

**MS30-2-5 Structure solution using 3DED of beam and vacuum sensitive carbazole-based di-phosphonic acid metal organic frameworks**

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**Abstract**

Metal-organic frameworks (MOFs) are characterized by metal nodes (inorganic building units, IBUs) linked by organic molecules (linker) resulting in a 3D network with pores that allow them to easily interact, absorb and release liquid and gas phases such as moisture, solvents... [1]. These materials are very challenging to investigate due to their tendency to crystallize as microcrystalline powders. Therefore, methods such as 3-dimensional electron diffraction (3DED) and XRPD are excellent tools to achieve structure determination [2]. In this research, we report the use of Transmission Electron Microscopy (TEM) to attain the structure solution of two new MOFs (Cu- and Zn-DPC), built by a new linker molecule. Both compounds were initially characterized using XRPD with the aim of determining their crystal structure. However, this approach was not successful. Therefore, 3DED was used to achieve the crystal structure through direct methods. One of the challenges of the study of these DPCs using 3DED is their beam and vacuum sensitivity. Since they contain guest molecules, upon introducing them inside the TEM, their structure starts to change due to water and/or solvent loss. These alterations result in a decrease in crystallinity, variation of length of the crystallographic axes, shearing of the cell, loss of volume and coordination change of the metallic cations. Therefore, in order to enable an ab initio structure solution, fast data acquisition is essential. In this project, using Fast Automated Electron Diffraction Tomography (Fast-ADT) we were able to achieve structure solution of such complex samples with room temperature measurements in an FEI TECNAI-F30 STWIN transmission electron microscope equipped with a ULTRASCAN4000 CCD camera. While the structures of these compounds feature similar building blocks, there are significant differences in their resulting networks; CuDPC can be described as a layered 2D coordination polymer, while ZnDPC features a layered IBU, but the interconnection through the linker molecules results in a 3D network. Both materials change within the TEM environment as a function of the time: the CuDPC shows a reduction of the distance between the IBUs accompanied with a shrinking of the lattice parameter *b*, and overall cell volume reduction upon removal of H<sub>2</sub>O from the IBU and the coordination environment of the copper ions (which changes from square pyramidal to square planar), while ZnDPC also shows lattice shrinking and volume reduction to a smaller extent, with  $\beta$ -angle changes being the more evident variation in the structure.

**References**

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- [2] T. Rhauderwiek, H. Zhao, P. Hirschle, M. Döblinger, B. Bueken, H. Reinsch, D. De Vos, S. Wuttke, U. Kolb and N. Stock. "Highly stable and porous porphyrin-based zirconium and hafnium phosphonates – electron crystallography as an important tool for structure elucidation", *Chemical Science* (2018), 9, 5467–5478.

Fig 1. Structure solution model of the ZnDPC

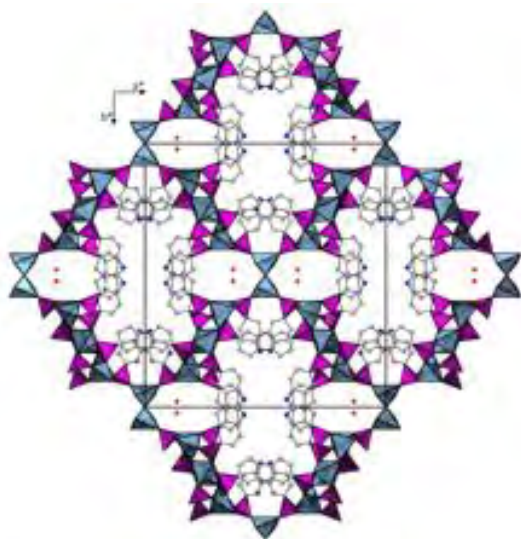


Fig 2. ADT3D volume reconstruction ZnDPC

