

MS17-P16 Using *in situ* X-ray diffraction to observe solvent exchange during MOF synthesis

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Metal-organic frameworks (MOF) materials are most commonly synthesised using solvothermal methods. Very often, MOFs contain solvent molecules coordinated to metal atoms in the framework skeleton; this solvent can then exchange with other species - for example, H₂O and DMF. To date, it has been impossible to quantify whether a framework is initially formed with one solvent that can be exchanged with another to reach the final product, or if the final product is the only species formed. Using time-resolved monochromatic high energy X-ray diffraction with a custom IR furnace cell ('ODISC', the Oxford-Diamond *In-Situ* Cell, Fig. 1, left),¹ we have been able to understand this behaviour in a laboratory-scale reaction at an unprecedented level of detail.

We present an *in situ* study of the solvothermal crystallisation of a new ytterbium MOF from a water/DMF mixture under solvothermal conditions. Analysis of high resolution powder patterns using Rietveld refinement reveals an evolution of lattice parameters and electron density during the crystallisation process. Quenching studies confirm that this is due to a gradual topochemical replacement of coordinated solvent molecules: the water initially coordinated to Yb³⁺ is replaced by DMF as the reaction progresses (Fig. 1, right). This study shows the possibility of studying very subtle changes in laboratory-scale reactions, which would be relevant not only to solvent exchange studies but also in the investigation of e.g. the preferential incorporation of different species mixed-metal and mixed-ligand frameworks.

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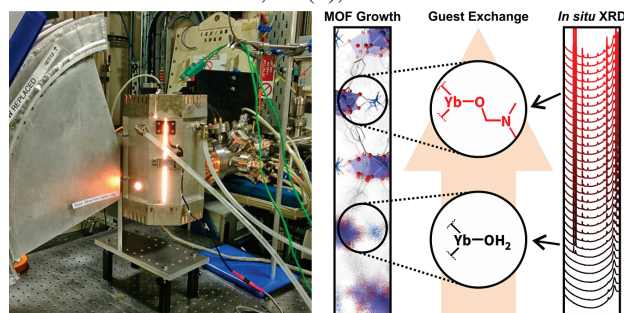


Figure 1. (left) ODISC furnace; (right) *In situ* guest exchange occurs during MOF growth

Keywords: in situ diffraction, MOF

MS17-P17 *In situ* investigation of the mechanochemical syntheses of new cadmium phenylphosphonates

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Metal phosphonates are metal organic compounds consisting of a metal ion and an organic phosphonic acid, usually deprotonated. Typically, metal phosphonates crystallize in layer structures where the organic part points into the interlayer space and can be classified as porous coordination polymers (PCP)^[1]. The research on this topic is of great interest because of their high potential of applications for gas storage^[2], catalyses^[3], proton conductors^[4], and surface modification^[5]. Usually, metal phosphonates are synthesized from solution, often under hydrothermal conditions for a reasonable crystallinity. Against this background, the syntheses of the crystalline cadmium phenylphosphonates Cd(O₂PPh)₂•H₂O (**1**), Cd(HO₂PPh)₂ (**2**), and Cd(HO₂PPh)₂(H₂O₃PPh) (**3**) from solid state reactions by grinding together cadmium acetate with respective equivalents of phenylphosphonic acid is presented. (**2**) and (**3**) can not be synthesized by any other synthesis method so far. The milling reactions were investigated *in situ* using synchrotron PXRD. The setup was developed by our group^[6]. Based on these data, the identification of intermediates is possible and the reactions mechanisms can be analyzed in detail.

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