Surface Mounted Metal-Organic Frameworks (SURMOFs)

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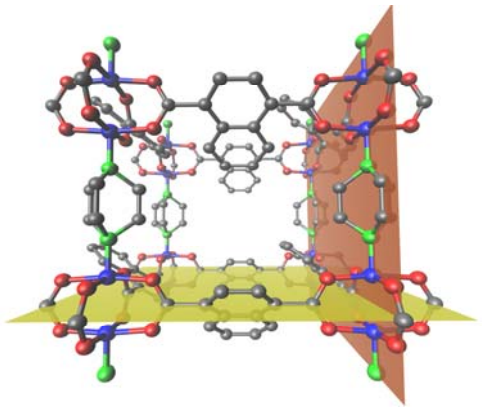
Metal-Organic Frameworks (MOFs) are Zeolite-like hybride organic-inorganic materials which combine unprecedented porosity with tailoring the chemistry of the coordination space and the control of the materials properties. Applications of bulk MOFs are ranging from hydrogen storage and carbon dioxide capture to gas separation, catalysis, drug-release and chemical sensing. However, much less work has been focused on the fabrication of MOF thin films and integration of MOFs into nano devices.

In particular, layer-based, multicomponent MOFs are well suited for stepwise liquid-phase epitaxy (LPE) of surface attached crystalline films of MOFs ("SURMOFs"), but only few cases have been reported, e.g. [Zn(bdc)(4,4-bipyridine)$_{0.5}$] (MOF-508; bdc = 1,4-benzene-terephtalate).[1,2] For our study we selected this series of well known MOFs [M(L)(P)$_{0.5}$] (**1**) which exhibit interesting responsive bulk properties [M = Zn, Cu; L = arene dicarboxylic acids, e.g. 1,4-naphtalene dicarboxylate (ndc); P = pillar ligands e.g. 1,4-diazabi-cyclo(2.2.2)octane (dabco) and functionalized derivatives of L and P]. In the figure, the structure is shown and the two principal growth directions [100] (red) and [001] (yellow) are highlighted, which are perpendicular to the most dense lattice planes.



The oriented growth of SURMOFs of type **1** on Au(111) surfaces modified with organic self assembled monolayers (SAMs) will be presented including multilayer heterostructures and homochiral structures. All SURMOFs were characterized by X-ray diffraction, AFM and IRRAS. Data on the evaluation of the (enantio-) selective gas adsorption properties will be discussed based on in situ monitoring by and quartz crystal microbalance techniques (QCM). A perspective will be given in order to target multivariate SURMOFs with programmed functions by the layer sequence.

References

[1] a) Shekhah, C.; Wang, H.; Kowarik, S.; Schreiber, F.; Paulus, M.; Tolan, M.; Sternemann, C.; Evers, F.; Zacher, D.; Fischer, R. A.; Wöll, C., *J. Am. Chem Soc.* **2007,** *129*, 15118. - b) Shekhah, O.; Wang, H.; Paradinas, M.; Ocal, C.; Schupbach, B.; Terfort, A.; Zacher, D.; Fischer, R. A.; Wöll, C. *Nat. Mater.* **2009**, *8*, 481. – c) D. Zacher, K. Yusenko, A. Bétard, S. Henke, M. Molon, T. Ladnorg, O. Shekhah, B. Schüpbach, T. de los Arcos, M. Krasnopolski, M. Meilikhov, J. Winter, Andreas Terfort, C. Wöll, R. A. Fischer, *Chem. Eur. Journal* **2011**, *17*, 1448-1455.

[2] D. Zacher, R. Schmid, C. Wöll, R. A. Fischer, "Surface Chemistry of Metal-Organic Frameworks at the Liquid/Solid Interface: A Perspective", *Angew. Chem.-Int. Edit.* **2011**, *50*, 176-199.