Layer-by-Layer Growth of Oriented Metal Organic Polymers on a Functionalized Organic Surface

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A metal–organic coordination polymer based on benzenetricarboxylic acid ligands and Zn(II) ions was grown on a COOH-terminated organic surface in a stepwise fashion. The deposited films were characterized using a number of surface analysis techniques, including X-ray absorption spectroscopy and X-ray photoelectron spectroscopy. IR measurements show that the metal–organic coordination polymer grows in a layer-by-layer fashion and can be reversibly loaded with NH₃. The deposition is very selective and occurs only on COOH-terminated regions of an organic surface, as demonstrated by AFM measurements.

The mesoscopic, inorganic/organic hybrid structures introduced by Yaghi et al.¹,² originally attracted interest because of their storage properties with respect to hydrogen and hydrocarbons. Recently, it has been demonstrated that these robust metal–organic coordination frameworks (MOFs) can also be loaded with organometallic precursors that can subsequently be converted to nanosized metal clusters inside the pores without severely disturbing the lattice.³,⁴ This opens the field for many more applications, in particular because it has been demonstrated recently that these coordination polymers can be deposited selectively on appropriately functionalized substrates.⁵ The surface anchoring is a key step, which is considered to be crucial for applications in the field of nanotechnology such as the manufacturing of sensor devices and devices comprising organic or molecular electronics.

Here, we focus on a different type of metal–organic coordination framework with synthesis conditions that are more compatible with the stability regime of SAMs. 1,3,5-Benzencarboxylic acid, C₆H₃(COOH)₃ (BTC), represents a prototype material for supramolecular self-assembly.⁶–⁷ This polyfunctional carboxylic acid with 3-fold symmetry comprising a phenyl ring and three chemically identical carboxyl end-groups in the same plane has been shown to assemble in diverse supramolecular structures as a result of the trigonal exodentate functionality. The reaction of BTC with Zn(II) salts yields different metal–organic coordination frameworks structures depending on the conditions (i.e., counterions (acetate, nitrate), solvents, and thermal treatment). These compounds have been shown to reversibly exchange small adsorbed molecules such as H₂O, NH₃, and C₂H₅OH.¹²,¹³

When investigating the deposition of BTC on a COOH-terminated organothiolate surface made from 16-mercaptopetanoic acid (MHPA), we found that the reaction can be carried out in a step-by-step fashion, making the layer-by-layer growth of metal–organic polymers on an organic surface possible by sequentially immersing the substrate into solutions of Zn(II) acetate and BTC, as illustrated in Figure 1.

The 16-mercaptopetanoic acid (MHPA)-SAM sample is immersed in a BTC solution without Zn(II) ions present, no adsorption of BTC on the COOH-terminated SAM surface is seen by infrared reflection absorption spectroscopy (IRRAS) (Figure 3b), X-ray photoelectron spectroscopy (XPS), and near-edge X-ray absorption spectroscopy (NEXAFS). However, if the MHPA-SAM is immersed in a Zn(II) acetate solution first, then XPS, IRRAS, and NEXAFS data reveal the adsorption of a BTC monolayer. The most direct demonstration that indeed a single layer of BTC was deposited is by way of atomic force microscopy (AFM).

The AFM micrograph that is reproduced in Figure 2 clearly shows the selective deposition of a BTC layer with a height of

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To make the height of the metal–organic coordination polymer adlayer easily visible, the organic surface was laterally patterned prior to immersion in the Zn(II) acetate and BTC solutions by microcontact printing (μCP) to yield a surface consisting of COOH-terminated squares (made from MHDA) and CH₃-terminated stripes (made from hexadecane thiol (HDT)). If the process is repeated, the polymer structures can be grown in a layer-by-layer fashion following the scheme depicted in Figure 1. Each step leads to a significant increase in the thickness of the deposited polymer, as revealed from the IRRAS data shown in Figure 3a and from XPS data (Supporting Information). The IRRAS data show the main characteristic bands (asymmetric and symmetric IR bands of the carboxylate groups of the BTC ligands) bonded to Zn(II) ions. Also, the increase in thickness per cycle is about the same up to a thickness of eight layers as shown in Figure 3b. Unfortunately, the thickness of the deposited polymer could not be accurately determined by our AFM setup operated under ambient conditions for layers with a thickness larger than two layers. Control experiments using XPS, NEXAFS, and IRRAS revealed that no deposition could be obtained on a CH₃-terminated organic surface. A sequential deposition of organic molecules employing metal ions to form layers with defined thickness has been reported for mercapto-hexadecanoic acids and polyelectrolytes but is here for the first time applied to the selective growth of metal–organic polymer structures on a substrate.

The height of the single deposited layers in the AFM data and the fact that the NEXAFS data reveal that the orientation of the BTC units is mainly perpendicular (average tilt angle 30°–40°) to the surface allow us to put forward the structural model displayed in Figure 4, where we propose a structure derived from that of the bulk, where the zigzag chains characteristic of the bulk structures of authentic Zn(II)–BTC MOFs run perpendicular to the surface.

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(17) The AFM-measurements carried out in ambient frequently suffered from artifacts due to the difference in hydrophilicity of the deposited metal–organic polymers (hydrophilic) and the CH₃-terminated regions of the SAM (hydrophobic).
normal to the surface, yielding a structure of almost vertical layers that are interconnected, as in the bulk structure, by water molecules. Attempts to obtain a powder X-ray diffraction pattern for metal–organic coordination polymers with a thickness of up to 10 layers were unsuccessful because of the small thickness of the metal–organic coordination polymer adlayers obtained so far. The details of the molecular structure of the deposited metal–organic polymers are therefore unclear, and further information is required to judge whether the structure is very regular and comparable to that of a MOF or more irregular as expected for an amorphous metal–organic polymer.

We could, however, successfully demonstrate the gas-loading properties of a four- and eight-layer metal–organic coordination polymers prepared using this novel layer-by-layer approach by an exchange experiment where the water in the BTC layer is repeatedly and reversibly exchanged by NH3. To this end, eight-cycle Zn(II)–BTC metal–organic coordination polymers was first exposed to gaseous NH3 (step 1) and then immersed in a water/ethanol mixture (1:50) (step 2). As evidenced by the IRRAS data shown in Figure 5, most of the water has been replaced by NH3 after step 1, which in turn is removed by water after step 2. These exchange experiments support the structural model presented in Figure 4 in that the deposited Zn(II)–BTC multilayer must contain similar adsorption sites and pores with sizes matching that of the corresponding bulk MOF structures (e.g., in case of [Zn2BTC3·12H2O]13 which reversibly exchanges water against ammonia to yield [Zn2BTC3·2H2O·10NH3]). Loading with other molecules such as C5H5N, CH3CN and C2H5OH was not successful. The deposited polymers also show high stability, where heating the samples up to 100 °C did not lead to the desorption of the polymer or a change in the IRRAS spectra, except for the decrease in the intensity of the water band at 3400 cm\(^{-1}\).

This layer-by-layer deposition on organic surfaces not only makes it possible to coat surfaces with polymer layers of defined thickness but, even more interestingly, may open up the possibility to synthesize completely new types of metal–organic coordination polymers or, possibly, even MOFs with compositions and structures not accessible by bulk synthesis routes (e.g., frameworks containing two different organic ligands arranged in an alternating fashion).

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**Supporting Information Available:** XP and NEXAFS spectra for an MHDA SAM after different cycles of immersion in Zn(II) ions and BTC solutions and IRRAS spectra of exchange experiments for H2O with NH3 on an eight-cycle sample. This material is available free of charge via the Internet at http://pubs.acs.org

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