MS25-1-3 3DED Experimental Parameter Optimization to Metal-Organic Frameworks
#MS25-1-3

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Abstract
3D Electron Diffraction (3DED) is nowadays one of the best techniques for structure determination of nano crystalline material. The basis for a successful crystal structure analysis are the acquired data quality and the completeness of expected reflections in the reciprocal space. Dependent on the materials beam sensitivity, micro-crystallinity, agglomeration state and crystal structure complexity, it can be challenging to perform. MOFs usually require cryo-handling, due to electron beam and vacuum sensitivity, and hybrid pixel detectors to maximize the signal-to-noise (S/N) ratio in order to achieve higher quality data, minimize experimental time and electron dose on the sample, avoiding structure modifications. [3,4]
Metal-Organic Frameworks (MOFs) are a class of porous materials with physicochemical properties strictly related to their crystal structure. These compounds, usually display pores of tunable sizes and a 3D crystalline network composed by the interaction between inorganic metal cations and organic ligands through coordination bonds. [1] Thanks to their porous structure, these materials are widely used for small molecules adsorption or guest replacement, heterogeneous catalysis, drug delivery, gas storage, sensing. [2]
In this work, we report a systematic investigation of Pyrazole-3,5-dicarboxylic acid-(acetate)(sulfate)/Iron MOF as synthetized and thermally activated, achieved from ED patterns acquired by a common CCD camera, in a FEI Tecnai F30/S-TWIN Transmission Electron Microscope (TEM), operating at 300 kV. In a first step, the crystal structure of both, the as synthesized and activated material, was solved. Both the previously unknown structures crystallize in the orthorhombic space group $Pna2_1$ and they are characterized by the presence of three iron cations, in a triangle shape and sharing an oxygen in the middle of it. There are two types of interconnections between the irons cations. The first type is bonding two irons by a sulfate and an acetate. Instead, the second one is bonding two irons by the acetate group of two linkers as shown in fig.1. Subsequently, a series of different data acquisition protocols (e.g. illumination, acquisition and camera parameters) were applied and the quality of the collected data sets were compared (fig.2).
Due to this optimization, Fast-Automated Diffraction Tomography (Fast-ADT), a semi-automatic tool for 3DED data acquisition and crystal tracking, could be applied more efficiently. [5] In this way, the electron dose could be minimized for the given setting especially if a CCD camera is used. It could be shown that the quality of crystal structure refinement of a beam sensitive and vacuum sensitive material was improved.

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Fig.1 Structure solution of FeMOF, view along c

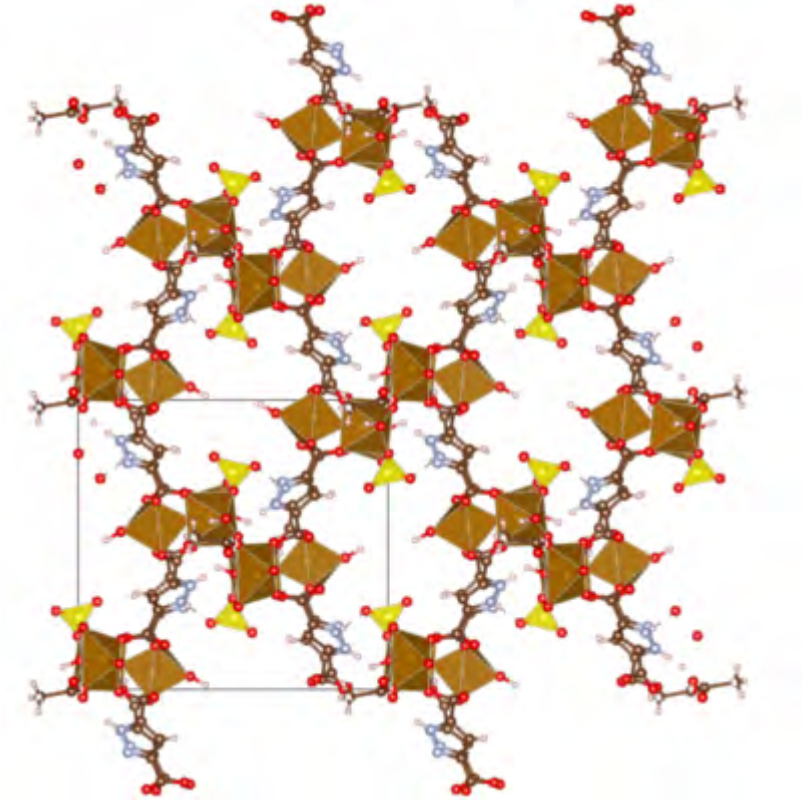

Fig.2 Static ED patterns at different time