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## **SURMOF**

(Anchoring of metal organic frameworks, MOFs, to surfaces)

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## Introduction

When the project was initiated in 2005, a new class of materials referred to as metal-organic frameworks (MOFs), porous coordination polymers (PCPs) or grid-type metal-ion architectures was receiving a huge attention. At this point in time, 2005, most of this attention resulted from the prospect to use this nanoporous materials for hydrogen storage in gas-tanks of automobiles. But, already then, four years ago, it was apparent that this class of materials with its ability to store small and medium-sizes molecules and objects, carries a huge potential for a number of other applications. While for gas storage the availability of the MOF-materials as powders is sufficient, for many of the more advanced applications of MOFs a reliable, reproducible and homogenous deposition on solid substrates is required. These more sophisticated applications include the use of MOFs as membranes for gas separation, in connection with electrical and electronic applications (including molecular electronics, organic electronics and optoelectronics) as well as sensor applications.

Realising that at this point in time, 2005, a reliable method to deposit of MOFs on solid substrate could not be achieved, we developed the plan for the present project SURMOF. The goals of SURMOF as defined in the original proposal were the development of methods to deposit MOFs on solid substrates and first tests with regard to possible applications in the area of sensor devices. Although the use of MOFs for sensor devices – and other applications different from gas storage – were certainly much too far ahead in the future to talk about more specific task we proposed to have – at the end of the project – a first proof-of-principle device available.

Today, at the end of the project (end of 2009), the general interest in MOFs is even larger than it was in 2005. Also in Europe the interest in this novel class of materials is still increasing, as reflected by the fact that in 2008 the first international conference on MOFs was held in Augsburg, Germany, and the next one, named MOF2012 will be organised in Marseille, France, in 2010.

While the interest in hydrogen storage has both in the US and in Europe decreased somewhat with respect of the situation in 2005, the general interest in MOFs and in particular with regard to the use of these nanoporous frameworks for other, more advanced applications, has seen an enormous increase. Many of these more advanced applications require, mentioned above, a safe method to anchor these methods on substrates. We thus conclude that the target of the SURMOF project defined in 2005 was a very timely one.

A brief inspection of the SURMOF results as described in more detail below reveals that the project has been a very big success. Certainly, this conclusion needs to be justified in more detail but basically, the following three facts already justify this very positive conclusion.

- 1) more than 30 papers describing the outcome of SURMOF were accepted for publication, some of them in high-ranked (impact factor larger than 3) and very high-ranked journals (impact-factor larger than 10).
- 2) the organisers of the EuroNanoForum 2009 in Prague accepted three talks proposed by members of the SURMOF consortium for on the main plenary sessions (one of which was presented by the SURMOF coordinator, Prof. Wöll, to describe the overall SURMOF results). In addition, there was a workshop with 9 contributions of MOF-applications, including one from another, MOF-related EU-STREP "MOFCAT". In addition, members of the SURMOF consortium presented 11 posters with their research results during the EuroNanoForum 2009
- 3) today, when it comes to anchoring MOFs on substrates, the contributions from the partners within SURMOF are recognized worldwide. All scientific work presently published on MOF deposition on substrates contain references to work done by partners within SURMOF. We are not aware of any exception to this statement.

The fact that – as characteristic for a high-risk research project – not all milestones defined in the original proposal could be ready does not put in question the very positive over-all judgement presented above. Before the very successful layer-by-layer method (also referred to as liquid-phase epitaxy) could be implemented first the problem related to the deposition on MOFs on substrates had to be investigated in more detail – and some negative results eventually helped to develop this novel method which is now the basis for MOF desorption on solid substrates.

With almost all main goals of the project reached the very successful project SURMOF has provided the basis for many new research projects. Now, upon completion of the SURMOF project, we not only foresee more than 10 additional publications describing the outcome of SURMOF but also a number of new research initiatives on the national level within EU member states and on the European level.

## Project Execution

### Scope of the SURMOF project

As illustrated in Fig. 1, the work done for this project can be assigned to the following steps:

#### SAM-formation.

Surfaces were modified to control nucleation and growth of metal-organic frameworks (MOFs). For this purpose, in most cases self-assembled monolayers (SAMs) were used. Major objectives within this part of the project were:

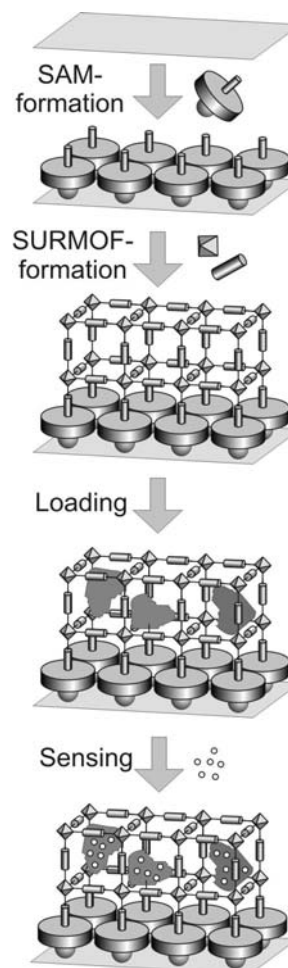
- the synthesis of suitable self-assembling organic molecules
- preparation and characterisation of the SAMs to be used for nucleation and growth of MOFs

Main contributions to SAM-formation: RUB A, GUF/UNIMAR.

#### SURMOF-formation.

MOFs were nucleated and grown to surfaces in a controlled, newly-established fashion using a step-by-step procedure for formation of single layers of the polymer frameworks. Additional to their preparation, the SURMOFs were extensively investigated with numerous surface-analytical methods. Major objectives within this part of the project were:

- Synthesis of building units of MOFs both for model studies and new MOF structures.
- Systematic study on the anchoring of MOFs to different inorganic surfaces (metal and metal oxides).
- Fabrication of model systems to study the interaction of the organic ligands with metal ions by using spectroscopic methods.
- Systematic study on the anchoring of MOFs to model organic surfaces by using a variety of analytical techniques.



**Figure 1.** Scope of the SURMOF project. Specifically designed self-assembled monolayers are used to control nucleation and growth of MOFs which, subsequently, serve as templates to control nanoparticle formation. Such a hybrid structure is then explored towards applications of which gas sensing.

- Development and improvement of theoretical methods to describe anchoring of SURMOFs to surfaces.
- Modification of existing MOF concepts to optimize the anchoring to surfaces (organic and inorganic).
- Strategies to deposit MOFs on predefined areas of the surface.

Main contributions to SURMOF-formation: RUB A, RUB B, USTAN A, USTAN B, CSIC A, CSIC B, ULI, UCL.

### **Loading.**

The loading of SURMOFs out of the gas phase and out of solution was studied to gain fundamental insight in SURMOF properties and applicability for gas sensing. Major objective:

- Fundamental studies on MOF structure-property relationships and their subsequent loading with metal-organic precursors.

Main contributions to loading: RUB B, ULI, CSIC B.

### **Sensing.**

As a demonstration for possible application of SURMOFs, the development of a SURMOF-based gas sensor was planned. Major objectives:

- Development of concepts to electrically contact MOF particles deposited on nonconducting substrates.
- Strategies to deposit MOFs on predefined areas of the surface.
- Fabrication of a functioning gas sensor based on SURMOFs.

Main contributions to sensing: GUF/UNIMAR, RUB A USTAN A.

**SURMOF project partners**

<b>Institution</b>	<b>Principal Investigator</b>	<b>Role in the Project</b>
Ruhr-University Bochum, Germany ( <b>RUB</b> )	1. Prof. Christof Wöll ( <b>RUB A</b> )	<i>Coordination</i> Surface Chemistry Surface Characterisation
	2. Prof. Roland A. Fischer ( <b>RUB B</b> )	MOF loading
Goethe-University Frankfurt, Germany ( <b>GUF</b> )	Prof. Andreas Terfort <sup>1</sup>	Lithography Synthesis Organothiols
University of Marburg, Germany ( <b>UNIMAR</b> )		
University of St. Andrews, United Kingdom ( <b>USTAN</b> )	1. Dr. Manfred Buck ( <b>USTAN A</b> )	Electrochemistry
	2. Prof. Neville V. Richardson ( <b>USTAN B</b> )	Physical Chemistry
Jagiellonian University Krakow, Poland ( <b>JUK</b> )	Prof. Marek Szymonski	Surface Physics
Consejo Superior de Investigaciones Cientificas, Spain ( <b>CSIC</b> )	1. Carmen Ocal ( <b>CSIC A</b> )	Microscopy (AFM)
	2. Prof. Jaume Veciana ( <b>CSIC B</b> )	Synthesis MOFs
University of Liverpool, United Kingdom ( <b>ULI</b> )	Prof. Matthew J. Rosseinsky	Synthesis MOFs
University College London, United Kingdom ( <b>UCL</b> )	Dr. Caroline Mellot-Draznieks <sup>2</sup>	Theoretical Chemistry
The Royal Institution of Great Britain ( <b>RIGB</b> )		

After the project started the research group of Prof. Thomas Bein, Ludwig-Maximilians-University Munich, applied to join the project. After the agreement of all partners and the EU scientific officer Prof. Bein became a member of the consortium. He did not receive any financial funding provided by the EU. This new partner took part in all meetings and acted as an advisor.

<sup>1</sup> Prof. Terfort's group worked at the University of Marburg until month 30, then moved to Goethe-University Frankfurt.

<sup>2</sup> Dr. Mellot-Draznieks' group worked at the Royal Institution of Great Britain until month 10 and moved to the University College London thereafter.

## ***The Workpackages***

### **WP1: Screening LBMOFs**

Workpackage leader was ULI. Contributions to this workpackage were made by ULI, UNIMAR/GUF, RIGB/UCL, CSIC, and RUB B.

WP1 started in month 1 of the project and involved the screening of existing LBMOFs for their growth onto  $-\text{CO}_2\text{H}$  and  $-\text{pyr}$  terminated SAMs on Au, in order to determine optimum conditions and techniques for SURMOF deposition and to permit an understanding of those factors that influence this growth, clearly enabling for the overall project objectives. Some of the initial targets were previously prepared by ULI, whereas others were well-studied thermally stable systems that exemplify this class of materials.

There were four milestones associated with this WP, all of which were reached:

#### **M1.1 "Information on which of the LBMOFs synthesized so far are compatible with anchoring to $-\text{CO}_2\text{H}$ terminated organic surfaces"**

One of the main objectives of WP1 was the screening of MOFs in order to determine which structures were most suitable for anchoring to *existing* carboxylic acid terminated SAMs. It was found that MOFs capable of forming stable highly-condensed oxide-based clusters such as the Cu-paddlewheels in HKUST-1 and MOF508, the  $\text{Zn}_4\text{O}$  units in MOF-5 and the  $\text{FeO}_6$  trimers in MIL-88B, form the best SURMOFs on these SAMs.

#### **M1.2 "Information on which of the LBMOFs synthesized so far are compatible with anchoring to pyridine-terminated organic surfaces"**

This milestone (due in month 10) was initially delayed due to problems experienced with the stability of the novel  $-\text{pyr}$  terminated SAMs; however, this work was fully completed in month 18. The LBMOF MOF 508,  $\text{Zn}(\text{BDC})(4,4'\text{-bipy})$ , was chosen as a model for growth on  $-\text{pyr}$  SAMs as it displays an axial N-heterocyclic group perpendicular to the layer. A 40 layer sample of the 508 MOF was grown on  $-\text{pyr}$  SAMs and fully characterized. MOFs containing ligands of this type, or an appropriate metal-site to bind the  $-\text{pyr}$  SAM to are best for growth on these SAMs.

#### **M1.3 "Generation of simple structures of MOFs using micro-contact printing with sub-micron dimensions"**

Gold surfaces were patterned using microcontact printing with two different thiols: one terminated by  $-\text{CO}_2\text{H}$  groups capable of framework formation, and the second terminated by an inert  $-\text{CF}_3$  or  $-\text{CH}_3$  group. MOFs were selectively grown on the  $-\text{CO}_2\text{H}$  terminated surface (shown by AFM and SEM measurements, RUB A) and no growth was observed



on surfaces terminated with  $-\text{CF}_3$  groups. The MOF structures were deposited as lateral stripes or as squares on suitably patterned surfaces.

#### **M1.4 "Understanding the basic principles governing LBMOF/organic surface anchoring"**

The basic principle of anchoring relates to the initial binding of a suitable metal ion to the  $-\text{CO}_2\text{H}$  or  $-\text{pyr}$  terminated surface, then building up the MOF in the presence of appropriate ligands. It appears necessary for the metal ion rather than the ligand to interact with the organic terminated surface, and is anion dependent. The organic surface can itself act as a template to influence the orientation of growth, and control the rate of this growth. MOF deposition can be achieved by 'sequential dipping' into solutions of the metals followed by solutions of the ligands which allows an ordered structure to be built layer-by-layer and can be done using more than one type of metal centre. *This method was pioneered by the RUB A group as part of the SURMOF project.* Immersion of the organic-terminated surface into a supersaturated solution of the framework forming components containing small clusters of the MOF (secondary building units) is a second, highly successful, method for growth (RUB B, *Bein* group).

#### **Nucleation studies on $-\text{CO}_2\text{H}$ (D1.2) and $-\text{pyr}$ (D1.3) terminated SAMs completed and results modelled"**

The objective of D1.2 and D1.3 is to understand the principles of the nucleation and surface growth of LBMOFs on  $-\text{CO}_2\text{H}$  and  $-\text{pyr}$  terminated SAMs, respectively, and to gain theoretical insight into the results obtained using molecular modelling techniques. These deliverables were both completed and the results are summarised below.

##### **Key results obtained:**

- MOFs can be anchored to and grown on organic-terminated surfaces through metal ions, which act as a linker between the SAM and the MOF. Nucleation occurs through the initial binding of a metal ion to the organic surface, and is enhanced when pre-formed SBUs are employed as observed for the significant differences in deposition of HKUST-1 when  $\text{Cu}(\text{OAc})_2$  (a framework SBU) or  $\text{Cu}(\text{NO}_3)_2$  are used as the metal source.
- Crystalline MOFs can be grown on to  $-\text{CO}_2\text{H}$ ,  $-\text{pyr}$  and  $-\text{OH}$  terminated SAMs from super-saturated solutions (where the nascent secondary building units present in solution interact with the surface and initiate surface growth) or from the bottom up using a layer-by-layer technique, and it is observed that the SAM terminus can strongly influence the rate of deposition.

- Growth of the MOFs can be selective on patterned SAMs where nucleation and subsequent growth is only observed on metal binding  $-\text{CO}_2\text{H}$  termini and not inert  $-\text{CF}_3$  termini.
- Growth of the MOFs on both  $-\text{CO}_2\text{H}$  and  $-\text{pyr}$  terminated SAMs using either of the growth techniques outline in M1.4 can be highly oriented, dependent on the SAM terminus, such that the organic interface can act as a template for growth. For example, a  $-\text{CO}_2\text{H}$  terminated SAM promotes HKUST-1 growth along the [100], whereas an  $-\text{OH}$  terminated SAM promotes growth along [111].
- Growth of MOFs onto SAMs can control interpenetration through symmetry breaking.

#### **WP2 and WP4: Synthesis of radical ligands and their screening for MOROFs-growth process, Design new optimized types of MOROFs**

Both workpackages 2 and 4 were lead by CSIC B. Further contributions were made by CSIC A, RUB, UNIMAR/GUF, USTAN, and UCL.

During the whole project time period, CSIC B offered its expertise in solution and synthetic chemistry, providing the organic building blocks for the Metal Organic Frameworks showing porosity as well as, thanks to the open- shell character of the PPM radical, magnetic properties. For their porous and magnetic properties the PPM based coordination polymers have been named Metal Organic Radical Frameworks, MOROFs. During the SURMOF project, CSIC B gained much expertise on surface science thanks to the fruitful collaboration with the project partners, experts in the fields of physical, inorganic and solid state chemistry. During this project, CSIC B has also been involved in the phenomenological studies (*i.e* in the unravelling of the mechanisms allowing the grafting of MOROFs onto the surfaces; frameworks of which it had good knowledge in *bulk* but that were never before studied on surfaces).

As a final result and accomplishing the not trivial task imposed by both Workpackages, CSIC B was able to show the feasibility of the anchoring, by means of coordination chemistry, MOROFs (Metal Organic Radical Open Frameworks) onto solid organic surfaces. Moreover the expertise gained by CSIC B researchers went beyond the limits of the project, leading the whole group to get valuable knowledge onto surface science, as represented by the many publications of his group in the last few years on the chemistry of PPM radicals onto surface and on the preparation of porous MOROFs as bulk crystalline materials.

Fulfilling the deliverables and milestones of WP2 and WP4, CSIC B was able to synthesize a PPM-based radical derivative able to graft directly to the gold surface. As reported in M2.1 and D4.3 this compound shows good anchoring properties and is able to preserve its magnetic character once covalently bound to the gold metal surface by means of thiol groups as anchoring units. Unfortunately, no synthetic route allows both the introduction of the thiol function and the generation of the carbon radical center, thus being an example of the no triviality of transferring solution knowledge to surface science. For this reason, a disulfide PPM molecule has been synthesized. By breaking of the S-S linkage, a well packed self-assembled monolayer has been prepared and fully characterized, both for its magnetic and electrochemical properties. CSIC B has been looking for a synthetic approach aimed to: 1) preserve the magnetic character of the PPM moiety; 2) introduce a site for direct anchoring to the gold surface; and 3) introduce sites for coordination with metal ions. Such kind of synthetic route turned out to be impossible. For this reason, CSIC B has been devoting much effort in the synthesis of radicals substituted with phosphonic acid groups: these functionalities present a larger number of ligating sites than carboxylic substituents, can covalently bind to oxide surfaces and might lead to multidimensional MOROF structures. This kind of ligands has been successfully synthesized but at very low yields, due to the very low reactivity of the PPM skeleton towards the introduction of bulky phosphonic substituents. (The details of the synthesis can be found in M4.1)

The possibility to directly graft PPM derivatives onto surfaces different from the gold, has opened the way towards the use of characterization techniques that do not necessarily need a gold substrate and also might help solving the problems encountered in the stepwise growth of MOROFs, such as the matching between the number of coordinating sites onto the inorganic adlayer and the number of coordinating sites on the PPM ligands and hence will allow obtain more robust devices. Within this objective, a few publications have been made which demonstrate the potentiality of PPM radicals for anchoring or physisorbing on surfaces of different nature.

Once obtained the organic open shell ligands described in all the deliverables of WP2, CSIC B researchers made a good use of the techniques available in the laboratories of the other project partners inside this European project, and got involved into new type of experiments, ranging from: 1) growth of PPM based MOROFs onto conducting solid surfaces (together with RUB A, JUK and CSIC A); 2) deposition of tri-carboxylic PPM and copper ions onto Au(111) in UHV-conditions to study the assembly of the hybrid framework onto such substrate (USTAN B).

1) CSIC B, in collaboration with RUB A and CSIC A, demonstrated and publish the surface driven growth of PPM based coordination complexes onto thiol-terminated SAMs. As a further step, CSIC B started addressing the growth of PPM based

coordination polymers onto –COOH terminated thiol SAMs using as metal centre either transition metal ions or rare earth ions, towards 3D surface-grafted structures. The obtained results have already been showed in front of specialised audiences during international congresses and will soon be collected and sent for publication. In the milestones and deliverables of WP2 and WP4 some experimental details have been given.

CSIC B has been addressing the growth mechanisms of PPM based MOROFs as well as their kinetics of formation by means of Surface Plasmon Resonance and Quartz Crystal Microbalance techniques (in collaboration with RUB A). The use of these two techniques to follow the stepwise growth of MOROFs is an example of a great achievement reached during this project: the use well established techniques in the field of either biochemistry or organic chemistry for surface characterization. By appropriate choice of the solid substrate, we could characterize the grown metal-organic adlayers by many different surface techniques, such as UV-Vis, EPR and SFM (CSIC A).

2) CSIC B, in collaboration with USTAN B, started a challenging project aimed to the *in situ* formation of MOROFs hybrid structures by co-deposition onto Au(111) in UHV-conditions of tricarboxylic PPM derivative and copper ions. Firstly the evaporation of only the organic ligand has been performed and the H-bonded network imaged and characterized by RAIRS. Then by co-deposition of tri-carboxy PPM radical and copper, we believed we were able to obtain the first example of MOROF physisorbed onto Au(111) in Ultra High Vacuum conditions. The preliminary RAIRS characterizations of the obtained surface as well as the STM imaging are very promising.

Thanks to the interplay of the different groups CSIC B could deliver along the three years of the project all the deliverables and no deviations from the work program were reported to the coordinator. Unfortunately, the only milestone CSIC B and RUB B could not achieve was that (M4.2) regarding the loading of a porous MOROF crystalline material with metal nanoparticles. The PPM derivative delivered to RUB B (D4.2), has been used by the researchers in *RUB B* to prepare and load the MOROF with inorganic particles, but with no positive results. After discussion with the experts in *RUB B* and with the project coordinator, CSIC B agreed to focus onto other types of surface characterizations of MOROFs and hence it was abandoned the loading experiments. However, as an alternative approach, we checked whether it would be possible to load the porous and magnetic open frameworks prepared by CSIC B with organic molecules. This approach appeared feasible (M4.2).

We believe that the impossibility to achieve the milestone M4.2 has been somehow an example of the continuous learning all over the three years by all the project partners: since nobody was a real expert in this emerging field tackling surface science. In addition the nanotechnology state-of-the-art can not answer all the key points necessary to know

to solve this complex problem at the moment of the writing of the project. This "learning by doing", turned out to be very much fruitful even if in one case did not allow us to reach our final goal. CSIC B is confident that this joint work will pave the way for a new concept in material science.

### **WP3: Design new types of LBMOFs**

This workpackage was lead by ULI. Further contributions have been made by UNIMAR/GUF, RUB and RIGB/UCL.

WP3 started in month 7 of the SURMOF project and related to the design of new types of LBMOFs. The central goal was the development of new types of ligands and their use to prepare new framework structures with optimised properties for surface adhesion and loading using an integrated approach of experiment and theory. There were two deliverables and two milestones associated with this WP, which are detailed below.

**M3.1 "Development of at least three new ligands for the generation of LBMOF structures by an integrated process involving synthesis, characterization and theory. The first ligand (in month 13) will be optimized for giving MOFs on –COOH terminated SAMs. The second ligand (in month 18) will be optimized for giving MOFs on pyridine-terminated SAMs. The third ligand (after month 25) will be optimized for loading surface anchored LBMOFs"**

**D3.1 "New ligands will be developed by ULI in order to optimize both, anchoring to organic surfaces and loading properties with metal organic molecules"**

One of the key inputs of the ULI partner to the SURMOF project was their synthetic expertise for the development of new ligands for the growth of optimised LBMOFs on surfaces. This involved the synthesis and characterisation of the ligands and their subsequent reaction with transition metal ions to generate new open framework structures (milestone M3.2 and deliverable D3.2 below). These ligands were grouped into 3 categories: (1) ligands for growth on –COOH terminated SAMs; (2) for growth on –pyr terminated SAMs and (3) ligand(s) optimised for nanoparticle loading. *ULI successfully prepared eleven new ligands covering all three classes, and so this milestone was clearly reached and the deliverable completed on time.*

We developed several extended trigonal ligands based on carboxylate donors for the optimised growth of metal-clusters for MOF formation on –CO<sub>2</sub>H terminated SAMs on Au. The extended ligands were also prepared in order to permit the formation of frameworks with the pore sizes necessary (> 1 nm) for nanoparticle loading studies,

including ligands that incorporated a potential metal-anchoring site for nanoparticle nucleation. Further, a complete range of extended and functional bipyridyl pillaring ligands was also developed in order to increase the interlayer separation in LBMOFs. Knowledge transfer from WP1 clearly indicated that the most stable SURMOFs were prepared from rigid ligands that could form highly condensed metal clusters, where the resulting framework was highly symmetrical. Based on this we designed and prepared an entirely new class of highly conjugated fluorescent pyrene-derived tetra-acid ligands for the promotion of SURMOF growth, and investigated their potential to form novel functional frameworks of diverse structure and properties.

### **M3.2 "Successful development of new LBMOF structures (at least two) with optimised adhesion and loading properties"**

#### **D3.2 "The structure of new MOFs will be determined to allow selection of those best suited to binding to SAMs. Stability and porosity of new LBMOFs will be tested by ULI."**

This part of WP3 relates to the screening of the ligands prepared for M3.1/D3.1 (above) for their ability to form new LBMOFs, characterisation of their structures and evaluation of stability and porosity using the ULI expertise in the field of MOF chemistry. Further, in conjunction with RUB A and RUB B, the new frameworks were assessed for their surface growth and loading properties with metal nanoparticles, respectively. Overall, and because of an extensive screening effort that included solvothermal, microwave and high-throughput synthesis techniques, ULI prepared and characterised ten new frameworks based on the ligands prepared in M3.1/D3.1, hence this milestone and deliverable were successfully completed.

Major MOF highlights of this work include control over network topology through the addition of small aromatic molecules to the MOF synthesis to form a rare example of a triply interpenetrated **tfz** net (article 1). The first stable and permanently porous framework derived from a long-lifetime fluorescent pyrene core and In(III), where the solid-state fluorescence of the ligand is enhanced through spatial separation in a coordination matrix, that also displays reversible guest-dependent fluorescence (article 2). Specific ligand rotations upon framework desolvation identified through solid state NMR that permit selective gas sorption in a Zn(II) pyrene framework, and demonstrable potential in the difficult industrially important m-/p-xylene separation. We also have several other frameworks that are structurally interesting from a crystal-engineering viewpoint, but which are unstable to guest loss or too interpenetrated to permit

nanoparticle loading. Manuscripts are currently in preparation for appropriate specialist journals.

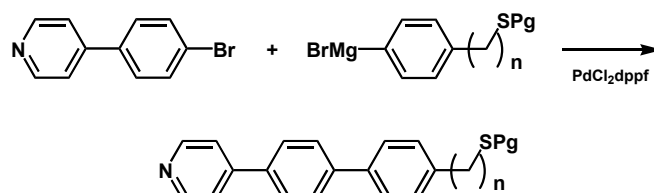
Several of the new frameworks were tested for their growth on  $-\text{CO}_2\text{H}$  and  $-\text{pyridyl}$  terminated SAMs using the layer-by-layer growth technique pioneered by RUB A. Growth was observed in a few cases and optimisation of these systems is ongoing. A notable difficulty however, was the production of only small amounts of each framework from the custom ligands that provided inadequate quantities of material for nanoparticle loading. Over the course of the project these syntheses have been gradually optimised.

### **WP5: Synthesis of OTs for SAMs / manufacture of $\mu\text{CP}$ materials**

Workpackage-leader was GUF/UNIMAR. Further contributions were made by RUB A, USTAN and CSIC A.

The central idea of the SURMOF project was to grow metal-organic frameworks (MOFs) onto solid surfaces in a directed manner to attain functionality which could not be accomplished with the micro-powders obtained by the traditional fabrication methods. For this, the surfaces had to be prepared in a very directed manner, so that this interesting microporous material would grow 1) only in certain desired areas and 2) with a defined orientation. To fulfil the first requirement, the surfaces need to be laterally structured by lithography. A very suitable manner for the controlled deposition of surface chemistry patterns is the so-called micro-contact printing ( $\mu\text{CP}$ ) of self-assembled monolayers (SAMs) onto certain substrates, most often of thiols onto gold. With this technique, lateral patterns in the micron-regime can be fabricated over areas of several tens of square centimetres. We cannot only produce the stamps for this printing process but also instructed the cooperation groups on the exact handling of technique. The second requirement, the oriented growth of the MOFs, can be induced by offering surface layers which basically mimic a certain cut through the MOF crystals by exposing predefined chemical groups. The advantage of SAMs is that this chemical functionalization can be "pre-programmed" into the SAM-forming molecules by synthesis. When the project started, almost no reliable strategy existed to form SAMs that would bind MOFs to surfaces, so we needed to develop suitable molecular structures as well as their synthetic realisation. The requirements for the molecules were the following: 1) The molecules needed to carry a suitable binding group to anchor them to the respective substrate. 2) On the opposite side of the molecules (the head group, which after SAM formation would be exposed) so-called donor groups needed to be mounted. These donor groups provide electron pairs to coordinatively bind the metal ions, which later become part of the metal-organic framework. 3) The molecular framework needed to be stiff to avoid distortions within the SAM by intermolecular interactions or interactions of the head

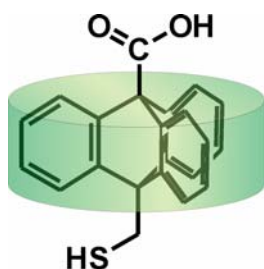
group with the substrate. For this a modular approach with aromatic subunits was chosen (Figure 1). This approach basically uses central compounds, so called node compounds, to which easily the required head group can be attached. This avoids the necessity of a full synthesis for each new SAM-forming molecule.



This approach proved to be very successful in particular after the respective protection group chemistry became optimised. In all investigated cases, the molecules form dense SAMs with their donor groups exposed, thus ready for binding.

An interesting question was, if the packing density of the

SAMs, or – to speak in other terms – its lattice constant, would affect the orientation or even the structure of the surface bound MOF (= SURMOF). For this, bulky derivatives, again with very stiff aromatic frameworks, in this case triptycenes, were synthesized (Figure 2). The advantage of these molecules is that they still carry their functionalities



**Figure 2:** An example for a triptycene thiol carrying a donor group for the MOF attachment.

along the central axis, which warrants a constant position for the MOF-binding while permitting the rotation of the triptycene unit.

With the help of these molecules, we could show that the nature of the head group (the donor) is much more important than the lattice defined by the SAM. Presumably, either the SAM or the first SURMOF layers can adapt to each other, so that this effect becomes overcompensated. At least in case of the denser oligophenyl SAMs (see Figure 1), an adjustment of the MOF structure can be excluded, since we succeeded in suppressing the intercalation of two equivalent MOF network by the layer-by-layer approach, that is presented in other parts of this final project report. If an adaptation of this network would be possible, the intercalation, which reduces the pore volume in the MOF significantly, could still take place.

In summary, the goal of developing a class of compounds, which would direct the growth of SURMOFs onto them, was reached. Our building block strategy permits the quick synthesis of surface active compounds with a multitude of head groups, which then determine the orientation of the MOF crystals grown onto them. This is an important precondition for the use of these materials in a very controlled manner.

n	Yield (%)
1	58
2	42
3	74

**Figure 1:** The modular approach exemplified for pyridine thiols. The thiol group shall bind to the substrate (gold) and the nitrogen atom is responsible for binding the MOF



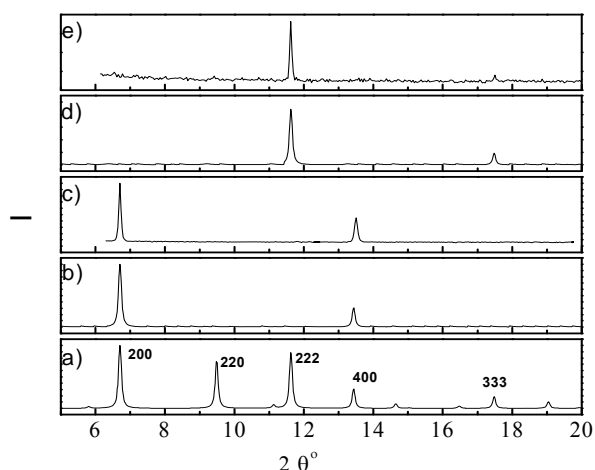
## WP6: MOF nucleation on SAMs

RUB A was the workpackage leader. USTAN, CSIC, ULI and RIGB/UCL also participated.

In this work package different types of SAMs with different functionalization group, have been tested for the step-by-step synthesis and controlled growth of MOFs on organic surfaces. Also different types of MOFs and LBMOFs were grown on these different functionalized organic surface, based on the sequential immersion of functionalized SAMs covered substrates in solutions of an organic ligand (e.g. benzenetricarboxylic acid (BTC), terephthalic acid (BDC) and DABCO) and an inorganic connector ( $ML_x$ , e.g. Cu(II), Zn(II)). The SAMs which have been used are:

### 1. COOH functionalized SAMs:

HUKST-1 [ $Cu_3BTC_2(H_2O)_n$ ] was synthesised and grown using this approach on a COOH terminated SAM, namely the 16 mercapto-hexadecanoic acid (HS(CH<sub>2</sub>)<sub>15</sub>-COOH) (MHDA). IRRAS data showed a linear increase in the thickness of the deposited MOF with the number of immersion cycles. AFM and SEM data demonstrated the homogenous and selective growth of the MOFs on COOH-terminated surfaces. In the case of Cu(II)-BTC the out-of-plane XRD-data (Fig. 1.c), reveal the presence of a highly ordered and preferentially oriented crystalline material, which exhibits the same structure for the bulk compound of HUKST-1.



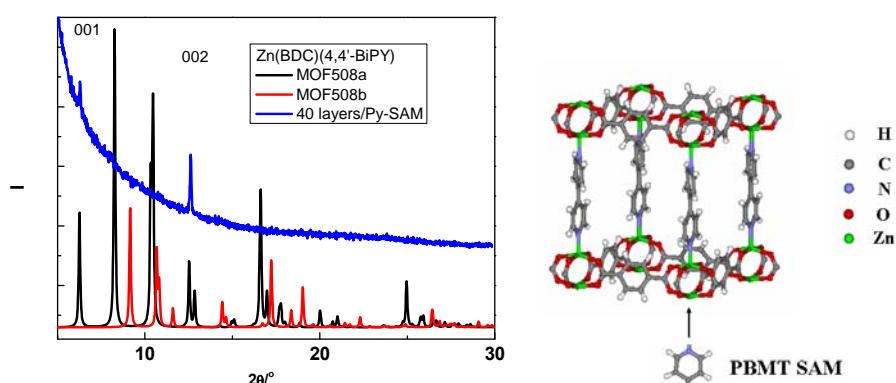
**Figure 1.** a) Out-of-plane XRD data for a  $Cu_3BTC_2 \cdot xH_2O$  MOF a) Bulk, b) growth on a MHDA SAM (Simulation), c) experimental growth on MHDA SAM (experimental), d) growth on MUD SAM (Simulation), e) grown on MUD SAM (experimental).

### 2- (OH) functionalized SAMs

HUKST-1 was also synthesised and grown using this approach on an OH terminated SAM, namely the 11-Mercapto-1-undecanol (HS(CH<sub>2</sub>)<sub>11</sub>OH) (MUD). IRRAS data showed a linear increase in the thickness of the deposited MOF with the number of immersion cycles. In the case of Cu(II)-BTC the out-of-plane XRD-data (Fig. 1e), reveal the presence of a highly ordered and crystalline material which has a preferentially different orientation from the COOH terminated SAMs.

### 3. Pyridine terminated SAM

The growth of layer based metal organic frameworks on the pyridine terminated SAM namely 4,4-pyridyl-benzenemethanethiol (PBMT) was done using the step-by step route developed in our group. The  $\text{Zn}(\text{BDC})(4,4'\text{-BiPy})_{0.5}$  MOF-508 was chosen as a test MOF for the growth on the both SAMs, a 40 layer sample of the 508 MOF was grown on the PBMT SAM and it was characterized with both IR and XRD. The out of plane XRD spectrum in Fig. 2. (blue) show that the grown  $\text{Zn}(\text{BDC})(4,4'\text{-BiPy})$  MOF fully agree with the bulk structure of the  $\text{Zn}(\text{BDC})(4,4'\text{-BiPy})_{0.5}$  MOF 508a and it is highly oriented.



**Figure 2.** The out of plane XRD spectrum (link) show that the grown on the PBMT pyridine SAM  $\text{Zn}(\text{BDC})(4,4'\text{-BiPy})$  MOF fully agree with the bulk structure of the non penetrated  $\text{Zn}(\text{BDC})(4,4'\text{-BiPy})_{0.5}$  MOF 508a (right) and it is highly oriented.

In addition to the  $\text{Zn}(\text{bdc})(\text{bipy})$  we have managed to grow  $\text{Zn}(\text{bdc})(\text{dabco})$ ,  $\text{Cu}(\text{bdc})(\text{dabco})$ ,  $\text{Zn}(\text{ndc})(\text{dabco})$  and  $\text{Cu}(\text{ndc})(\text{dabco})$  on the PBMT SAM in an oriented fashion.

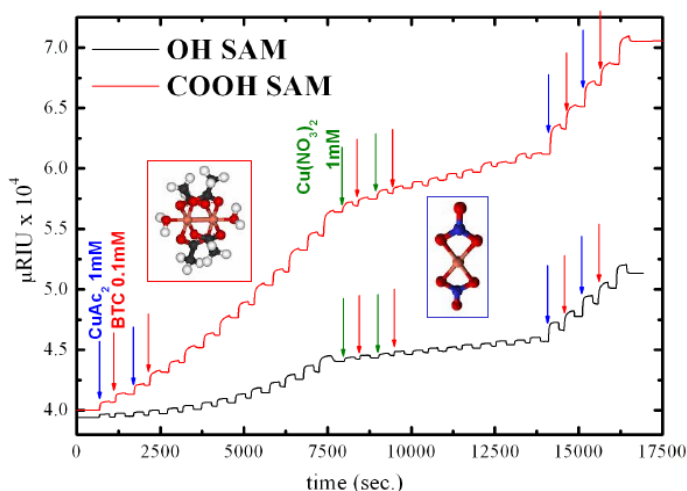
In this work package also different types of inorganic precursors ( $\text{ML}_x$ , e.g.  $\text{M}=\text{Cu}(\text{II})$ ) with benzenetricarboxylate (BTC) have been tested in order to study the role of the SBUs in the mechanism of the HUKST-1 [ $\text{Cu}_3\text{BTC}_2(\text{H}_2\text{O})_n$ ] MOF synthesis and growth on SAMs. Also different SAMs with different functionalization groups have been also tested in order to study the template effect of the substrate.

HUKST-1 was synthesised and grown using the step-by-step approach on a COOH terminated SAM, (MHDA) and an OH terminated SAM, (MUD). In the step-by-step approach the template effect of the SAMs allows the formation of MOFs already at room temperature. The deposition rate has been determined using surface plasmon resonance (SPR) spectroscopy, and the structure of the deposited MOF was determined using x-ray diffraction (XRD):

Fig. 3 shows SPR data recorded during the deposition of HUKST-1 using copper(II)acetate ( $\text{Cu}(\text{Ac})_2$ ) as a metallic precursor, on a COOH and an OH-terminated SAMs. An inspection of the growth curves reveals that the time constant for the deposition of the organic building block, BTC, is quite similar to that seen for the metal ions ( $\text{Cu}^{2+}$ ) delivered from the  $\text{Cu}(\text{Ac})_2$ . In case of the usual synthesis protocol for HUKST-1 copper(II)nitrate was used as a metal precursor. In our step-by-step growth experiment we can change the metal precursors in a straightforward fashion. The data shown in Fig. 1 reveal that virtually no deposition of MOF is observed on a MOF-substrate when using Cu-nitrate as a precursor. If after several cycles involving exposure to Cu-nitrate the substrate is exposed to Cu-acetate again, a very regular growth is observed (Fig. 3) with rates undistinguishable from those seen before switching to the Cu-nitrate. This interesting finding of Fig. 1 can be rationalized by considering that in solutions of Cu-acetate the dominant unit present actually is the Ac-bridged paddle wheel  $[\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot 2\text{H}_2\text{O}]$ . This is important, since the HUKST-1 framework is composed of very similar, just BTC-bridged  $\text{Cu}^{2+}$ -dimers. In contrast, the structural chemistry of solvated copper(II)nitrate compounds is rather diverse.

In order to further investigate the general importance of preformed SBUs for the growth of  $[\text{Cu}_3\text{BTC}_2]$  crystallites it was necessary to study the growth along other crystallographic directions as well. While such a monitoring of deposition rates on different faces of MOF crystals is virtually impossible for other in situ growth studies of

MOFs carried out recently in solution. The most promising strategy to obtain such a growth in a different direction is to use a different template for the liquid phase epitaxy. Considering the high density of OH-groups along the [111]-planes in the hydrated bulk structure of HUKST-1 we have chosen a OH-terminated organic surface to initiate growth. The X-ray diffraction data (XRD) shown in Fig. 2 clearly demonstrates the success of this strategy. Whereas on a COOH-functionalized the growth of HUKST-1 proceeds along the [100]-direction, on an OH-terminated surface MOF-layers with a



**Figure 3.** SPR signal as a function of time recorded in situ during sequential injections of Cu-acetate ( $\text{Cu}(\text{Ac})_2$ ), BTC and Cu-nitrate ( $\text{Cu}(\text{NO}_3)_2$ ) in the SPR cell containing MHDA SAM (red) and MUD SAM (black). (inset) Molecular structure of copper(II)acetate hydrate  $[\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot 2\text{H}_2\text{O}]$  ( $\text{Cu}(\text{Ac})_2$ ) in the solid state and in solution.

[111] surface termination are grown. This is an interesting observation in itself, since it reveals that the organic surface not only nucleates the MOF growth but also controls the growth direction.

The generation of micropatterns of MOFs on substrates using nanolithography is described in more detail in the section on workpackage 13.

### **WP7: MOF growth on SAMs**

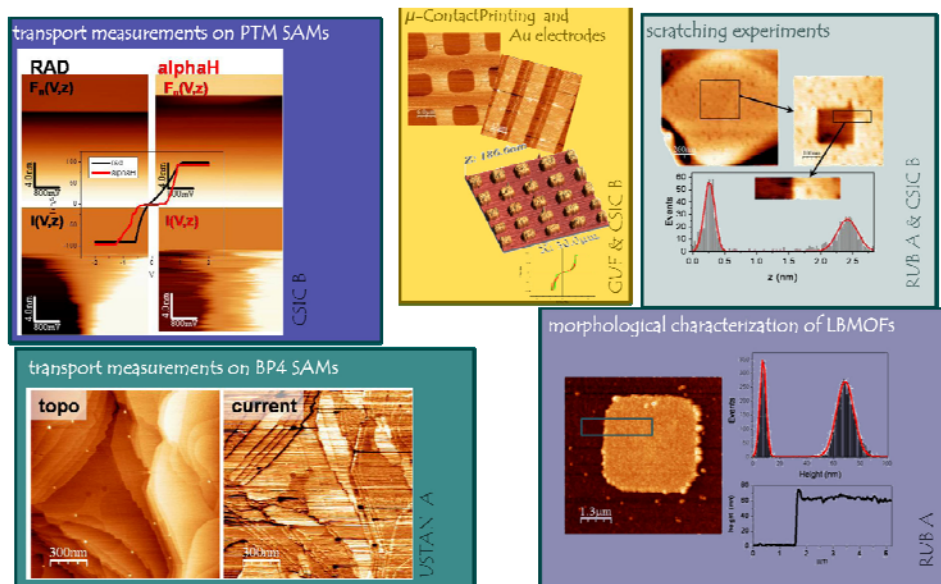
The WP7 activities have been carried out in collaboration between workpackage leader CSIC A with groups of other project partners from CSIC B, JUK, UCL, RUB, GUF and USTAN. The work package leader group offered the expertise in surface science techniques for the preparation and characterization of substrate surfaces and, during the project has developed a series of SFM-based strategies, implemented in the already existing equipments and specifically designed to get insight in the problems emerged during SURMOF, thus fulfilling all steps needed to achieve the corresponding work package deliverables.

The growth of ordered films thicker than few monolayers is frequently required for technological applications. Then, whereas in other work packages of the project, the nucleation of MOFs on SAM surfaces has been addressed mainly using spectroscopic methods, in this work package we have made an effort to grow thicker layers and, in accordance to the original DoW, the growth process has been investigated by exploiting atomic force microscopy in connection with both, continuous films and laterally patterned SAMs. Because, in particular, for the goal of the whole STREP activity it was stated as very important to obtain a selective growth of MOF in attempts to obtain a controlled orientation.

Using this approach the amount of deposited MOFs and the orientation of the MOF crystallites has been determined. An important aspect of this work package was also the optimization of growth parameters, in particular, for those more promising cases. The growth protocols for the production of high-quality have been explored to establish the growth conditions (e.g. concentration of constituents, temperature) to optimize the quality of the deposited MOF layers and the deposition speed. The control of the structure of the grown films is a big challenge, inherently related to the size and symmetry of the molecules and the complexity of the chemical and physical interactions involved in the ordering process.

Systematic and periodic test experiments performed on the HKUST-1 patterned and unpatterned samples have indicated that no significant aging is observed for elapsed times up to nine months.

Local and long-range order of the grown layers as well as the full assessment of structure and orientation was studied by combining the scanning probes investigations of CSIC A, USTAN and JUK as well as with spectroscopic and diffraction studies USTAN and RUB. During the project, most experiments were devoted to determine the quality of both SAMs and the grown MOFs. In the former case, using either commercial molecules or those provided by GUF or synthesised by CSIC B, complete aromatic-based SAMs grown in USTAN and patterned alkane-based SAMs prepared by  $\mu$ C-printing in CSIC A have been characterized. The main tasks involved sample preparation and Scanning Force Microscopy (SFM) measurements. The objectives were focused to elucidate the role of the differently functional groups, molecular order and surface potential on the final properties of the SAMs. Motivated by the interest of tuning the substrate work function, we systematically investigated the conductivity response (by means of conducting SFM or C-SFM) and surface potential (by Kelvin SFM or KPM) of the different types of SAMs employed for the ulterior MOF growth. In particular, the study of radical and non-radical PTM based SAMs as well as BP4 monolayers with two coexisting molecular phases. Measurements of electrostatic forces by means of the developed for these purposes 3D-SFM modes were also made to cross-check all data. Figure 1 serves to illustrate some of the inter-SURMOF collaborations, between CSIC A and other partners:



**Figure 1.** Examples of SURMOF inter-partners collaborations: 3D Transport measurements on PTM SAMs (CSIC A and CSIC B), Patterned substrates using micro-contact printing (CSIC A, GUF and CSIC B), Scratching experiments (CSIC A, RUB and CSIC B), Transport measurements in BP4 SAMs (CSIC A and USTAN), Morphological characterization of LBMOFs (CSIC A and RUB)

The overall strategies have helped to know the best growth conditions via determination of the film quality. The effort has been devoted to different tasks performed in coordination with other SURMOF partners:

- Conducting Force Microscopy (C-SFM) studies (3D modes, current imaging and I-V curves. The methodology was published in *Nanotechnology*, 18; 125505-125512 (2007)
- Work function changes and Surface Potential measurements (KPM) and electrostatic force differences (Force versus voltage measurements by 3D modes)
- Comparison between Scanning Tunnelling Microscopy (STM) and a combination of SFM and C-SFM.
- Thickness determination of MOFs (LBMOFs and MOROFs) by two different methods.
- Surface quality determination by means of morphological SFM test and surface roughness (rms) analysis.

Though details on deliverables and milestones are given in the periodic reports, it is worth to mention that, in general, most objectives were achieved within each milestone except complete selectivity in the case of radicals (M7.3). However, the results obtained so far demonstrate that we are not far of getting a good selective and high-quality system with roughness and scalability good enough for their use.

### **WP8: MOF-metal (vacuum)**

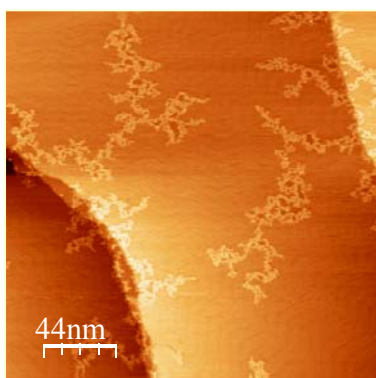
USTAN B lead the workpackage. Further contributions came from RUB A and JUK.

The aims of the workpackage were: fundamental studies on the interaction of ligands used in MOF synthesis with metal surfaces; preparation conditions optimization in order to prepare layers which can be used as seed or template for 3D MOF growth; determination of the binding energies of the species involved for possible change in coordination and layer ordering/reordering, desorption.

Copper and gold are widely used as interconnects and electrodes, mainly because of their high conductivity. For different reasons, in particular the ease of obtaining ordered and clean surfaces, they are also widely used in surface studies as model surfaces. Therefore, they were thought to be a good choice as substrates in these studies.

The criteria governing the choice of molecules was that they should have a variety of functional groups allowing them to bind to the metal surfaces, to coordinate with a guest metal and open the possibility of three dimensional MOF growth. Attention was directed to ligands comprising aromatic systems containing multiple carboxylic acid groups and

with additional substituents. In particular, carboxylic acid groups coordinate well with copper, because of the possibility of copper displacing the hydrogen from the carboxylic group. Furthermore, it has been demonstrated that such molecules can form 2d networks and also adopt differing coordination schemes (flat-lying and/or upright) when on a metal surface, depending upon surface coverage, preparation conditions and presence of other metal ions. Among the ligands used, some are commercially available (benzoic acid, 4-aminobenzoic acid, TAPB), others were obtained from other groups in the consortium (H<sub>3</sub>BTB, TATB, RH1044 from ULI,  $\alpha$ -PTMTC and PTMTC radical from CSIC B), thereby establishing some collaborative work.



**Figure 1.** STM topographic images of H<sub>3</sub>BTB and Cu co-adsorbed onto Au(111). A disordered MOF network is prepared over the  $(22 \times \sqrt{3})$  Au(111) reconstruction ( $220 \times 220 \text{ nm}^2$ , 1.2 nA, -1.2 V).

Using ligands with carboxylic acid groups on non-interacting substrates, such as Au(111), results in the formation of H-bonded networks which, in specific cases, with the introduction of another guest metal, can incorporate this second metal into the organic network and form a MOF layer. Pursuing this strategy, H<sub>3</sub>BTB, was dosed onto a clean Au (111) surface and studied by vibrational spectroscopies and scanning tunneling microscopy (STM) with a view to characterising orientation with respect to the substrate.

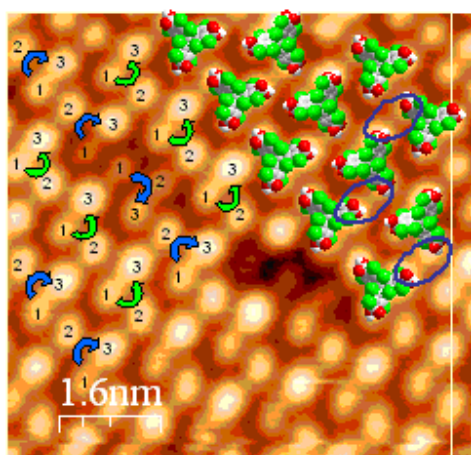
The co-adsorption of H<sub>3</sub>BTB with copper onto a clean Au (111) surface at room temperature resulted, after subsequent annealing to ca. 650 K, in a reaction leading to filaments and networks concentrated near step-edges but also extending onto terraces (figure 1). Copper is necessary for H<sub>3</sub>BTB adsorption and limits the amount of ligand that can be adsorbed. By the addition of small amounts of copper a disordered MOF was obtained, whereas, when high amounts of copper were dosed, copper clusters of varying sizes separated and were decorated by H<sub>3</sub>BTB ligands, which prevent coalescence and alloying with the gold.

Preliminary investigations via STM of the adsorption of the closely related ligand 1,3,5-tri(4-aminophenyl)benzene (TAPB) adsorbed on Au(111) were carried out. The three-fold symmetry of this molecule can be easily resolved and the image clearly indicates a flat-lying orientation for this species.

The modification of the Au (111) surface by adding Cu atoms opened up a new series of studies regarding this particular metal on metal system, which was found to have been characterised by many all electrochemical technics, but never comprehensively in UHV environment. Our STM investigation shows that, at an early deposition stage, Cu adsorbs at the elbows of the Au (111) herringbone reconstruction, forms clusters which eventually coalesce into a single layer when approaching the monolayer regime. When a

critical size is reached, to relieve the stress induced by the lattice mismatch, the new layer reconstructs in a herringbone fashion. Nucleation also occurs at step edges; however, the clusters appear to grow faster than the layer nucleated at step edges.

Attention then turned to polyfunctionalized ligands considering them more effective in the preparation of 3D MOF networks. Polychlorotriphenyltricarboxyl radical (PTMTC), because of its propeller-like shape should allow the formation of three dimensional networks. The ligand was deposited onto a Au(111) surface in UHV conditions at different temperatures. Low temperature (180–190 K) deposition produces honeycomb patterned islands whose sides coincide with the herringbone directions. With the help of vibrational spectroscopies as well as DFT calculations, we proposed the following model. The PTMTC radical adsorbs on the Au (111) surface via the chlorine atoms and appears as a set of three separate intensity maxima (figure 2). The imaged state is likely the one reflecting the HOMO electron densities. Each of the maxima, having a cross section of



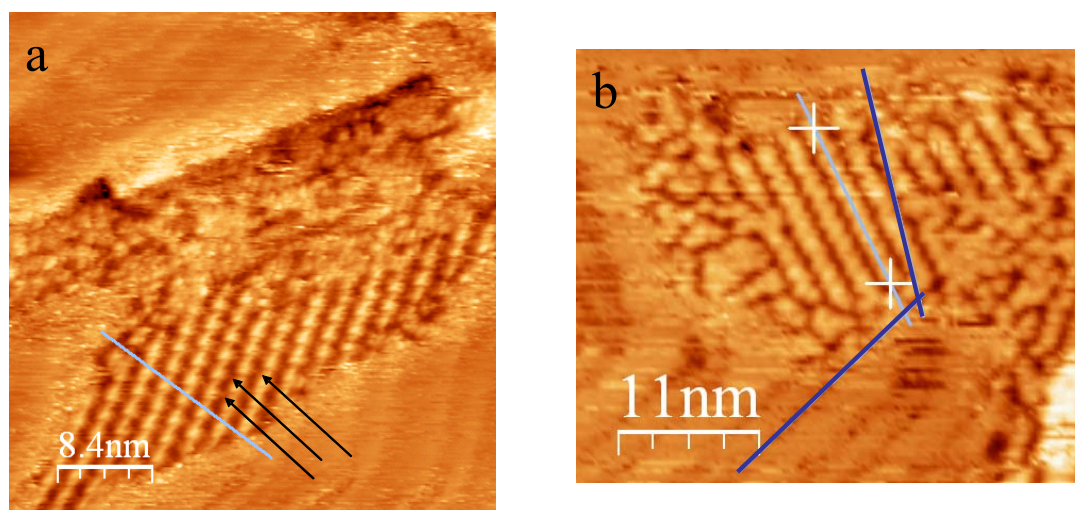
**Figure 2.** proposed model of the PTMTC radical adsorbed and forming a racemic domain on the Au (111) surface ( $6.8 \times 7 \text{ nm}^2$ , 0.2 nA, -1.3 V).

ca. 0.6 nm, comprises an aromatic ring, four chlorine atoms and a carboxyl/carboxylate group. Intensity analysis, assigning the highest priority to the brightest of the spots, reveals that each set of three electron densities has a well defined orientation. Also, half of the molecules present positive rotation (P, blue arrows) and the other half negative rotation (N, green arrows), making the resulting domain racemic. Evidence of H-bonding between a P molecule and the two adjacent N molecules is also present and is indicated by the relative intensity between the molecules (blue ovals in figure).

The effects on PTMTC adsorption induced by the pre-addition of copper onto the Au(111) surface were also studied. When the PTMTC is dosed onto this system, the radical molecule appears to coordinate in a disordered fashion in the proximity of, but not onto, the copper particles. This might be due to the presence of a mixed Cu-Au system, in the area immediately surrounding the copper particles; this new system might be due to copper atoms leeching out of the Cu particle and intermixing with the gold atoms. Annealing to ca. 350 K promotes reorganization of the PTMTC radical into hexagonal and linear domains. Inside the hexagonal domains, triangular units can be identified (figure 3a); each unit is attributed to a single PTMTC radical molecule laying flat and likely coordinating through the chlorine atoms with the gold surface. The systematic presence of ‘dots’ a little offset with respect to the ideal triangular shapes give some



indication of metal incorporation within the organic layer. The features visible into the rectangular domains are of a different nature (figure 3b). Here, the PTMTC radical is likely have an upright configuration, co-ordinating through one of the carboxylic groups to copper atoms and exposing the remaining two carboxylic groups to the vacuum side. Because of this configuration, with both flat laying molecules and standing up molecules, this system can be considered as a good candidate for 3D-MOF growth in vacuum.



**Figure 3.** STM topographic image showing hexagonal (a) and rectangular (b) domains formed by adsorption of PTMTC radical on Cu / Au (111) and annealing to ca. 350 K. The arrows in a) indicate features attribute to single Cu atoms; the dark blue lines in (b) indicate closed packet directions; a)  $42 \times 43 \text{ nm}^2$ , 0.37 nA, -1.32 V; b)  $40 \times 35 \text{ nm}^2$ , 0.18 nA, -1.2 V.

### **WP9 and WP12: MOF-metal (electrochemistry), MOF loading (electrochemistry)**

These workpackages were lead by USTAN A. The partners CSIC, JUK and ULI contributed to them.

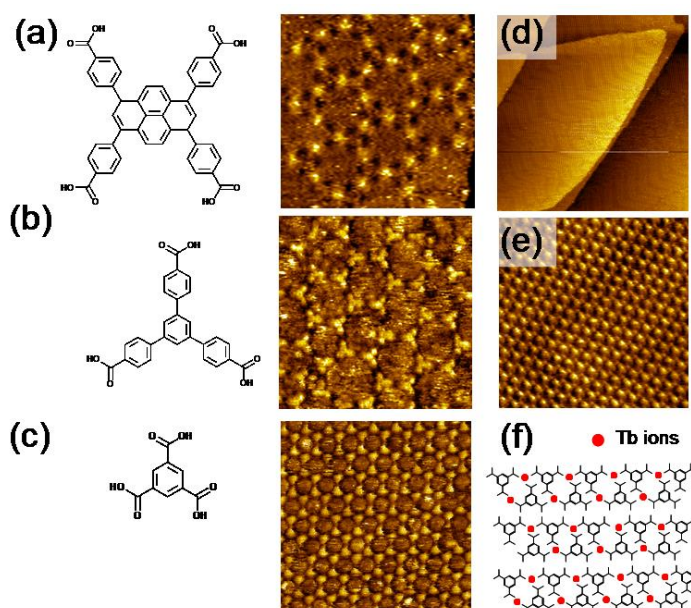
The workpackages led by USTAN A focused on surface based MOFs at electrified interfaces. This involved electrochemistry in two different ways, on the one hand as part of MOF preparation and, on the other hand, MOFs as systems to control electrochemistry. Accordingly, the associated workpackages (WP9, WP12) concentrated on the preparation of MOFs and studies of their electrochemical behaviour.

### **MOF preparation**

Contrasting other work packages (e.g. WP6/7) where MOFs were grown on thiols based SAMs, it was an important goal within WP9 to grow MOFs directly on an electrode surface, i.e. without a self-assembled monolayer (SAM) as templating layer. This approach was taken since thiol SAMs represent barrier layers which impair interfacial charge transfer and, thus, electrochemical processes.

The underlying idea was to first grow a porous two dimensional metal-organic coordination network (2d-MOCN) on a surface which then acts as template for the growth of MOF films. This work entered new territory in several respects. Firstly, the methodology to prepare MOCNs from solution had to be developed. In contrast to studies in ultrahigh vacuum (UHV) where two dimensional MOCN networks on surfaces are easily prepared<sup>3</sup>, it was not clear how and to what extent this is feasible from solution. Secondly, it had to be demonstrated that such 2d-MOCNs can act as templates for oriented MOF growth into the third dimension. Within WP9, attempts to prepare 2d-MOCNs adopting protocols established in UHV were unsuccessful. The stepwise preparation through a sequential deposition of metal and organic ligand did not produce ordered MOCN layers. However, highly ordered ones formed when deposition was performed from the mixture of the MOCN components but, in contrast to preparation

from UHV where porous networks are formed, only dense structures were obtained despite extensive variation in systems and preparation conditions (ion, molecule, temperature, solvent, concentration, time). In contrast to hydrogen bonded systems which form easily open networks (Fig. 1 a-c), all molecules studied, including those synthesized by partner ULI (Fig. 1 a,b), formed only dense structures as exemplified by Fig. 1 d-f. Upon variation of parameters

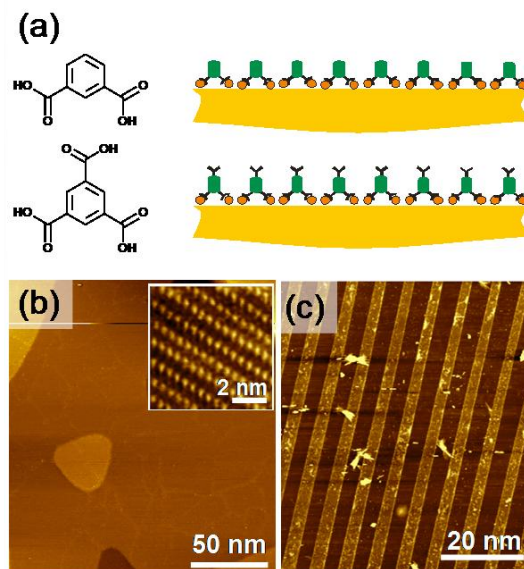


**Figure 1.** STM images of different hydrogen bonded systems of carboxylic acids (a-c) and MOCN of trimesic acid and terbium (d-f) on Au/mica. Model of MOCN shown in (f). Image size  $15 \times 15 \text{ nm}^2$  (a-c, e) and  $100 \times 100 \text{ nm}^2$  (d).

<sup>3</sup> J. V. Barth, Fresh perspectives for surface coordination chemistry, *Surf. Sci.* 603, 1533 (2009).

only different dense structures were obtained. A tentative explanation of the striking difference between systems prepared in UHV and from solution is that, for the former, the process is kinetically controlled whereas in solution a thermodynamically preferred dense structure forms due to lowering of activation barriers caused by a solvent facilitated rearrangement of molecules and interference of the solvent with the coordination centre. Experiments studying nucleation of MOFs on the dense MOCN structures did not produce layers. Only localised crystal growth was observed, most likely triggered by nucleating at defects.

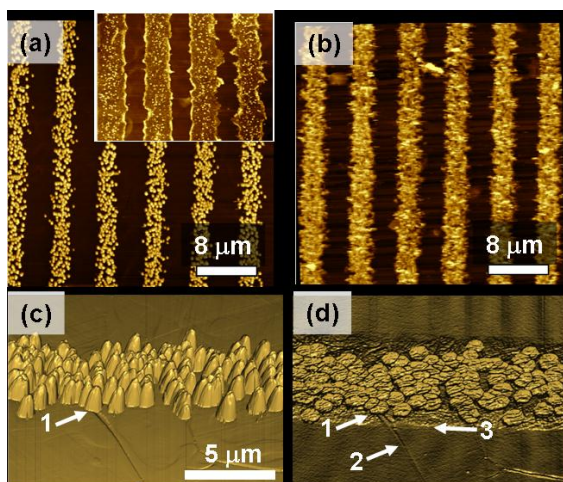
In search for routes to produce open networks, an unexpected behaviour of molecules with an isophthalic acid (IA) like structure was observed which resulted in the discovery of a new type of SAM and which has the potential of a more general approach to structurally very well defined templates not only for MOFs but for surface functionalisation in general. Instead of flat lying, IA and TMA molecules stand upright (Fig. 2a) when the substrate is modified by a Cu layer, thus forming monolayers with an exceptional molecular order as seen from the inset in Fig. 2b. This finding is remarkable in several respects which makes them very interesting for wider exploitation. Firstly, in contrast to other SAMs such as those based on thiols which have only one anchoring group, the isophthalic acid moiety provides two anchoring sites and, thus, a rigid structure. This will enable a much better structural definition of the SAM surface. Secondly, these layers are quite stable, e.g. weeks in ambient does not result in a degradation and, thirdly, the preparation does not require any sophisticated protocol, just a simple electrochemical metal deposition step and subsequent immersion in a solution of the molecule. That such generated layers are well suited as templates for the growth of MOCN layers is demonstrated in Fig. 2c which shows lines of Cu-TMA MOCN deposited in a layer by layer fashion onto a patterned substrate consisting of TMA as surface active and alkane thiols as passivating parts, respectively.



**Figure 2.** (a) cartoon of isophthalic acid (IA) and trimesic acid (TMA) on a Cu modified Au surface. (b) STM images of IA, large scale showing uniformity of layer, inset demonstrating the excellent molecular order. (c) Cu-TMA MOCN layer grown on a TMA pattern.

### Electrochemical experiments on MOF modified electrodes

Studies of SURMOFs in an electrochemical environment are of interest for several reasons. As porous structures whose dimensions can be tailored they have the potential of controlling interfacial processes by acting as selective diffusion barriers. Furthermore, they offer the possibility of electrochemical deposition at exactly defined distances from the electrode thus providing unprecedented opportunities for the generation of ultraprecise hybrid structures. The results obtained within the project which demonstrate the possibility to deposit metal onto MOF modified electrodes and the dependence of electrochemical



**Figure 3.** AFM images of Cu electrochemically deposited on a MOCN line pattern. Lines consist of 8 cycles of Cu/TMA deposition and a SAM of hexadecane thiol for the passivated areas. (a) Metallisation after 60 s (inset after 10 s) deposition from aqueous 50mM CuSO<sub>4</sub> at -0.1 V vs Cu<sup>2+</sup>/Cu. (b) after dissolution of Cu. (c,d) 3d image of deposition showing topography (c) and friction (d). Arrow 1 points to the same particle, 2 to a grain boundary in the Au substrate and 3 marks the boundary between the MOCN deposit and the thiol SAM.

activity on the type of MOF have to be considered as the first steps of a promising new direction in MOF research, where SURMOF is merged with electrochemistry.

Since MOF stability can be an issue, it was a crucial step to establish conditions under which electrochemical experiments can be performed. Depending on the type of experiment this required either proper selection of the solvent (e.g. ethanol instead of water) or set restrictions on the duration of an experiment. The successful electrochemical deposition of metal on top of a SURMOF is illustrated in Fig. 3 which shows the deposition of isolated Cu particles at different stages. This opens a flexible way to deposit either isolated particles of defined size on a MOF layer or, upon longer deposition time, to grow a continuous layer. Since the thickness of the SURMOF can be controlled with molecular precision through layer by layer growth, MOF films can be exploited as ultraprecise spacer layers for the generation of electrode structures. The important result of these studies is that the MOF structures are stable under the conditions of electrochemical metal deposition and, thus, can be used as templates to control electrochemical processes. Beyond metal deposition, the influence of MOF layers on electrochemical redox reactions was studied using ferrocene as probe. In these studies which were performed in collaboration with partner RUBA, two different types of SURMOFs were used which showed a distinctly different influence on the charge

transfer. While a tricomponent SURMOF prepared from 1,4-diazabicyclo[2.2.2]octane (dabco), 1,4-naphthalenedicarboxylic acid (ndc) and Cu-acetate results only in a moderate reduction in the redox currents, a film prepared from TMA and Cu-acetate blocked the charge transfer. Even though the detailed mechanism of charge transfer is still under investigation, it can be already concluded that SURMOFs are most interesting for tailoring charge transfer properties at interfaces. Given the unique opportunities of MOFs to control dimensions both with respect to pore size and thickness of SURMOF layers, it is easy to foresee from the accomplished results that the combination of electrochemistry with SURMOFs open new opportunities for nanotechnology.

### **Achievements**

With USTAN A focussing on electrochemical aspects of MOFs, the two associated workpackages (WP9/WP12) entered new territory not only with respect to the behaviour in an electrochemical environment but also with regard to the preparation of SURMOFs without the presence of thiol SAMs. As a result not all milestones were reached in a way originally anticipated. While the suitability of SURMOFs for electrochemistry has clearly been demonstrated (D9.1/9.2) and, through structural and kinetic studies (D9.3), a new way was found to grow MOCNs without the use of thiols SAMs, it remains to be clarified whether the growth of oriented MOFs (M9.1) is not only possible on thiols SAMs but also on IA-type SAMs. With regard to studies on growth mechanism (D9.3/M9.2) results are very encouraging as with the new IA-type SAMs one can, for the first time, monitor the initial stages of MOF nucleation down to molecular resolution. However, since both ordered and disordered areas of metal coordination are observed the picture is not yet conclusive and, therefore, milestone M9.2 has only be partially achieved. This has a direct consequence for the second part of M9.2 which relates to electrochemistry. While parameters for electrochemical deposition have been established it is still open where the optimum values lie. Within WP12 it was clearly demonstrated that MOFs can be exploited to control electrochemical metal deposition (D12.1-3) and that deposition can be used to influence the dimension of deposits (M12.1). However, the results are not limited to metal deposition but go beyond the stated milestone. The finding that MOFs can be used to control electrochemical activity of other redox systems marks the start of an unexplored and exciting area of MOF research. M12.2 was achieved by demonstrating structured metal electrodeposition on patterned MOFs. While this is the first demonstration towards the exploitation of MOFs for the generation of hybrid materials, the full potential of this approach has yet to unfold as the influence of the MOF structure has been beyond the time frame of the project.

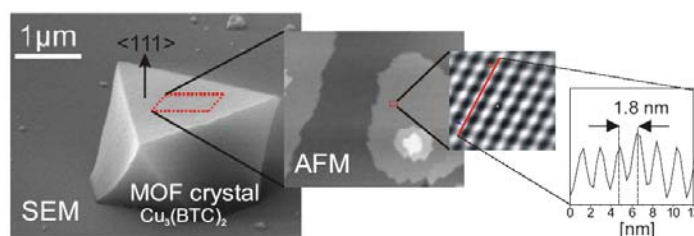
## WP10: MOF-oxide, characterisation MOF surfaces

The workpackage was lead by JUK. Additionally, RUB and USTAN worked on the project.

The general aim of the SURMOF project was to develop methods of surface controlled growth of thin metal-organic framework (MOF) films. So far MOF materials were produced in the form of powder. The possibility of their controlled formation on the surface in the form of well oriented film clearly opens up new possibilities to combine their fascinating storage and sensing possibilities with the techniques and experimental approaches realized in the development of what is known as nanotechnology. To really achieve the possibility of processing MOF materials on the nanometer scale it is important to develop both proper sample preparation techniques and microscopic approach to actually monitor this films at the nanometer scale. This problem was exactly the main issue of the WP10 work package. In more details we have carried out research on two issues:

- (1) analyzing already formed MOF crystals obtained by different preparation methods to find out the possibility of imaging them with so called scanning probe microscopy technique at the nanometer scale
- (2) finding combination of the metal-oxide substrate and the ligand molecule (ligands play a role of linkers in the MOF structure) which allow formation of well defined monolayers of ligands on metal-oxide surface enabling thus in future formation of MOF films on metal oxide substrate.

During the WP10 project duration we have managed to realize both of these tasks. Regarding first of them we have analyzed three different methods for MOF formation (layer-by-layer deposition, solvothermal growth of single crystals, and microwave stimulated solvothermal growth of crystals). For one of them (solvothermal preparation) we have demonstrated not only the possibility of the MOF surface analysis at the nanoscale but also application of such analysis for finding way to improve MOFs preparation procedure for better control their surface structure (see Figure 1). Most recent results show that it is another method (microwave stimulated solvothermal) which seems to be even more interesting since it unites benefits of layer-by-layer deposition and solvothermal growth which are formation



**Figure 1.** Overview of SEM and AFM microscopic analysis for single MOF crystal

of a complete MOF film consist of well-defined crystals suitable for analysis at the nanoscale. Further research of these aspects goes beyond duration of this project and will be continued.

Regarding the second topic we have manage to find out that one of the most popular linker in MOFs i.e. the TPA (terephthalic acid) molecule forms well ordered monolayers on the (110) TiO<sub>2</sub> surface (see Figure 2). Importantly, TPA molecules in this film exhibit their functional -COOH groups outside the surface what is necessary for potential building of the MOF structure on that template surface. Moreover, we have also demonstrated that despite such structure is prepared in ultra high vacuum conditions it can be taken out to the ambient conditions without destruction. This means that it can be of use for MOF formation which takes place out of vacuum conditions. The research using other linker molecules is under investigation, and will be continued beyond duration of the SURMOF project.

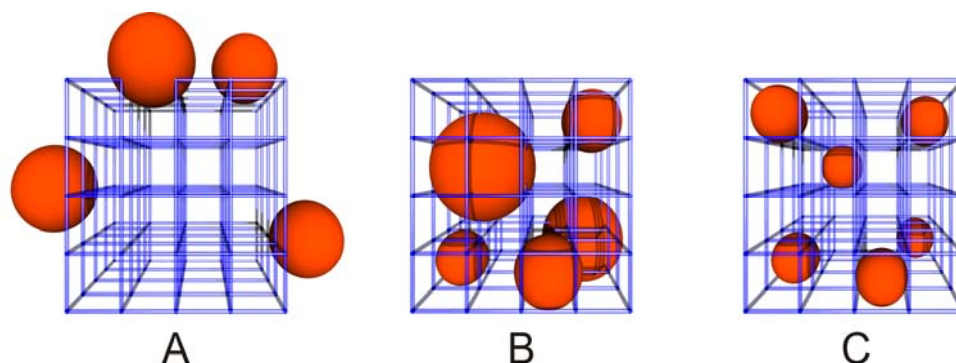
### **WP11: MOF loading (CVD)**

This workpackage has been lead by RUB B. Contributions were made by UCL.

Metal Organic Frameworks are a fascinating class of artificial porous Designer-Materials. They offer perfect molecular control on the so-called coordination space for host/guest Chemistry. The Large void storage volume within molecular-organic frameworks can be used to put in many molecular materials, be they hydrogen for fuel cells or drugs. This idea would even be possible for metal nano particles for catalysis, were there not one little hindrance: if the void spaces in the MOF are too large, a second embedded framework system automatically develops during the synthesis process. This "uncontrolled proliferation" leads to a significant reduction in the size of the voids. A major break-through in the field of MOF research and host guest chemistry was to suppress this interpenetration by a novel growth technique of MOFs at surfaces (SURMOFs). This was developed with contributions of WP 11 (RUB B, Fischer group) an published in *NATURE Materials*, the leading journal in Materials Science.

The loading of MOFs with functional nanoparticles was the particular speciality of the Fischer group within the SURMOF cooperation network. Tailored volatile organometallic precursor compounds were used. These compounds can penetrate through the channels and pores of the MOF material and will be weakly adsorbed inside the matrix. This can be done by simple exposure of the MOF material, also deposited as a thin film on a surface just by exposure of the MOF to the vapor of the particular precursor. In a second step, the adsorbed precursor will be converted to the desired nanoparticles inside the MOF cavities. At least, this was the idea.

In fact, this concept works for selected, well behaved cases, but not for all. The situation turned out to be very complex. Also, the microstructure of the hybride composite materials called "metals@MOFs" is an important issue. Figure 1 below depicts the three cases.



**Figure 1.** Three characteristic cases A, B and C of microstructures for nanoparticles supported by Metal-Organic Frameworks are shown.

A quite general aspect of the deposition of metals at MOFs as studied in WP 11 is the question whether the particles are distributed evenly over the volume of the MOF crystallite with a size dispersion matching with the dimensions of the channels or cavities or if the particles accumulate preferentially at the outer surface regions of the MOF with a pronounced tendency to exceed the pore size substantially (Figure 1). The former case may be called "metals@MOF" (or "metals $\supset$ MOFs"). The abbreviation "@" (or " $\supset$ ") emphasizes the preferred inclusion of the particles *inside* the cavities *throughout* the MOF volume (Figure 1, B and C), while deposition at the outer surfaces may be better written as "metals/MOFs" as this is the notation for supported catalysts in general (Figure 1, A). There might be a substantial local damage of the MOF support matrix if the particle sizes are significantly larger than the typical pore dimensions (cases A, B). We selected a case study and found that so-called Au@ZIF-90 approaches the ideal, limiting situation C of matching size particles being homogeneously distributed throughout a defect-free matrix which appears to host very small Au<sub>55</sub> (magic number) clusters as the majority species. We thus finally achieved a concept of MOF loading with metal particles which is likely to be transferred from our well-behaved test case (ZIFs) to suitably functionalized other MOFs, also fabricated at surfaces.

### WP13: Growth of patterned MOFs

Leader of this workpackage was RUBA. Further contributions were made by UNIMAR/GUF and CSIC.

There are different concepts for the grow MOFs on surfaces, like the direct deposition from solvothermal mother solutions or the assembly of preformed, ideally size and shape selected, nanocrystals have been used. The disadvantages of these methods are that the films formed are not homogenous and that the growth could not be controlled.

In this work package in contrast to the established synthesis protocols of MOFs, where the educts (primary building blocks, typically two) are mixed and reacted under solvothermal conditions, the stepwise layer-by-layer growth mode of MOFs was



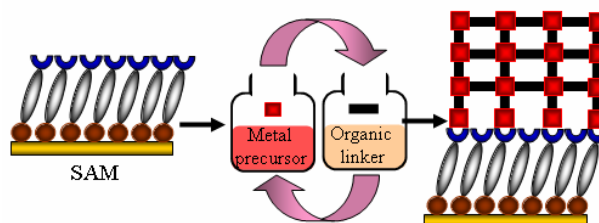
introduced, which is based on the combination of the reaction partners in a sequential, stepwise fashion and removing unreacted components via rinsing with a solvent separates the individual steps see Fig. 1.

The ideal substrates to start with such a layer-by-layer deposition of organic ligands or metal-oxo coupling units, are organic surfaces as exposed by SAMs. Since a fairly large number of MOF structures reported so far are based on carboxylate coupling units, the choice of COOH-terminated SAMs exposing a COOH-terminated surface is quite

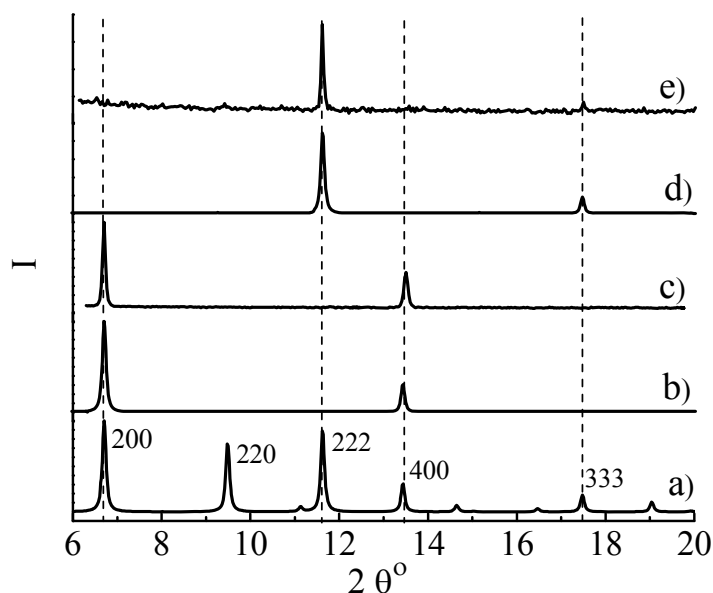
obvious. Using the COOH functionalized organic surface of a mercaptohexadecanoic acid SAM (MHDA) as a 2D anchoring and nucleation site, the growth of homogenous, structurally well-defined MOF structures in a step-by-step fashion was demonstrated by Shekhah et al. for the case of HKUST-1.

The two components, copper(II)acetate ( $\text{CuAc}_2$ ) and 1,3,5-benzenetricarboxylic acid ( $\text{H}_3\text{btc}$ ), were separately dissolved in ethanol and the substrate was immersed into each solution in a cyclic way, while each step was followed by rinsing with pure ethanol. By starting with  $\text{CuAc}_2$ , a linear increase of thickness of the deposited HKUST-1 layer with the number of (alternating) immersion cycles in  $\text{CuAc}_2$  and btc could be demonstrated by infrared reflectance absorption spectroscopy (IRRAS) and in situ by surface plasmon resonance (SPR) spectroscopy.

Most importantly, XRD data recorded for these deposited MOF layers revealed that only one orientation is grown, with the [100] direction perpendicular to the



**Figure 1.** A schematic diagram for the step-by-step growth of MOFs on SAMs by repeated growth cycles separated by washing: first immersion in a solution of metal precursor and subsequently in a solution of the organic ligand.



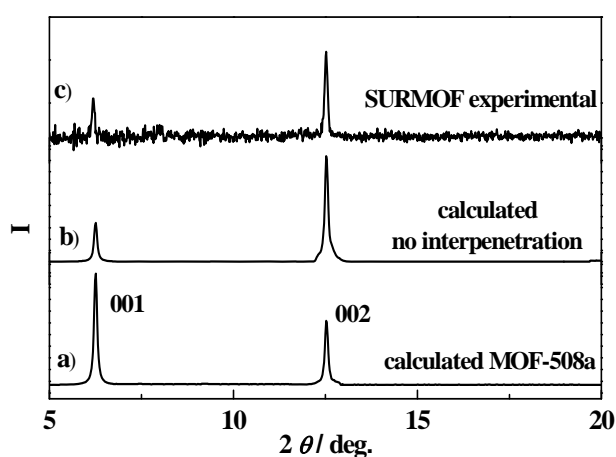
**Figure 2.** Out-of-plane XRD data for a  $[\text{Cu}_3\text{BTC}_2(\text{H}_2\text{O})_3]$  (hydrated HKUST-1). a) Bulk, b) growth on a MHDA SAM (calculated), c) growth on MHDA SAM (experimental), d) growth on MUD SAM (calculated), e) growth on MUD SAM (experimental).

surface. Interestingly, when replacing copper(II)acetate with zinc(II)acetate, instead of the growth of oriented MOFs, only the deposition of a non-porous, amorphous  $Zn^{2+}/btc$  polymer was observed, in contrast to the known solvothermal chemistry, which leads to MOFs. When the MHDA SAM (COOH-terminated surface) was replaced by a mercaptoundecanol (MUD) SAM (OH-terminated surface) again an oriented growth of HKUST-1 takes place. This time, however, with the [111] direction of HKUST-1 orientated normal to the substrate surface. The observation that on a COOH-terminated surface, HKUST-1 grows along the [100] direction and on an OH-terminated surface along the [111] direction, is in full accord with the observation reported by Biemmi et al., who observed that the deposition of MOFs from a “mother liquor” at elevated temperature also leads to poly-crystalline, but well-ordered, MOF films with the same preferential orientations. A particular advantage of the layer-by-layer method is the possibility to directly monitor the deposition of both ligands and coupling units using SPR spectroscopy.

The step-by-step method has been tested to grow different types of MOFs on different types of functionalized organic surfaces. Using this new method it was possible to grow the HKUST-1 MOF on a COOH and an OH functionalized SAM modified substrate.

Different types of LBMOFs like (Cu(bdc)(dabco), (Cu(ndc)(dabco), Zn(bdc)(dabco), (Zn(ndc)(dabco) and (Zn(bdc)(bipy)) have been also successfully grown in a highly oriented way on a pyridine functionalized SAM modified substrate. We have also managed to demonstrate the potential to synthesize new classes of MOFs not accessible by conventional methods. In the case of Zn(bdc)(bipy) or what is known as MOF-508, the formation of the second, interpenetrated framework has been suppressed by using liquid phase epitaxy on an organic template as the XRD data in Fig. 1 shows.

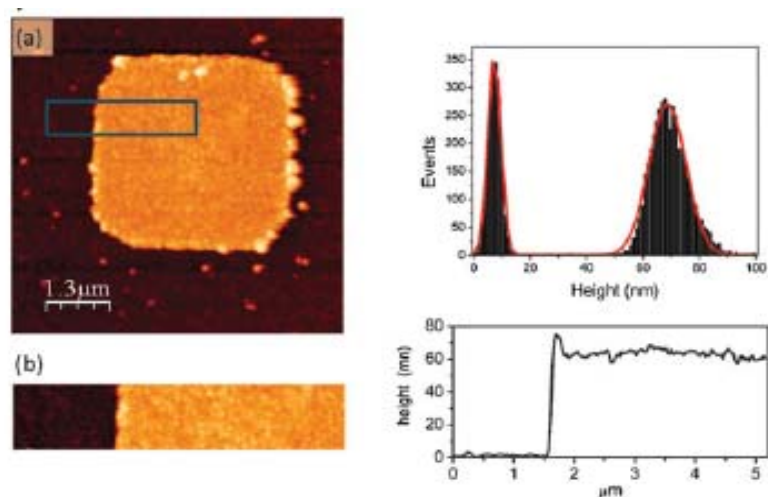
We explain the suppression of the second, interpenetrating lattice in the SURMOF by the pyridine-terminated organic surface acting as nucleation template. The other sub-lattice does not match with this template. Another particular advantage of using the organic surfaces exposed by Au/organothiol SAMs is the



**Figure 3.** XRD patterns for a) Calculated diffraction pattern expected for an oriented MOF layer of type MOF-508a on the surface including interpenetration, b) Calculated diffraction pattern expected for an oriented MOF layer of type MOF-508a (no interpenetration) on the surface and c) SURMOF-1

availability of methods to laterally pattern the organic surface, e.g. via micro contact printing ( $\mu$ CP) and electron beam lithography (EBL), and thus to achieve a selective growth of MOF films on pre-defined areas of the surface. In our work, such patterned SAMs have been used in connection with quantitative AFM to follow the growth of oriented MOFs on the COOH-terminated surface and to study their morphological characteristics (Fig. 4).

The results verify the selective growth of the HKUST-1 on the COOH-terminated surface (Fig. 4) and the homogeneity of the deposited layers. It also demonstrates the strength of the step-by-step preparation procedure employed and its capability to fabricate high quality MOFs films on surfaces. The observed monotonous thickness



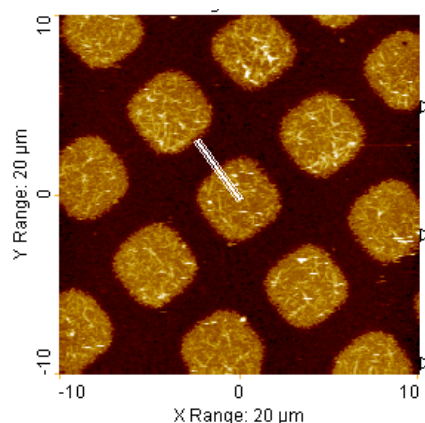
**Figure 4.** a) a topographic image (6.5 x 6.5 mm) and (b) a selected area for accurate thickness estimation; right: the corresponding height histogram (top) and averaged profile (bottom) calculated over the whole area in (b). The red lines in the histogram represent the corresponding Gaussian fits.

increase indicates that, within experimental error, the number of layers grown is proportional to the number of immersion cycles, implying that once the first  $[\text{Cu}_3\text{btc}_2(\text{H}_2\text{O})_n]$  layer nucleates on the COOH-terminated regions, all of the subsequent material is deposited on top of the previously nucleated layers. Interestingly, in this work it was observed that the increase in thickness per immersion cycle amounted to half a unit cell in the [100] direction. With regard to applications, it is particularly relevant that the topmost film surface roughness is fairly low and does not increase substantially with SURMOF thickness. In contrast to the immersion of substrates into preconditioned solvothermal mother liquors, the step-by-step synthesis yields extraordinary homogeneous films of 4100 nm thicknesses and a roughness in the order of only one elementary cell in regions in the range of several  $\text{mm}^2$ . As a result, the layer-by-layer approach may also be suited for the fabrication of thicker layers with a very homogenous, flat surface, e.g. in sensor applications and for fabricating membranes.

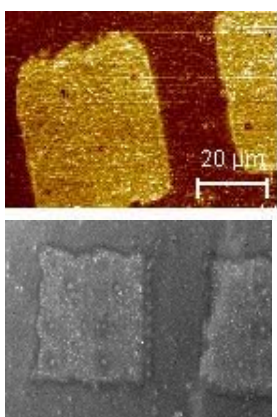
A new pyridine terminated SAM has been optimized to selectively grow LBMOFs. Using  $\mu$ CP a sample consisting of pyridine- terminated squares (PP1 SAM) and CH-terminated stripes (Adamantine SAM) was laterally patterned and used for the growth of a  $\text{Cu}(\text{ndc})(\text{dabco})$  LBMOF.

(Fig. 5) The AFM data demonstrates the selective and homogenous growth of Cu(ndc)-(dabco) MOF (30 cycles) on the patterned sample. The AFM data demonstrates also that using the step-by-step route method for the synthesis of LBMOFs leads to a selective growth of the LBMOF layers and yields homogeneous thin films, which are in addition grow in a highly ordered and preferentially oriented crystalline fashion. The top surface roughness is fairly small less than 5 nm.

The same was done for the MUD SAM, but the problem was it was difficult to stamp the MUD SAM, that is why we have done the reverse in which we have stamped at first the hexadecane thiol to yield a surface consisting of CH<sub>3</sub>-terminated 3 X 3 μm<sup>2</sup> squares and OH-terminated stripes (made from MUD SAM) separating the squares. The SEM-data showed clearly that the growth of HKUST-1 is selective on the MUD SAM.



**Figure 5.** A topographic image a laterally patterned samples by μCP consisting of pyridine- terminated squares (PP1 SAM) and CH-terminated stripes (Adamantine SAM) used for the growth of a Cu(ndc)(dabco) LBMOF.



**Figure 6.** AFM (up) and SEM (down) images of a laterally patterned sample by EBL method consisting of squares terminated by COOH- and stripes terminated by CH<sub>3</sub> used for the growth of HKUST-1.

A conventional electron beam lithography method (EBL) was also used to pattern self-assembled monolayers in addition to the micro contact printing method used before. The EBL is one of the techniques used to pre-pattern the surface with different types of structures like line, squares and other different patterns. At first a non patterned sample was functionalized with MHDA SAM and exposed under different condition to electron beam, then immersed after that in a solution of HDT for 24 hrs. The sample was then characterized with IRRAS, in order to find the best condition for the replacement of the MHDA SAM with the HDT SAM. After optimizing the conditions two types of patterns using two types of Quant-foil were generated on a sample functionalized with the MHDA SAM. The pre-patterned sample was then used as a substrate to grow the HKUST-1 MOF on it using the step-by-step method. The data in Fig. 6 demonstrates clearly that the EBL method has been successfully used for the selective growth of the HKUST-1 MOF as the SEM

and AFM images in Fig. 6 shows. The SEM and AFM data revealed that it is possible using the EBL method to laterally patterned samples for the selective growth of HKUST-1 as shown in Fig. 6. Using an AFM tip right lines in a predefined SAM was not successful. Regarding the growth of MOROFs on laterally patterned surfaces, even μCP

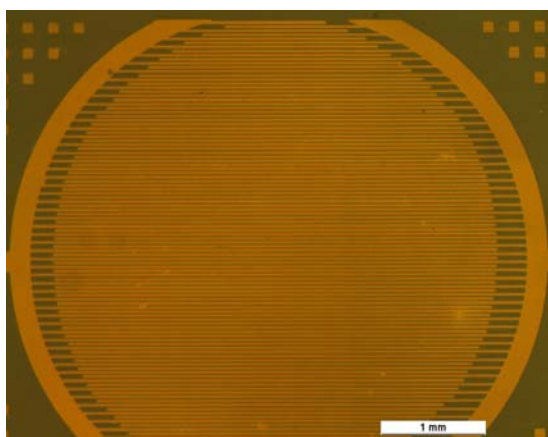
was not successful due to the minor selectivity of the MOROFs to differently terminated functionalized surfaces (see reports on related workpackages). None of the other nanolithography methods were employed since they are considerably more challenging than  $\mu$ CP.

### WP14: Fabrication of MOF-based gas sensor

Workpackage-leader was GUF/UNIMAR. Further contributions were made by RUB A and USTAN A.

The regular porosity of their networks makes MOFs interesting for many applications beyond mere gas storage. As cooperating groups within this project have shown, the pores also can be loaded with organometallic molecules which might be decomposed to the respective metals in form of nanoparticles. These particles are fixed within the network as if localized in a three-dimensional shelf. If the loading is high enough, what can be adjusted by the loading parameters, electronic communication between these particles becomes possible. This communication is not only inherent to the size and kind of nanoparticles and their distance, but also to the immediate environment. This basically means that if a molecular species becomes co-adsorbed in the system, the charge-transport through the nanoparticles should be altered. We considered this as a basis for a sensoric system.

The first problem that had to be addressed was the contacting of the SURMOF materials with metal electrodes. Although evaporation of electrodes onto the MOFs might intuitively be the first thing to suggest, soft materials (such as MOFs) are usually destroyed by this method. We therefore rather figured that it would be advantageous to directly

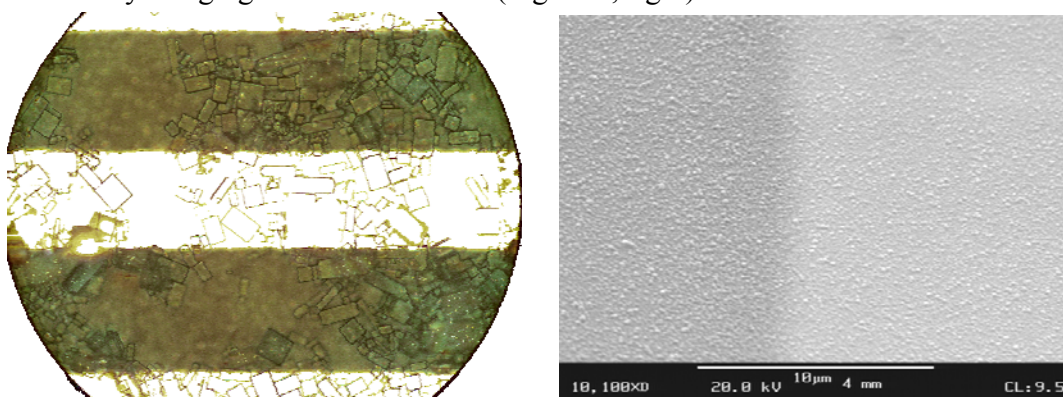


**Figure 1:** Micrograph of the interdigitating electrodes in the devised sensor.

deposit the MOFs onto the electrodes. As electrode pattern we went for a design with two interdigitating electrodes, what maximises the channel length but at the same time minimises the channel length (Figure 1). These sensors were manufactured using softlithographic methods, in particular a combination of micro-contact printing ( $\mu$ CP) and galvanics. For the deposition of the SURMOFs, the surface chemistries of the metal surface as well as the insulating dielectric had to be

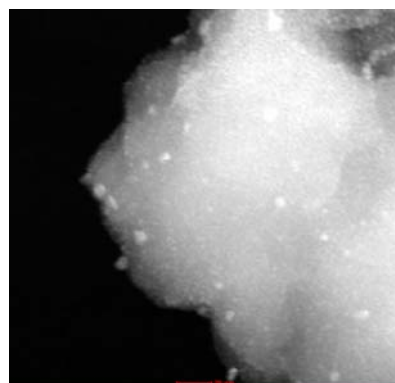
adapted to each other to warrant a homogeneous growth of the MOF effectively bridging both electrodes. This was accomplished by a combination of two plasma processes with

SAM chemistry: The first step generated hydroxyl groups on both kinds of surfaces, while the last plasma step generated carboxyl groups at the surface. These groups interact with the metal clusters in the MOF structures, thus permitting the attachment of the MOFs. Two strategies for this attachment have been tested. The traditional hydrothermal route yielded well-oriented crystals, which nevertheless were too small to cross the gap between the electrodes (Figure 2, left). Although the crystals often are in contact, we expect that this is not sufficient to warrant a good percolation. We therefore turned to the layer-by-layer method developed by one of the project partners. With this, we were able to grow SURMOF layers homogeneously covering the entire sensor surface, thus effectively bridging the two electrodes (Figure 2, right).



**Figure 2.** Results of the two different SURMOF deposition methods. Left: Optical micrograph of the hydrothermal deposit. Well-oriented crystals on a sensor array (electrode distance 50  $\mu\text{m}$ ). Right: SEM image of a layer-by-layer deposited SURMOF growing over the boundary between a gold electrode and the dielectric (glass).

To make these SURMOF layers functional, they had to be loaded with nanoparticles. Although initially one of the partners initially reported that loading of SURMOFs would not be possible, we succeeded in substituting the solvent molecules in the pores of the SURMOF network by an organo-palladium compound (cyclopentadienylpalladiumallyl) which later was transformed into metallic nanoparticles either by the action of hydrogen or light (Figure 3). We chose palladium nanoparticles, since this metal interacts with a variety of analytes, such as hydrogen, carbon monoxide, or organic compounds with unsaturated bonds in a basically reversible manner. Because of these interactions, the electronic communication between the particles would be changed, leading to a different macroscopic conduction of the system.



**Figure 3:** TEM image of a SURMOF particle loaded with Pd nanoparticles (bright spots).

At the present state, nevertheless, the loading density of the MOFs turned out to be too low for an efficient communication. The research is continued to increase the loading density (presumably a factor of about 10 is needed), to fabricate a functional device.

In summary, within this work package the principles for SURMOF-based sensors have been identified and most of the fabrication steps successfully implemented. The final problem, the loading density, has been recognized, what will permit to find a viable approach soon.

## Dissemination and Use

The main use and dissemination of this basic research take place via scientific publications (journal articles and conference contributions). Apart from this, a project related website has been established<sup>4</sup>.

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#### **By cooperating scientists**

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#### **Contributions to Scientific Conferences**

##### **By members of the SURMOF consortium**

1. J. Prauzner-Bechcicki, S. Godlewski, A. Tekiel, P. Cyganik, J. Budzioch, and M. Szymonski, *Functionalised surfaces – a TiO<sub>2</sub>(110) case (key note lecture)*, in *2nd IRUN Symposium on Nanotechnology*. 2009, 8-9 October: Krakow.
2. V. Mugnaini, *Grafting Metal-Organic Radical Open Frameworks onto surfaces: A first step towards magnetic and porous solid devices (oral presentation)*, in *European Conference on Molecular Magnetism (ECMM)*. 2009, 7-10 October: Warsaw.

3. V. Mugnaini, *Perchlorotriphenylmethyl radicals: new trends (invited talk)*. 2009, 29 September: Department of Organic Chemistry, University of Bologna.
4. S. Godlewski, J. Prauzner-Bechcicki, A. Tekiel, P. Cyganik, J. Budzioch, and M. Szymonski, *Self-assembly of terephthalic acid on rutile TiO<sub>2</sub>(110): toward chemically functionalized metal oxide surfaces (oral presentation)*, in *ACSIN-10 ("Atomically Controlled Surfaces and Interfaces 10")*. 2009, 21-25 September: Grenada.
5. M. Buck, *Surface Based Self-Assembly of Organic Molecules as Platform for the Nanoscale (invited talk)*, in *ECOSS26*. 2009, 30 August-4 September: Parma.
6. C. Shen and M. Buck, *Self-Assembled Monolayers as Templates for Electrochemical Nanotechnology (oral presentation)*, in *ECOSS26*. 2009, 30 August-4 September: Parma.
7. K. Barbe, H. Thomas, and A. Terfort, *Fabrication of Sensors by Soft Lithography (poster)*, in *EuroNanoForum 2009*. 2009, 2-5 June: Prague.
8. Cebula, C. Shen, C. Silien, and M. Buck, *Supramolecular Networks on Gold Surfaces Prepared from Solution (oral presentation)*, in *EuroNanoForum 2009*. 2009, 2-5 June: Prague.
9. P. Cyganik, J. Prauzner-Bechcicki, S. Godlewski, A. Tekiel, J. Budzioch, and M. Szymonski, *High-resolution scanning tunneling microscopy studies of Terephthalic Acid Molecules on Rutile TiO<sub>2</sub>(110)-(1x1) Surface (oral presentation)*, in *EuroNanoForum 2009*. 2009, 2-5 June: Prague.
10. P. Cyganik, K. Szlagowska-Kunstman, M. Goryl, and M. Szymonski, *Surface Structure of Metal-Organic Frameworks (oral presentation)*, in *EuroNanoForum 2009*. 2009, 2-5 June: Prague.
11. F. Grillo, M. Oliveros, V. Mugnaini, J. Veciana, S.M. Francis, and N.V. Richardson, *Supramolecular 2D network of PTMTC radical adsorbed onto Au(111) and Cu/Au(111) (oral presentation)*, in *EuroNanoForum 2009*. 2009, 2-5 June: Prague.
12. F. Grillo, M. Oliveros, V. Mugnaini, J. Veciana, S.M. Francis, and N.V. Richardson, *Supramolecular 2D network of PTMTC radical adsorbed onto Au(111) and Cu/Au(111) (poster)*, in *EuroNanoForum 2009*. 2009, 2-5 June: Prague.
13. R. Heck, J. Rabone, S. Chong, J. Bacsá, M.J. Rosseinsky, and D. Bradshaw, *Flexible sorption responses in a nanoporous framework material identified through an integrated approach (oral presentation)*, in *EuroNanoForum 2009*. 2009, 2-5 June: Prague.

14. R. Heck, J. Rabone, S. Chong, J. Bacsá, M.J. Rosseinsky, and D. Bradshaw, *Flexible sorption responses in a nanoporous framework material identified through an integrated approach (poster)*, in *EuroNanoForum 2009*. 2009, 2-5 June: Prague.
15. M. Meilikhov, K. Yusenko, and R.A. Fischer, *Loading of porous coordination polymers with metalorganic precursors and metal nanoparticles (poster)*, in *EuroNanoForum 2009*. 2009, 2-5 June: Prague.
16. C. Mellot-Draznieks, *Designing New Nanoporous Metal Organic Frameworks (poster)*, in *EuroNanoForum 2009*. 2009, 2-5 June: Prague.
17. C. Mellot-Draznieks, F.-X. Coudert, and A. Torrisi, *Interplay between simulations and experiment in the study of metal organic frameworks surfaces (oral presentation)*, in *EuroNanoForum 2009*. 2009, 2-5 June: Prague.
18. V. Mugnaini, M. Oliveros, N. Roques, M. Paradinas, H. Wang, O. Shekhah, C. Wöll, C. Ocal, and J. Veciana, *Surface based Coordination Chemistry: The case of the selective grafting of Metal-Organic Radical Open Frameworks (oral presentation)*, in *EuroNanoForum 2009*. 2009, 2-5 June: Prague.
19. V. Mugnaini, M. Oliveros, N. Roques, M. Paradinas, H. Wang, O. Shekhah, C. Wöll, C. Ocal, and J. Veciana, *Surface based Coordination Chemistry: The case of the selective grafting of Metal-Organic Radical Open Frameworks (poster)*, in *EuroNanoForum 2009*. 2009, 2-5 June: Prague.
20. B. Schüpbach and A. Terfort, *Donor-terminated Self-Assembled Monolayers as Anchoring units for Surface-Mounted MOFs (oral presentation)*, in *EuroNanoForum 2009*. 2009, 2-5 June: Prague.
21. B. Schüpbach and A. Terfort, *Putting Organic Functionalities onto Surfaces (poster)*, in *EuroNanoForum 2009*. 2009, 2-5 June: Prague.
22. O. Shekhah, H. Wang, R.A. Fischer, and C. Wöll, *Step-by-Step Approach for the Synthesis and Growth of Metal-Organic Frameworks (MOFs) Thin Films on Organic Surfaces (oral presentation)*, in *EuroNanoForum 2009*. 2009, 2-5 June: Prague.
23. O. Shekhah, H. Wang, R.A. Fischer, and C. Wöll, *Step-by-Step Approach for the Synthesis and Growth of Metal-Organic Frameworks (MOFs) Thin Films on Organic Surfaces (poster)*, in *EuroNanoForum 2009*. 2009, 2-5 June: Prague.
24. C. Silien, M.T. Räisänen, C. Shen, I. Cebula, and M. Buck, *Solution Based Supramolecular Self-Assembly on Surfaces: Towards a Toolbox for the Nanoscale (oral presentation)*, in *EuroNanoForum 2009*. 2009, 2-5 June: Prague.

25. H. Thomas, L. Roeder, B. Schüpbach, M. Paradinas, C. Ocal, and A. Terfort, *Metal Contacts on Organic Monolayers formed by Electroless Metal Deposition (poster)*, in *EuroNanoForum 2009*. 2009, 2-5 June: Prague.
26. Torrisi, C. Mellot-Draznieks, and R.G. Bell, *Impact of Ligands on CO<sub>2</sub> Adsorption in Metal-Organic Frameworks: DFT Study of the Interaction of CO<sub>2</sub> with Functionalised Benzenes (poster)*, in *EuroNanoForum 2009*. 2009, 2-5 June: Prague.
27. Wöll, *Anchoring metal-organic frameworks, MOFs, to surfaces (oral presentation)*, in *EurNanoForum 2009*. 2009, 2-5 June: Prague.
28. H. Wang, *Step-by-Step Route for the Synthesis and Controlled Growth of MOFs on Functionalized Organic Surface (poster)*, in *Bunsentagung 2009*. 2009, 21-23 May: Köln.
29. Torrisi, C. Mellot-Draznieks, and R.G. Bell, *Towards the Design of MOFs: the impact of the ligand on CO<sub>2</sub> sorption (oral presentation)*, in *Workshop on CO<sub>2</sub>*. 2009, 13-16 May: Liblice.
30. Torrisi, C. Mellot-Draznieks, and R.G. Bell, *Towards the Design of MOFs: the impact of the ligand on CO<sub>2</sub> sorption (oral presentation)*, in *UCL "Get Together" meeting*. 2009, 6 April: London.
31. J. Prauzner-Bechcicki, S. Godlewski, A. Tekiel, P. Cyganik, J. Budzioch, and M. Szymonski, *Functionalised surfaces – a TiO<sub>2</sub>(110) case (poster)*, in *COST D-41*. 2009, 2-3 April: London.
32. Cebula, M. Buck, R. Heck, D. Bradshaw, and M.J. Rosseinsky, *Supramolecular Networks on Gold Surfaces Prepared from Solution (oral presentation)*, in *ISSC17*. 2009, 30 March-2 April: Reading.
33. F. Grillo, M. Oliveros, V. Mugnaini, J. Veciana, S.M. Francis, and N.V. Richardson, *Supramolecular 2D networks of PTMTC radical adsorbed onto Au(111) (poster)*, in *ISSC 17*. 2009, 30 March-2 April: Reading.
34. Shen and M. Buck, *Self-Assembled Monolayers as Templates for Electrochemical Nanotechnology (oral presentation)*, in *ISSC17*. 2009, 30 March-2 April: Reading.
35. Silien, M.T. Räisänen, and M. Buck, *Nanometre scale confinement of electrochemical metal deposition at thiol-modified Au(111) electrodes (oral presentation)*, in *ISSC17*. 2009, 30 March-2 April: Reading.
36. Ocal, *Using SAM-based heterogeneously functionalized surfaces for selective*

- growth (keynote talk, invited)*, in *NanotechInsigth*. 2009, 29 March-3 April: Barcelona.
37. Torrisi, C. Mellot-Draznieks, and R.G. Bell, *Towards the Design of MOFs for CO<sub>2</sub> Adsorption: The Role of the Organic Ligands (poster)*, in *RSC Christmas meeting*. 2008, 17-18 December: Southampton.
  38. P. Cyganik, K. Szelagowska-Kunstman, M. Goryl, A. Szpak, and M. Szymoński, *Badania AFM struktur metaloorganicznych powstałych na powierzchni samoorganizujących się monowarstw organicznych (oral presentation)*, in *V Seminarium STM/AFM*. 2008, 26-30 November: Zakopane.
  39. Munuera, O. Shekhah, H. Wang, C. Wöll, and C. Ocal, *Following the selective growth of MOFs on patterned substrates by Scanning Force Microscopy (talk)*, in *Second Spanish Workshop on Nanolithography*. 2008, 10-13 November: Bellaterra.
  40. M. Buck, *Self-Assembled Monolayers and Networks as Templates to Control Electrochemical Metal Deposition (invited talk)*, in *PRIME conference*. 2008, 12-17 October: Honolulu.
  41. V. Mugnaini, *A first step towards the construction of porous and magnetic radical-based metal-organic frameworks on top of self-assembled monolayers (poster)*, in *MOF 2008 - 1st International Conference on Metal Organic Frameworks and Open Framework Compounds*. 2008, 8-10 October: Augsburg.
  42. C. Munuera, O. Shekhah, H. Wang, C. Wöll, and O. C., *Following the selective growth of MOFs on patterned substrates by Scanning Force Microscopy (talk)*, in *MOF 2008 - 1st International Conference on Metal Organic Frameworks and Open Framework Compounds*. 2008, 8-10 October: Augsburg.
  43. O. Shekhah, *Step-by-step route for the synthesis and controlled growth of metal-organic frameworks on functionalized organic surfaces (oral presentation)*, in *MOF 2008 - 1st International Conference on Metal Organic Frameworks and Open Framework Compounds*. 2008, 8-10 October: Augsburg.
  44. J. Veciana, *High-Dimensional Metal-Organic Frameworks Based on Free Radicals Showing Magnetic Properties (oral presentation)*, in *MOF 2008 - 1st International Conference on Metal Organic Frameworks and Open Framework Compounds*. 2008, 8-10 October: Augsburg.
  45. C. Rovira, *Multifunctional Organic Radicals on Surfaces (invited lecture)*, in *The 11th International Conference on Molecule-based Magnets ICMM 2008*. 2008, 21-24 September: Convitto della Calza, Florence.
  46. J. Veciana, *Multi-Functional Magnetic Organic-Inorganic Hybrid Surfaces by*

- Self-Assembling of Polychlorotriphenylmethyl Radicals (invited lecture)*, in *Global COE International Symposium on Perspectives in Inorganic-Organic Hybrid Materials*. 2008, 1 August: Tohoku University, Sendai.
47. J. Veciana, *Future perspectives for devices based on magnetically active molecules. Magnetic Porous Molecule-based Materials (invited lecture)*, in *The 57th Fujihara Seminar on New Prospects on Molecular Magnetism*. 2008, 28-31 July: Tomakomai.
  48. Cebula and M. Buck, *Metal-Organic Networks on Au Surfaces Prepared From Solution (poster)*, in *ECOSS 25 - European Conference on Surface Science*. 2008, 27 July-1 August: Liverpool.
  49. Grillo, R. Heck, D. Bradshaw, S.M. Francis, and N.V. Richardson, *Co-adsorption of copper and multifunctional carboxylic acids on Au(111) (poster)*, in *ECOSS 25 - European Conference on Surface Science*. 2008, 27 July-1 August: Liverpool.
  50. K. Szelagowska-Kunstman, P. Cyganik, M. Goryl, D. Zacher, Z. Puterova, R.A. Fischer, and M. Szymonski, *AFM investigation of Cu<sub>3</sub>(btc)<sub>2</sub> metal-organic framework microcrystals formed selectively on silica surface modified with organic self-assembled monolayers (poster)*, in *ECOSS 25 - European Conference on Surface Science*. 2008, 27 July-1 August: Liverpool.
  51. V. Mugnaini, *A first step towards the construction of porous and magnetic radical based MOFs on top of self-assembled monolayers (oral presentation)*, in *2nd NANOSEA*. 2008, 7-10 July: Villa Mondragone-Monte Porzio Catone- Roma.
  52. K. Szelagowska-Kunstman, P. Cyganik, M. Goryl, D. Zacher, Z. Puterova, R.A. Fischer, and M. Szymonski, *Badania AFM powierzchni mikrokryształów struktur metaloorganicznych powstałych na powierzchni samoorganizujących się monowarstw organicznych (poster)*, in *II Krajowa Konferencja Nanotechnologii*. 2008, 25-28 June: Krakow.
  53. Szpak, K. Szelagowska-Kunstman, P. Cyganik, O. Shekhah, C. Wöll, and M. Szymoński, *Metaloorganiczne struktury typu MOF otrzymane poprzez wzrost warstwa po warstwie – Badania AFM (poster)*, in *II Krajowa Konferencja Nanotechnologii*. 2008, 25-28 June: Krakow.
  54. Tekiel, J. Prauzner-Bechcicki, S. Godlewski, J. Budzioch, and M. Szymonski, *Funkcjonalizacja powierzchni TiO<sub>2</sub>(110)-(1×1) molekułami kwasu tereftalowego (poster)*, in *II Krajowa Konferencja Nanotechnologii*. 2008, 25-28 June: Krakow.
  55. P. Cyganik, K. Szelagowska-Kunstman, M. Goryl, and M. Szymoński, *Badanie powierzchni struktur metaloorganicznych typu MOF (oral presentation)*, in *III Krajowa Konferencja Nanotechnologii*. 2008, 22-26 June: Warszawa.



56. R.A. Fischer, *Selective, oriented and phase controlled growth of metal-organic frameworks at surfaces and trapping of nano-MOF crystallites in colloidal solution (invited talk)*, in *235th ACS National Meeting 2008*, 6-10 April: New Orleans.
57. O. Shekhah, *Step-by-step route for the synthesis of Metal-organic frameworks (oral presentation)*, in *235th ACS National Meeting*. 2008, 6-10 April: New Orleans.
58. J. Veciana, *Nanoporous Molecular Magnets (invited lecture)*, in *IDECAT-MAGMANet-NANOFUNPOLY NoEs Joint Workshop 2008*. 2008, 17-19 March: Florence.
59. J. Veciana, *Metal-Organic Frameworks based on Organic Free Radicals showing Magnetic Properties (invited talk)*, in *2008 Eurasia Conference on Chemical Sciences*. 2008, 7-11 January: Manila.
60. J. Veciana, *Open-Framework Molecular Showing Porosity and Magnetic Ordering (invited talk)*, in *4th International Conference of Africa Materials Research Society*. 2007, 10-14 December: Dar es Salaam.
61. J. Veciana, *Functional porous molecule-based materials. Introduction, general concepts and applications (invited lecture)*. 2007, 13 November: Facultad de Químicas; Universidad de Santiago de Compostela.
62. J. Veciana, *Functional porous molecule-based materials; Magnetic nanoporous molecular materials" (invited lecture)*. 2007, 22 May: University of Fribourg, Département de Chimie.
63. J. Veciana, *Functional porous molecule-based materials; Introduction, general concepts and applications (invited lecture)*. 2007, 21 May: Basel University, Departement für Chemie.
64. R.A. Fischer, *Selective Growth and MOCVD Loading of Thin Films of Metal Organic Frameworks on Various Substrates (invited talk)*, in *211th ECS Meeting*. 2007, 6-10 May: Chicago.
65. N. Roques, D. Maspoeh, A. Dacu, D. Ruiz, C. Rovira, and J. Veciana, *Magnetic Porous Materials with Purely Organic and Metal-Organic Frameworks*, in *ESF Exploratory Workshop on Genesis and Applications of Active Metal-Organic Frameworks (invited lecture)*. 2007, 25-28 April: Dourdan.
66. O. Shekhah, *Layer by layer growth of Metal Organic Frameworks (MOFs) on organic surfaces (poster)*, in *DPG Jahrestagung*. 2007, 25-30 March: Regensburg.

67. J. Veciana, *Functional porous molecule-based materials. Magnetic Nanoporous Molecular Materials (invited lecture)*. 2006, 14 November: Yokohama State University.

### **By cooperating scientists**

1. R. Blom, *Functional Metal-Organic Frameworks as Heterogeneous Catalysts - the MOFCAT project (oral presentation)*, in *euroNanoForum 2009*. 2009, 2-5 June: Prague.
2. C. Scherb, J. Williams, R. Köhn, and T. Bein, Sorption behaviour of oriented films of metalorganic frameworks (poster), in *EuroNanoForum 2009*. 2009, 2-5 June: Prague.