Materials that show strong responses to external stimuli are of vital importance for the development of future functional devices. We have recently characterised a series of 3D coordination frameworks, LnFe(CN)$_6$, that are extremely flexible by virtue of competition between the framework rigidity and the counteracting effect of their locally-unstable trigonal prismatic lanthanoid (Ln = La–Lu, Y) coordination geometries, which exert an internal pull on the structure.[1] This flexibility yields anomalous structural responses to temperature and pressure.

Using a wide array of X-ray and neutron structural and dynamic techniques, we have characterised the negative thermal expansion properties of this series, wherein the materials contract upon warming. Through inelastic neutron scattering and DFT-based calculations we find that the origin of this behaviour is a new torsional mechanism wherein the non-rigid Ln coordination geometry twists at unusually low vibrational energies.[2] High pressure neutron diffraction measurements show a freezing-in of this twisting mode, with the Ln coordination geometry reversibly and progressively transformed from trigonal prismatic at ambient pressure to octahedral at 1 GPa, with further twisting at higher pressures (see Figure). This change is accompanied by a coiling up of the framework, and an extremely high compressibility which is one of the largest for any crystalline material.[3]

This discovery opens the door for pressure-tuneable luminescent and magnetic behaviour in these frameworks and has implications for the strategic design of next-generation responsive materials.

Figure 1. Progressive, reversible crumpling of the YFe(CN)$_6$ structure under increasing hydrostatic pressure. Shown are a single slice of the network structure (top) and the Y coordination environment (bottom).