

Nanostructured MOFs through defect engineering

Matthew Cliffe¹, Clare P. Grey¹

¹Department Of Chemistry, University Of Cambridge, Cambridge, United Kingdom
E-mail: mjc222@cam.ac.uk

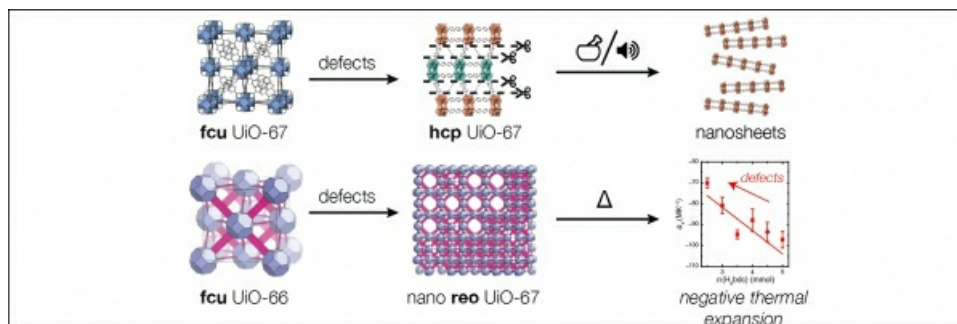
The crucial role that defects play in the chemistry of metal-organic frameworks (MOFs) is becoming increasingly clear, with recent studies revealing the existence of defects, especially ligand vacancies, in many important families of MOFs. The presence of defects has been shown to dramatically improve sorption properties [1], catalytic activity [1] and ionic conductivity [2] of MOFs. In many materials, particularly at higher defect concentrations, the interactions between defects lead to nanostructures that determine the behaviour of a material.

We have investigated the role of defects in the canonical UiO-66 family of MOFs, and shown that at high concentrations these defects are accommodated by introducing correlation. Just as for oxide frameworks, this ordering leads to a diversity of structures. We have focussed on two examples, where defect correlations lead to very different nanostructures: UiO-66(Hf) (benzenedicarboxylate ligand), where defects are accommodated through a nano-domain phase in which correlated ligand absences lead to metal cluster absences [4] and UiO-67(Hf) (biphenyldicarboxylate ligand), where condensation of the metal cluster secondary building units leads to the formation of layered phases.

Making use of a wide-range of complementary techniques (including pair-distribution function analysis, in situ diffraction of MOF growth and transmission electron microscopy) we further demonstrated that the structures of the resultant defect phases depend critically not only on the concentration of defect-promoting modulator, but also on the identity of the ligand and the reaction time and temperature.

The control over structure provided by defects allowed us to tune the physical and chemical properties of the UiO family of MOFs. By varying the concentration of defects we were able to tune the very large isotropic negative thermal expansion of UiO-66(Hf), and the introduction of chemical anisotropy into UiO-67(Hf) meant it was possible to delaminate it into nanosheets.

[1] Vermoortele, F. et al., J. Am. Chem. Soc. 135, 11465, 2013. [2] Taylor J. et al., Chem. Mater. 27, 2286, 2015. [3] Cliffe M.J. et al, Nat. Commun. 5, 4176, 2014.



Keywords: [metal-organic frameworks](#), [defects](#), [nanosheets](#)