

Poster Presentations

[MS37-P12] Correlated disorder and structured nanodomains in Group 4 MOFs
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UiO-66(Zr) was the amongst the first very stable metal-organic frameworks (MOFs) to be discovered[1], and as it is thermally stable to above 400 °C and chemically stable to 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 $Zr_6O_4(OH)_4$ clusters, linked together by 1,4-benzenedicarboxylate (BDC) ligands. This high connectivity has been posited as an explanation for the structural stability of the framework. This framework has also proved extremely versatile, with a wide range of other dicarboxylate ligands also forming isoreticular MOFs. Substitution of Hf for Zr is also facile[7],[8].

The relatively simple topology and the structural stability give only a partial picture of this material, and there have been 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 of broad 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 correlated defects. We have further shown that the size and concentration of these defects are amenable to chemical control through the use of modulators. These defects are an integral part of the structure of the material,

and as relatively 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 lower connectivity on the mechanical properties. These will be particularly pertinent for calculations of the properties of this material. It also highlights that the idealised topologies of MOFs may not provide the complete story for these useful and fascinating materials.

References:

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