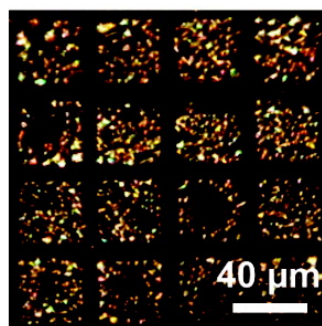
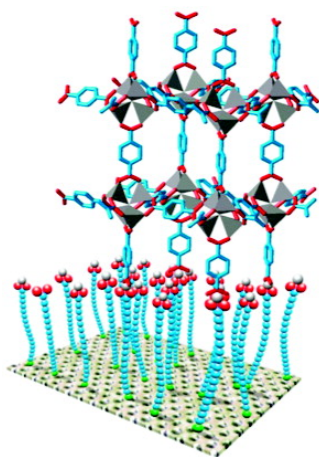


Selective Nucleation and Growth of Metal–Organic Open Framework Thin Films on Patterned COOH/CF-Terminated Self-Assembled Monolayers on Au(111)

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J. Am. Chem. Soc., **2005**, 127 (40), 13744–13745 • DOI: 10.1021/ja053523l • Publication Date (Web): 14 September 2005

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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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The ultrahigh porous and chemically robust Metal–Organic open Framework coordination polymers (MOFs) based on zinc carboxylate structural motifs pioneered by Yaghi et al. are fascinating because of extraordinary gas-storage capacities for hydrogen and hydrocarbons.^{1,2} Other interesting applications are emerging, as well, including gas separation, gas sensing, and catalysis.^{3,4} Fine-tuning size, shape, and chemical functionality of the nanoscale cavities and the internal surface offers prospects for a unique supramolecular host–guest chemistry of these zeolite-type organic–inorganic hybrid materials. We have demonstrated the size-selective gas-phase loading of MOF-5 and IRMOF-8 with typical OMCVD precursors to yield well defined intercalation compounds which were converted into catalytically active nanocomposites, such as Pd@MOF-5 and Cu@MOF-5.⁵

Beyond this use as bulk (powder) materials, it is obvious that the integration of MOFs as novel building blocks and functional units for bottom-up nanotechnology raises the challenge to direct and control the growth of MOFs at surfaces (Figure 1), similar to zeolite thin films.⁶ Self-Assembled Organic Monolayers (SAMs) in combination with soft lithographic techniques (Micro Contact Printing, μ CP) play a dominant role in designing chemical and physical functionalities at surfaces on a molecular level.⁷

SAMs and LB films with carboxylic acid surface groups are well-known to coordinatively bind metal cations $M(\text{solv})^{n+}$ from solution phase, and much work has been done to study biomineralization processes by employing those tailored model surfaces.⁸ Homogeneous nucleation of Yaghi's MOFs is likely to proceed via the formation of the so-called secondary building units (SBUs), which in the case of MOF-5 is a tetrahedral $[\text{Zn}_4\text{O}]^{6+}$ cluster ion with the six Zn···Zn edges bridged by terephthalate. These octahedral connectors then fuse together and form the network and eventually cubic macrocrystals.^{1,2} Directed heterogeneous nucleation on solid substrates should thus be possible if solvated or polynuclear Zn^{2+} complexes, such as SBUs, or even larger MOF-5 nuclei selectively bind to carboxylate-terminated SAMs^{9,10} via a terephthalate bridge connected to a surface-bound Zn^{2+} cation. Figure 1 illustrates this idea, not excluding a variety of alternative structures of the linkage.

When a μ CP-patterned SAM of 16-mercaptohexadecanoic acid and 1*H*,1*H*,2*H*,2*H*-perfluorododecane thiol on Au(111)¹¹ was immersed into a clear, supersaturated reaction mixture typically used in our laboratory for synthesis of well-shaped MOF-5 macrocrystals,⁵ a thin film of MOF-5 particles was obtained and anchored selectively at the carboxylate-terminated areas of the SAM, as shown in Figure 2. The AFM data, also shown in Figure 2, clearly reveal that virtually no crystallization takes place on the CF₃-terminated stripes. The protocol to achieve that is as follows: Dissolve $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (3.14 g) and terephthalic acid (0.67 g)

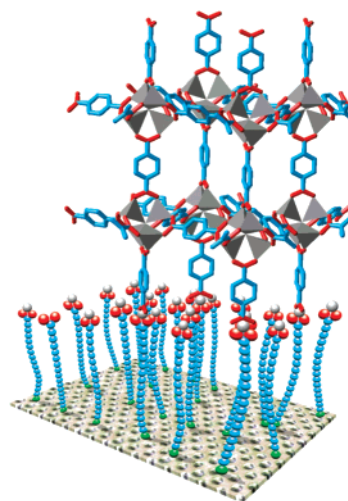


Figure 1. The concept of anchoring a typical MOF-5 building unit to a carboxylic acid-terminated SAM. The figure represents a simplified model, not excluding alternative possibilities of the linkage.

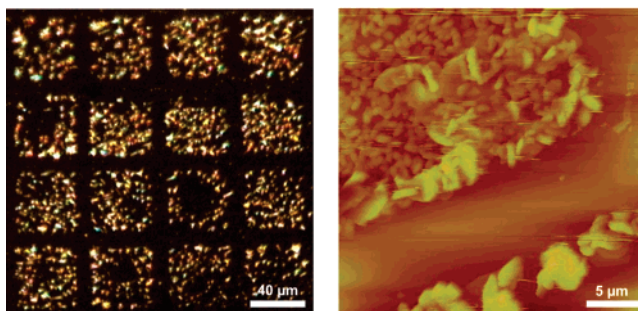


Figure 2. Optical microscope (left) and an AFM image (right) of a selectively grown film of MOF-5 on a patterned SAM of 16-mercaptohexadecanoic acid and 1*H*,1*H*,2*H*,2*H*-perfluorododecane thiol on Au(111) from the mother solution at 25 °C. The MOF-5-coated squares are 40 × 40 μm , and the crystallites are about 100–500 nm in size.

in 200 mL of pure diethylformamide (DEF, Merck), and keep this mother solution at 75 °C for 72 h. Then heat to 105 °C until beginning crystallization, and then cool to 25 °C. Filtrate the slightly turbid solution before contact with the SAMs, and then allow crystallization at 25 °C for 24 h. Neither immersing the SAM directly into the mother solution at 105 °C nor shortening the incubation period at 75 °C gave satisfying results. Such variations resulted in nonselective growth. Note that under the conditions used here the surface carboxylate groups of the SAMs are fully protonated¹⁰ prior to immersion in the MOF solution.

Our MOF-5 films adhere well to the surface, as evidenced by the fact that the crystallites could be imaged in AFM (Figure 2).

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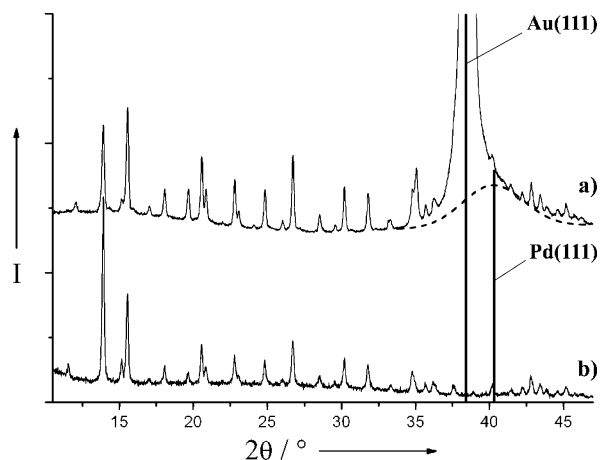


Figure 3. A PXRD pattern of Pd@MOF-5@SAM is shown in comparison to a sample of an authentic polycrystalline MOF-5 (trace below). Reflections from Au(111) (substrate) and Pd(111) are marked.

In addition, the MOF films remained on the surface even after several washing cycles with ethanol. Similar experiments were carried out with bare Au(111), CF₃-, and COOH-terminated nonpatterned SAMs. Only in the latter case were well adherent MOF-5 films formed. The chemical composition of the MOF-5@SAM thin films was characterized by SEM-EDX and XPS, revealing the expected elemental constituents (e.g., Zn, O, F). The grazing incidence PXRD pattern shown in Figure 3a compares well with an authentic polycrystalline sample of MOF-5 (Figure 3b),⁵ thus giving unambiguous evidence of the retained cubic structural motif of the MOF-5 crystallites composing the thin film. The lower signal-to-noise ratio and the broadened reflections of the MOF-5 thin film are due to the very small quantity of the MOF-5 material and the rather small typical crystal domain size of about 100 nm (PXRD line profile analysis), matching the data from SEM and AFM studies (Figure 2) at a film thickness of about 500 nm (SEM cross-section). Currently, we are seeking conditions for a controlled layer-by-layer growth, choosing MOFs with a two-dimensional layered structure.

The as-synthesized MOF-5@SAM thin films are likely to contain solvent molecules (DEF) inside the cages of the MOF-5 lattice.^{1,2} The immersing of the films into chloroform for 24 h, thus allowing for diffusive exchange of the low volatile DEF, and keeping the treated films in a dynamic vacuum of 1 Pa at 100 °C for 6 h results in the removal of all adsorbed species, as it is known from the as-synthesized microcrystalline MOF-5 powder material.⁵ At present, we are unable to accurately measure the specific (internal) surface area (Langmuir) of our thin MOF-5 films due to instrumental limitations. However, to provide proof of concept that the films can be conveniently loaded with functional materials of various types, the following experiment was performed by taking advantage of the extraordinary properties of gas absorption of the MOF: An emptied MOF-5@SAM film was exposed to the vapor of $[(\eta^5\text{-C}_5\text{H}_5)\text{Pd}(\eta^3\text{-C}_3\text{H}_5)]$ (**1**), which is an auburn colored, moderately volatile compound and is well-known as a clean precursor for OMCVD of palladium.¹² The bright cinnabar color of the resulting film indicates the loading of the MOF-5 cavities with **1** (Figure 4). In analogy with the intercalation compound $[(\eta^5\text{-C}_5\text{H}_5)\text{Pd}(\eta^3\text{-C}_3\text{H}_5)]@MOF-5$, each cavity of the present materials could accommodate up to four molecules of **1**.⁵ Subsequent treatment of the loaded film with hydrogen gas at 25 °C converts

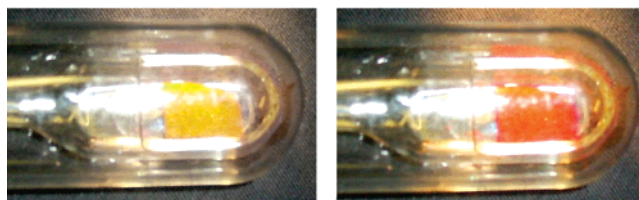


Figure 4. An empty, 5 μm thick MOF-5 thin film on a 16-mercaptohexadecanoic acid SAM on Au(111) before (left) and after (right) the exposition to the vapor of the deep-red OMCVD precursor, $[(\eta^5\text{-C}_5\text{H}_5)\text{Pd}(\eta^3\text{-C}_3\text{H}_5)]$ (**1**).

1@MOF-5 instantaneously into Pd@MOF-5, visible by the color change to deep black. The size of the imbedded Pd nanoclusters ranges around 1.5 nm, according to the Pd(111) line broadening (Figure 2). The organic ligands are likely to be catalytically hydrogenated and released as cyclopentane and propane in vacuo.⁵

The resulting thin film [Pd@MOF-5]@SAM represents a novel example of an organic–inorganic, hierarchical nanocomposite functional material bridging scales from the molecular regime over mesoscopic to the micro and macro regime. It seems obvious that the particular combination of SAMs and μCP techniques with the broad variability of coordination polymers together with the integrative potential of OMCVD and Atomic Layer Deposition (ALD)¹³ for thin film and surface technology hold much promise. For example, we are currently investigating a related SAM-type modification of the internal surface of membranes, such as anodic alumina (AAO). This allows the selective filling of the channels and pores of the membrane with MOFs, which in turn act as getters for OMCVD precursors for functional inorganic nanoclusters, a subject we will soon report elsewhere.

Acknowledgment. The authors wish to acknowledge generous support by the Fonds der Chemischen Industrie.

Supporting Information Available: Infrared spectra, SEM pictures, and XPS spectra of the thin films. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA053523L