A045-06-260823 Using High-Pressure Diffraction to Design and Understand Functionality

Dual-cell, high-pressure studies of porous, flexible frameworks from 20 to 30,000 bar

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Metal-organic frameworks (MOFs) are at the heart of porous materials research, due predominantly to the framework pore spaces accessible after activation for molecular adsorption. Most research in this area has centred on rigid MOFs; we are still at the beginning, however, of understanding structure-property relationships of flexible framework materials. Increasing numbers of MOFs are being investigated in relation to their dynamic deformation under various external stimuli such as temperature or pressure [1], in order to map out structure-property relationships for utility in various applications including gas separations.

The SHF (Sheffield Framework) family of MOFs [2,3] are a series of two-fold interpenetrated diamondoid indium-based frameworks with aminoterephthalate-based organic linkers (Figure 1a,b). The parent SHF-61 MOF exhibits large-amplitude continuous 2D “breathing” with a *pseudo*-wine rack motion, as well as prominent host-guest chemistry which leads to gas separation capabilities [2]. Post-synthetic modification of the pendant amine groups to form acetamide yields the MOF SHF-62, which exhibits 3D breathing behaviour, where channel-length expansion/compression accompanies the dynamic deformation of channel cross-section [3]. Recently, the family has been extended through a series of cation-exchanges, whereby the parent dimethylammonium can be exchanged for larger cations, which has implications for the dynamic range of the materials. The large-amplitude dynamic motion observed upon removal/uptake of guest molecules raised questions around the structural response of these materials to other external stimuli, namely *pressure*.

In this work, we used a combination of different pressure cells to facilitate X-ray diffraction studies of SHF MOFs across multiple pressure ranges. A recently-developed sapphire capillary liquid-pressure cell [4] facilitated visualisation of the initial framework deformation at a mid-pressure range (20-1,500 bar), before higher pressure ranges were reached using the more commonly utilised diamond anvil cell (~0.1–3 GPa; 1,000–30,000 bar) (Figure 1c). Marked differences in framework behaviour were observed between using framework-penetrating and non-penetrating pressure-transmitting media (Figure 1d). This combination of pressure cells enables a uniquely detailed insight into the nuances of the dynamic response of these flexible frameworks across a wide pressure range.

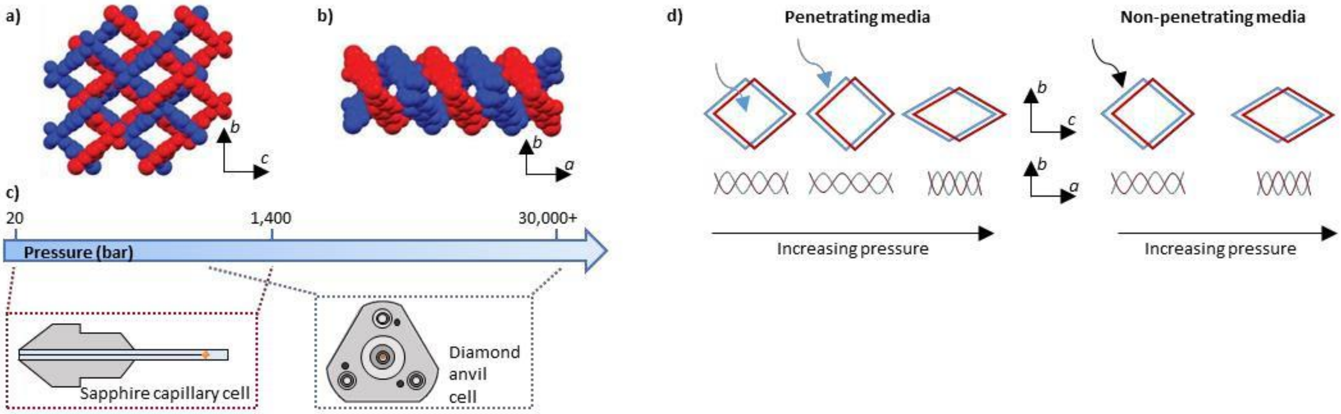

Figure 1. View down the a) *a*-axis and b) *c*-axis of the SHF-61 MOF; c) pressure ranges accessed with sapphire capillary and diamond anvil cells; d) schematic of framework deformations under from pressure.

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