Communication

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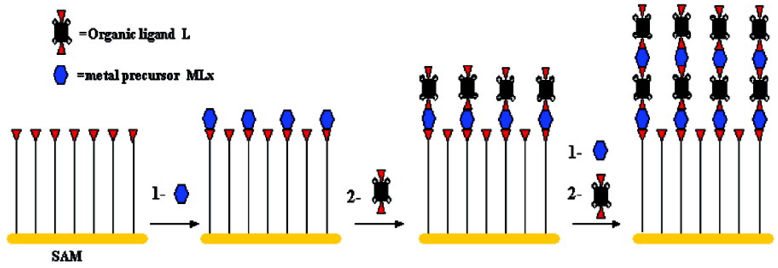

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Step-by-Step Route for the Synthesis of Metal−Organic Frameworks

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Supramolecular chemistry holds unique prospects for the fabrication of novel functional materials. Molecular precisely defined subunits (which may already be rather complex self-assemblies) form even more complex structures that exhibit functionalities not provided by the individual building blocks. The coupling of the covalently bonded subunits by noncovalent interactions is a key requisite for this type of supramolecular assembly.[1] In two dimensions, the understanding of such an assembly of organic molecules (ligands) interacting through hydrogen bonds or ionic interactions has been significantly advanced in recent years.[2,3] A major reason for this progress is the availability of molecular-resolution microscopic data, which allows following directly the self-assembly process taking place after the building blocks are placed on a “tablet”. For appropriate tablets like Au(111) or Ag(111) surfaces, scanning tunneling microscopy (STM) can be applied in a straightforward fashion to obtain high-resolution images not only of the ordered structures present after the completion of the self-assembly process but also of intermediate, nonperiodic structures. In several cases it was possible to apply microscopic methods and spectroscopic methods in parallel to study important steps in the self-assembly process, i.e., the deprotonoation of organic acids and the subsequent formation of carboxylates in a step-by-step fashion, by cooling the metal substrates to cryogenic temperatures.[4,5]

It is difficult to study self-assembly processes occurring in three dimensions on the same level of detail. For metal−organic frameworks (MOFs), a class of hybrid porous solid material introduced by Kitagawa, Ferey, and Yaghi about 10 years ago,[6−8] there have been attempts to characterize the formation process by in situ spectroscopic techniques in more detail.[9,10] Although it was possible to demonstrate that the formation of the highly ordered MOFs occurs first via an assembly of the primary building blocks to defined secondary building blocks (SBUs), and then to the MOF crystallites,[9] a thorough understanding of the formation process is still lacking.

In order to study the formation of MOFs in a more rational way, we have taken a rather different approach. In contrast to the established synthesis protocols, where the educts (primary building blocks, typically two) are mixed and treated under solvothermal conditions, we combine them in a sequential fashion. By using an appropriately functionalized organic surface as a (two-dimensional) nucleation site, we can grow MOF structures in a step-by-step fashion (see Figure 1). This not only allows us to study the kinetics of the individual steps but also provides the potential to fabricate structures possibly not accessible by bulk synthesis (Figure 1). We have chosen [$Cu_3BTC_2(H_2O)_n$] (**1**, HKUST-I) for our study (see Figure 1 in Supporting Information)). The synthesis and structure of this MOF have been described in detail previously, but the details of its formation are still unknown.

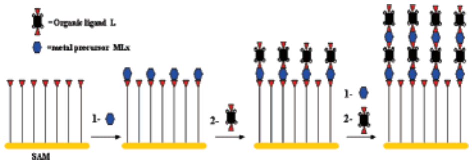

Figure 1. Schematic diagram for the step-by-step growth of the MOFs on the SAM, by repeated immersion cycles, first in solution of metal precursor and subsequently in a solution of organic ligand. Here, for simplicity, the scheme simplifies the assumed structural complexity of the carboxylic acid coordination modes.

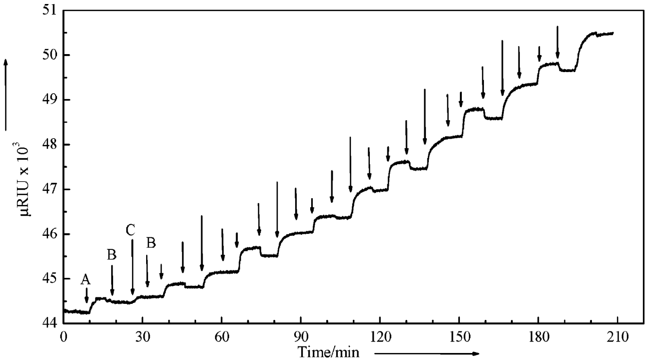

Figure 2. SPR signal as a function of time recorded in situ during sequential injections of CuAc (A), ethanol (B), and BTC (C) in the SPR cell containing a COOH-terminated SAM.

In Figure 2 we present data obtained by surface plasmon resonance (SPR) for the growth of **1** on a COOH-terminated SAM surface fabricated by immersing the Au substrate into an ethanolic solution of mercaptohexadecanoic acid (MHDA). The SPR technique, which has not previously been applied to MOF synthesis, allows monitoring the deposition of molecular species on surfaces with submonolayer resolution. The data show that subsequently adding copper(II)acetate (CuAc) and 1,3,5-benzenetricarboxylic acid (BTC) leads to step-by-step deposition of multilayers. Data obtained by IR spectroscopy (Figure 2 in Supporting Information) fully support this finding.

The deposition of organic layers using such sequential processes has been reported previously (see ref 17 for the case of multilayers of organosulfur/Cu compounds and ref 18 for the deposition of ionic polymers). However, evidence of a three-dimensional long-range ordering of the deposited multilayers with structural features identical to a coordination polymer with the same composition has not yet been presented. In a recent work by us on the sequential deposition of Zn/BTC, which has a different structure from HUKST-1, no X-ray diffraction data could be obtained, thus

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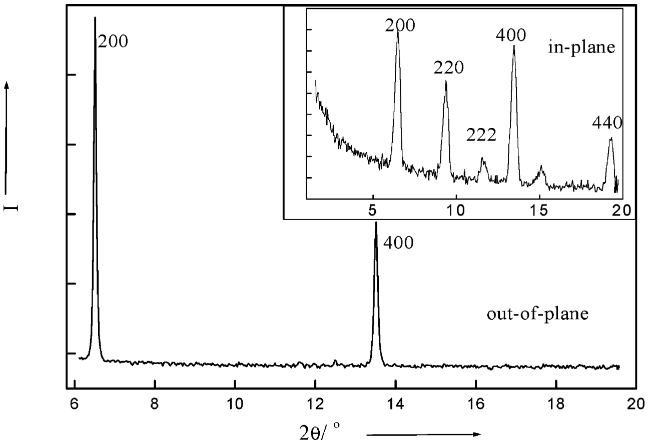

Figure 3. Out-of-plane XRD data for a $Cu_3BTC_2{\cdot}xH_2O$ MOF sample (40 cycles) grown on a COOH-terminated SAM, the in-plane spectra are also shown as an inset.

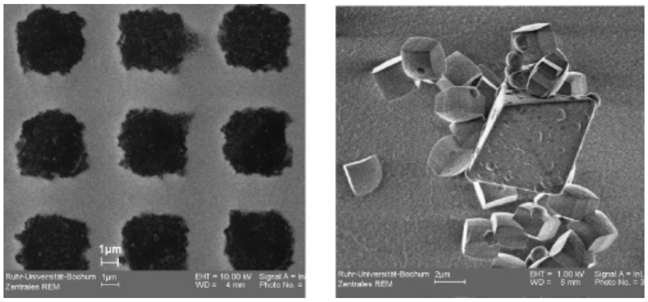

Figure 4. Scanning electron micrographs of $Cu_3BTC_2{\cdot}xH_2O$ MOF (40 cycles) grown on a SAM laterally patterned by microcontact printing (μCP) consisting of COOH-terminated squares and CH_3-terminated stripes (left), and $Cu_3BTC_2{\cdot}xH_2O$ MOF crystallites grown on a COOH-terminated SAM using the method described in ref 21 (right).

pointing to the presence of rather disordered material. In the present case, however, we were able to obtain high-quality XRD data, both for out-of-plane and in-plane conditions. The experiments were carried out using a laboratory (Cu Kα) as well as a synchrotron radiation source (DELTA, Dortmund). A typical diffraction scan for a 40 cycles Cu/BTC multilayer is shown in Figure 3. This out-of-plane diffraction scan clearly demonstrates the presence of a highly ordered and preferentially oriented crystalline material with a periodicity of 6.5 Å normal to the surface. Together with the in-plane data (see Figure 3, inset) this demonstrates unambiguously that the deposited multilayer exhibits the same structure as observed for the bulk compound $[Cu_3BTC_2(H_2O)_n]$ **(1)**.

Of course the finite number of layers perpendicular to the surface should result in an increased width of the out-of-plane diffraction peaks, which is given by $\beta = \lambda/(Nd \cos \theta)$, with λ denoting the wavelength of the X-ray radiation, Nd the length of the unit cells, and θ the diffraction angle. Under our conditions ($\lambda = 1.54$, $N =$ number of layers, $d = 13$ Å for the (200) reflex peak) the width for a 40-layer film amounts to 0.03°, which is below the experimental resolution used in the present case and is fully consistent with the data shown in Figure 3.

It is interesting to note that on our COOH-terminated surface **1** grows with the same orientation as observed previously by Bein and co-workers, when immersing an organothiol-based COOH-terminated SAM into an aged (8 days) and filtered mother solution of the solvothermal synthesis of **1** at room temperature, but different from that obtained for COOH-terminated silane-based SAMs. Obviously, the (100)-face of **1** matches particularly well with a COOH-terminated MHDA-SAM initiating a highly regular growth at mild conditions. The gas-loading properties of MOF layers grown by the step-by-step method were studied via NH_3/water exchange experiments. IR and NEXAFS data (see Supporting Information) reveal a nonreversible behavior similar to that seen in the bulk.

Together with the SEM data shown in Figure 4 we can thus conclude that the step-by-step synthesis yields homogeneous, highly crystalline MOF films exhibiting the HKUST-I bulk structure. Note that the immersion method used in previous work[21−24] leads to very heterogeneous, rough MOF coatings consisting of fairly large, single crystallites. A second advantage of our new method is the lower temperature (room temperature vs 75 °C required in the one-step synthesis.[21] Aside from the possibility to use the novel preparation method to study the kinetics of the film formation in more detail using SPR and to model it using theoretical approaches, the step-by-step method offers the unique opportunity to grow novel MOF-like ordered structures which consist of alternating layers, possibly with nonperiodic combinations of different metal ions and/or different linkers.

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Supporting Information Available: IRRAS and NEXAFS spectra recorded for samples prepared after cycles of immersion in $Cu(Ac)_2$ and BTC solutions. IRRAS spectra monitoring the loading of the surface-deposited MOFs with NH_3. This material is available free of charge via the Internet at http://pubs.acs.org.

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