in Fig. 1a. The technique captures information comprehensive enough to image and analyse dislocations in a one-time data collection with very mild beam exposure, at a pristine specimen state. Taking inspiration from historical defect imaging techniques such as dark-field

TEM (DF-TEM) and large-angle convergent-beam electron diffraction (LACBED), the authors develop data-mining workflows to map the dislocations.

DF-TEM has been the major workhorse to image dislocations in inorganic systems since the 1950s for its superior nanometre spatial resolution and diffraction contrast mechanism⁴. Such resolution is important because dislocations often appear as extended networks with geometric configurations such as loops or stair-rods that interact with one another. However, DF-TEM requires prior knowledge of the system's symmetry, or the invisibility criteria, to correctly image and identify Burgers vectors (**B**) of a dislocation line (**u**). Burgers vectors can characterize the magnitude and direction of a displacement field. As a result, using DF-TEM alone to study dislocation networks in organic crystals has been difficult because one cannot achieve invisibility criteria either from the complex symmetry of molecular crystals or from the trial-and-error sampling of different crystal orientations, which can accumulate damage due to the electron beam sensitivity of organic crystals. However, the LACBED technique developed in the 1980s can unambiguously determine Burgers vector using at least three LACBED patterns without prior knowledge of the system⁵. Based on the rules of Cherns and Preston, diffraction intensity in a large disc formed by electrons of a range of incident angles interacting with a dislocation can be further analysed⁶. However, the diffraction method does not have the necessary spatial resolution to image dislocation networks.

Collins and co-workers take advantage of the high sensitivity of electron diffraction to dislocations, much like in LACBED, but performed in the SED mode. In SED, the electron beam interacts with the sample locally at nanometre-by-nanometre area, at nearly parallel and low convergence, to collect diffraction patterns during a raster scan of sample in the (*x*, *y*) plane in real space (Fig. 1a). The diffraction patterns at each location of interaction, or each pixel, store the information of multiple beams on a pixelated detector in one shot, so that post-collection analysis and visualization of defects can be performed on virtual dark-field (VDF) images (Fig. 1b,c). The authors leverage the unique bending of the organic crystal films to mimic the large incident angle condition in LACBED and to use multiple diffraction discs available in SED to generate multiple imaging conditions required in DF-TEM. All data are collected in one scan, successfully circumventing the beam damage challenge while maintaining the spatial resolution.

In addition to pushing the forefront of electron microscopy-based dislocation imaging, another major contribution of the work is the construction of a geometric model that allows the determination of Burgers vectors and the sign from fitting multiple beams. This model construction is important, as it allows the consideration of the generic structural flexibility of organic molecule crystals, and thus the sampling of different molecular and packing structures. The authors have conducted an extensive series of experiments, showing the broad applicability of the model. These experiments include organic semiconductors such as *p*-terphenyl and anthracene that are packed in the most naturally occurring space group, *P2₁/a*, and also the pharmaceutical

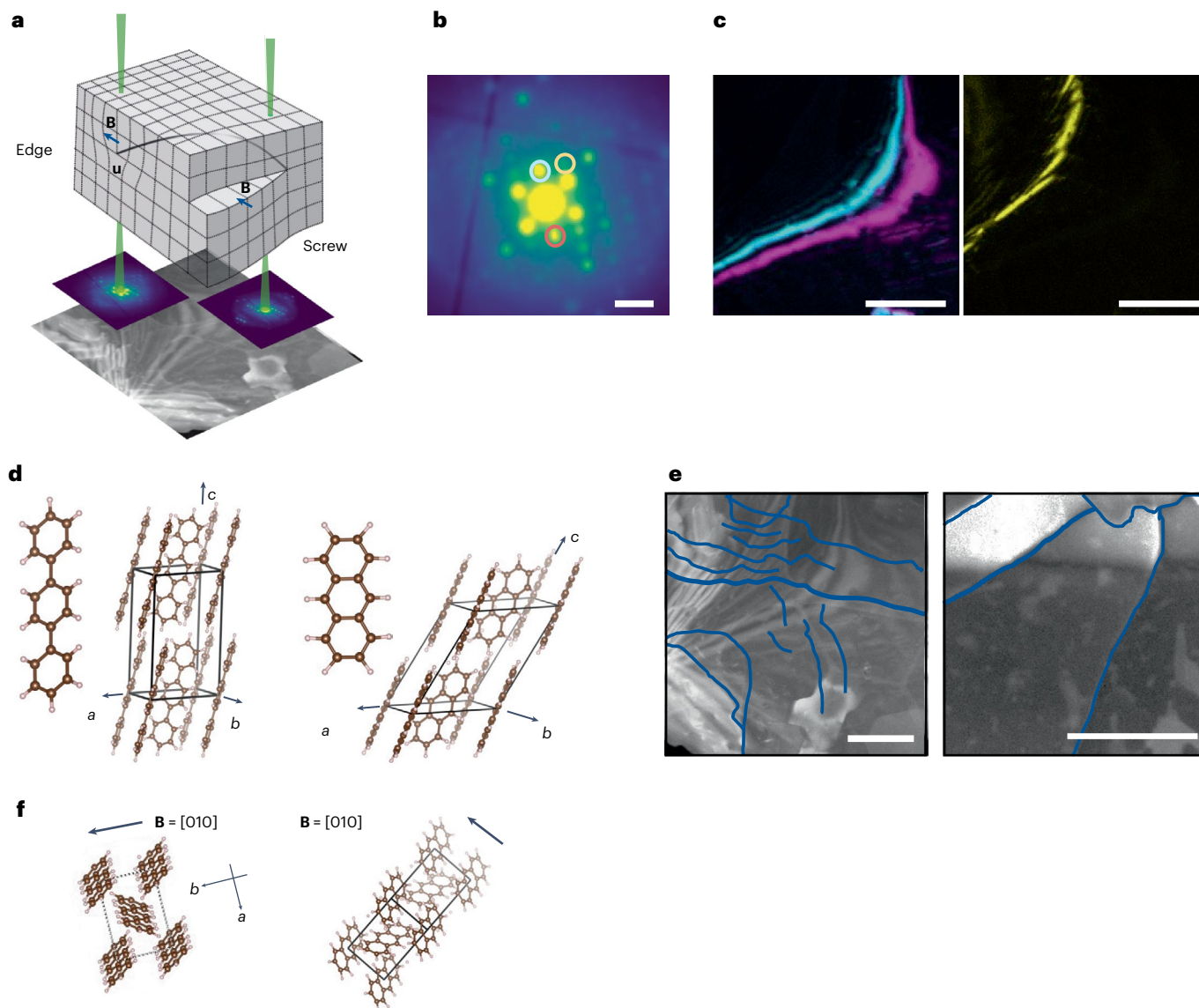


Fig. 1 | Imaging and characterization of dislocation networks in deformed organic thin films using SED. **a**, Illustration of SED on a deformed lattice with dislocation (**u**) with Burgers vectors (**B**). The resulting bottom image is a virtual annular dark-field image reconstructed from all the diffraction spots in an SED dataset. **b**, Diffraction pattern of *p*-terphenyl at [001] zone axis. Circled diffraction spots are used to form VDF images in **c**. **c**, Left: the VDF image formed by the (200) spot in cyan and the (-200) spot in magenta that satisfy the invisibility criterion. Right: the VDF image of the (210) spot in yellow does not

satisfy the criteria and shows broken line features corresponding to dislocation lines. **d**, The molecular and packing structures of *p*-terphenyl (left) and anthracene (right). **e**, The annular dark-field images of *p*-terphenyl (left) and anthracene (right) overlaid with their dislocation networks in blue. **f**, Results of the Burgers vector from the characterizations of *p*-terphenyl (left) and anthracene (right) and how it corresponds to the respective packing structures. Scale bars, 500 nm (virtual images); 0.25 Å⁻¹ (diffraction pattern). Figure adapted from ref. 3, under a Creative Commons licence CC BY 4.0.

compounds of theophylline and waxy *n*-hentriacontane with long and linear carbon chains, as shown in Fig. 1d–f.

These systems are relevant to a variety of applications for organic crystals, ranging from flexible electronics to pharmaceutical tableting. Notably, in these applications, organic crystal films can be bent, possibly causing visible cracks and mechanical failure. It will be desirable, for example, if the films can maintain macroscopic structural integrity with stress-induced dislocations locally contained. Imaging dislocations thus can be the foundation for such

predictive engineering of their structural responses to deformation⁷. Although the Burgers vectors are yet to be fully identified in three dimensions, it is remarkable to envision, based on the opportunities provided in this work³, how planar or long-chained molecules preferentially slip and slide along the path of least resistance when subjected to mechanical force. If extended beyond bent thin films, the method could potentially offer a more fundamental understanding of the structural response along with the weak and highly anisotropic interactions therein.

Broadly, this work has forged the connections of two communities – the materials scientists studying the mechanical properties of molecular materials and the chemists synthesizing and crystallizing them. This defect imaging method can find applications in other organic molecule systems such as molecular actuators, piezoelectric and triboelectric devices⁷, catalytic activity⁸ and electrochemical properties of oxides⁹. For the grand goal of autonomous materials discovery and property design, this work contributes to filling the gap in characterizing defects, as one important aspect of complexity in modern materials.

Oliver Lin¹, Zhichu Tang² & Qian Chen^{1,2,3,4}✉

¹Department of Chemistry, University of Illinois, Urbana, IL, USA.

²The Grainger College of Engineering, Department of Materials Science and Engineering, University of Illinois, Urbana, IL, USA. ³Beckman Institute for Advanced Science, University of Illinois, Urbana, IL, USA.

⁴Materials Research Laboratory, University of Illinois, Urbana, IL, USA.

✉ e-mail: qchen20@illinois.edu

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Competing interests

The authors declare no competing interests.