# Post-synthetic modification of epitaxially grown, highly oriented functionalized MOF thin films†‡

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Thin films of MOFs grown on solid substrates offer a huge potential with regard to tailoring the properties of a surface, in particular if used in connection with post-synthesis modification (PSM). Here, we report on the PSM of surface-supported crystalline MOFs, with target molecules using an amine-based coupling strategy.

One goal of interfacial systems chemistry[1] is the flexible modification of substrates to achieve multi functionality. With regard to this goal, surface supported, crystalline metal organic frameworks (MOFs) offer a huge potential for a number of applications, including membranes and optical coatings, and in homogenous as well as heterogeneous catalysis, selective separation, and chemical sensing.[2] These applications are based on the ability to adjust crystal size, shape, orientation and functionality of the MOF thin films.[2,3]

The anchoring of MOF crystallites to a modified Au substrate can be carried out in a rather straightforward fashion,[3] but the polycrystallinity and fairly rough morphology of these coatings somewhat limit their applications. High quality MOF films prepared by the liquid phase epitaxy (LPE) approach, on the other hand, are crystalline, of well defined thickness and very homogenous,[4,5] thus providing the basis for developing a general platform for surface functionalization. Briefly, in contrast to conventional MOF synthesis protocols, where the reactants are mixed and then reacted under solvothermal conditions, in the LPE approach appropriately functionalized
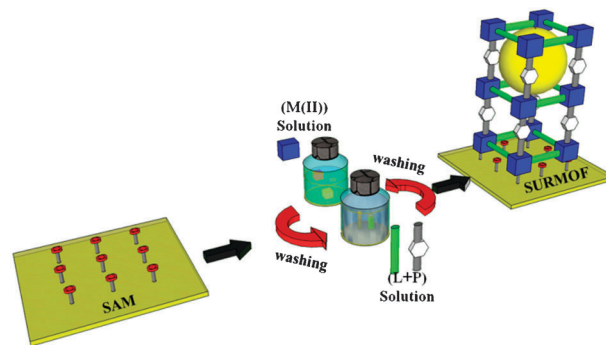
Scheme 1 Schematic diagram for the LPE growth of SURMOFs on substrates functionalized with SAMs. The preparation is done by repeated immersion cycles first in solution of the metal precursor and subsequently in the organic ligand solution, with solvent rinsing in between.

substrates are immersed into solutions of one of the individual reactants in an alternating fashion[6] (see Scheme 1).

The resulting SURMOFs (surface anchored, highly crystalline MOFs) exhibit high crystalline order and an adjustable thickness proportional to the number of immersion cycles.[7] The nucleating organic surface typically prepared by fabricating thiolate based self assembled monolayers (SAMs) acts as a structure directing element and can control the orientation of the SURMOF.[8] In special cases LPE has been shown to yield MOFs not accessible *via* bulk synthesis routes.[4,9]

Layer based MOFs (LBMOFs) with the general formula $[M(L)(P)_{0.5}]$ (M: Cu^{2+}, Zn^{2+}; L: dicarboxylate linker; P: dinitrogen pillar ligand) are particularly well suited for the SURMOF process. LBMOFs generally consist of dicarboxylate ligands bridged by metal dimers to form 2D sheets, and linear connectors like 1,4 diazabicyclo[2.2.2]octane (dabco) to connect the 2D lattices.[10–12]

Although the self assembly process of LBMOFs based on fourfold coordinated metal dimers linked by dicarboxylate benzene ligands is quite robust with regard to adding a functionality on the bdc unit (*e.g.* an amino group),[13,14] sterically more demanding functionalities may interfere with the assembly process thus prohibiting the formation of a well defined MOF lattice. In addition, in the case of SURMOF, for certain applications it may be desirable to laterally pattern a coating, *i.e.* to only functionalize certain areas of a deposited film.

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In this context, post synthesis modification (PSM) is an important option, as a MOF built from organic ligands with a reactive functionality like *e.g.* an amino group is modified after the assembly of the porous coordination polymer.[15] In fact, PSM opens the possibility of advanced porous solid engineering.[14,15] Whereas in previous work for bulk MOFs, reactive functionalities like NH_2, pyridyl and aldehyde functional groups have been demonstrated to be well suited for the PSM process,[14] this process has not yet been studied in connection with SURMOFs.

In this work, we first report the synthesis of a SURMOF containing the organic ligand NH_2 bdc (NH_2 bdc 2 amino 1,4 benzenedicarboxylate), and then demonstrate that using the amino group for a PSM process carries a huge potential with regard to SURMOF functionalization. The starting point for this project is a layer pillar type of MOF with a layered structure consisting of $[Cu_2(NH_2\ bdc)_2]$ sheets connected by dabco pillars, the synthesis of which has recently been reported by Savonnet *et al.*[14] The XRD results shown in Fig. S1 in ESI‡ demonstrate that this MOF is well suited for the SURMOF process; the data reveal the presence of structurally well defined frameworks supported on an OH terminated organic surface. As expected, the high affinity of the Cu^{2+} dimer axial coordination site results in a growth of the SURMOF with the [001] direction perpendicular to the surface.[8] These SURMOFs were then used as a platform for PSM with various synthons such as isocyanates to generate urea derivatives (see Scheme S1 in ESI‡).

In this study, Au(111) surfaces covered with an OH terminated SAM fabricated from 11 mercaptoundecanol (MUD)[16,17] were used as a substrate for the LPE process. As evidenced by quartz crystal microbalance (QCM) data the LPE process leads to a stepwise growth of the $[Cu_2(NH_2\ bdc)_2(dabco)]$ MOF, as observed before for other ligand/metal ion combinations.[4] The out of plane and in plane XRD results displayed in Fig. S1 in the ESI‡ reveal a diffraction pattern fully consistent with the presence of a [001] oriented $[Cu_2(NH_2\ bdc)_2(dabco)]$ SURMOF with a thickness of 40 layers erected on the OH terminated MUD SAM. The positions and relative intensities of the diffraction peaks are fully consistent with the XRD patterns calculated for the bulk material.[14] The out of plane XRD confirmed that $[Cu_2(NH_2\ bdc)_2(dabco)]$ grows highly oriented along the [001] direction.

The infrared (IR) data showed the characteristic bands of the carboxylate groups in the region between 1200 and 1700 cm^{-1}, as well as the amine symmetric (3498 cm^{-1}) and antisymmetric (3384 cm^{-1}) N H stretching vibration (Fig. S2 in ESI‡).

After having demonstrated the suitability of the $[Cu_2(NH_2\ bdc)_2(dabco)]$ MOF for the SURMOF process we now turn our attention to the covalent attachment of iso cyanates to the MOF lattice using the amine groups as anchoring points. The first tests were done with *n* butyliso cyanate by exposing the $[Cu_2(NH_2\ bdc)_2(dabco)]$ SURMOF to the gaseous isocyanate (vapour pressure of *n* butyliso cyanate: 10.6 mm Hg) at 20 °C for 2 days. After rinsing with ethanol the samples were thoroughly characterized. The IR results (Fig. S3 in ESI‡) still show the carboxylate bands being characteristic of the $[Cu_2(NH_2\ bdc)_2(dabco)]$ MOF.

The signals from the symmetric (3498 cm^{-1}) and antisymmetric (3384 cm^{-1}) N H stretching vibration are found to be weakened after the reaction. Unfortunately, the N H stretch vibration of the urea group (R NH C O NH R), which is expected at around 3400 cm^{-1},[18] could not be seen in the experimental IR data. The intensity increase of the bands in the CH stretching regimes, *i.e.* between 2800 3000 cm^{-1}, is fully consistent with the presence of asymmetric and symmetric stretching bands of the CH_2 and CH_3 moieties in the *n* butyl group of the isocyanates.

The XRD results depicted in Fig. S5 in ESI‡ show that the peak positions are unaffected by the reaction, only a small change in the relative intensities of the 002/001 peaks is observed. We thus conclude that the PSM reaction does not change the periodicity, crystallinity and orientation of the SURMOFs, the backbone of the frameworks is not affected by the coupling reaction.

In order to demonstrate the versatility of PSM for SUR MOFs in a more straightforward fashion, we have used a larger synthon, 4 fluorophenylisothiocyanate (F C_6H_4 NCS), as a PSM reagent. Again the reaction was triggered by exposing the pristine $[Cu_2(NH_2\ bdc)_2(dabco)]$ SURMOF to vapour (vapour pressure of F C_6H_4 NCS: 0.122 Torr at 25 °C). The IR (Fig. S4 ESI‡) and XRD (Fig. 1) data were recorded after an exposure time of 2 days. In this case, the reduction of the NH_2 band intensities at 3498 and 3384 cm^{-1} indicated a reaction yield of ∼50%. After the reaction, the XRD pattern of the SURMOF showed the same pattern but with slightly lower overall intensity; again revealing that the SURMOF does not lose its crystallinity after reaction. The presence of the fluorinated aryl groups was conveniently demonstrated by X ray photoelectron spectroscopy (XPS), a quantitative analysis yielded about 3 4 4 fluorophenylisothio cyanate molecules per SURMOF pore.

Finally, an even larger compound, 1 ferrocenylmethy lisocyanate, was used as a PSM reagent. In this case the reaction was carried out in the liquid phase, a pristine $[Cu_2(NH_2\ bdc)_2 (dabco)]$ SURMOF was immersed in a solution of 1 ferrocenyl methylisocyanate (1 mM in dichloroethane) at 30 °C.
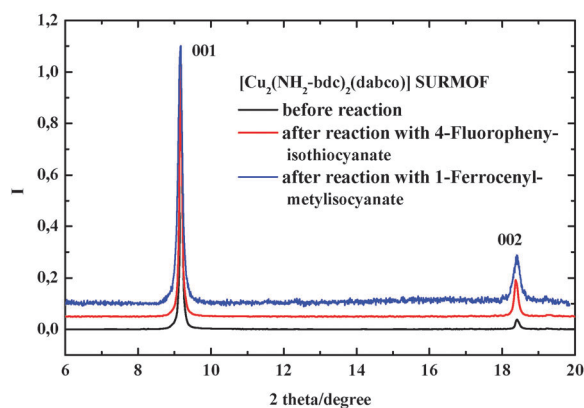
Fig. 1 Comparison of XRD patterns from as synthesized $[Cu_2(NH_2\ bdc)_2(dabco)]$ (black), prepared by the LPE method. After reaction with 4 fluorophenylisothiocyanate (red). After reaction with 1 ferrocenyl methylisocyanate (blue). The individual patterns were normal ized with regard to the (001) diffraction peak. Note the pronounced changes in the relative intensity of the (002) to the (001) peak.
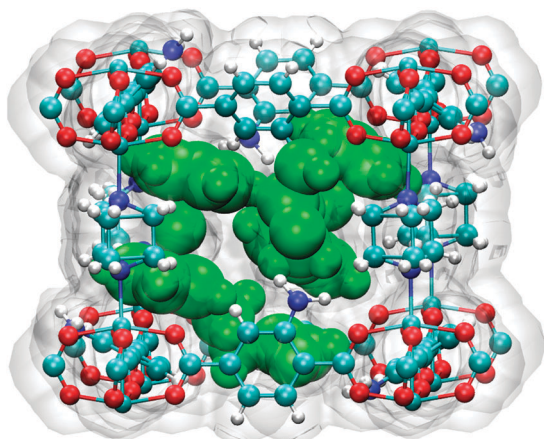
Fig. 2 Geometry of a [Cu$_2$(NH$_2$ bdc)(dabco)] MOF after covalently attaching two 1 ferrocenylmethylisocyanate units (green) per pore, as obtained from MD simulations. The grey surface indicates the free space in the unit cell of the empty MOF before the PSM process.

The IR and XRD data recorded for the modified SURMOFs are shown in Fig. S4 ESI‡ and Fig. 1.

The reduction of the NH$_2$ stretch at 3498 and 3384 cm^{-1} indicates that 30% of the NH$_2$ groups in the lattice have been reacted. The presence of the ferrocene groups was demon strated also by XPS (Fig S6 in ESI‡), a quantitative analysis yielded the presence of about 1 2 of the 1 ferrocenylmethyl isocyanate molecules per SURMOF pore. Very importantly, in this case the change in the relative intensities in the XRD data was quite pronounced, as expected from the presence of a heavy iron atom in the moiety attached to the MOF framework. Simulations of XRD data (not shown) for the hypothetical structure shown in Fig. 2 also reveal a pronounced increase in the (002) diffraction peak intensity.

In order to get more insights into the precise structure of the SURMOF after the PSM process we have performed molecular dynamics simulations (MD) using the Amber10 molecular modeling package.[19] As a starting point for the calculations we used a [Cu$_2$(NH$_2$ bdc)$_2$(dabco)] framework with the known bulk structure parameters. The different synthons were then connected to the lattice *via* the amino groups of the NH$_2$ bdc ligands. Separate calculations were carried out for different numbers of synthons grafted to the backbone of the framework. The molecular arrangement of the synthons within the MOF lattice was optimized while keeping the corners and unit cell size of the structure fixed. In Fig. 1 we display the results for a PSM process carried out with a 1 ferrocenylmethylisocyanate synthon. Optimization was carried out by "heating" the start geometry from 0 to 300 K using a time step interval of 2.0 fs. We find that the competing effects of the covalent grafting of the 1 ferrocenyl methylisocyanate to the NH$_2$ bdc ligands, the non covalent interaction with the benzene ring units of the MOF structure and the steric repulsion allow for a maximum density of 2 ferrocene molecules per pore. The resulting geometry is displayed in Fig. 2. Calculations carried out for an additional

ferrocene unit per pore revealed that there is not enough space to fit a third unit. The presence of a maximum number of two ferrocene units per SURMOF pore is fully consistent with the XPS data (see above). Simulations for the loading with 4 fluorophenylisothiocyanate are shown in Fig. S7 of the ESI.‡

The functionalization of supported MOF thin films can be readily achieved by post synthetic modification (PSM). The experiments presented here demonstrate that layer pillar based SURMOFs employing an NH$_2$ modified dicarboxy benzene ligand offer a robust platform for attaching synthons containing an isocyanate group. The grafting of ferrocene inside the SURMOF pores has important consequences for the SURMOF electrochemical properties.[20] In future work we plan to extend the PSM of SURMOFs to other coupling units (*e.g.* azide units for employing click chemistry) and to laterally pattern SURMOFs by inducing the coupling reactions on selected areas of the SURMOFs.

Notes and references

1 A. Golzhauser and C. Woll, *ChemPhysChem*, 2010, **11**, 3201 3213.
2 O. Shekhah, J. Liu, R. A. Fischer and C. Woll, *Chem. Soc. Rev.*, 2011, **40**, 1081 1106.
3 D. Zacher, O. Shekhah, C. Woll and R. A. Fischer, *Chem. Soc. Rev.*, 2009, **38**, 1418 1429.
4 O. Shekhah, *Materials*, 2010, **3**, 1302 1315.
5 O. Shekhah, H. Wang, S. Kowarik, F. Schreiber, M. Paulus, M. Tolan, C. Sternemann, F. Evers, D. Zacher, R. A. Fischer and C. Woll, *J. Am. Chem. Soc.*, 2007, **129**, 15118 15119.
6 D. Zacher, R. Schmid, C. Woll and R. A. Fischer, *Angew. Chem., Int. Ed.*, 2011, **50**, 176 199.
7 C. Munuera, O. Shekhah, H. Wang, C. Woll and C. Ocal, *Phys. Chem. Chem. Phys.*, 2008, **10**, 7257 7261.
8 D. Zacher, K. Yusenko, A. Betard, S. Henke, M. Molon, T. Ladnorg, O. Shekhah, B. Schupbach, T. de los Arcos, M. Krasnopolski, M. Meilikhov, J. Winter, A. Terfort, C. Woll and R. A. Fischer, *Chem. Eur. J.*, 2011, **17**, 1448 1455.
9 O. Shekhah, H. Wang, M. Paradinas, C. Ocal, B. Schupbach, A. Terfort, D. Zacher, R. A. Fischer and C. Woll, *Nat. Mater.*, 2009, **8**, 481 484.
10 W. Mori, S. Takamizawa, C. N. Kato, T. Ohmura and T. Sato, *Microporous Mesoporous Mater.*, 2004, **73**, 31 46.
11 K. Seki, S. Takamizawa and W. Mori, *Chem. Lett.*, 2001, 122 123.
12 D. N. Dybtsev, H. Chun and K. Kim, *Angew. Chem., Int. Ed.*, 2004, **43**, 5033 5036.
13 E. Dugan, Z. Q. Wang, M. Okamura, A. Medina and S. M. Cohen, *Chem. Commun.*, 2008, 3366 3368.
14 M. Savonnet, D. Bazer Bachi, N. Bats, J. Perez Pellitero, E. Jeanneau, V. Lecocq, C. Pinel and D. Farrusseng, *J. Am. Chem. Soc.*, 2009, **132**, 4518 4519.
15 K. K. Tanabe and S. M. Cohen, *Chem. Soc. Rev.*, 2011, **40**, 498 519.
16 R. Arnold, W. Azzam, A. Terfort and C. Woll, *Langmuir*, 2002, **18**, 3980 3992.
17 M. Kind and C. Woll, *Prog. Surf. Sci.*, 2009, **84**, 230 278.
18 Y. Mido, *Spectrochim. Acta, Part A*, 1973, **29**, 431 438.
19 D. A. Case, T. E. Cheatham, T. Darden, H. Gohlke, R. Luo, K. M. Merz, A. Onufriev, C. Simmerling, B. Wang and R. J. Woods, *J. Comput. Chem.*, 2005, **26**, 1668 1688.
20 A. Dragasser, O. Shekhah, O. Zybaylo, C. Shen, M. Buck, C. Woll and D. Schlettwein, submitted for publication.