

## Structural and thermodynamic analysis of the compound $\{[\text{Zn}(2,5\text{-pdc})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}\}_n$ and its dehydrated and delaminated forms.

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**Abstract:** In recent decades, a new class of porous solids was reported, the Metal-Organic Frameworks (MOFs), and it is known as a subclass of the coordination polymers. These solids bring together the selective function of the pore modulation with the electronic properties. In general, they typically have crystalline structure formed by coordination of primary organic units and inorganic construction and thus generate infinitely extended structures with different dimensions: 1D (chains), 2D (layers) or 3D (networks) [1]. In particular, the 2D functional materials attracted much attention for the development of a new generation of electronic and optoelectronic devices due to their high surface area and synthetic approach robustness [2]. The two dimensional MOF studied in this work was the network  $\{[\text{Zn}(2,5\text{-pdc})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}\}_n$  (2,5-pdc = 2,5-pyridinedicarboxylate), ZnPDC2D. The MOF 2D was synthesized [3] and characterized by different experimental techniques and was also studied by computer simulation. Two optimized ZnPDC2D structures were obtained by distinct methods (PBE and PBE-D2) with a good agreement of their parameters. The structure obtained from the simulation of the dehydration process suggest the formation of three new phases (d1-ZnPDC2D, d2-ZnPDC2D and d3-ZnPDC2D). The temperature at which ZnPDC2D undergoes amorphization was determined by X-ray powder diffraction measurement with in situ temperature rise and it could be inferred that the amorphous phase undergoes a reversible transformation after being exposed to the environment. The thermodynamics of the first stage of dehydration shows that the PBE functional is adequate to describe the minimum temperature at which this process is spontaneous (142 °C to PBE and 227 °C to PBE-D2). The experimental results from TGA (termogravimetric analysis) show that the ZnPDC2D has a endothermic peak in the range of 130-250 °C. These work also reports the simulation of the monofilament by the PBE and PBE-D2 methods. The analyses



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of electronic properties for all the cited structures were performed and discussed according to the processes and changes involved. The elimination of the water molecules caused a change of the geometry especially for the metal center and also a decrease of the band gap energy for the totally dehydrated structure. The monofilm formation energy was obtained and the DOS calculations showed that the band gap energy increased.

**Key-words:** Metal-organic frameworks. Two-dimensional metal-organic frameworks. Structural transformation. DFT.

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