

Received 21 October 2015
 Accepted 4 November 2015

Keywords: metal–organic frameworks; high-pressure crystallography; nanoporous materials.

Metal–organic frameworks: the pressure is on

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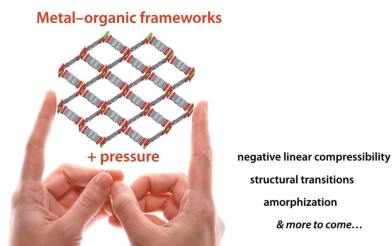
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Metal–organic frameworks, or MOFs, demonstrate a wide variety of behavior in their response to pressure. A growing number of materials in this topical family have been shown to be stimuli-responsive (Coudert, 2015), with most of the attention paid to structural transitions upon temperature change and guest adsorption or evacuation – including some eye-catching phenomena with names such as gate opening and breathing. However, as McKellar & Moggach (2015) show in their Feature Article, ‘pressure is a powerful thermodynamic variable’ which can be varied within a wide range (four orders of magnitude) and is tensorial in nature (compared with *e.g.* the scalar nature of temperature). Being built partly on weaker interactions (coordinative bonds, π – π stacking, hydrogen bonds *etc.*) than traditional inorganic microporous materials, and because they reach ultra-high porosities, MOFs tend to be generally more compressible than, say, zeolites. This magnifies their unusual responses to the application of high pressures, with large-scale changes of structure and properties upon modest stimulation, and can in turn be leveraged into devices and applications. McKellar & Moggach (2015) have reviewed the recent literature in this rapidly growing field, highlighting some of the key behaviors that have been observed in MOFs (Fig. 1).

One of the striking behaviors emerging among MOFs is the high prevalence of materials with anomalous mechanical properties. This category includes properties such as auxeticity (the existence of negative Poisson’s ratio) and high elastic anisotropy, but one that has recently attracted significant interest and is perhaps the most counter-intuitive is negative linear compressibility (NLC; Cairns & Goodwin, 2015). A material displaying NLC, upon compression under hydrostatic pressure, expands along one or several directions – rather than contract. Because thermodynamics requires that $(\partial V/\partial P)$ be negative, NLC is associated with large positive compressibility along at least one direction. NLC is rare among crystalline materials in general yet it was reported in several framework materials, dense or porous. Therein it is often associated with specific network topologies or structural motifs, including wine racks, honeycombs and helices. The common occurrence of these motifs in MOF topologies could lead to a vast increase in the number of known NLC materials in the coming years, with potential application in pressure-sensing devices and actuators.

A second class of phenomena highlighted by McKellar & Moggach (2015), which has seen a recent surge in activity, is the occurrence of pressure-induced structural transitions observed by compression of a framework material immersed in a fluid, either penetrating or non-penetrating. The past decade has seen a rapidly growing number of high-pressure single-crystal X-ray diffraction studies reported in the literature, providing high-quality structural information in the gigapascal range of pressure – typically 0.1 to 10 GPa – using diamond–anvil cells (Moggach *et al.*, 2008). Indubitably the most widely studied systems from this point of view are a family of MOFs featuring four-connected zeolite-like nets, the zeolitic imidazolate frameworks (ZIFs). Such studies have helped advance significantly our fundamental understanding of structural transitions and polymorphism among MOFs, as well as their mechanical properties and the way in which the presence of guest molecules can dramatically affect these properties.

This knowledge of mechanical properties and stability is crucial for applications of MOFs at the industrial level. For stimuli-responsive material to be of practical use, they need to strike a delicate balance between the desire to discover novel mechanical responses and leverage them into new functions, and a need for materials with sufficient mechanical stability. An important milestone in this direction was the realisation that amorphization of MOFs, which was once thought of as the death of a (possibly expensive!) sample, can actually be of practical interest. Amorphous phases of MOFs can be



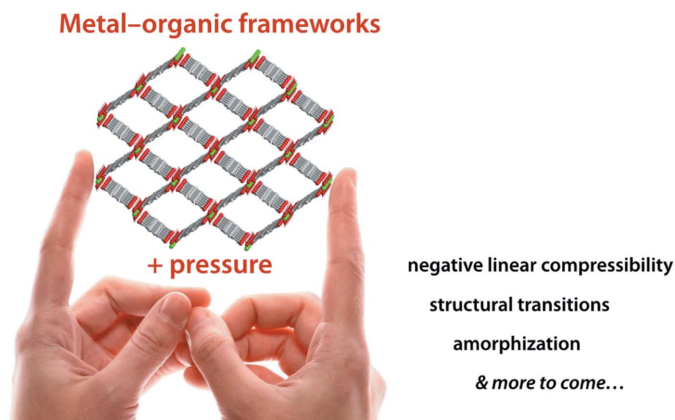


Figure 1
Metal–organic frameworks demonstrate a wide variety of behavior in their response to pressure.

produced by controlled pressure-induced amorphization, either through hydrostatic compression or ball-milling (Bennett & Cheetham, 2014). These amorphous structures partially retain the porosity of the parent crystalline MOF, and feature improved mechanical strength. Amorphous MOFs could thus prove beneficial for the traditional applications such as adsorption and catalysis, but they have also been proposed for specific purposes, *e.g.* irreversible trapping of

species such as radioactive iodine (Chapman *et al.*, 2011). However, we still have a lot to learn about the disordered phases of MOFs and the mechanisms of crystal-to-disordered transitions, as illustrated by the recent discovery of glass-forming liquid MOFs (Bennett *et al.*, 2015) and the evidence that correlated disorder can play a strong role even in crystalline MOF structures (Cliffe *et al.*, 2014).

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