

**WP n°: WP2 – PL3**

**Title:** Active site engineering of UiO-66 type metal-organic frameworks by intentional creation of defects: A theoretical rationalization

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**Summary** (max 200 words):

Hybrid framework compounds including both inorganic and organic moieties have recently developed into an important new class of crystalline porous materials, also known as metal-organic frameworks (MOFs) [1]. As MOFs contain many metal sites, which might be catalytically active, they have the potential to replace homogenous catalysts in important industrial applications [2]. Within the family of Zr-benzenedicarboxylate (Zr-BDC or UiO-66) type MOFs, missing linkers were found to be responsible for the catalytic activity [3]. Experimental procedures were developed to create more of such active Zr-sites by adding an excess of modulator (MDL) to the synthesis mixture [4]. Subsequently, the incorporated modulators can be removed by a post-synthesis treatment at elevated temperature, thereby creating new active Zr-sites. In this contribution, we aim at explaining experimental observations with computational insights, focusing on the modulating species trifluoroacetic acid (TFA), HCl and H<sub>2</sub>O [5]. At synthesis conditions, the coordination strength of these species predicts the stability (from high to low): BDC > TFA > HCl > H<sub>2</sub>O. High MDL:BDC ratios are thus required to achieve incorporation. Post-synthesis removal of the defect-coordinating species follows, as expected, the opposite trend: H<sub>2</sub>O > HCl > TFA > BDC. The dehydroxylation from inorganic Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub> bricks happens spontaneously at high temperatures as BDC decoordination leads to freed hydroxyl groups.

[1] Férey, G., *Chemical Society Reviews* 37 (2008) 191.

[2] Czaja, A. U., Trukhan, N. and Muller, U., *Chem. Soc. Rev.* 38 (2009) 1284.

[3] Vermoortele, F., Vandichel, M., Van de Voorde, B., Ameloot, R., Waroquier, M., Van Speybroeck, V., De Vos, D. E., *Angew. Chem. Int. Ed.* 51 (2012) 4887.

[4] Vermoortele, F., Bueken, B. Le Bars, G., Van de Voorde, B., Vandichel, M., Houthoofd, K., Vimont, A., Daturi, M., Waroquier, M., Van Speybroeck, V., Kirschhock, C., De Vos, D., *Journal of the American Chemical Society* 135 (2013) 11465.

[5] Vandichel, M., Hajek, J., Vermoortele, F., Waroquier, M., De Vos, D., Van Speybroeck, V., *CrystEngComm*, accepted for publication.