

Microcontact Click Printing for Templating Ultrathin Films
of Metal–Organic Frameworks[†]

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The controlled growth of metal–organic frameworks (MOFs) over surfaces has been investigated using a variety of surface analytical techniques. The use of microcontact printing to prepare surfaces, patterned with regions capable of nucleating the growth of MOFs, has been explored by employing copper-catalyzed alkyne–azide cycloaddition (CuAAC) to pattern silicon wafers with carboxylic acids, a functional group that has been shown to nucleate the growth of MOFs on surfaces. Upon subjecting the patterned silicon surfaces to solvothermal conditions, MOF thin films were obtained and characterized subsequently by AFM, SEM, and grazing-incidence XRD (GIXRD). Large crystals (~0.5 mm) have also been nucleated, as indicated by the presence of a bas-relief of the original pattern on one surface of the crystal, suggesting that it is possible to transfer the template surface pattern onto a single crystal of a MOF.

Introduction

The porous crystalline families of metal–organic frameworks (MOFs) are a rapidly developing class of materials^{1–5} derived from organic linkers spatially segregated by nodes of transition-metal ion clusters. The surface area of these materials, depending on the linker size and geometry, can extend up to 6000 m²/g.^{6,7} They have been investigated extensively in the context of gas storage applications,^{8–11} drug delivery,¹² and separation science.¹³ The controlled deposition of MOFs on capillary surfaces has led to the separation of gas-phase compounds,¹⁴ and there continues to be much promise for sensing applications² as well as hetero-

geneous catalysis^{4,15} with these systems. Anchoring and nucleating the growth of MOFs to surfaces has emerged¹⁶ as a novel strategy to broaden the potential applications of these unique materials. The ability to direct MOF growth, which has been demonstrated^{17–25} rather elegantly, reveals that, under select conditions, crystal growth can be achieved on appropriately functionalized surfaces. For instance, spatial control over seeded crystal growth of MOFs on patterned self-assembled monolayers on gold surfaces has been demonstrated²³ by employing an approach that was also recently used to template the growth of organic materials for electronic devices.^{26,27} Although these results have proven attractive, self-assembled monolayers (SAMs) on gold suffer from instability to light²⁸ and heat²⁹ and, in addition, are susceptible to diffusion,³⁰ limiting the utility of these SAMs in certain applications, particularly in separation methods requiring high temperatures and exposure to light. Beyond the application limitations arising from thermal sensitivity, SAMs of organothiols on gold exposed to solvents are known³¹ to desorb spontaneously, a process exacerbated by heat.

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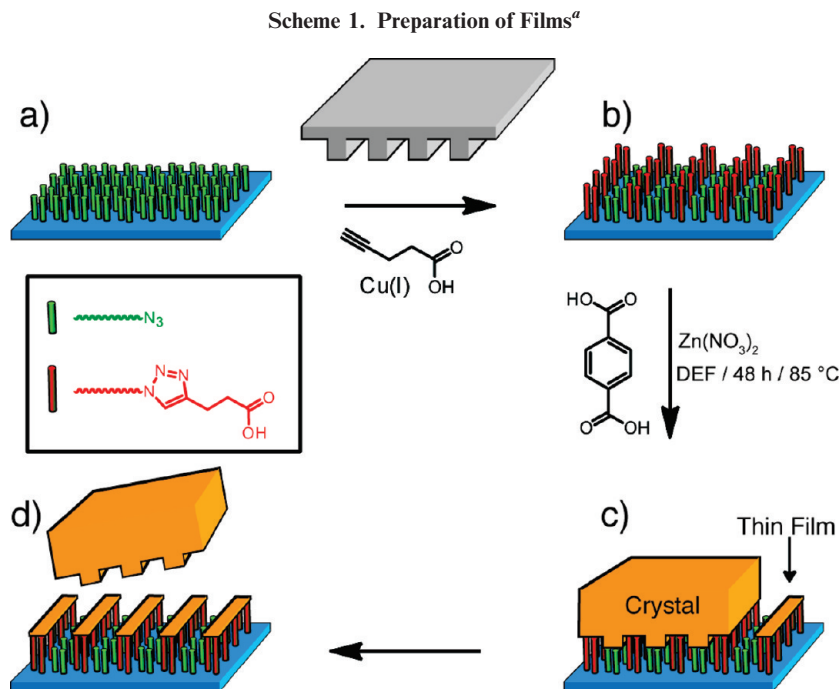
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^a (a) Silicon wafers functionalized with a monolayer of alkylazides are subjected to microcontact click printing with pentynoic acid and a source of copper to form (b) repeating rows of pentynoic acid and leave rows of unreacted azide. These wafers are subjected to solvothermal syntheses, in the case of MOF-5, using terephthalic acid and $\text{Zn(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in freshly distilled DEF to form (c) substrates that contain thin films, in addition to larger crystals. (d) The large crystals (>0.5 mm) are mechanically removed by hand and analyzed by optical microscopy. The substrates are further characterized by SEM and AFM after sonication.

As a result, organothiols on gold are not ideal for use in the purely solvothermal synthesis of MOFs, a procedure that is becoming ubiquitous²¹ in MOF preparation. Indeed, it was pointed out recently¹⁶ that MOF syntheses from pretreated mother liquors generally failed to produce smooth, uniform MOF thin films.

Functionalized self-assembled monolayers on silicon oxide and silica surfaces offer an attractive alternative to gold–thiol SAMs for certain applications on account of much more robust surface attachment. Furthermore, certain monolayers can be postfunctionalized using microcontact printing to create patterned surfaces with regions of substantially different surface chemistries. Hence, we were inspired to use the copper-catalyzed azide–alkyne cycloaddition^{32–34} (CuAAC) to pattern oxidized silicon surfaces with carboxylic acids, a functional group that has been shown to nucleate the growth of MOFs on surfaces.²³ Subjecting the patterned silicon surfaces to solvothermal conditions for 48 h produced thin films of polycrystalline MOF-5 that were approximately 40 nm in height and were subsequently characterized by atomic force microscopy (AFM), scanning electron microscopy (SEM), and grazing incidence X-ray diffraction (GIXRD). In addition, a mixed film in the isorecticular³⁵ series of MOFs consisting of IRMOF-10 and IRMOF-9 could be prepared using the same solvothermal reaction conditions. The resulting films have different height profiles than those found with MOF-5. Finally, the patterns created on the functionalized silicon surface templates transferred as a bas-relief onto the faces of individual large crystals (~ 0.5 mm) of MOF-5.

Experimental Section

Preparation of Thin Films. Preparation of the films follows a three-step process (Scheme 1), beginning with an azide-terminated monolayer (Supporting Information) formed on the surface of silicon plates. Patterned surfaces of pentynoic acid were prepared from a poly(dimethylsiloxane) (PDMS) stamp that was inked with ethanolic solutions of Cu(II)SO_4 , ascorbic acid and pentynoic acid in an approximately 2:1:10 ratio. After allowing the solution to soak into the PDMS stamp, a stream of nitrogen was used to remove the excess fluid and the stamps were carefully placed onto the azide substrates and left in contact with the surface for 3 h without applying additional pressure. The patterned surfaces were washed rigorously and sonicated in solutions of EtOH, dimethylformamide (DMF), and then H_2O to remove any unreacted compounds and adsorbed PDMS. Thin films of MOF-5 were subsequently grown on the patterned silicon wafers by immersion into a freshly distilled diethylformamide (DEF) solution of terephthalic acid and $\text{Zn(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ at 85°C for 48 h, after which time the substrates were removed and allowed to cool to room temperature over the course of several hours. The large MOF crystals (>0.5 mm) were removed carefully for further characterization by optical microscopy. The silicon substrate was sonicated for 5 min in DMF and characterized using AFM, SEM, and XRD.

Results and Discussion

Microcontact click printing was developed^{36–38} to covalently link an azide-terminated SAM on a substrate with an alkyne through triazole formation using CuAAC chemistry, a so-called³³

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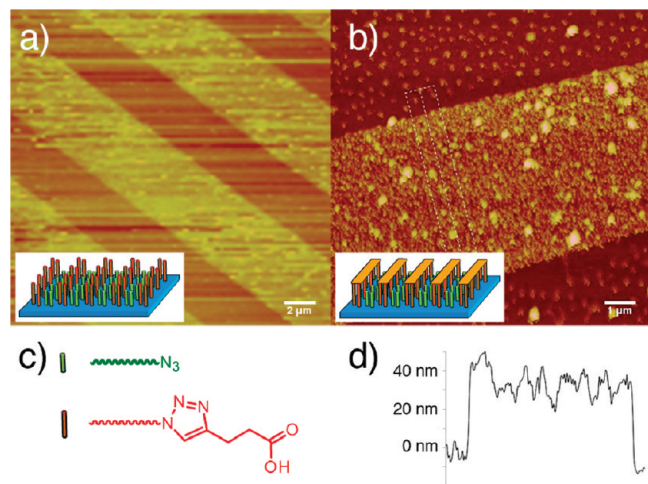


Figure 1. Tapping-mode AFM images of (a) the surface after reaction with pentynoic acid and (b) following the solvothermal treatment of the samples with terephthalic acid and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in freshly distilled DEF at 85°C for 48 h. The higher topography (brighter) regions are films of MOF-5, and the lower (darker) areas correspond to the azide surfaces. (c) Graphical representations of the surface are shown in the insets. (d) The height profile for the surface of MOF-5 shows even coverage approximately 40 nm above the surface of the azides.

click reaction. The CuAAC reaction is orthogonal to numerous other chemical transformations, and the process has been demonstrated with several alkyne reagents under homogeneous and heterogeneous catalytic conditions. A patterned elastomeric stamp, which has been inked with the Cu catalyst and alkyne reagent, generates a concomitant surface. The resultant triazole-lined monolayers, under homogeneous reaction conditions, form in yields exceeding 95% within 400 min, creating a surface that is uniformly patterned by the desired product. After employing this general procedure, we analyzed the resulting surfaces by AFM and found (Figure 1a) a 1 nm height increase over the azide SAM where the stamp had been in contact with the substrate, a value consistent with previous investigations.³⁷ The wettability of the overall surface was also greater, an observation that was consistent with the transformation of a hydrophobic azide-terminated surface to that of a more hydrophilic pentynoic acid. Another useful feature of this type of substrate is that there is no need to backfill the unpatterned areas afterwards. Although it is possible to react the azide groups, which remain on the surface after microcontact click printing with inert functional groups such as perfluoro allyl chains that have been shown to prevent the nucleation of MOF growth, we decided to investigate the effectiveness of using the surfaces with the azides “unprotected.” In our experiments, the unfunctionalized azides weakly nucleate MOF-5 growth, a result that is in line with the expectation that azides are very poor ligands and are generally considered to be hydrophobic functional groups. After being rinsed (section 3S in the Supporting Information), the final samples were analyzed once again by AFM, and the final height of the MOF-5 layer was found to vary around 40 nm (Figure 1b) across the surface. To rule out the possibility that adventitious PDMS oligomers had been transferred from the stamp and were responsible for nucleation, we performed the stamping procedure again without the pentynoic acid only to find that there was minimal crystal growth on the surface. This observation is consistent with our predictions that MOF crystals are nucleated by the hydrophilic functional groups. The carboxyl-terminated surfaces also nucleated the

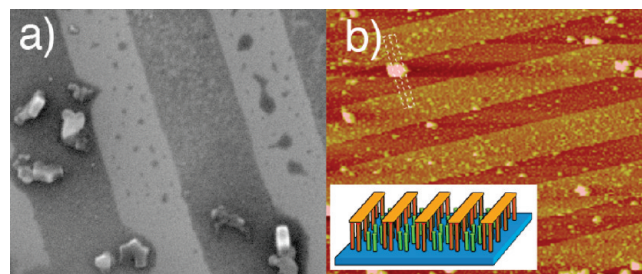


Figure 2. (a) SEM image of the surface of the patterned silica including large ($10\ \mu\text{m}$) crystals. The dark areas are films of MOF-5, and the lighter-colored areas are the azide surfaces. (b) The AFM image shows a surface that is covered in stripes of MOF-5 punctuated by large crystals approximately 700 nm in height. Higher-topography (brighter) regions are films of MOF-5, and lower (darker) areas correspond to the azide surfaces.

growth of larger crystals ($\sim 10\ \mu\text{m}$), which were visible by AFM (Figure 2a) and SEM (Figure 2b). SEM analyses revealed that several of these medium-sized crystals appeared to have ingrowths from second nucleation events (Figure S1), producing six-pointed stars. The low surface coverage and small size of these crystals made their isolation difficult, preventing further characterization. The film samples were bound strongly to the surface of the substrate, as evidenced by the fact that neither AFM tapping mode nor contact mode perturbs the layers to any visible extent. In fact, we were able to sonicate samples in CH_2Cl_2 to remove (Scheme 1d) the larger crystals ($< 700\ \text{nm}$) from the surfaces prior to AFM analysis.

To characterize the thin films formed on patterned surfaces further, we determined their chemical composition by energy-dispersive X-ray spectroscopy (EDX), a technique that revealed the expected elemental constituents (Zn, O, and C in Figure 3c). Analysis by grazing incidence GIXRD indicated (Figure 3a) that the films formed are polycrystalline samples of MOF-5. We further explored the utility of our approach by considering other MOF struts³⁵ besides terephthalic acid, namely 4,4'-biphenyldicarboxylic acid, which is used as the strut of IRMOF-10. This compound has limited solubility in DMF at room temperature, and thus the higher temperatures used under solvothermal reaction conditions are imperative for the synthesis to be successful. Although IRMOF-10 possesses pores that are more than twice the size of MOF-5, it forms in combination with an interpenetrated MOF variant, namely, IRMOF-9. Using the same solvothermal conditions, we were also able to obtain thin films of a mixture of IRMOF-9 and IRMOF-10. Grazing incidence GIXRD showed that the material is multicrystalline. However, an analysis of these films by AFM did not reveal the same uniform appearance as for samples containing MOF-5. Instead, the regions of the thin film grew (Supporting Information, Figure S3) to heights ranging from 5 to 10 nm with isolated regions of nucleation of up to 500 nm. This difference most likely stems from the fact that the longer struts allow for mixtures of noninterpenetrated and penetrated frameworks, a conclusion born out by GIXRD measurements (Figure 3b).

The analysis of the larger crystals of MOF-5 ($> 0.5\ \text{mm}$) revealed an unanticipated artifact of the crystal growth on the thin films. Because the crystals are grown on covalently anchored surfaces under solvothermal conditions, we were able to obtain large crystals that showed an imprinted negative of the pattern formed by microcontact click printing. We tentatively suggest that larger crystals are grown from the surface and that the thin crystalline films are part of the large single-crystal domain. The bas-relief pattern is consistent with the detachment of larger

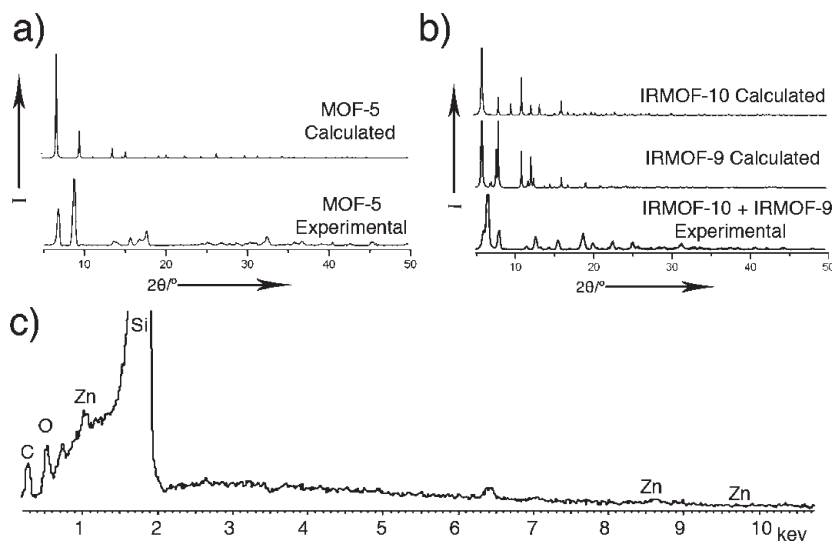


Figure 3. GIXRD traces of (a) MOF-5 and (b) IRMOF-10. The top spectra are calculated, and the bottom are experimental. Also shown is (c) the EDS spectrum of the MOF films, indicating the presence of carbon, oxygen, and zinc.

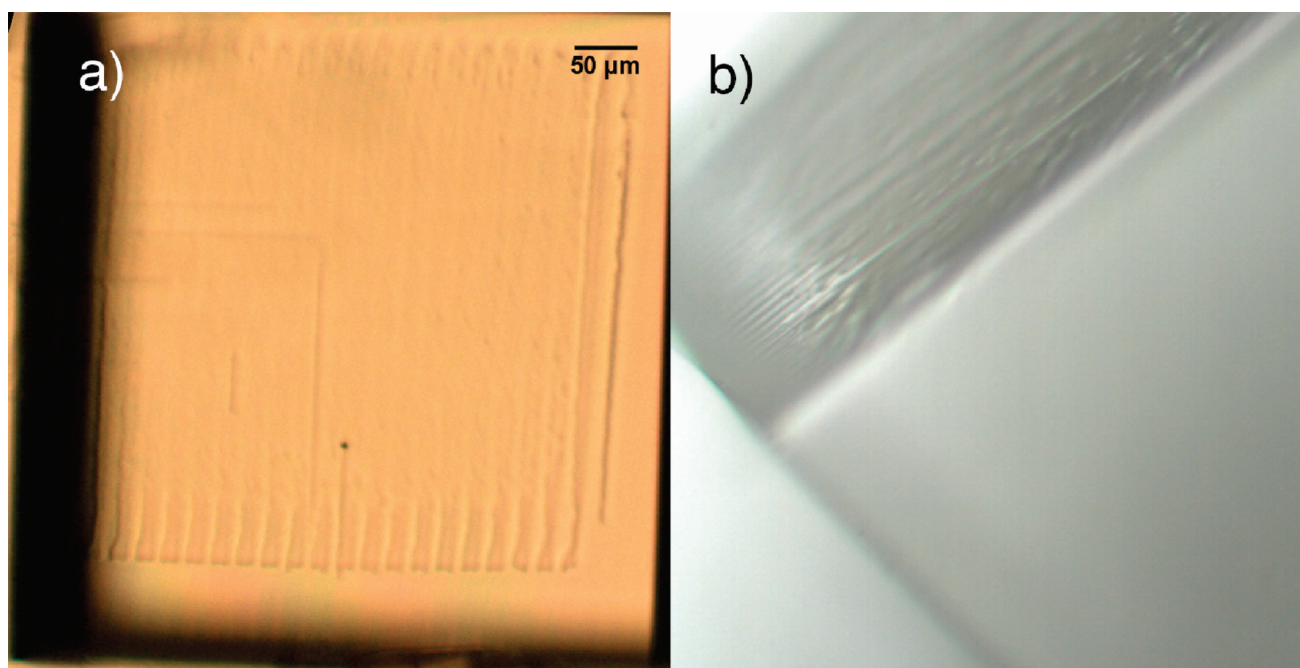


Figure 4. The surface of MOF-5 after being gently removed from the silicon wafer has the same surface features (vertical lines, 20 μm), indicating the transfer of the pattern neatly onto the surface of the crystal. Shown from both the (a) face and (b) side of the crystal. Note that the pattern appears on only one side of the crystal and that the scale bar is the same as that shown in (a).

crystals from patterned surfaces, with the wider stripes corresponding to regions where the large crystals were previously attached to the substrate. The patterns (Figure 4) cover a single face of the crystals, with the other five unaffected sides showing no indication of surface imperfections. Attempts to analyze these surface features to obtain topological data by AFM and SEM turned out to be unproductive because of crystal surface destabilization as a result of solvent evaporation and instrument limitations in the presence of DMF or DEF. Nevertheless, the procedure of pattern transfer onto the surface of MOF-5 was repeatable and clearly visible by optical microscopy.

Conclusions

We have developed microcontact click printing as a means of creating domains for the nucleation of MOF growth for both

MOF-5 and IRMOF-9 and -10. The process is simple, requires no special equipment, and can be performed on the benchtop. The azide monolayer serves as an inert, poorly nucleating surface, which removes the need to backfill unreacted surfaces. Furthermore, this system takes advantage of the robustness of monolayers formed on silicon-based surfaces, a property that imparts stability to the functionalized substrates that is compatible with the solvothermal process of MOF synthesis. In the case of large, macroscopic crystals, the patterns formed on the surface are transferred to a facet of the crystal. Ongoing efforts to evaluate this phenomenon will be the subject of another publication when the research has been completed.

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Supporting Information Available: Synthesis and characterization details. This material is available free of charge via the Internet at <http://pubs.acs.org>.