[MS37-03] Correlated disorder and structured nanodomains in Group 4 MOFs

Matthew J. Cliffe and Andrew L. Goodwin,

Department of Chemistry, University of Oxford.
matthew.cliffe@chem.ox.ac.uk

UiO-66(Zr) was the amongst the first very stable metal-organic frameworks (MOFs) to be discovered[1], and as itis thermally stable to above 400oC and chemically stableto acid, base and boiling water it has been extremely well-studied. In addition to the exploitation of its porosity for gas and liquid separations[2][3], UiO-66 and its derivatives have been shown to be active Bronsted catalysts[4], photocatalysts[5], and sensors[6].

UiO-66 has a face-centered cubic like topology, consisting of twelve coordinate Zr6O4(OH)4 clusters, linked together by 1,4-benzenedicarboxylate (BDC) ligands. This high connectivity has been posited as anexplanation for the structural stability of the framework.This framework has also proved extremely versatile, witha wide range of other dicarboxlyate ligands also formingisoreticular MOFs. Substitution of Hf for Zr is also facile[7],[8].

The relatively simple topology and the structural stabilitygive only a partial picture of this material, and there havebeen early indications of structural complexity and dynamic behaviour, with TGA evidence suggesting that there are ligand vacancies[9], and post-synthetic transformations, such as ligand and metal exchange possible[10]. Some of the most striking evidence of structural complexity in this family is the presence ofbroad primitive superlattice reflections in samples of UiO-66, especially UiO-66(Hf)[8]. We show that these peaks are in fact consistent with diffuse scattering produced by the existence of nanodomains of correlateddefects. We have further shown that the size and concentration of these defects are amenable to chemical control through the use of modulators. These defects arean integral part of the structure of the material, and asrelatively energetic sites, may present opportunities for reactivity and catalysis.

The existence of these defects and disorder could well have important implications for the properties of UiO-66, from the presence of wider pores to the effect of lowerconnectivity on the mechanical properties. These will beparticularly pertinent for calculations of the properties ofthis material. It also highlights that the idealised topologies of MOFs may not provide the complete storyfor these useful and fascinating materials.

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