

Lively crystals – on the mechanism of thermally induced structural adjustments in elastically adaptable coordination polymers

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From delivering essential pharmaceutical components that resolve numerous health issues to providing incredible soft and delicate machines, crystals tend to amaze the world of science daily with their endless and often surprising possibilities. [1, 2] The past several decades of research on crystal engineering have yielded a wide variety of crystalline compounds equipped with remarkable properties, such as electrical, optical, and magnetic, that ensure a bright future of crystals' utilisation in the development of emerging technologies. [3] Even the major impediment of the usual fragile and static nature of crystals has been transcended with the discovery of dynamic crystalline materials capable of adjusting to a wide variety of external stimuli by displaying extraordinary mechanical movements. [4] Crystals being able to bend, jump, explode, or endure considerable changes in their dimensions, thus mimicking the behaviour of biological systems, show significant potential in finding novel solutions in the design of advanced materials. Although up to this moment a significant number of dynamic crystals have been found, structural features which enable this incredible dynamic adaptability of crystalline compounds, and the mechanism of the movements are still not entirely elucidated. Recent studies demonstrated that even slender crystals of relatively structurally rigid one-dimensional coordination polymers of d-block metal cations such as cadmium(II), lead(II), and zinc(II) with heterocyclic organic ligands can adapt to the application of mechanical force by displaying elastic and/or plastic bending motions.[5–11] It was found that inducing slight structural modifications directly impacts the ability of a crystal to bend, the extent, as well as the type of bending. In addition to mechanically triggered motions, it was found that a handful of compounds of this type are also able to display thermally and light-stimulated motions. [11]

To get a deeper insight into the structural prerequisites which enable stimuli-triggered dynamic motions together with structural adjustments that take place during the mechanical response, an in-depth examination of the structure–property correlation was executed for two one-dimensional crystalline coordination polymers of cadmium(II) with halides (Cl⁻, Br⁻) and pyrazinamide ligand. Crystals of both compounds display mechanically induced adaptability; 2D anisotropic elastic bending upon the application of the mechanical force in a three-point bending fashion, and notable elastic deformation during the static tensile experiments from which Young's moduli of these materials were determined. In addition to mechanically initiated dynamic responses, these crystals also exhibit slight mechanical movements provoked by the elevation of the temperature. To examine the source of thermally initiated motions, adjustments of the structural characteristics of each crystal in a wide temperature range were monitored. The results demonstrate that the application of thermal stimulus triggers changes that involve several structural features. Apart from a clear impact on parameters of the unit cell, i.e., increase of crystallographic axes and overall volume, and concurrent decrease of the majority of angles with elevation of the temperature, subtle changes in spatial orientation of specific molecular fragments in the structures were also noted, such as changes in the tilting angle between the heterocyclic ligand and the plane of Cd–X (X – halide ion) chain, rotation of the heterocyclic ligand and changes of the angles in a polymeric chain. All these adjustments prove the complexity of the thermal mechanism of this astonishing family of elastically adaptable coordination polymers. The results of this research contribute to the understanding of the dynamic nature of crystals by providing the basis for further enlightenment of the tangled world of adaptable crystalline solids.[12]

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