MS44-O1 **Uncovering the molecular assembly of metal organic frameworks through scanning force microscopy**
Pablo Cubillas, Pak Y. Moh, Michael W. Anderson, Martin P. Attfield *School of Chemistry, The University of Manchester, UK.*
E-mail: pablo.cubillas-gonzales@manchester.ac.uk

Understanding the fundamental aspects of the crystal growth of metal organic frameworks (MOFs) is critical to develop better materials for new and enhanced applications. Some of the most pressing questions in this regard are the formation of the structure around the voids in the framework or the factors that control the morphology of the crystals. Only direct observations at the nanoscale under growing conditions can reveal the answers to these fundamental questions. Atomic force microscopy (AFM) can provide these kind of detailed observations. In this paper we report results from in-situ AFM growth experiments for three different MOFs: MOF-5, ZIF-8 and ZIF-76. AFM images of the three types of crystals growing under low supersaturation conditions reveal similar results. In all cases growth was observed to take place by a birth and spread and/or spiral growth mechanism. Detailed height analysis of 2-D nuclei as a function of lateral spreading revealed a complex mechanism of terrace growth for all three systems. For ZIF-76 five different heights were measured: 0.6, 1.0, 1.4, 1.8 and 2.3 nm. The last height is equal to that of a full monolayer height or d_{100} spacing, which corresponds to a double four ring (D4R) plus a sodalite (SOD) cage of the LTA-type structure of ZIF-76. The other heights correspond to the height of single D4R (0.6 nm) or the sum of a D4R plus an incomplete SOD cage. For ZIF-8, a similar stepwise building process was observed with heights corresponding to the addition of Zn ions or methylimidazole linkers to complete the constituent sodalite cages that provide the step stable termination. In the case of MOF-5 only two heights were measured during 2-D nucleation and growth, corresponding to addition of the Zn clusters and benzendicarboxylic (bdc) linker. These measurements indicate that MOF crystal growth takes place by the nucleation and spreading of successive metastable unenclosed sub-layers to eventually form the stable, enclosed framework structure. This process is dependent on the presence of non-framework species that bridge the developing pores during growth. During the experiments on MOF-5, it was also observed that varying the stoichiometry of the MOF-5 growing solutions resulted in a dramatic change in terrace morphology. Solutions with a Zn/H_2bdc ratio > 1 produced square terraces with steps parallel to the d directions. However, if the Zn/H_2bdc ratio is approximately one, the steps become parallel to the o direction, resulting in a rhomboid terrace morphology. Additionally, a change in MOF-5 crystal shape was observed from the pure cubic morphology to blunted cubes and octahedra expressing the {111} facets indicating a change in the relative growth rates of the different faces that define the crystal morphology. These results provide a modulator-free route to control the crystal morphology of MOF-5 and potentially other MOFs.

MS44-O2 ***In situ*** **observations of impurity effects during protein crystallization.**
Mike Sleutel, Dominique Maes, [a]*Structural Biology Brussels, Flanders Interuniversity Institute for Biotechnology (VIB), Vrije Universiteit Brussel, Pleinlaan 2, 1050, Elsene, Belgium*
E-mail: mike.sleutel@vub.ac.be

Laser confocal microscopy combined with differential interference contrast microscopy (LCM-DIM) has emerged as one of the most powerful mesoscopic techniques for *in situ* observation of the protein crystal-liquid interface. We employ this technique to visualize noninvasively the surface topography of protein crystals that are in non-equilibrium with the surrounding mother liquor. From snapshots of growing crystals the dominating growth mechanisms are determined. Subsequent time-lapse imaging of a single observation area is then used for the study of growth and/or dissolution dynamics in response to the system's super/undersaturation. From the kinetics of elementary steps growing from high purity solutions, fundamental kinetics coefficients are determined. These measurements then serve as a benchmark for further studies of crystal growth kinetics in impure conditions. Two topics in particular will be highlighted. First, the concept of time-dependent impurity uptake will be discussed. Different growth mechanisms expose the crystal surface to the surrounding bulk liquid with varying characteristic times, coined the terrace exposure times. The ratio of the terrace exposure time with the characteristic time for impurity adsorption onto the crystal surface is put forward as an intrinsic constant that governs impurity incorporation. This model is then applied to the two main crystal growth mechanisms, i.e. spiral dislocations and two-dimensional nucleation, and differences will be commented upon. Secondly, we discuss the growth mechanism of a non-model protein crystallization system, i.e. xylanase. We will show that by departing from well-established purified protein model systems (e.g. lysozyme), unconventional growth mechanisms are obtained that result in highly complex protein crystals with nontrivial surface topography.

Keywords: proteins;crystal growth;impurities