Tetrahedral structures like silica are capable of a large structural variety. The class of ZIFs, which are based on metallic linkers tetrahedrally coordinated by imidazolate ligands, feature porous networks, which are thermally and chemically stable. Ligand substitution allows for easier property tuning than inorganic zeolites. For gas adsorption, porosity is a critical parameter, which can be affected by network topology. A complete scan of possible ZIFs materials uses therefore the language of nets to enumerate all possible topologies and extract all compatible space groups. While standard structure prediction methods tend to fail, topological enumeration is extremely powerful for ZIFs. In the combination with DFT techniques, accurate energy landscapes of ZIFs compounds can be obtained, prior to ZIFs synthesis.

The free energy landscape of ZIFs is complicated, not only due to the potentially large number of metastable compounds with distinct topologies, but also by the variety of conformational polymorphs, resulting from ligand internal degree of freedom. Additionally, dispersion interactions require interatomic potentials beyond standard models. This makes the investigation of polymorphism and phase transitions in MOFs and ZIFs challenging, and subtly involved. A complete knowledge of the free energy landscape is critical for affecting properties, from structural (porosity), to bulk and mechanical properties.

The prediction of MOFs and ZIFs crystalline structures yields a rather accurate estimate of the likelihood of a structural motif, beyond bare space group or network occurrence statistics. In practice however, in order to turn a predicted structure type into an actual compound, ligand substitution may be a key ingredient. SOD, RHO and lcs topologies for example can be realised in zinc 4,5-dichloro imidazolate ZIFs only, but remain elusive if the ligand is unsubstituted [1-3].

Despite an advanced understanding of structural details, and a growing variety of synthesised compounds, we are still not able to fully predict which compound is going to be formed. To elucidate the reasons for the selection of a particular MOF/ZIF topology, nucleation and growth details at times of compound formation must be understood, as the formation of a particular network is associated with a kinetic mechanism.

Mechanisms for solid-solid polymorphic transformations, currently still rare, can provide insights into the (meta)stability of a certain polymorph, and help augmenting energy-based rankings by a precise knowledge of energy barriers, which favour or disfavour a polymorph stability [3].

Crystallisation appears more and more as the fundamental process during which the selection of metastable topologies is taking place. While still involved and demanding in terms of computational resources, the use of topological MOF descriptors in combination with advanced numerical tools can provide additional guidance in understanding at which stage a metastable motif can be expressed, and subsequently grow, or what can assist the formation of “complicated” topologies, otherwise unlikely as structurally less simple.


Keywords: ZIF polymorphism, crystallisation, phase transitions