



References:

- [1] P F Tavares et al, (2014), *J. Synchrotron Rad.*, 21, p. 862.
 [2] U Johansson, U Vogt and A Mikkelsen, (2013), *Proc. SPIE* 8851, 88510L.
 [3] B. Enders P. Thibault, (2017), *Proc. R. Soc A* 472 20160640

Keywords: Nanofocus, Hard X-ray, diffraction

MS24-P04

Correlated disorder in a metal-organic framework

Emily Reynolds¹, Mia Baise², Alistair Overy¹, Arkadiy Simonov³, Jamie Gould⁴, Ben Slater², Andrew Goodwin¹

1. University of Oxford, Oxford, United Kingdom
 2. University College London, London, United Kingdom
 3. University of Freiburg, Freiburg, Germany
 4. University of Leeds, Leeds, United Kingdom

email: emily.reynolds@chem.ox.ac.uk

At the heart of creating and developing functional materials is understanding structure - a task often complicated by disorder, be it compositional or orientational, static or dynamic. Whilst diffraction techniques have become adept at describing periodicity and understanding atomic structure, deviation from perfect order occurs in most real materials. Traditional crystallographic techniques fail to describe such deviations from periodicity, and while we understand the importance of disorder we are yet to understand how to describe, characterize and control disordered states.

A very specific disordered state is correlated disorder. This state arises when dominant interactions - i.e. chemical bonding - dictate fixed local atomic arrangements that need not result in long-range 3D order but may result in aspects of the structure being correlated. These correlations can produce signature patterns in the measured diffraction pattern in the form of diffuse scattering. In a class of materials known as metal-organic frameworks (MOFs), the local interactions driving formation usually result in long-range periodic arrangements. However, we can introduce disorder in MOFs through asymmetry in the linker, which acts in an analogous way to cyanide in transition-metal cyanides.[1] second-order Jahn-Teller displacements in BaTiO₃ [2] and hydrogen bonding in square ice.[3]

We substitute terephthalate linkers with asymmetric pyrazole-carboxylate and show that while powder and single crystal diffraction data suggest the linkers are disordered, the highly structured diffuse scattering visible in single-crystal X-ray patterns indicates correlated disorder along the linker rows. By comparing experiment with models calculated using simple local rules, we are able to understand the specific type of correlations giving rise to the diffuse, and prove the presence of correlated disorder in a MOF-5 analogue. The fixed local arrangements in the structure results in specific pore chemistry and binding sites important for adsorption and catalytic applications. More generally, these results contribute to the ability to identify specific types of correlated disorder within analogous systems, and therefore a greater understanding of structure on the nanoscale.

References:

- [1] Karyakin, A. (2001). *Electroanalysis*, 13, 813-819.
 [2] Senn, M., Keen, D., Lucas, D., Hriljac, J. & Goodwin, A. L. (2016). *Physical Review Letters*, 116, 207602.
 [3] Pauling, L. (1935). *Journal of the American Chemical Society*, 57, 2680–2684.

Keywords: Disorder, framework, diffraction