

Correlated Linker Disorder in Metal-Organic Frameworks

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The first developments on metal-organic frameworks, or MOFs, were made approximately four decades ago, marking the discovery of a novel class of porous materials. Initially thought to be ordered and truly crystalline, there is now an increasing realisation that defects and disorder are prevalent in MOFs, and that nontrivial arrangements can be important in physical properties [1]. Though, disorder in MOFs does not necessarily imply randomness. In fact, depending on the interactions between components, MOF structures can exhibit short-range order and long-range disorder simultaneously. This is what we refer to as correlated disorder [2]. Thorough understanding is achieved through investigation of the interactions involved in causing these states, with the aim of controlling physical properties via their manipulation.

Generally, there are three types of disorder observed in MOFs: vacancy defects, compositional disorder, and orientational/conformational disorder [3]. The latter forms the focus of this project. A key factor is the distinction between molecular point symmetry (*i.e.* the local structure) and that of the corresponding position in the lattice (*i.e.* the average structure). Namely, molecular components are arranged on a lattice of which the geometry is determined by that of the MOF, giving control over the molecular orientational degrees of freedom [4]. Since MOF geometry is often highly symmetric, lowering the symmetry of nodes and/or linkers can enable targeted design of correlated conformational disorder (Fig. 1).

In this work, correlated disorder is introduced to the highly symmetric (hypothetical) parent framework $\text{ZnO}_4(\text{BTC})$ (BTC = benzene tricarboxylic acid) by reducing the linker symmetry from D_{3h} to C_{2v} , giving $\text{ZnO}_4(1,3\text{-BDC})$ (BDC = benzene dicarboxylic acid) (Fig. 1). The resulting linker disorder is characterised via diffuse scattering observed in single crystal X-ray diffraction (SCXRD) patterns, 3D Δ -pair distribution functions (3D Δ -PDFs), and Monte Carlo code. Ultimately, we want to understand how to control defective structures in MOFs to optimise their properties, enabling utilisation in real-life applications.

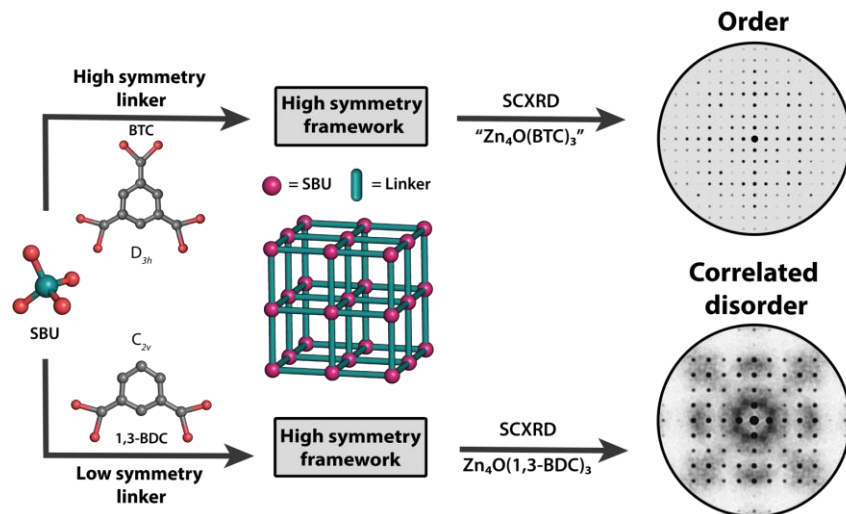


Figure 1. Approach of introducing correlated disorder into MOF structures, showing an example relevant to this project – replacing the highly symmetric BTC linker with 1,3-BDC.

[1] Bennett, T. D., Cheetham, A. K., Fuchs, A. H., Coudert, F.-X. (2017). *Nat. Chem.* **9**, 11.

[2] Keen, D. A. and Goodwin, A. L. (2015). *Nat.* **521**, 303.

[3] Meekel, E.G. and Goodwin, A.L. (2021). *CrystEngComm*.

[4] Simonov, A. and Goodwin, A. L. (2020). *Nat. Rev. Chem.*

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