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Chemistry of SURMOFs: Layer-Selective Installation of Functional Groups and Post-synthetic Covalent Modification Probed by Fluorescence Microscopy

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Supporting Information

ABSTRACT: Layer-selective installation of functional groups at SURMOFs (surface-attached metal−organic framework multilayers) is reported. Multilayers of [Cu(ndc)-(dabco)$_{0.5}$] grown in [001] orientation on pyridine-terminated organic self-assembled monolayers on Au substrates were functionalized with amino groups by step-by-step liquid-phase epitaxy. The method allows the growth of samples exhibiting one monolayer of functional groups at the *external* thin-film surface. In situ quartz crystal microbalance monitoring confirmed the presence of amino groups by turning the multilayer film from a non-reactive to a reactive material for covalent binding of fluoresceinisothiocyanate, and fluorescence microscopy displays the expected luminous property.

Metal−organic frameworks (MOFs) or porous coordination polymers (PCPs) have emerged as a class of crystalline materials with well-defined structures of designable topologies, high porosities (*internal* surface), and a variety of applications such as guest molecule sorption, catalysis, sensors, etc.[1] The *external* surface of MOFs, the first barrier for incoming molecules, plays a critical role. In this spirit, it is of general interest to develop methodologies for tuning the surface properties of MOF crystallites, such as hydrophilicity/hydrophobicity, affinity, and functionality.

Much effort has been undertaken to introduce functional groups (FGs) to MOFs.[2,3] Most reported MOFs are synthesized as polycrystalline powder materials by solvothermal one-pot complexation of metal ions and organic ligands in sealed vessels. In this case, any FGs present in MOFs must be incorporated into ligands prior to MOF synthesis, and this strategy is limited by their compatibility with solvothermal reaction conditions, i.e., thermal stability and coordinating capability with metal ions. Post-synthetic modification (PSM) of MOF bulk structure has been established for pore surface modification, i.e., by means of "click chemistry".[2] A protection−complexation−deprotection process was reported to incorporate FGs into MOFs that were compatible with the solvothermal formation of the MOFs.[3] In all these cases, however, FGs are *homogeneously* distributed over the bulk of the MOF crystallites. Besides these *internal* surface modifications, the selective modification of the *external* surface of MOF crystallites or the interface between different MOF crystallites remains a significant challenge.[4] Macro-scale BAB-type heterocrystals of MOFs (or PCPs) were prepared via solvothermal, liquid-phase epitaxial growth, taking advantage of matching lattices of specific crystal surfaces.[5] Some related, pioneering studies exist on the hybridization of extended coordination structures.[6] Kitagawa and co-workers demonstrated immobilization of functional monolayers on the PCP microcrystal *external* surface by coordination bonding.[7] Consequently, this method must consider the properties of crystal faces, e.g., terminal structure, and the particular coordination equilibrium. Related post-synthetic fuctionalization of a MOF thin film or a MOF multilayer has not been reported so far.

Herein, we demonstrate, to the best of our knowledge, the first example of a selective covalent functionalization of the *external* surface of a MOF multilayer film with emphasis on two aspects: transferring the concept of post-synthetic (covalent) modification to SURMOFs (surface-attached crystalline and oriented metal−organic framework multilayers) and achieving a monolayer resolved incorporation of FGs at the linkers in order to alter its external or interfacial surface properties with retention of the framework bulk structure.

SURMOFs are fabricated by step-by-step liquid-phase epitaxy (LPE) as was introduced recently.[8] It is simply described as alternating application of the inorganic and organic building blocks to a substrate, for example using thiolate-based self-assembled monolayers (SAMs) on gold as templates for MOF crystallization (Supporting Information (SI), Figure S1). This method offers unique possibilities for investigation of MOF chemistry that cannot be accessed by conventional one-pot solvothermal reactions and MOF single (macro)crystals. For instance, in this latter case, the composition of the external surface (including different crystal faces) is not obvious and is difficult to controlled precisely. In contrast, SURMOFs can be deposited in selected orientations with well-defined terminal compositions.[8] In the following, we demonstrate our concept by introducing amino groups selectively to the external surface of a SURMOF of [Cu(ndc)(dabco)$_{0.5}$] in [001] orientation (ndc = 1,4-naphthalene dicarboxylate;

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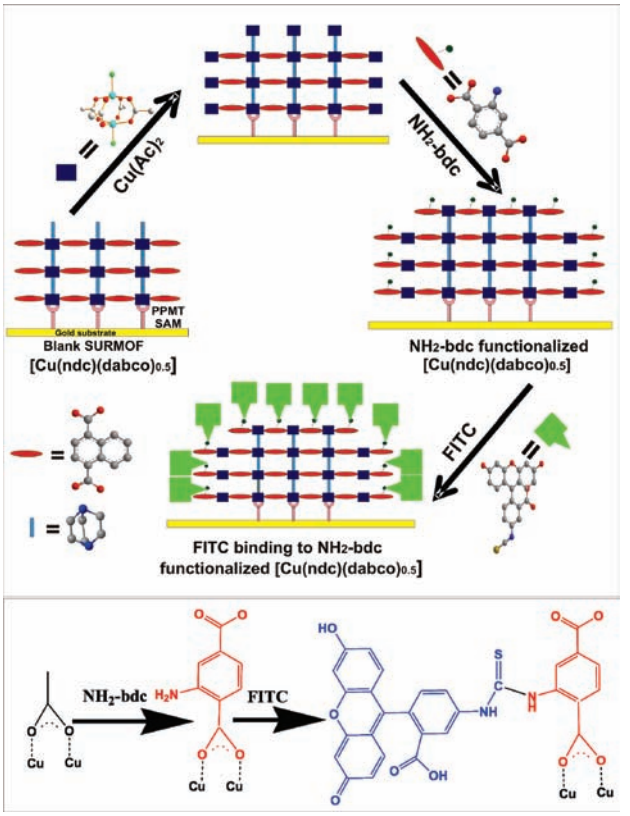
Scheme 1. (Top) Stepwise Approach for External Surface Functionalization of the Pre-formed [001]-Oriented SURMOF $[Cu(ndc)(dabco)_{0.5}]$ at Pyridine-Terminated PPMT SAM[a] and (Bottom) Ligand Exchange between Acetate and NH_2-bdc and Reaction of NH_2-bdc with FITC



[a] $Cu(Ac)_2$ is used as a commutator to change the external surface composition from ndc and dabco to acetate groups before subsequently exchanging acetate groups with NH_2-bdc at each crystal face and then amino labeling with FITC molecules.

dabco = 1,4-diazabicyclo[2.2.2]octane). The amino fuctionalization turns the SURMOF from a non-reactive to an active material for capturing a fluorescent dye marker solely at the external surface (Scheme 1). For clarity, we summarize our experiments in Table 1, which we will discuss in the following.

The well-known layer-based MOF $[Cu(ndc)(dabco)_{0.5}]$ (**1**),[9] containing two coordination modes of ndc-Cu and dabco-Cu with an anisotropic tetragonal crystal system, was selected as a model case. Dinuclear Cu_2 units with a paddlewheel structure are bridged by ndc linkers to form a 2D square grid [Cu(ndc)], and the axial sites of the Cu_2 paddlewheels are occupied by dabco pillars to extend the 2D layers to a 3D network, in which four faces are terminated by copper-ndc (denoted as [001] faces) and other two surfaces are terminated by copper-dabco (denoted as [100] faces) (SI, Figure S2). Usually, 10−40 layers of **1** were grown on a pyridine-terminated SAM on a gold substrate by alternating deposition of $Cu(Ac)_2$ and an equimolar mixture of ndc/dabco solutions, separated by washing with absolute ethanol, according to the procedure developed by our group.[10] As characterized by X-ray diffraction (SI, Figure S3), a typical SURMOF sample **1** is obtained in a preferred [001] orientation, due to the templating effect of the pyridine-terminal SAM.[11] Note that the pyridine group of a 4,4′-pyridylphenylmethanethiol (PPMT) SAM will occupy the axial site of Cu_2 paddlewheels of $Cu(Ac)_2$, which regulates the orientation. Subsequent ndc/dabco deposition results in the coordination of dabco pillars on the other axial site of Cu_2 paddlewheels in the [001] direction and coordination of ndc in the [100] direction, respectively, and then proceeds in this way with next cycle's growth (SI, Figure S4).[10,11] Because of a final deposition step with ndc/dabco, the external surfaces of **1** are terminated with ndc linkers in the [100] direction and dabco in the [001] direction (Scheme 1).

Based on **1**, the concept of layer-selective introduction of FGs onto such a pre-formed (crystalline and oriented) SURMOF sample is as follows. After additional deposition of $Cu(Ac)_2$ on the pre-formed SURMOF, copper dimers can be coordinated with terminal ndc and dabco ligands in [100] and [001] directions (Scheme 1), respectively, as they do in the stepwise growth of **1** (see quartz crystal microbalance (QCM) data). In this critical step, $Cu(Ac)_2$, behaving as a commutator, substantially changes the external surface composition from ndc and dabco to acetate groups (around Cu_2 sites for charge compensation) in all directions.[10,11] Further exposure to NH_2-bdc (2-amino-1,4-benzeneterephtalate) will afford a NH_2-bdc-modified SURMOF $[Cu(ndc)(dabco)_{0.5}]$ (**2**) by replacing acetate groups with NH_2-bdc, as the ndc ligand does. Thus, NH_2-bdc is located on each external SURMOF surface for both the [100] and [001] directions (Scheme 1). This replacement between acetate groups and NH_2-bdc ligands is independent of terminal ndc-Cu or dabco-Cu coordination modes. It is noteworthy that axial coordination sites of dinuclear Cu_2 units cannot be occupied by carboxylate owing to the tetragonal pyramid coordination mode of Cu^{2+} ions in MOFs.[9−12] In comparison, *coordinative* immobilization of a dye monolayer in the [100] direction can only be made by substituting ndc (not dabco) with dye molecules containing the same carboxyl group, subject to the composition and properties of the crystal external face.[7] Formation of the NH_2-bdc monolayer does not require lattice-matching with pre-formed $[Cu(ndc)(dabco)_{0.5}]$ at the interfaces, which is essentially different from the concept of core−shell PCP heterocrystals.[5a] Consequently, functionalization of the whole external surface in a controllable fashion by introducing FGs at the linkers should be possible with the step-by-step LPE method.

The QCM is an ultrasensitive weighing device capable of sensing mass changes in the nanogram range. In situ QCM data indicate that continuous mass gain upon alternating deposition of $Cu(Ac)_2$ and ndc/dabco (Figure 1a), another deposition of $Cu(Ac)_2$, and subsequent NH_2-bdc deposition on pre-formed sample **1** is also detected by QCM (Figure 1b), which provides us direct proof that NH_2-bdc has been installed successfully (SURMOF sample **2**).

The installed surface amino groups of **2** should allow permanent labeling by fluoresceinisothiocyanate (FITC), which is an ideal species to probe the presence of amino groups because it can react with amine under mild conditions in ethanol solution to form robust thioureas, and it is convenient to detect due to its strong fluorescent properties.[13] Permanent mass gain, indicating FTIC adsorption, was indeed observed by QCM upon flowing FITC ethanol solution over sample **2** grown on QCM substrate at room temperature (black curve in Figure 1c), which results in the formation of sample **3** (FITC@**2**). This mass adsorption could not be removed by extensive washing with ethanol, obviously due to the formation of a robust thiourea covalent linkage.[13] XRD and SEM studies demonstrated that the film morphology and the crystallinity of the $[Cu(ndc)(dabco)_{0.5}]$

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Table 1. Summary of Experiments

sample	preparation	FITC adsorption by QCM	luminous properties by FM
1, blank SURMOF [Cu(ndc)(dabco)$_{0.5}$]	step-by-step LPE	NO	NO
2, NH_2-bdc-functionalized **1**	one cycle of $Cu(Ac)_2$ and NH_2-bdc deposited on **1**	YES	NO
3, FITC@**2**	FITC solution flowing over **2**	nd[a]	YES
4, FITC@**1**	FITC solution flowing over **1**	nd[a]	NO
5, bdc-functionalized **1**	one cycle of $Cu(Ac)_2$ and bdc deposited on **1**	NO	nd[a]
6, SURMOF ($N+1$)	one cycle of $Cu(Ac)_2$ and ndc/dabco on **2**	YES	YES[b]
7, SURMOF ($N+2$)	two cycles of $Cu(Ac)_2$ and ndc/dabco on **2**	NO	NO[b]

[a] Not determined. [b] After FITC flowing.

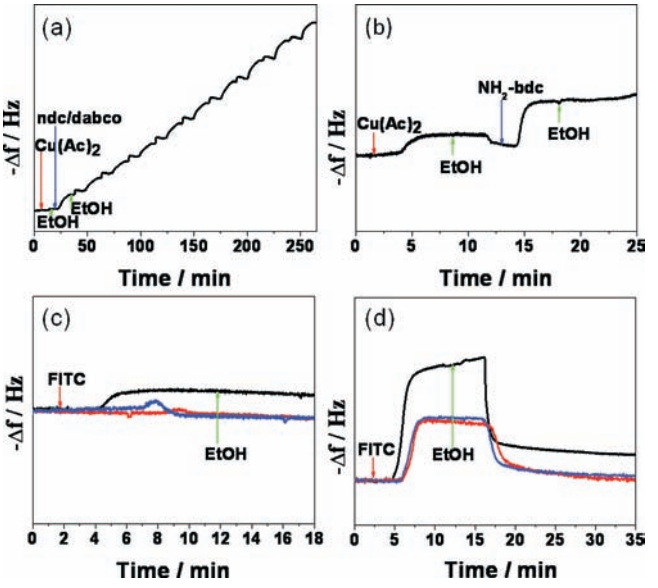

Figure 1. QCM curves for the deposition of (a) SURMOF [Cu(ndc)-(dabco)$_{0.5}$] (sample **1**, 10 cycles) fabricated on a pyridine-terminated SAM in a step-by-step fashion; (b) sample **2** fabricated by one cycle of $Cu(Ac)_2$ and NH_2-bdc deposition on the preformed **1**; (c) FITC solution flowing over samples **1** (blue), **2** (black), and **5** (red); (d) FITC solution flowing over samples **6** (black), **7** (red), and SURMOF (N+3) (blue). See Table 1 for sample specifications.

framework remained intact after FITC labeling (SI, Figures S5 and S6). Interestingly, when FITC solution was directly applied over sample **1** (sample **4**, FITC@**1**), no mass adsorption was observed by QCM, as expected (blue curve in Figure 1c). The small transient mass increase is attributed to a weak and reversible physisorption of FITC and **1**. In addition, FITC cannot be captured by bdc-modified **1** (sample **5**, red curve in Figure 1c). There are two types of FGs, carboxyl and amino groups, present on the external surface of sample **2**. According to our parallel experiments, it is clear that carboxyl groups make no contribution to catching FITC. Consequently, it is rational to conclude that the FTIC capture is caused only by the introduced amino groups. Obviously, a single deposition cycle of H_2N-bdc turned the inert SURMOF **1** into a reactive material (sample **2**) for permanent FITC binding. The FITC molecular dimensions (5 × 10 × 10 Å) are larger than the free pore sizes of [Cu(ndc)(dabco)$_{0.5}$] (4 × 8 × 8 Å), which suggests that FITC was chemisorbed at the external SURMOF surface only. This reasoning is substantiated by comparison of the fluorescence microscopy images of **1** and **2** (Figure 2a,b) with those of FITC@**2** and FITC@**1** (Figure 2c,d).

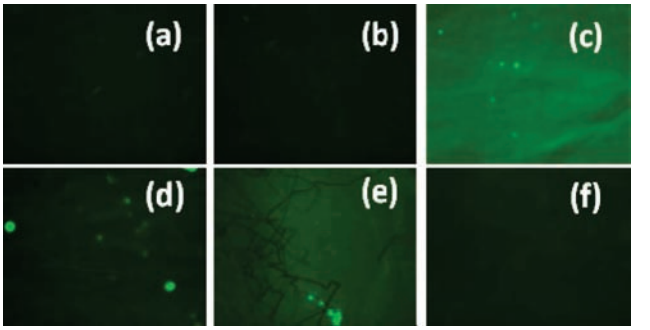

Figure 2. Fluorescence microscopy images for the samples of (a) **1** (40 cycles), (b) **2**, (c) **3**, (d) **4**, (e) **6**, and (f) **7**. All SURMOF base samples **1** were fabricated on transparent SAM-modified Au-glass substrate, and all image sizes are 334.8 × 443.8 μm. See Table 1 for sample specifications.

A very significant fluorescence intensity increase is observed for FITC@**2**, which is consistent with the QCM data. Note that some bright spots present in fluorescence microscopy images arose from agglomerates (parasitic deposition of MOF particles) on the SURMOF, which can be seen on SEM images (SI, Figure S6). All the samples that displayed FITC adsorption in QCM curves showed higher fluorescence intensity with reference to samples **1** and **2**, although it is difficult to derive quantitative data on the FITC adsorption of FITC@**2** (e.g., the density of the FTIC monolayer). Unfortunately, no new characteristic vibration in routine IRRAS spectra was detected for FITC@**2** in comparison with blank sample **1** (SI, Figure S7), owing to the very small, monolayer amount of FITC and overlap with the framework bands. In order to further probe the surface- and layer-selective anchoring of FITC, we buried the introduced terminal H_2N-bdc linkers by additional cycles of $Cu(Ac)_2$ and ndc/dabco deposition. After one additional cycle was applied to sample **2**, leading to sample **6**, some FITC adsorption could still be monitored by QCM (Figure 1d) and fluorescence microscopy (Figure 2e). One additional MOF layer (N+1) may be not thick enough to prevent linear isothiocyanate groups of FITC from reacting with amino groups of the layer (N) below, and crystallite defects may play a role as well. SURMOF roughness is known to be on the order of 1−2 layers.[8] Therefore, more layers (i.e., deposition cycles $N+k$) of [Cu(ndc)(dabco)$_{0.5}$] are needed to completely prevent the adsorption of FITC. As expected, physisorbed FITC can be washed away with ethanol quantitatively (Figures 1d and 2f) when $k \geq 2$. Samples of $N+1+k$ multilayers with only a single H_2N-bdc internal layer fully retain the crystallinity and [001] orientation of the overall SURMOF (SI, Figure S8). These observations provide additional support to the conclusions that

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H_2N-bdc was only anchored to the external surface of **1** and the covalent bonding of FTIC to the SURMOF can only take place between surface-exposed amino groups and isothiocyanate groups from FITC. The data prove monolayer selectivity of the introduction of chemical functionality at LPE-grown SURMOFs. We recently reported on related SURMOF block heterostructures of type AB with variation of both metal and linker for the respective A and B blocks.[14] Our present study suggests the feasibility of SURMOFs ABA with only one or a few layers of B as the interface between homoepitaxially grown multilayers A (SI, Figure S9).

In conclusion, we have demonstrated a methodology to install functional (amino) groups in an ultraselective way on MOF multilayers with SURMOF $[Cu(ndc)(dabco)_{0.5}]$ as the model case. The key to ensure this layer-selective installation relies on switching terminal ndc and dabco to acetate groups by using $Cu(Ac)_2$ as a commutator. This amino modification by H_2N-bdc turned inert $[Cu(ndc)(dabco)_{0.5}]$ into an active material for covalent FITC binding, as identified by in situ QCM monitoring and fluorescence microscopy. The amino groups were located only on the external surface of the deposited MOF multilayers. We propose a wide applicability of this SURMOF-based concept for investigation and development of MOF surface, interface, and host−guest chemistry in general. For example, a precise layer-selective incorporation of functional groups by LPE may enable us to decorate pre-formed multilayers with various functional groups not only at the external surface but at certain distances in the volume, creating sharp internal interfaces. These options are under current investigation, i.e., anchoring hydrophobic groups to protect SURMOFs from moisture, introduction of molecular gates at the external surface, and tailored post-synthetic modification of interfacial layers by diffusion of small reactive molecules.

■ ASSOCIATED CONTENT

Supporting Information. Experimental details, LbL protocols, XRD patterns, SEM images, and IRRAS. This material is available free of charge via the Internet at http://pubs.acs.org.

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