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 covalently bonded subunits by noncovalent interactions is a key formation even more complex structures that exhibit functionalities not subunits (which may already be rather complex self-assemblies)

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 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.

In Figure 2 we present data obtained by surface plasmon resonance (SPR) for the growth of I 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
COOH-terminated MHDA-SAM initiating a highly regular growth of mild conditions. The gas-loading properties of MOF layers grown by the step-by-step method were studied via NH3/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 work21–24 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).23 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 NH3. This material is available free of charge via the Internet at http://pubs.acs.org.

References


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