

Interfacial Systems Chemistry: Surface-templated assembly of three-dimensional functional networks

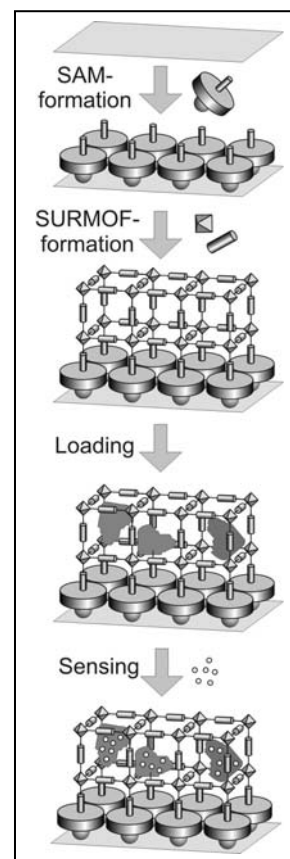
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Supramolecular chemistry holds unique prospects for the fabrication of novel functional materials. Molecularly precisely defined, nanometer-sized subunits which may already be rather complex self-assemble to form even more complex structures which exhibit functionalities not provided by the individual building blocks. In two dimensions, the understanding of a surface-templated assembly of organic molecules (ligands) interacting through hydrogen bonds or ionic interactions has been significantly advanced in recent years.[1]

Here we extend the fabrication of surface-anchored networks beyond the formation of planar, two-dimensional adlayers by demonstrating the synthesis of highly-ordered, three-dimensional porous metal-organic frameworks (MOFs) nucleated on organic surfaces exposed by different types of self-assembled thiolate-based monolayers (SAMs). We will demonstrate the principle of liquid phase epitaxy [2] for the case of $[\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_n]$ (HKUST-1) grown on COOH- and OH-terminated SAMs using Cu(II) acetate as the metal precursor and BTC (benztricarboxylic acid) as the organic ligand. SPR (surface plasmon resonance) spectroscopy is used to monitor the growth in-situ. XRD data reveal the formation of highly ordered crystalline MOF thin-films with a structure identical to that observed in the bulk on both SAMs. The XRD data also reveal different growth orientations, depending on the termination of the SAM. AFM characterization of patterned substrates by micro-contact printing (μCp), shows clearly the selective and homogeneous deposition on both surfaces [3]. It should be noted, that the LPE-process not only allows for fabricate very homogenous coatings but also provides rather detailed insight into the basic mechanisms of the MOF synthesis process, in particular about the role of secondary building blocks (SBUs)[4]. In addition, the rather different fabrication mechanisms underlying the LPE-process – alternating exposure to the reactants in contrast to the standard solvothermal synthesis – allows to access novel MOF-structures and makes it possible to control the phenomenon of interpenetration [5].

The availability of porous frameworks rigidly anchored to solid surfaces opens the prospect of adding additional functionality to these ultrathin surface coatings by placing nanoobjects inside the pores within the MOFs, e.g. metal clusters or dye molecules [6]. We will demonstrate the potential of this approach by loading the three-dimensional porous scaffolds with metal-containing molecules such as ferrocene.



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