

Self-Assembled Monolayers as Templates for Metal-Organic Framework Thin-Films - Preparation and Applications

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Abstract. *One major concern in several thin film applications of metal-organic frameworks is the need for highly ordered crystals with well defined crystal orientations. This report summarizes their most important growth methods on self assembled monolayers like layer-by-layer growth, crystallization from mother solution and solvolthermal synthesis. Methods regularly used to achieve high quality, as well as methods yielding less well oriented thin films are evaluated with respect to possible applications. A special focus lies on thin films grown on top of self assembled monolayers and how thereby induced crystal properties, like reduced surface roughness, are related to possible sensor or chromatographic applications for these materials.*

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1. Introduction

With the growth of the field of metal-organic frameworks (MOFs), comprising metal centres connected by organic linkers according to coordination chemistry and thereby forming a crystal, in recent years, research has gone into several directions like molecular recognition, catalysis or gas storage^{1–5} as well as their electrical and optical properties.^{6,7} Furthermore, MOF thin films, pioneered by Fischer, Shekka and Zhuang, have become increasingly more popular. In addition to the same applications^{8–10} possible for bulk MOF, their interface with other materials, often oxides or metals, promise use in further fields.^{11,12} Due to the variety of building units that can be used to form MOFs, an enormous amount of structures, and thereby properties and applications, can in principle be obtained by this porous designer material. MOFs exhibit an enormous internal surface area¹³ and porosity making them interesting for several applications such as gas separation,¹⁴ and sensors.¹² Their metal centres are inductive for catalytic and magnetic properties, while the organic linkers are interesting because of arising optical applications (luminescence, chirality). "SURMOFs", surface mounted metal-organic frameworks, are micrometer thick films on solid state support, that promise further applications as sensors, membranes for gas separation or even in electronic devices, where one major problem so far is to mount MOFs on different substrates.⁷ While originally not deemed an interesting field, an increase in research on photovoltaic and other electronic devices^{15–17} over the

last years has been observed. Each developing field has yet to overcome their own obstacles. For example in the application as separation membrane, one of the requirements for a MOF thin film is the formation of an uniform, ordered crystal with correct orientation of exhibited pores with respect to the film surface. A problem that is often symptomatic for MOF thin film technology. Only if the MOF fulfills this criterion, can gas of the correct size efficiently pass through the material.¹⁸ Fischer divides growth of MOF thin films into three categories: direct growth on (modified) substrate, step-by-step growth on a (modified substrate) and assembly of previously grown nanocrystals on a substrate.¹⁹ Of those, one approach to obtain appropriate thin films is by growth of MOF thin-films on self-assembled monolayers (SAMs) which promotes high crystallinity and ordering^{20,21} of the grown MOF thin film and, if the correct growth method is chosen, results in almost completely defect free crystals.^{22,23} Another interesting property is, that depending on the tail functional group in the SAM and other factors, different well-defined crystal orientations are accessible even using the same MOF.²¹ Thus, the orientation of pores can be controlled. However, the usual solvothermal synthesis method cannot be easily transferred from bulk to thin film synthesis due to the instability of most SAMs, like those consisting of alkanethiols at high temperature.²⁴ Instead, several other techniques have been developed which have been reviewed by several authors.^{25–27}

This paper reviews different preparation methods of MOF thin-films and their effect on applications, i.e. where advantages and disadvantages of different methods lie. A focus lies on the SAM-MOF interface properties and characteristics, as well as, how they differ from directly grown MOF thin films. Therefore, introductions into the concepts of MOF thin films and SAMs are given below. Afterwards, several of the most important methods and how they grow MOFs are given and compared to each other. To conclude, SAM-MOF thin films are, based on their properties resulting from growth, put into context with bulk MOFs, as well as thin films that do not use SAMs as a template. A prediction of how the field might develop, as well as where several major obstacles have to be overcome, concludes this review.

1.1. Concepts of Metal-Organic Framework Thin Films

Several definitions regarding the nature of MOFs are described in literature. Each may include more or less subtle differences, demonstrating that the borders of the term "metal-organic framework" have yet to be conclusively defined. This is especially true with respect to the term "coordination polymers" and how they differ. The core of every definition, however, is the same. MOFs are crystals, where metal centres are linked via coordination bonds to organic linker molecules which bind two or more metal centre together. Often MOFs are included as a subgroup of coordination polymers, but sometimes they are differentiated. A major differences is, that the term "polymer" generally connotes that polymers or oligomers, of which the exact structure is unknown, are present. This is not the case in MOFs since they build, aside from defects that are inherent to crystal structures, a crystalline solid with long range order, that is not present for polymers.²⁶

Figure 1. shows several secondary building units (SBUs). These are metal centres consisting of more than a single central metal atom and find wide use in MOFs since they increase the stability of the produced material.²⁹ $M_2(CO_2)_4$ for example is used in the MOFs called IRMOF 2 to 16, where the only difference between each MOF is the variation of organic linkers.⁵ How organic linkers and SBUs lead to a MOF is shown in

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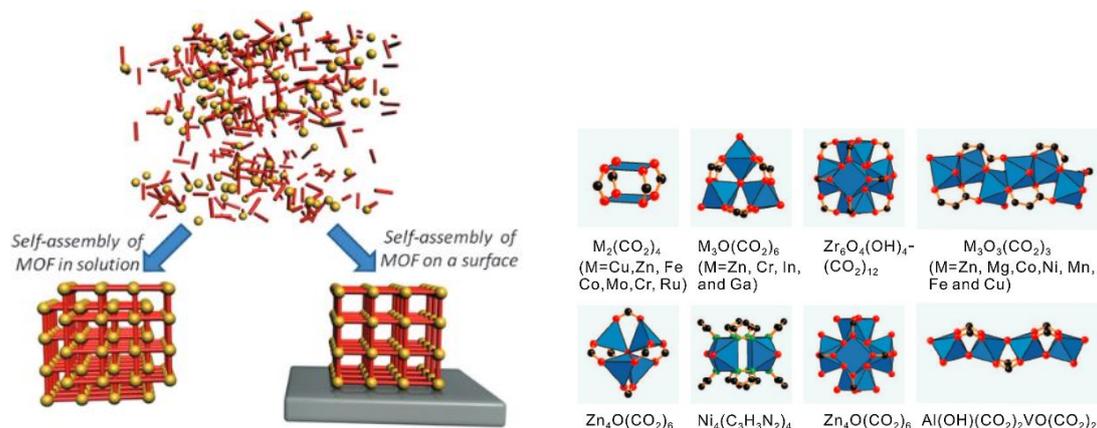


Figure 1. Left: MOF grown either as thin film or in solution. A simplification of the results of several growth methods is shown. Generally, in-solution growth promotes interlattice growth, while thin film growth on substrate yields a well-ordered and controlled system.²⁷ Right: Different possible SBUs often used in MOFs functioning as coordination sites for organic linker molecules.²⁸

the same figure. Since organic linker libraries are even more extensive than for those of SBUs, no structures are shown.

In recent years, not only bulk MOFs have been intensively studied, but also a big interest in thin-film MOFs or "SURMOFs" has arisen, both as a model system for general MOF properties, as well as their own possible applications in gas separation and as sensors. In those, thin-films of MOFs are generally grown on a solid state surface with a thickness up to several micrometer (see section 2 for various growth methods). When compared to the bulk MOF, no interwoven substrates can grow inside the lattice due to the lack of docking points on the substrate, that are needed as nucleation sites.²⁷ Nucleated primers are washed away during preparation of thin films, but not bulk. Thereby, intergrowth of crystals is, usually, prevented. Of main importance is the linkage of the thin-film to the surface. Depending on the substrate, this happens in several possible ways, often involving coordination bonds, if SAM functionalized surfaces are used. Otherwise non-covalent bonding is the reason for surface attachment.²⁰ The substrate not only provides support for thin films, it sometimes also influences the obtained MOF.³⁰ Due to breaking the symmetry at the boundary, a conformation different from the bulk can be induced, as was reported by Scherb et. al for Fe-MIL-53 which formed Fe-MIL-88B instead on a functionalized gold interface. This is an interesting phenomenon which may be utilised to obtain MOFs, that are otherwise inaccessible in bulk conformation like the case described. Until now, the only way to obtain SURMOFs, is to grow the material directly on the substrate, either step-by-step or via assembly of nanocrystals. A linkage of a MOF thin film after synthesis has not yet been reported. The main problem is surface roughness which prevents a tight binding of the substrate with the MOF, since instead of numerous connecting bridges, much less bonding interactions per area are possible.

1.2. Introduction to Self-Assembling Monolayers

Self-assembled monolayers (SAMs) are a reversible assembly of molecules formed on an interface under thermodynamically controlled conditions. They are formed by the

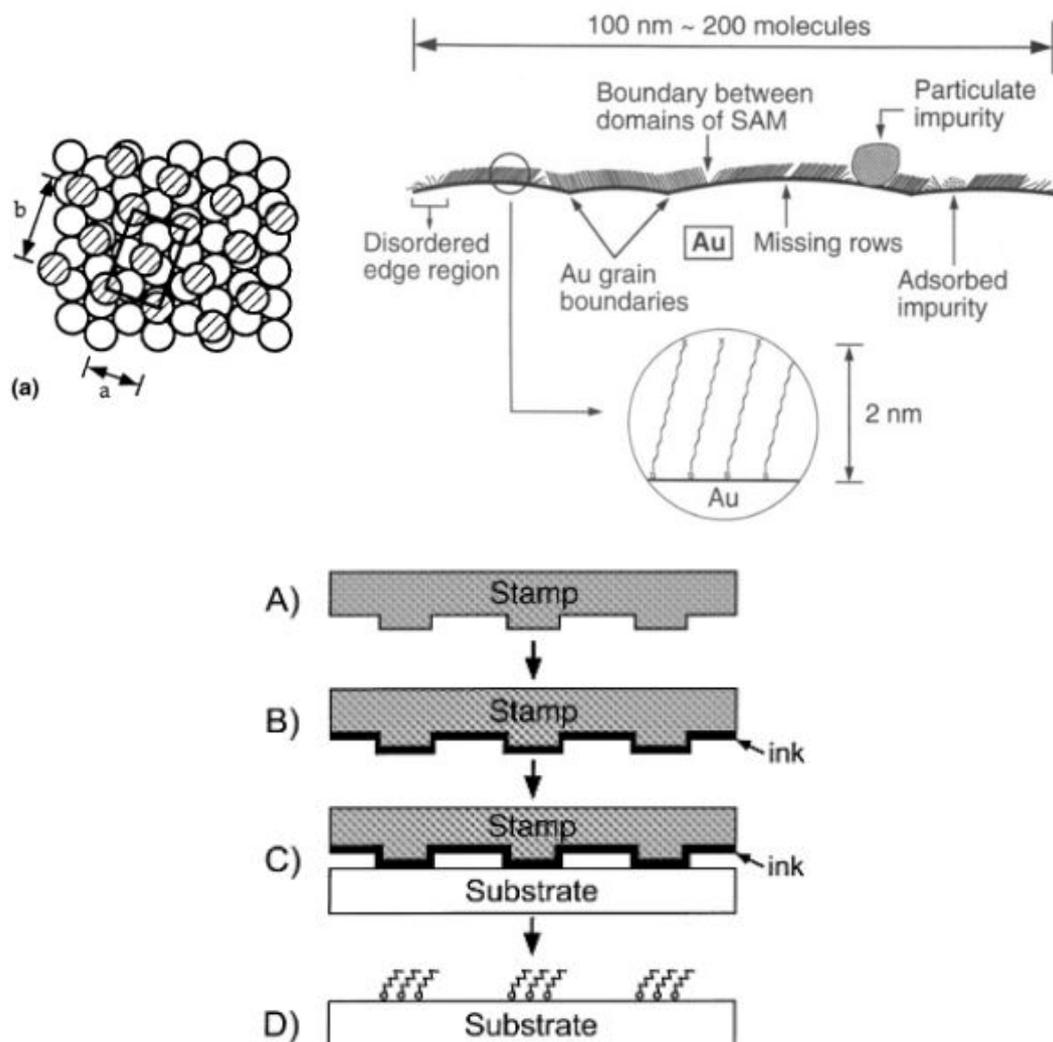


Figure 2. Top left: An adsorbed thiollattice on Au without bulky head groups forming a well-ordered 2D structure.³¹ Top right: A typical thiol-covered interface showing common impurities and defects like grain/domain boundaries, vacancies, foreign bodies and disordered regions which interrupt the lattice.³² Below: Showing a micro contact printing scheme. A stamp, often comprising PMMA, is coated with ink consisting of thiols or other functional molecules depending on the substrate. The coated stamp is pressed on the surface, where the connecting areas leave the molecules after stamp removal in a well-ordered fashion.³¹

molecules' interactions of so called head groups with the interface that are competing with several other interactions, like intermolecular interactions or interactions of tail-/face group with the interface. These different kind of interactions lead to molecule specific alignment on the interface. Are head group-surface interactions to weak, assembly does not occur. Are intermolecular interactions to weak, only individual molecules assemble at the interface, but no dense monolayer is formed due to lack of intermolecular attraction. If on the other hand, these interactions are to strong, the molecules will not assemble on the surface.³³

There are several kinds of SAMs that are documented (e.g. porpheryines on HOPG, BTB-1) but left out here, since they are only of minor importance to the field.³⁴ The type of SAM that is used, heavily depends on the substrate choice and only few enable SAM growth on their surface. Common substrates in this field are Al₂O₃, Au, SiO₂, Cu, quartz and TiO₂.²⁶ Alkanethioles on gold and alkylsiloxanes on siliconoxide are most intensively studied (see fig. 2 for structure and common defects), even if later are strictly speaking not self-assembled monolayers, since interactions formed by these building units are not under thermodynamic control and non-reversible. Still, they are often studied systems and are in literature treated as SAMs and for this reason included here. In these two types of monolayers, the head group is adsorbed on the solid state surface via chemisorption and the tail groups lead to alignment of the individual molecules via van der Waals interactions.^{24,33,35} The tail group can be functionalized with e.g. -OH, -COOH or -NH₂ groups to modify SAM surface properties like hydrophobicity and thereby wettability.³⁶ In this paper, growth conditions and methods of SAM formation will not be a focus. Good literature can be found elsewhere.^{31,37} Not only can a wide variety of SAMS with functional groups be grown, after assembly it is even possible to modify the tail groups chemically. It has to be considered however, that the high density of molecules may influence the mechanism of a reaction. A nuclear substitution where the head group is attacked from the back, is for example sterically hindered, by the molecules' neighbours. Nevertheless, several reactions are known to circumvent these problems and many functional groups are achievable.³⁸ Reversible interactions lead to a high surface quality, but bring several problems with them as well. Generally depending on the type of monolayer building monomers, temperatures over 90°C lead to dissociation of the adhered monolayer by removing the thiol with an attached gold atom from the surface.²⁴ The same occurs after some time, if the SAM is removed from equilibrium, by, for example, removing the sample from the thiol-containing solution. In cases where such environments are necessary, usually alkylsiloxanes are used due to strong binding interactions in the silicon oxide substrate. Recently, also selenolates have been investigated due to their improved crystallinity when compared alkanethioles.^{39,40} They do, however, suffer from the same limitations as thioles, since the instability stems from the substrate's properties.

An advantage of SAMs formed by thioles is their easy processability(see fig.2). A wide range of different patterning techniques like microcontact printing are known and can be used to cover only certain surface areas or even substitute thioles in one region with another thiole-type.^{32,41} Several possible applications arise therefrom in e.g. electronic devices.^{7,20,42} Due to their strong bonding, alkylsiloxanes cannot be processed as easily.

1.3. Metal-Organic Framework Thin Film Growth on Self-Assembling Monolayers

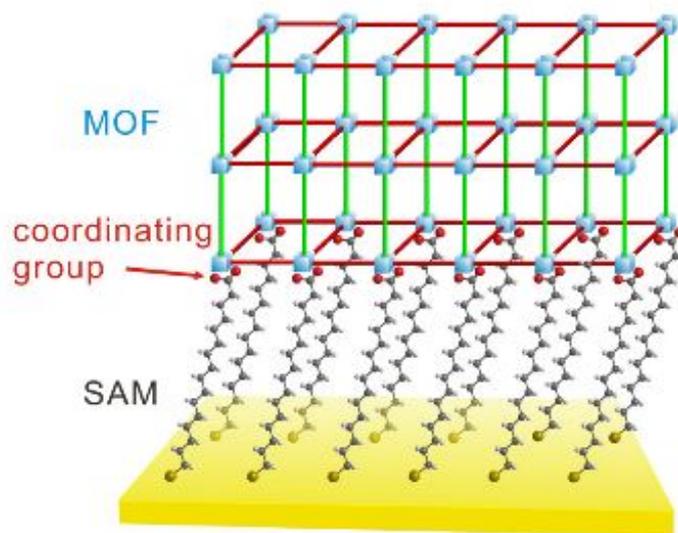


Figure 3. An example of a common configuration used to connect MOF thin-films to a surface. A functionalized gold interface is interacting via their thiole tail-groups with the SBUs of a MOF by forming coordination bonds between organic moieties and metal centre atoms.²⁰

Combining both SAMs and MOF thin films results in the relatively new field of SUR-MOFs. Via growing thin films on a SAM instead of the pure substrate, in general a higher crystal uniformity and smoother surface can be achieved. An example structure is shown in Fig. 3. While there are several cases known, where it was possible to achieve similar results via direct deposition on bare substrate, those are more exception than the norm, unlike for deposition on SAMs. Later even offer the possibility to adjust the crystal orientation by changing the functional group exposed on the SAM surface.⁴³ Something that is difficult on bare surfaces. A well studied case is the HKUST-1 thin film, where upon deposition on a -COOH terminated SAM, a [100] orientation was measured by X-ray diffraction(XRD), while for -OH termination [111] was observed. However, the SAM composition is not the only parameter that effects crystal growth. Ohnsorg et al. reported a change of crystal orientation with a change from 25 to 50 °C.²³ Indicating, that crystallisation is even more complex than at first assumed. The change in crystallographic direction can in some cases be attributed to the change in binding group density at the surface of SAMs. With -COOH as an example, higher and lower densities of ligand tail groups were tested by using different thioles with the same functionality to find, whether crystallographic growth direction is affected. It was indeed found that thereby a certain growth direction was forced on the MOF thin film. This is attributed to inflexible linker molecules lengths. They have to bridge the metal centres in a well defined distance, since torsion or other deformations are energetically unfavourable.⁴⁴ This also indicates that there could be more parameters like pH or linker concentration/ratio (if more than one linker is used) that could influence the growth of the thin film. Later was proven by Zacher et al.⁴⁵ Combined with patterning techniques for SAMs, it was shown^{46,47} that good shape control over MOF thin-films can be obtained, something that could in the

future be important for electronic device fabrication. Using unmodified surfaces, such a fine control over shape and properties of MOF thin-films has to the authors knowledge not yet been achieved. While in general, closed films are achieved by standard deposition techniques, it is important to note that crystal growth often does not follow the Frank-van der Merwe model, i.e. layer by layer growth, until a thickness that depends on the individual MOF is achieved. Instead, a Volmer-Weber growth is observed, where until a "critical thickness" is reached, islands grow instead of the expected film.²³ Thereby, often the minimal thickness of a closed SURMOF is limited. Via X-ray diffraction,⁴⁶ information about morphology and homogeneity can be won from the in-plane and out-of-plane diffraction patterns, as well as an estimate of film thickness via the Scherrer relation. Due to their small thickness of often between 20-50 nm, a synchrotron source is generally needed to get sharp diffraction peaks. Ellipsometry, while also often used,^{47,48} has the limitation, that the refractive index of the bulk MOF must be known for the technique to yield reliable results. For smaller devices Raman spectroscopy is used to prove MOF growth and to identify a specific crystal.¹² The morphology can be found by AFM⁴⁹⁻⁵¹ or SFM studies. Another technique that is easily applicable, is surface area evaluation via gold coated quartz microbalances, on which the MOF can easily be grown and the uptake of guest molecules be studied via change in resonance frequency of the device.⁵²

2. Metal-Organic Framework Thin Film Preparation

Today, there are numerous techniques and subtechniques that are used to grow SURMOFs, whether with or without SAM assistance, each exhibiting their own disadvantages and advantages.^{19-22,25,27,53} Here, only the most important techniques are explained and characterized. The correct film preparation is of utmost importance, not only for film quality, but also crystal orientation, as there has been reported that both can change upon using different preparations methods.^{43,54} While this may not always be the case, it is important to note, since this indicates, that it is not safe to assume that the same crystal is obtained via the same starting materials but different preparation methods. The preparation method choice depends on many parameters, such as growth time, preferred crystal quality, crystal orientation, growth temperature and substrate.^{20,23} Often a compromise between growth time and crystal quality has to be made, especially if commercial applications are considered and the growth of a few dozen nanometer must not take several days of undisturbed rest. Further, while there are several substrates, like SiO₂, glass, mica, Au, Al₂O₃ or quartz available for SURMOF growth, relatively few have been studied in detail, such that currently for many of those no synthesis methods with enough control over film properties exist.²⁶ Only Au and SiO₂ have been studied intensely, mainly due to the ease with which SURMOFs can be prepared on their surfaces, when compared to others, due to SAM induced orientational growth.⁴³ There, different SAM constituents are, however, of interest, since MOF growth follows a growth similar to epitaxial growth²³ and control over the position of dangling functional groups might lead to an increase of possible crystal directions that can be deposited on the surface and would therefore be interesting for possible applications.

2.1. Solvothermal Synthesis

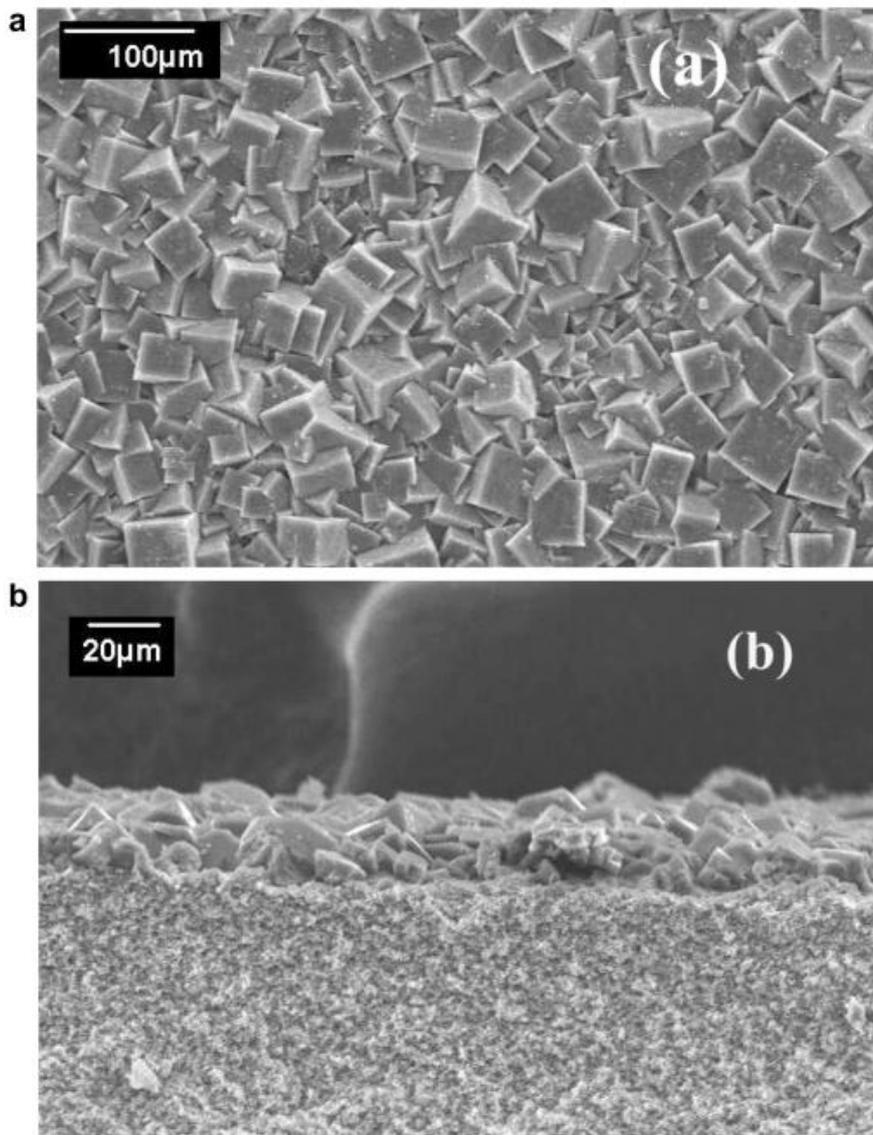


Figure 4. MOF thin films obtained by solvothermal synthesis usually show high density but poor crystal orientation. Image taken via scanning electron microscopy (SEM). Here: MOF-5 on porous α -alumina, taken at room temperature. (a) Top view of a continuous, intergrown thin film with high surface roughness and random crystal orientation. (b) Side view of the same film. Clear differences between thin film and substrate in roughness and orientation are visible.¹⁴

As shown in fig. 4, films that are formed by this technique are usually intergrown, since crystals are first grown, then deposited; and denser, but less oriented and rougher films are formed, when compared to other growth methods. Sometimes this results in non-closed films for very thin films ($<50\text{nm}$). One concern is the problem of connecting growing crystals tightly to the surface. As theorized by Zacher et al., the linkers acid-base character has influence on connectivity to the substrate if no SAM is applied. Acidic surfaces

hardly interact with acidic linker molecules, while basic linker molecules often show favourable interactions. Thereby substrate nature is important for MOF growth with this method.⁵⁵ Solvothermal synthesis is a method often used to produce bulk MOFs in solution for which many growth conditions are known. Research in the last years has tried to transfer this knowledge to MOF thin film technology. Solvothermal synthesis typically is performed by incubation of both organic linker and metal centres dissolved in a solution covering the substrate and includes heating of the substrate above 100°C in often harsh reaction environments.¹⁴ As such, gold that is coated with alkanethioles are often not viable for growth of a thin film on a surface, since high temperatures lead to dissociation of the linked SAM. Instead silica substrates covered by alkylsiloxanes or bare alumina surfaces are often used in this technique. Film thickness is controlled by incubation time. Sometimes growth is aided by microwave induced nucleation of MOF nanocrystals.⁵⁶ Even crystal orientation is achieved in some, but not all, cases.^{55,57}

2.2. Crystallization from Aged Mother Solution

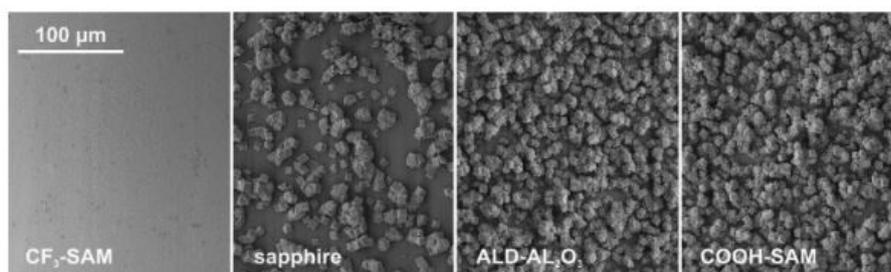


Figure 5. Growth of MOF-5 thin film on differently functionalized alumina surfaces, indicated in the image. In all cases where thin films were produced, high surface roughness is evident, showing that with crystallization from aged mother solution, high density but poor crystallinity films can be obtained.⁵⁸

In contrast to the common preparation technique for bulk MOFs, this technique allows for processing at room temperature.⁵⁹ Thereby, it is possible to use a SAM on a solid state support as substrate. Here, the first step consists of MOF nucleation under solvothermal conditions in e.g. ethanol, resulting in the mother solution used later. During this step, that takes several days, the solution stays separated from the SAM. After nucleation, where exact synthesis time depends on the MOF that is to be synthesized, the mother solution is added to the SAM for several hours. Consequently, the precipitating MOF crystals selectively bind to the SAM, since a certain direction of the crystal shows preferred binding.⁴³ Ultimately, the SAM controls the crystallographic direction of the MOF, yet does not yield a smooth thin film surface, due to the grain sizes that constitute the smallest, binding MOF building blocks (see fig. 5). A growth on $-CH_3$ functionalized SAM tail groups results in a less ordered MOF, probably originating from hydrophobic interactions as only anchoring interaction, while $-CF_3$ prevents binding entirely. Later functionalization's property is often used for patterning. The observed growth happens under such mild conditions, that it was possible to view the growth via AFM.

A very similar method is the gel layer growth of MOF thin films. The thin-films are in principle grown via the same technique, but instead of a liquid, a polymer gel is

situated above the SAM, acting as mother solution. Via this technique, a higher concentration of nucleated MOFs is present near the phase boundary, which can result in a different orientational growth than in liquid mother solution. In a study performed with HKUST-1, the obtained crystal orientation showed [111] growth independent of the underlying SAM, a property that other growth methods did not exhibit.⁵⁴

2.3. Solvent Evaporation Induced Crystallization

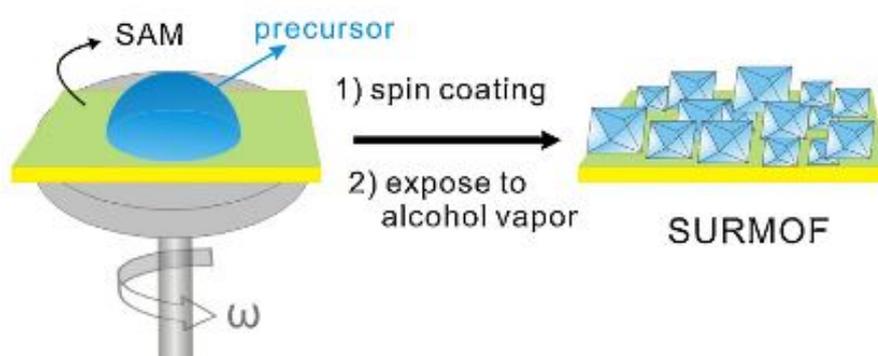


Figure 6. MOF layer formation via solvent evaporation and applied by spin coating. After drying, a layer of relatively low density and poor crystal quality is obtained. Spin coating on a patterned substrate yields thin films only on previously templated areas, if these can be wetted by the mother solution.⁶⁰

With this method, a solution of metal ions and linker units are in a solution where the solvent molecules bind strong enough to metal ions to prevent aggregation, but weak enough to be removed by evaporation.⁶¹ Once the solvent is evaporated or removed by spin coating (see fig. 6), the MOF thin film forms, but unexpectedly always takes the same crystal orientation when building a HKUST-1 thin film on SAMs, no matter which surface functionalization is present.⁶⁰ Surprisingly, the same [111] orientation was found as with gel layer growth. Whether, this similarity is reproducible for other MOF thin film types has not been studied yet. With this technique, patterned deposition is easily achieved allowing for easy position control, yet it yields poor crystal quality. When using this growth method and patterning is intended, it is important to take wettability of the surface with utilized solvents and present surface modification into account. In a study by Carbonell for example, it was found that DMSO solvent was unable to pattern structures on -COOH and -OH terminated thiole SAMs due to complete covering of the surface, while -CH₃ and -CF₃ terminated thioles were able to maintain their applied drop form, and developed after drying into a crystal with well defined boundaries. Thus a surface with low wettability is needed for this method.⁶² Another problem is the huge variety of shapes, individual crystals produced via this technique can take. This may lead to problems during device manufacture and poor bonding. An advantage is the possibility to screen a multitude of MOF solutions with different characteristics like pH and concentration to find an optimum for crystallization and desired MOF properties.

2.4. Layer-by-Layer (LbL) Deposition

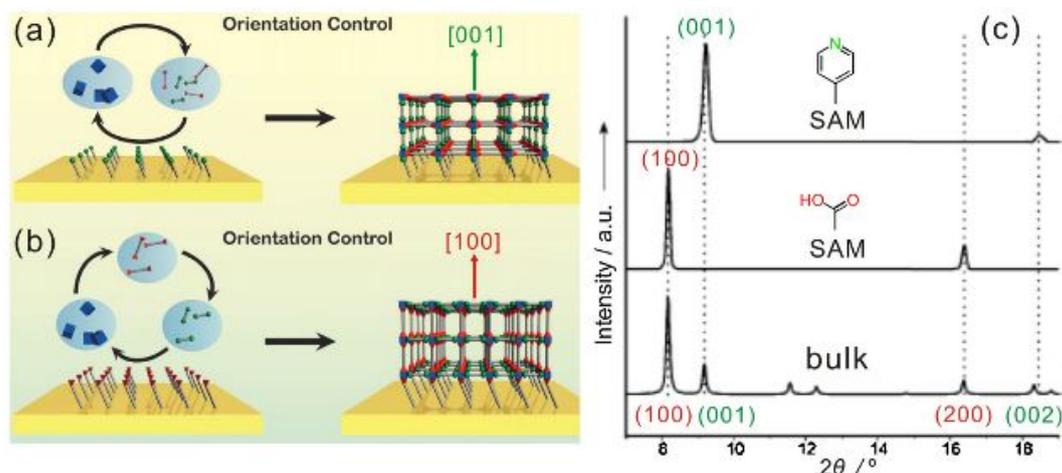


Figure 7. Example process of Layer-by-Layer deposition of $[\text{Cu}_2(\text{ndc})_2(\text{dabco})]$. Since layers are added step by step, high crystallinity and well defined orientation are achieved. a) Two step cycle, where linking molecules are added as mixture, resulting in the (001) orientation. b) Three step cycle, dividing different linking molecule addition steps. A (100) orientation of the crystal is produced.²⁰ c) Influence of different SAM tail group in this process on crystal orientation as detected by XRD.⁴⁵

Layer-by-Layer deposition, despite intuitively thinking otherwise, achieves the formation of non-closed films only after several deposition cycles have occurred.²³ A deposition cycle consists of exposure of the interface to the metal ions or SBU, washing, exposure to the organic linkers in solution and washing.⁶³ For a scheme, see Fig. 7. While this does separate the growth phase from nucleation, it does not prevent the nucleation of MOF units after the initial washing step since there is no closed layer formed after just one deposition cycle and surface-ligand interaction is in principle weaker than ligand-ligand interaction. Only after several cycles does the SURMOF close above the surface. Due to the separation of nucleation and growth, this technique may be used at room temperature and thereby with surface functionalization by SAMs. However, while a very smooth surface and precise orientation are achievable by this method, one main disadvantage becomes quickly apparent.⁶⁴ A very slow growth of the thin film results from the cyclic growth, which can take up to several days for a hundred nanometer thin film. Furthermore, it has been reported by Nijem et al., that loss of orientation may onset after a limited number of cycles. For HKUST-1, 60 cycles were reported as the amount of repetitions it took to lose SAM-induced orientation.⁶⁵ Instead, a [200] orientation started to dominate irrespective of the underlying SAM the film was grown on. The number of cycles probably depends on several parameters such as MOF, concentration and temperature; but those influences have yet to be tested. Therefore, while this growth characteristic may not be shown by all MOFs, for HKUST-1 not only the minimum but also maximum thickness of a closed, highly oriented SURMOF is limited.

Since this technique is very time intensive, a similar method was developed to reduce the amount of time needed to form the SURMOF. For a film that would otherwise take 72h to grow, only 30min are needed. The Spray assisted LBL method uses the

same principle, but instead of immersing the surface into solution, the building block containing solutions are sprayed in fine droplets onto the surface, while following the same cycle scheme shown in figure 7, also including intermediate rinsing.⁴⁶ The finely distributed solvent evaporates and leaves the MOF thin-film with an additional layer. Why this method works so much faster, is not known, but films prepared by this method are of slightly less high quality than the original technique, yet still exhibit preferred orientational growth and closed layers.²⁰

2.5. Langmuir-Blodgett LbL Deposition

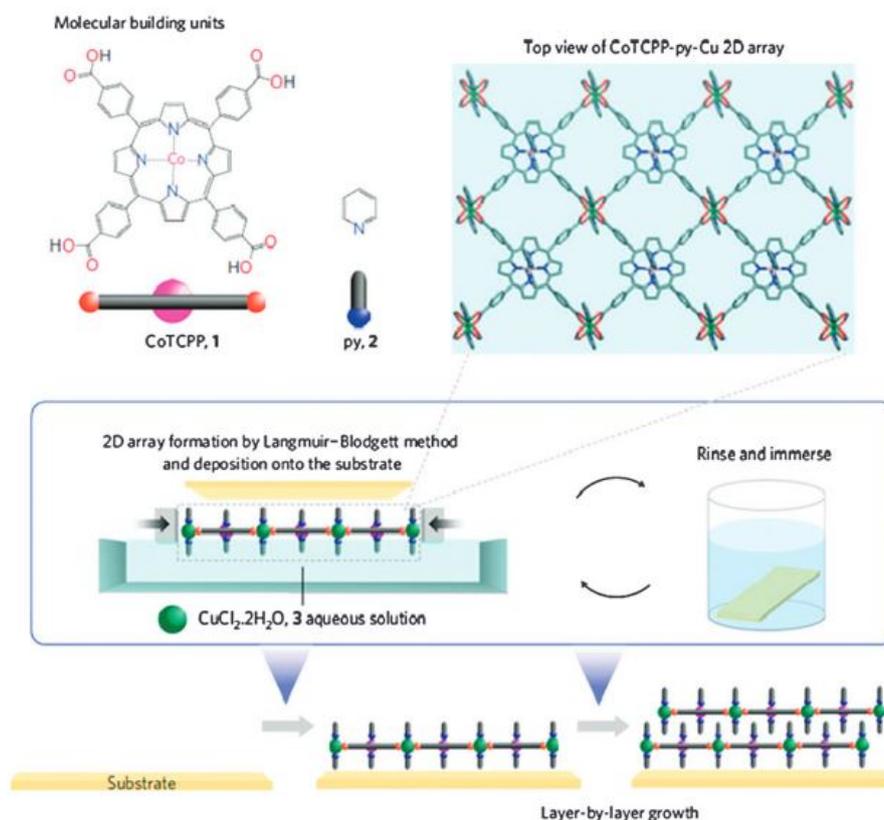


Figure 8. Principle of Langmuir-Blodgett LbL deposition of a Co-Porphyrine with pyridine on silicon. A MOF monolayer forms at the air-liquid interface and is transferred to the substrate. Each applied layer is bound by non-covalent interactions to connecting layers. Here shown with NAFS-1 as model system.⁶⁶

This deposition technique works analogously to the normal Langmuir-Blodgett method for amphiphilic molecules. Layer by layer, is transferred from a liquid-air interface to the substrate which does not necessarily need an attached SAM to produce highly oriented thin films (see fig. 8).⁶⁷ The technique was developed by Makiura et al. for use on silicon and can also be used on quartz.⁶⁸ It is performed with extensive, combined linker-ion complexes in deposition cycles, depositing one layer per cycle and providing films of a quality similar to those prepared by spray assisted LBL deposition. The individual layers are held together by weak non-covalent interactions. One major limitation is the small variety of MOF thin films that can be accessed by this technique, since the requirement to

build amphiphilic structures at the air-liquid boundary is rarely fulfilled by MOF monolayers. Furthermore, harsh environments that are often used in solvothermal synthesis of MOFs, cannot be applied in this method.²⁶ Thereby limiting the amount of accessible MOF thin films and possible applications with this technique further. As a result, there are only few studies performed on this growth method in literature, despite this methods precise control over crystal direction and morphology.

3. Properties and Applications of SAM Grown MOF Thin Films

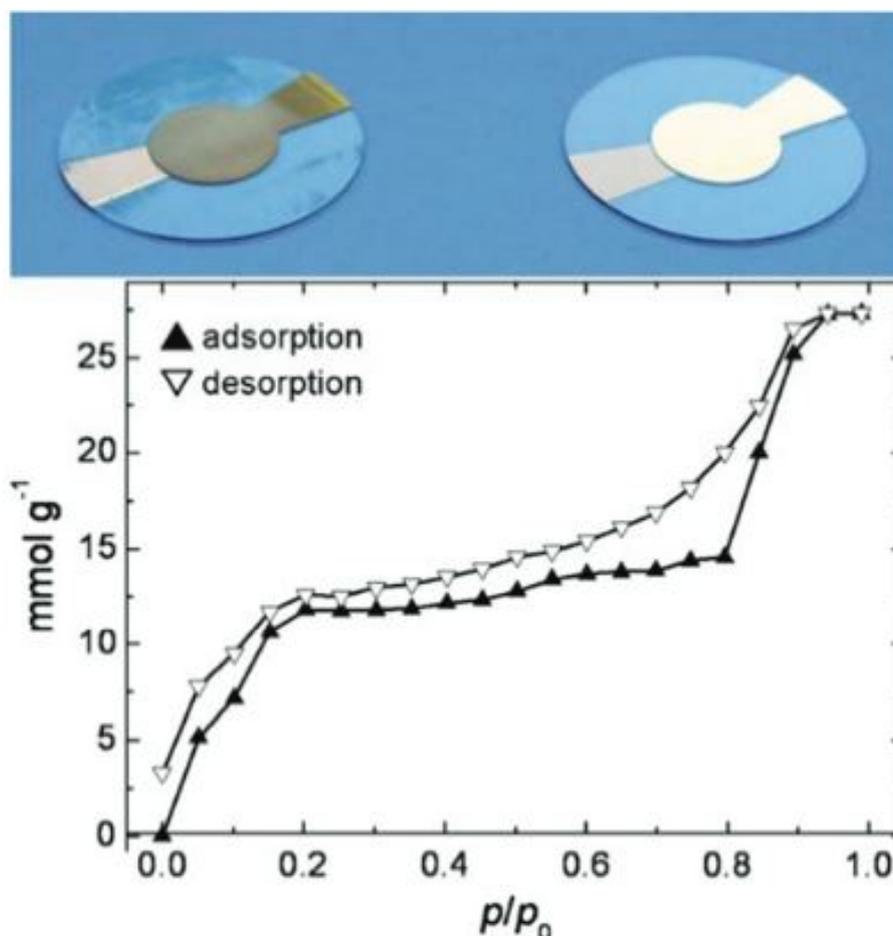


Figure 9. Gold QCM coated with MOF on SAM. Top left: Au coated with HKUST-1 on SAM. Top right: Au reference sample without any coating. Below: Adsorption and desorption isotherm of water on QCM, derived from change in QCM vibration frequency due to gain in weight.²⁶

While bulk MOFs promise a wide variety of applications like gas storage⁶⁹ or heterogeneous catalysis,⁷⁰ due to the highest surface area per weight ratio currently exhibited by any material,⁷¹ several applications that have become of interest, are better prepared as thin films. Bulk MOFs are insoluble and generally show a multitude of orientations in powder form. A property that would be inadequate for example in gas separation applications, where orientation of pores and a continuous crystal without defects are essential for functionality.⁷² SURMOFs might solve those problems, if the right fabrication technique

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is used. Characteristics for all methods treated in this review are described in table 1. MOF thin films often show good morphology and crystal quality which is of interest for gas separation, sensing applications and chromatography, especially when high crystal orientation is present. SAM grown SURMOFs show dense packing and very tight binding to the surface, due to numerous connecting coordination bonds between metal ions and SAM functional groups and would therefore be ideal. Both properties are not easily obtained via after-growth immobilization to the surface which, to the authors knowledge, has not been achieved yet. If SAM grown MOF thin films and SURMOFs grown on bulk material are compared, it is easily seen that later are inferior due to their often random orientation and intergrown lattices and the lack of easily achievable patterning. However, due to the higher amount of possible substrates their use is more flexible and not bound to Au and SiO₂ interfaces. It is, however, possible to find preparation techniques for directly grown thin films, that yield crystal orientation, if not as well as in SAM grown thin films. When grown on quartz crystal microbalances (QCMs), shown in fig. 9, selective uptake that is influenced by crystal quality and orientation, MOF thin films grown on SAMs are more important for this application and may in the future lead to very precise sensors. The change in resonance frequency upon binding can give information not only about presence, but also amount of ligands on very small weight scales. The ability to modify MOF structures to increase selectivity, makes this an application with a variety of prospects. Currently, only few studies have been carried out and selectivity still poses a problem.⁴³

Method	Characteristics	Substrates	References
Solvothermal	No SAM on Au, but SiO ₂ ; rarely directional, poor morphology, high density, intergrowth, slow	Dependent on organic linker acid/base character	14, 55-57
Mother solution	directionality possible, rough film, high density, slow	SAM covered surfaces; alumina,	43, 58, 59
Solvent Evap.	poor crystal quality, rough surface, patterning possible, limited directionality, fast	SAMs on Au and SiO ₂	60-62
LbL Deposition	highly directional, very smooth surface, very slow, patterning possible, directional film thickness limited	SAMs on Au and SiO ₂	20, 23, 63-65
Langmuir-Blodgett LbL	directional, high crystal quality, MOF choice very limited	Quartz, SiO ₂	26, 66-68

Table 1. A summary of the characteristics of thin film growth methods discussed in this review and where to find them documented.

Another promising application comprises MOF thin films in chromatography. While separation by bulk MOFs in chromatography has already been reported for several organic molecules,^{73,74} it would be interesting for gas chromatography to use a capillary with MOF coating instead.²⁶ In that regard, the working principle was proven by a SAM covered silica capillary on which MOF-5 was grown via layer by layer deposition.⁷⁵ Another group later reported even enantiomeric separation by using a similar technique.⁷⁶ After 80 cycles, a sufficiently thick layer was achieved and separation was compared to

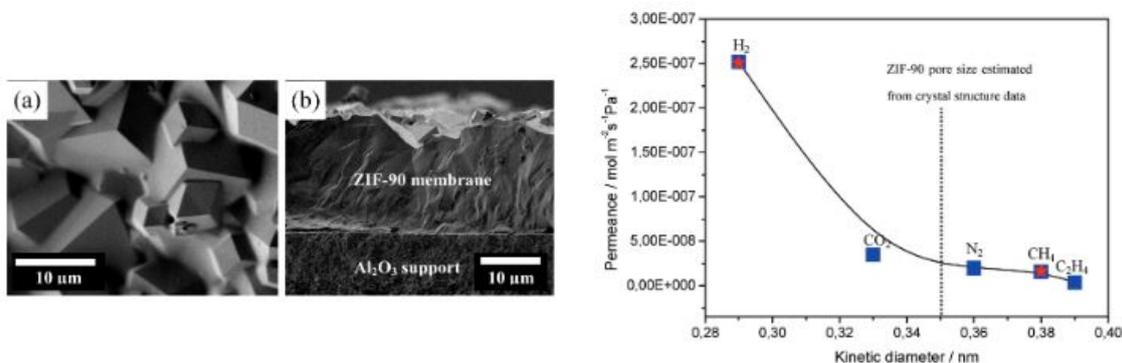


Figure 10. Left: ZIF-90 membrane grown on with APTES modified Al_2O_3 support. a) Top view showing high surface roughness and random crystal orientation. b) Side view of the same sample. Right: Graph showing gas permeation for different gases at 200°C as a function of kinetic diameter.⁷⁷

a commercial PLOT column used for gas separation. Comparable separation, but on a faster time scale for the MOF column was observed.

Films grown directly on metal oxide show poor permeance but if prepared optimally, exhibit selective gas transport with a reported ratio of 23/1 for H_2/N_2 for ZIF-90 (shown in fig. 10). Thereby, a use as gas separating membrane becomes conceivable.⁷⁷ Rather rough surfaces are produced via direct growth on metal oxides, yet seem sufficient for this application. If higher separation factors are reached, this method can be used for gas purification. Molecules with larger diameter than pore size still passed through the membrane, if at a lower rate, due to what is thought to be MOF lattice flexibility. A better filtration could be reached by MOF on MOF structures, that can bind common gas impurities.

4. Advances on SAM Grown MOF Thin Films

A main advantage thin film MOFs present over their bulk analog lies in their processability in devices. Using thin films it is possible to form almost completely defect free and connected surfaces, which prevents leakage through e.g. a possible molecular sieve. Meanwhile bulk MOFs would not be able to prevent leakage when pressed into a film due to their numerous orientations and discontinuous grain boundaries. So far, the compromise between crystal quality and growth time results in one of several major factors that prevent MOFs from widespread applications in industry, especially if performed on a large scale.⁴² While there are still many fields and much basic research to be performed in order to control and understand MOF properties better, improvement of fabrication techniques are necessary to manufacture thin films that exhibit specific properties, only depending on the thin film and not the preparation method. Where later also often has unwanted influences on film quality. Especially for membrane technologies in gas separation or possible electronic applications, high quality films with high crystalline order and continuity are needed for them to work as intended and for their features not to be dominated by defects. Until now, SAM grown SURMOFs exhibit the overall "best" properties for demanding applications as those mentioned previously. They are, however, restricted in their application, since only gold and silica can be functionalized with strongly binding SAMs.

While the groundwork is laid and several interesting applications, like MOF beads in chromatography⁷⁸ and separation properties of individual MOF types^{79,80} on different substrates have recently been investigated, it is needed to transfer what was learned to other substrates to increase the number of potential substrates where highly ordered thin films can be grown on, in a controlled fashion. Only then are several new possible applications, for example in optical^{6,81} or electronic⁴² devices, truly accessible. In these fields, a wide variation of substrates are needed and especially in electronics, energy level matching is performed via matching the correct materials. This is not possible with the limited amount of substrates on which thin films can be applied in a fashion, that fulfills the high requirements towards film quality this field poses as well. One recent development was the growth of a MOF on indium tin oxide, a substrate very common in organic-inorganic hybrid electronics which could lead to more interesting applications.⁸² Another problem in this field, where MOFs could be used for energy harvesting⁸³ and as designer materials, exhibiting well controlled conducting^{7,84} and magnetic⁸⁵ properties, is the current lack of metallic MOFs that research is currently working with.⁸⁶⁻⁸⁸ Especially changing and modifying linker groups and loading of MOFs with TCNQ have recently shown great promise and indicate more possibilities, should a generalization of the yet unknown^{89,90} transport mechanism be found. In that regard, it is of interest, how SAM templates impede their properties and how directly grown MOF thin films compare in their properties, something that has not been investigated as far as the author knows. Connecting two different substrates with the MOF thin film is as of now still a new field⁷ and has not been investigated deeply. The formation of a strong contact with two surfaces is often not possible via deposition of metal with vapor deposition methods due to MOF porosity and thermal instability of the material. A possible solution might be growth on both surfaces towards a meeting point in between both surfaces, since LbL growth indicates a Volmer-Weber growth mechanism that would lead to good connectivity. This poses, however, again difficult, with possibly different growth directions observed on both substrates.

In most articles, only case studies on already well known MOFs, like HKUST-1 or MOF-5 were performed. Currently, there is seemingly a lack of generalized understanding in the field of how different parameter influence thin film properties. While it is for example known, that a change of temperature in LbL deposition of HKUST-1 changes the preferred crystallographic orientation,²³ it is not known how this comes to be, for which other MOFs the same or similar processes may influence the growth and for which not at all or at different temperature. The same is true for pH influences, if certain linker molecules or mixture compositions of several linkers are used. It is a major interest to unify theories behind those influences in order to control MOF formation of thin films better and to further the knowledge still needed for a wide variety of applications MOF thin films promise. The same holds true for different aging effects that may appear with time and influence the performance of devices. Changes in flexibility, oxidation, film quality and others are likely to appear with time and will undoubtedly change device behavior. Recently, a study examining the effect of aging on chromatographic performance for MOF-5⁷⁵ has been conducted and is one of the first of presumably many that will investigate long term behaviour and performance of MOFs that are of interest for example in catalysis, where a catalyst needs to show high performance for many catalysis cycles. Connectivity to the sample via a SAM might also be one of several points of interest, that could be effected by time. Long term connectivity has to be granted in many cases, since

flaking of MOF thin films may not only impact device performance negatively, but also be detrimental for the environment, since interactions of these often reactive materials with biological systems are not well studied yet.

5. Conclusion

Self-assembled monolayers are an often used template to grow MOF thin-films on gold or silica, yielding so far, a control over orientation and surface smoothness that is hard to achieve using other substrates. This is done by applying layer-by-layer deposition techniques that come at the prize of long preparation times. While growth methods can also influence the layer properties greatly, today there are a variety of techniques to choose from. Consequently, it is possible to manufacture thin films with preferred properties on these substrates. Yet, ultimately, the applications that are achievable using only those two substrates are limited and for the technology to make it's way into industry, further substrates have to be investigated in detail. Growth properties of MOFs on SAMs yield useful information about nucleation and film growth, that likely can be transferred to other solid state supports as well as bulk preparation methods. The understanding of direct growth on surfaces in the last years has consequently made strides into the direction of achieving similar control over film properties as SAM grown films. While MOF thin-films are a useful model system and may have several future applications, industry tends to minimize production and time cost and therefore it is probable that alternative substrates have to be found to realize MOF thin-films potential. While MOF thin films are closely connected to bulk MOFs and thereby yield valuable information about their properties, they exceed their potential in certain areas like optical applications, due to the possibility to form very homogeneous, highly oriented and smooth surfaces. So far, only studies of individual and the most common MOF thin films were performed and a closer relation between SURMOFs constituents and their growth properties has not been investigated. A closer look at building units and their effect on crystal nucleation and growth on thin films has not been studied on a large scale, but might provide useful insight to obtain novel thin films with interesting properties due to, for example surface template induced chirality, that have no parallel in bulk MOFs. Until now, sensing applications using QCMs have not accomplished what they aimed for. The recognition of molecules is often unreliable and a roughly correct size with right functional groups are often enough to be "recognized", such that a single molecule cannot be detected accurately. While MOFs are often described as designer materials, they face the same problems as supramolecular chemistry in the regard, that binding pockets cannot be manufactured so precisely that only one molecule is selected for uptake. Unlike proteins, where due to a huge backbone, subatomic resolution is possible, MOFs show limited size resolution due to by atoms quantized size dimensions. Gas chromatography by SAM grown thin films on the other hand has already shown it's viability. Only one of the early studies was discussed in this paper, yet already a commercial device did not show better separation. Different binding affinity and retention due to pore size even make it possible to engineer MOFs to fit individual needs in industry. It is therefore no surprise, that in the last years, this field has become of major interest. Still, the long fabrication time prevents commercialization. Yet, this should pose no problem with the advance of new growth methods. For other applications like optoelectronic devices, still too little is known about MOF thin film properties and at this point in time it is too early to judge viability. As such, MOF thin films pose an interesting research area that has yet to cool down.

6. Acknowledgements

The Author is grateful to Dr. M. Pchenitnikov, Dr. R. Gengler and Prof. R. Chiechi for their support during and with writing the report, especially later who also functioned as the authors supervisor for this research paper. Numerous fruitful discussions with and feedback from colleagues are also gratefully acknowledged.

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