

Supplementary Information

Selective Nucleation and Growth of Metal-Organic Open Framework Thin Films on Patterned COOH/CF₃ Terminated Self Assembled Monolayers on Au(111)

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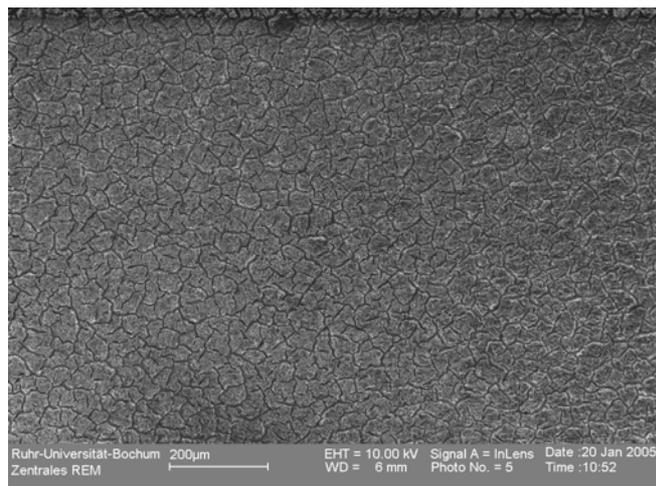


Figure S1. SEM image of a MOF-5@SAM thin film grown on a uniform SAM of 16-mercaptohexadecanoic acid (without μ CP patterning) after desorption of included solvent molecules. The SEM reveals typical cracks across the densely covered MOF-5 surface of a 5 μ m thick film, being a result of the drying process, which certainly may be optimized. This MOF thin film sample was used to be loaded with the OMCVD precursor **1** (see Fig. 4 of the article).

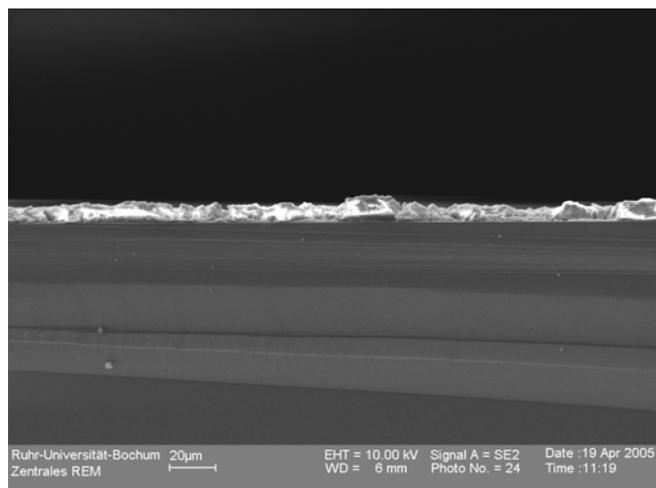


Figure S2. SEM cross section of the 5 μ m thick MOF-5 film of Figure S1 (above) giving evidence of the dense structure and uniform film thickness together with Figure S1.

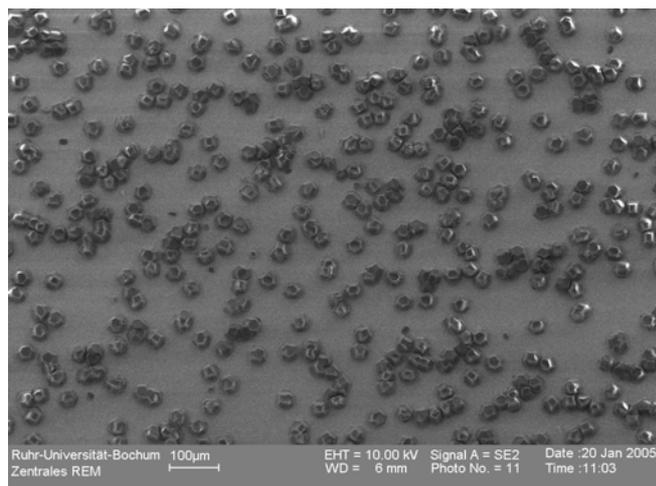


Figure S3. SEM of a patterned SAM directly immersed at 105 °C into the MOF-5 mother solution. At this rather harsh conditions, the patterned structure of the SAM is destroyed and the selectivity of the growth of MOF-5 is lost completely. See below the details and comments referring to the preparation of MOF-5@SAM.

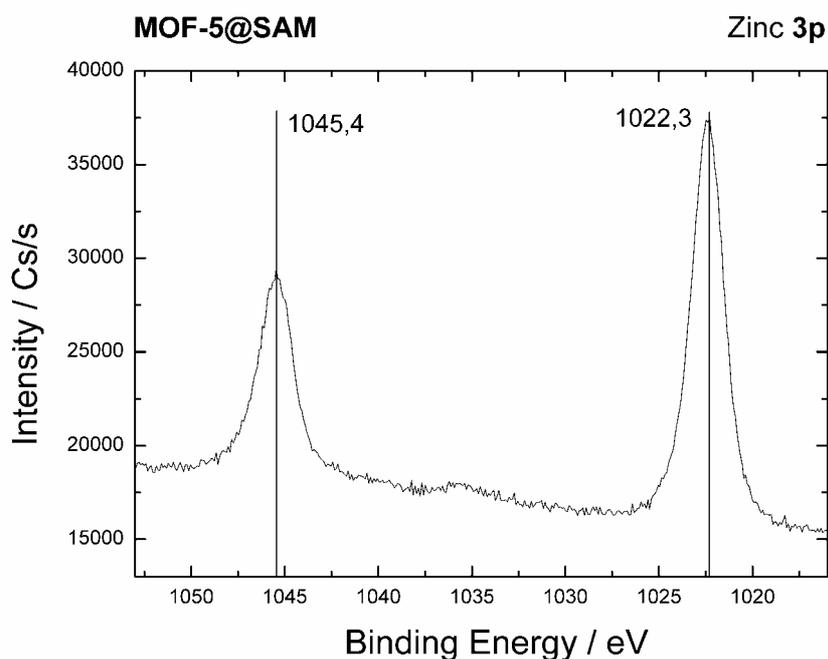


Figure S4. XPS at the Zn 3p levels of the MOF-5@SAM of Figure S1. This spectrum compares with a reference sample of polycrystalline MOF-5 powder of Figure S5 (below). This comparison gives evidence of the expected significant Zn^{2+} surface concentration as a consequence of the presence of a MOF-5 thin film attached to the SAM.

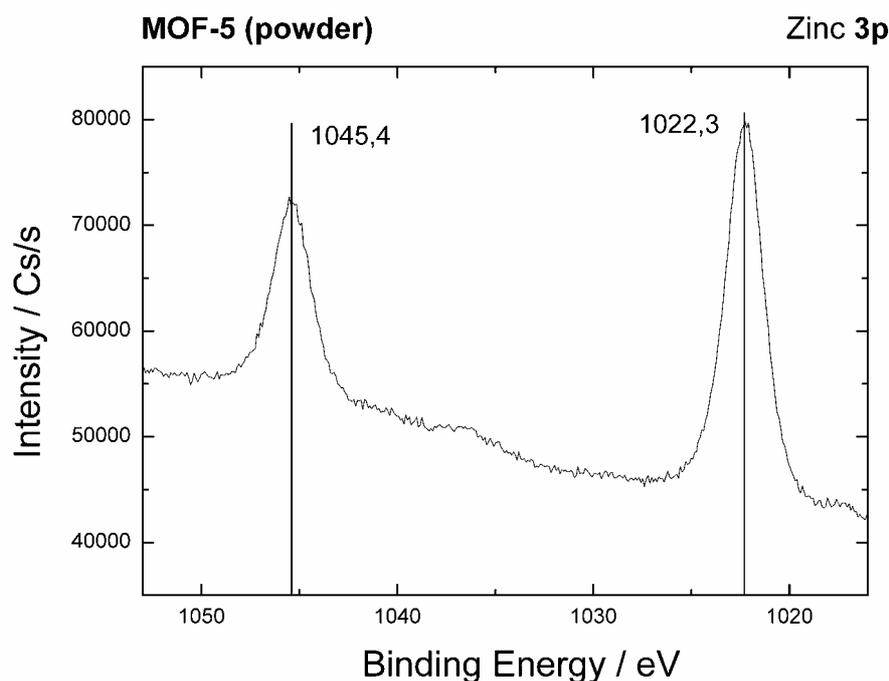


Figure S5. XPS at the Zn 3p levels a reference sample of polycrystalline MOF-5 powder corresponding to the MOF-5@SAM of Figure S1 and its XPS data of Figure S4 (above). This comparison gives evidence of the expected significant Zn^{2+} surface concentration as a consequence of the presence of a MOF-5 thin film attached to the SAM.

Preparation of MOF-5 thin film on carboxylic acid terminated SAMs

Protocol. $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (3.14 g) and terephthalic acid (0.67 g) were dissolved in 100 ml pure diethylformamide (DEF, Merck) at 75 °C and the mixture was kept at this temperature for 72 hrs. Then a short heating to 105 °C initiates crystallisation of MOF-5 which can be detected with the unaided eye as a faint turbidity of the solution. After rapid cooling to 25 °C and filtration, the SAM coated substrate was immersed into the clear supersaturated MOF-5 mother solution and was left there in an upright position at 25 °C for 24 hrs. Then, the sample was taken out of the solution and was consecutively washed with dimethylformamide, toluene and finally with ethanol. MOF-5 growth occurred only the SAM covered side of the substrate.

Explanation. According to our still ongoing studies, the crystallisation of MOF-5 in diethylformamide without the presence of any additional base is initiated by the heating to 105 °C because of the gradual thermal decomposition of diethylformamide which produces small amounts of diethylamine (identified by GC/MS) especially in the presence of Zn^{2+} as catalyst. With rising levels of the in situ produced basic diethylamine, the formation of MOF-5 is accelerated. A base (diethylamine) is needed for efficient deprotonation of the terephthalic acid. At temperatures below 60 °C the decomposition of diethylformamide is too slow for MOF-5 crystallisation. At temperatures above 60 °C the SAM thin films tend to decompose and in particular patterned SAMs loose their structural perfection and finally disintegrate. It is critical to control the rate of MOF-5 nucleation and particle growth at low temperatures of 25 °C for a selective attachment to the SAM and to achieve a densely packed thin film. The above protocol allows that.