MS13 Structural Characterization of Functional Materials

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A walk through the valley of weak interactions and diverse mechanical responses of crystals

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Abstract

The amazing ability of crystalline matter to adapt to external stimuli while consequently achieving outstanding mechanical movements, such as bending, jumping, crawling, or exploding, has enabled the evolution of a new direction in advanced materials design and development. [1] However, with a growing number of literature reports describing dynamic crystalline compounds, it becomes clear that the structural background behind these materials is not straightforward, and to get to the point where mechanically responsive crystalline solids become the material of choice, a thorough structure-property correlation must be delivered.

One-dimensional crystalline cadmium(II) coordination polymers emerged as a perfect model system to investigate structure-property interconnection, as they displayed an unexpected diversity of mechanically induced responses – a wide spectrum from purely elastic bending motions to variable plasticity. [2–5] These motions were found to be dependent not only on the crystals' composition but also on the direction of the force application, therefore making a clear distinction between 1D and 2D bendable crystals. Recently, it was observed that the latter could additionally be divided into two subcategories, 2D-isotropically and 2D-anisotropically flexible. Upon investigation of this intricate spindle of crystal flexibility and structural characteristics, intermolecular interactions were found to be one of the key factors which guide the behaviour of the crystal towards the desired mechanical output. [5]

To investigate the influence of the weak intermolecular interactions on the mechanically induced crystal adaptability more closely, we opted for another family of crystalline Cd(II) coordination polymers equipped with methyl derivatives of pyridine or pyrazine. By introducing slight structural changes around the cadmium(II) metal centre, via exchanging bridging anion or inducing small changes in heterocyclic ligand, we were able to alter the crystals' morphology, the dimensionality of resulting polymers, crystal packing arrangement, the strength of the intermolecular interactions, and consequently the crystals' mechanical response. While with pyridine-based ligands we isolated 1D coordination polymers whose crystals displayed a variety of elastic mechanical responses, crystalline compounds with pyrazine-based ligands formed 2D polymeric networks and displayed primarily plastic flexibility upon the applied stress. Furthermore, a detailed inspection of mechanical and structural properties using a variety of advanced and custom-designed experimental methods provided us with a deeper insight into the origin and a mechanism of mechanically induced bendability, thereby allowing us to get one step closer to unraveling the puzzle of an extraordinary world of flexible crystals.

References

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