Chapter VI
Conclusion

Metal Organic Frameworks (MOFs), as the focus of this thesis, are considered as one of the most promising multifunctional hybrid inorganic-organic solid materials, which might be useful for diverse technical applications such as catalysis, gas adsorption, separation or storage, etc. While looking forward to the prospect of application, the ability to control the arrangements of channels of porous modules is critical for various nanodevices, e.g. chemical sensors, smart membranes, catalytic coating etc. However, most of present research is concentrated on the synthesis of novel MOFs and structure/property/function correlations, in particular searching responsive, flexible frameworks and introducing interesting chemical functionality. These µm-sized microcrystal materials are insoluble in any solvent and therefore hard to prepare in a thin layer form. Thus, the study of how to fabricate thin films with defined porosity has been put on the agenda. The goal is the deposition or growth of MOF thin films on substrates, ideally in a dense homogeneous and oriented fashion and also the preparation of size-, shape-, and surface-functionalized MOF nanocrystals, which can act as wells, wires, rods and dots. Firstly, the direct deposition/growth from solvothermal mother solutions was used to fabricate MOF thin film onto substrates. In the report of Fischer and co-workers, MOF-5 can be selectively nucleated and grown on a modified Au substrate. Subsequently, Bein and co-workers also demonstrated the oriented growth of HKUST-1 film on different functionalized substrates with similar method. However, the grown MOF thin film direct from solvothermal solution is considerably inhomogenous and uncontrollable. The prepared MOF thin films are also far from the requirement for applications.

In this thesis, a new layer-by-layer (LBL) method has been developed to synthesize and grow MOFs on surfaces, namely surface-mounted MOFs (SURMOFs). This concept is based on surface chemistry and is in principle related to the solid-phase synthesis of complex (bio-) organic polymers, such as peptides, DNA etc., by using an appropriately functionalized organic surface as a 2-dimensional nucleation template. Differing from the established solvothermal synthesis protocol of MOFs, the LBL growth mode of MOFs is achieved by the sequential contact and reaction of the individual reactants with the substrate, respectively. By using this route, different types of MOFs (e.g. HKUST-1 and various LBMOFs) have been synthesized and grown on
organic surfaces modified by functionalized SAMs. With the combination of different analytical techniques, such as IRRAS, XRD, SPR etc., it is demonstrated that the LBL growth process is controllable and the synthesized SURMOFs are a homogenous thin film on surfaces, possessing highly ordered and preferentially oriented crystalline structure.

Firstly, the LBL growth of HKUST-1 thin film on COOH- and OH-terminated surfaces has been presented. From IRRAS and XRD data, the synthesized thin film exhibits the same chemical component and crystalline structure with the bulk HKUST-1 material. And the growth of HKUST-1 film reveals different orientation on different functionalized surface: the LBL growth proceeds alone [100] direction on COOH-terminated surface and along [111] direction on OH-terminated surface. Moreover, by combining AFM and µCp techniques it is demonstrated a selective growth of HKUST-1 obtained only on the COOH-terminated, not on the CH₃-terminated surface, and a linear increasing of the film thickness with the number of immersion cycles. It is calculated that the increase of HKUST-1 film thickness for one immersion cycle is 1.317 nm corresponding with half of the length of crystal unit cell along [100] direction. In addition, the rather homogenous HKUST-1 film is also presented in AFM images.

LBL method not only provides the chance for synthesis of homogenous SURMOF thin film on substrates, also makes it possible for the study of the growth mechanism of MOFs which is hard to realize in the conventional synthesis process. As is well known, there are two fundamental structural compositions in MOF: organic linker which is directly supplied by organic reactant and SBUs which have to be formed in the synthesis process from the metallic precursors. The formation of the SBUs appears to be crucial for the MOF assembly process. However, it is difficult to study the importance of SBUs, because in the conventional synthesis process the two reactants are mixed in the solution. On the contrary, during the SURMOFs growth the two reactants are kept separated, making it possible to study the role of the individual reactants in the process of MOF formation, in particular the SBUs. Thus, SPR technique has been used to in situ monitor the growth of MOFs on surfaces. In case of the growth of HKUST-1, with Cu(OAc)$_2$ as metallic precursor and H$_2$bdc as organic linker, a typical LBL growth has been observed on COOH- and OH-terminated substrates in the SPR data. However, when Cu(NO$_3$)$_2$ is used as metal precursors instead of Cu(OAc)$_2$, no growth has been obtained in SPR data. And when Cu(OAc)$_2$ was used as Cu$^{2+}$ source again, the LBL growth also comes back. This result can be rationalized by considering that in the solution of Cu(OAc)$_2$, the dominant unit present is the acetate-bridged paddle-wheel cluster similar to the SBUs in the structure of HKUST-1, just btc-bridged Cu$^{2+}$ dimers. On the contrary, the structure of solved Cu(NO$_3$)$_2$ is rather diverse, in general, considered a monomeric form with two nitrate ligands chelating the Cu$^{2+}$ ion in a square planar arrangement. Clearly, at the continuous-flow conditions of LBL growth experiment these monomeric Cu$^{2+}$
species absorb much less efficiently to a btc-terminated surface than the preformed SBU-like acetate bridged Cu$^{2+}$ dimers. Consequently, the growth is significantly delayed when Cu(NO$_3$)$_2$ is used. With Cu(OAc)$_2$ as the Cu$^{2+}$ source, one or two OAc$^-$ ligands of the dinuclear species are displaced by the free carboxylate units of the btc groups, which are exposed at the [100] surfaces of the HKUST-1 SURMOF. This simple ligand-exchange reaction allows the anchoring of a preformed SBU at the growing surface and the formation of a monolayer of adsorbed SBUs, most likely terminated by acetate groups.

Furthermore, as start point, the functionalized substrates play a role of 2-dimentinal template to initiate and control the LBL growth of MOFs. Apparently, this template effect allows that the LBL growth carries out at room temperature, in comparison with the conventional solvothermal synthesis of MOFs, where the high temperature between 70 and 150° is necessary. Besides, by choosing different functionalized substrates to simulate the different crystalline planes of MOFs, the SURMOF growth can be controlled along the different directions. And after completion of the first deposited layers further growth proceeds in fact as a MOF-on-MOF homoepitaxy, which providing chance to study the growth kinetic of MOFs along different crystalline directions. In case of HKUST-1, the different growth orientation observed on COOH- and OH-terminated surface has verified it. Since in HKUST-1 [100] crystalline plane contains high density of COOH-group, the LBL growth proceeds along [100] direction on COOH-terminated substrate. Similarly, HKUST-1 growth proceed along [111] direction on OH-terminated substrate because of the high density of H$_2$O molecule on [111] plane. In addition, the SPR data reveals that the growth rate on the OH-terminated surface is somewhat delayed and also the maximum growth rate under steady-state conditions is about half that on the [100] oriented surface. This result demonstrates that for different MOF surface terminations different growth rates are to be expected.

Besides HKUST-1, LBMOFs are another study object in this thesis. At first, 2-dimensional planar LBMOFs consisting of paddle-wheel SBUs and dicarboxylate linkers have been studied. Cu/bdc and Zn/bdc films have been successfully synthesized on COOH-terminated surfaces by using LBL method. The formed Zn/bdc and Cu/bdc films possess highly ordered and preferential oriented crystalline structures, however, differing from the known structure of bulk MOF (e.g. MOF-2 [Zn(bdc)-(H$_2$O)]). Thus, a proposed crystalline structure is given, where the Cu/bdc and Zn/bdc 2D layers, being the rhombic lattice with certain tilted angle, stands on the COOH-terminated surface. The hydrogen bridges bind the two neighbor 2D layers together. Because of the lack of the in-plane XRD data, the distance between two neighbor 2D layers cannot be determined.

Afterwards 3-dimensional LBMOFs have been introduced in my work. By adding a linear pillar N-terminated ligand, 2-dimensional layers are connected together, forming a nearly cubic 3-
dimensional framework. A series of $[\text{M}_2(\text{dicarboxylate})_2(\text{N-ligand})]$ LBMOFs have been successfully grown on pyridine-terminated substrate in LBL fashion. The highlight of this part is that the by using LBL grown $[\text{Zn}_2(\text{bdc})_2(\text{bipy})]$ thin film on pyridine-terminated substrate has exhibited a similar crystalline structure with MOF-508, but without interpenetrated. As we know, in pursuit of big pore size of MOF with a given topology, the simplest way is to increase the length of the rigid organic linker without changing SBUs. However, when the pore size of MOFs is expanded to extremely large by using an extra long organic linker, a fundamental complication, i.e. interpenetration, ineluctably occurs. The large pores in MOFs can accommodate a second network (or subnetwork). The interpenetration in structure commonly favors the simple cubic frameworks as well as the steric non-demanding SBUs and linkers. Here, MOF-508 is just a well-known example. From a topological point of view, interpenetration is hard to avoid because the different frameworks bear translational symmetry and are therefore equivalent within the bulk. However, while MOF-508 has been synthesized on organic functionalized surfaces by using LBL method, a new structure without interpenetration was found on the surface. Herein, the presence of an appropriately functionalized substrate breaks the symmetry of the bulk MOF, rendering the different interpenetrating frameworks inequivalent. Only the framework have a plane of coupling units in common with the organic surface of the substrate is favored, whereas the growth of other frameworks is strongly suppressed.

In conclusion, by using LBL method the homogenous SURMOF thin film, which possesses a highly ordered and preferentially oriented crystalline structure, can be synthesized and grown on organic functionalized substrates. The growth is controllable and selective, and also can prevent interpenetration which is hard to avoid in the conventional synthesis process of MOFs. Furthermore, LBL method provides possibility for the study the mechanism of MOF synthesis.