## COMMUNICATION

## Assessing the adsorption selectivity of linker functionalized, moisture-stable metal-organic framework thin films by means of an environment-controlled quartz crystal microbalance†‡

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The stepwise thin film deposition of the robust, hydrophobic  $[Zn_4O(dmcapz)_3]_n$  (dmcapz = 3,5-dimethyl-4-carboxy-pyrazolato) is reported. The adsorption of small organic probe molecules, including alkanols, toluene, aniline and xylenes, was monitored by an environment-controlled quartz crystal microbalance setup. The adsorption selectivity was tuned by introducing alkyl side chains in the dmcapz linker.

The processing of metal-organic frameworks (MOFs) as thin films and coatings is relevant for a wide range of applications, such as separation by membranes, gas chromatography, catalysis and sensing.<sup>1</sup> For integration into practical devices, good air, water and thermal stability as well as an easy and quick thin film fabrication method at low temperature, compatible with the substrate limitations, is required. The stepwise deposition is one of these methods, in which the metal and the linker components are kept separate from each other and are successively put into contact with the growing film on the substrate.<sup>2</sup> It has been used for the coating of textile fibers,3 the coating of gas chromatography columns,<sup>4</sup> the fabrication of membranes for gas separation<sup>5</sup> and of sensing devices.<sup>6</sup> However, until now only few MOFs have been grown as dense coatings in a stepwise fashion, namely: HKUST-1  $[Cu_3(btc)_2]_n^2$  (btc = 1,3,5-benzenetricarboxylate), pillared-layered  $[M_2L_2P]_n$  structures where  $M = Cu^{2+}$  or  $Zn^{2+}$ , L = dicarboxylate linker, P = dinitrogen pillar ligand,<sup>7,8</sup> and MOF-5  $[Zn_4O(bdc)_3]_n$ (bdc = 1.4-benzenedicarboxylate). The drawbacks associated with these MOFs are either their limited functionalization possibilities, i.e. for HKUST-1, or their limited resistance to moisture; MOF-5 is even only attainable when working in a dry environment. For device applications more robust and easily tailored MOFs are desirable. The stepwise film growth of such a candidate is reported below.

Barea, Navarro and co-workers<sup>9</sup> recently reported the synthesis of a fairly robust MOF with interesting adsorption properties:  $[Zn_4O(dmcapz)_3]_n$  (dmcapz = 3,5-dimethyl-4-carboxypyrazolato). This MOF exhibits the same secondary building unit

(SBU) and the same topology as MOF-5.<sup>10</sup> That is, the structure is cubic with the Zn<sub>4</sub>O tetrahedron sitting at the vertices and linked by six molecules of dmcapz to the next vertex. Unlike MOF-5,  $[Zn_4O(dmcapz)_3]_n$  is highly water and air stable as a result of the presence of both the pyrazole group at one side of the linker and the two methyl groups which point toward the carboxylic acid group, protecting the more labile Zn–O bonds from nucleophilic attacks.  $[Zn_4O(dmcapz)_3]_n$  was reported to capture toxic gases even in the presence of moisture.<sup>9</sup> The high stability and cubic structure make it an ideal candidate for applications in filters or membranes, chromatography and pervaporation. Its close structural relationship to MOF-5 strongly suggests its compatibility with the stepwise film deposition method using the Controlled SBU Approach (CSA).<sup>4,11</sup>

We first synthesized polycrystalline powder samples of  $[Zn_4O-(dmcapz)_3]_n$  as reference by employing the CSA. A solution of basic zinc acetate  $[Zn_4O(OAc)_6]$  was mixed with a solution of H<sub>2</sub>dmcapz in the presence of ethanol and water (for details see ESI<sup>‡</sup>). Phase pure  $[Zn_4O(dmcapz)_3]_n$  was formed as proven by powder X-ray diffraction (XRD) (Fig. 1b).

Interestingly, the same experiment without water led to the formation of another and yet unknown phase, whose powder XRD pattern could be indexed in an orthorhombic space group (Fig. S2, ESI<sup>‡</sup>). Following these results, stepwise deposition of  $[Zn_4O(dmcapz)_3]_n$  was performed. A gold coated substrate suited for quartz crystal microbalance (QCM) measurements was functionalized with a COOH-terminated SAM (self-assembled monolayer) and was then exposed alternately to a solution of basic zinc acetate [Zn<sub>4</sub>O(OAc)<sub>6</sub>] in ethanol and to a solution of H<sub>2</sub>dmcapz in an ethanol-water mixture, using a computer controlled automatic deposition setup described previously.<sup>12</sup> These growth steps were separated by rinsing steps with ethanol only. Characterization by XRD and scanning electron microscopy (SEM) (Fig. 1, top) revealed the deposition of phase pure material with preferred orientation along the [100] direction. This corresponds to cubic crystallites preferably attached to the surface by their bottom facet. A dense coating of intergrown crystallites is achieved after approximately 30 cycles (Fig. 1c), leading to an overall film thickness in the range of  $0.5-1 \mu m$ . The deposition method is compatible with a wide range of substrates: gold surfaces functionalized with SAMs of COOH, OH or pyridyl termination, as well as unmodified flat or porous silica and alumina substrates

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**Fig. 1** (top) SEM micrographs of a 30-cycle film grown on COOHterminated gold (bottom). Comparison of the X-ray diffraction patterns (a) simulated from published data, (b) of a powder obtained by the CSA and (c) of a film grown on COOH-functionalized gold.

(Fig. S4, ESI‡). Note that the growth of  $[Zn_4O(dmcapz)_3]_n$  was carried out with low-cost technical ethanol, making the film deposition much less expensive as compared with other so far reported stepwise depositions of MOFs on SAMs as surface templates, which all required very pure and dry ethanol for achieving crystalline, densely packed, phase-pure and oriented (SUR)MOFs.<sup>2,7,8</sup>

The methanol adsorption isotherm (0-95% rel. humidity) of a typical film of  $[Zn_4O(dmcapz)_3]_n$  grown on the abovementioned substrates was obtained by using an environmental controlled QCM setup as described in the ESI‡. The isotherm has the expected type I shape (Fig. S5, ESI‡) and nicely demonstrates the microporosity of the MOF film. The amount of methanol adsorbed at 20 °C and relative humidity of  $0.95 p/p_0$  was 7.6 mmol g<sup>-1</sup>. This represents a pore volume of  $0.36 \text{ cm}^3 \text{ per cm}^3$  of MOF (calculated from the density of liquid methanol) whereas a value of  $0.45 \text{ cm}^3 \text{ per cm}^3$  of MOF has been measured on bulk samples with standard N<sub>2</sub> adsorption.<sup>9</sup> The difference can be attributed to the size of the methanol molecules which cannot fill every empty space in the structure and to the activation process, carried out for the thin film samples *in situ* (see ESI‡) and which might be incomplete to some extent.

As a model for pervaporation or chromatographic separation, we studied the adsorption selectivity of our films for a choice of volatile organic compounds using the environment controlled QCM equipment mentioned above. At t = 0 min, a helium flow with a partial vapor pressure  $p/p_0 = 0.85$  of the desired analyte reached the QCM adsorption cell and the mass change over time was monitored. We first investigated the adsorption of a series of simple alkanol molecules of increasing sizes: methanol, ethanol, isopropanol and *tert*-butanol.



**Fig. 2** Time dependent mass uptake of a  $[Zn_4O(dmcapz)_3]_n$  film for alkanols of increasing size at a rel. humidity of 85% at 20 °C (1 atm).

The uptake curves are presented in Fig. 2. A striking difference can be seen between methanol and ethanol, for which 4 to 5 molecules per cavity are absorbed within a few seconds, compared with isopropanol, for which the kinetic uptake is much slower; tertbutanol is not adsorbed. From these measurements the effective size of the pore window can be estimated to be around 5.3 Å, which is somewhat smaller than the value of 5.6 Å estimated from crystallographic data.9 We then studied in some detail the adsorption of molecules whose sizes are close to this characteristic pore opening. Toluene and aniline were chosen on one hand, and the xylene series on the other. A very good selectivity of toluene over aniline (4.9 at 90 min), despite their very close sizes (about 5.3 Å), is evident from the recorded mass gain over time (Fig. 3, left). The observed differences in the adsorption rate and saturation level can be explained by the different polarities of the analytes:  $[Zn_4O(dmcapz)_3]_n$  is highly hydrophobic and therefore shows a higher affinity for non-polar molecules over polar ones. A significant selectivity of *p*-xylene over m-/o-xylene (5.3 at 90 min) was also observed, which is certainly based on the molecular size: in this case *p*-xylene is slightly smaller than the pore opening, whereas the other isomers are slightly larger.

In order to vary the pore size and to modulate the adsorption response of the films, a range of derivatives of the parent linker were chosen bearing various substituents other than just methyl on the pyrazole ring, *i.e.* ethyl (Et), *n*-propyl ("Pr), isopropyl ('Pr), cyclopropyl (°Pr). The respectively functionalized 4-carboxy-pyrazoles  $H_2L$  were synthesized *via* a facile and efficient two-step route starting from acetoacetate and the respective derivatives. This allows us to vary independently the substituents on the two sides of the linker, giving access to non-symmetrically substituted linkers, thus affecting the



**Fig. 3** Time dependent mass uptake of a  $[Zn_4O(dmcapz)_3]_n$  film for toluene *vs.* aniline (left) and for *p*-xylene *vs. o*-,*m*-xylene (right) at a rel. humidity of 85% at 20 °C (1 atm).



**Fig. 4** Amount of analyte adsorbed at saturation (or after 90 min) of linker functionalized films  $[Zn_4O(L)_3]_n$  at rel. humidity of 85% (20 °C, 1 atm). The analytes are close in size but different in polarities.

multivariate complexity of the structures. Surprisingly, however, we failed to prepare most of the target MOFs  $[Zn_4O(L)_3]_n$  as phase-pure polycrystalline powder materials. The orthorhombic phase of so far unknown crystal structure, already mentioned in the case of parent  $[Zn_4O(dmcapz)_3]_n$ , was nearly always present as a (minor) contaminant which could not be avoided or separated.

Nevertheless, phase-pure films were finally obtained by using the seeding layers concept (details in the ESI<sup>‡</sup> and Fig. S7–S9).<sup>8</sup> The seeding approach consisted in depositing some parent  $[Zn_4O(dmcapz)_3]_n$  material (just one deposition cycle) on the substrate surface prior to the deposition of the functionalized  $[Zn_4O(L)_3]_n$ , in order to direct the nucleation and growth of the desired phase. The respective methanol adsorption isotherms (0-95% rel. humidity) of the deposited films were then recorded at 20 °C (Fig. S10 and S11, ESI<sup>‡</sup>). They all represented type I isotherms and from this the accessible pore volumes were derived (Table S2, ESI<sup>‡</sup>). As expected, a constant decrease of the pore volume  $V_p$  is observed upon the addition of increasingly more bulky alkyl substituents. Moreover, a striking difference appears between "Pr ( $V_p = 0.15 \text{ cm}^3 \text{ g}^{-1}$ ) and 'Pr  $(V_{\rm p} = 0.052 \text{ cm}^3 \text{ g}^{-1})$  substitution. This is certainly due to the high rigidity of <sup>*i*</sup>Pr, which therefore blocks the pore entrance more efficiently than the conformationally flexible "Pr. This high rigidity has an effect on the accessibility of the MOF bulk structure. Indeed, we failed to obtain the MOF-5-analogue phase when the linker was symmetrically functionalized with *two* <sup>*i*</sup>Pr groups, whereas a symmetric functionalization with two <sup>n</sup>Pr groups led to the formation of the desired material. (The characterization and structural elucidation of the obtained phases are out of scope of this communication.)

We then estimated the pore size opening of the functionalized derivatives  $[Zn_4O(L)_3]_n$  by studying the uptake of the deposited films at the saturation limit (for 85% rel. humidity) after 90 min for some analytes of similar size. The results are grouped in Fig. 4. Isopropanol is somewhat smaller (5.12 Å) than toluene and aniline (5.3 Å), and is therefore more readily adsorbed, in general, than the other analytes. However, with increasing bulkiness of one substituent, the uptake of toluene and aniline decreases dramatically due to a smaller pore size of the functionalized MOFs. The (mono) <sup>*i*</sup>Pr functionalized film does not adsorb any isopropanol, suggesting that its pore size is smaller than 5.1 Å. These data clearly demonstrate the possibility of fine tuning the adsorption selectivity for quite similar molecules by the choice of substituents at the linker L.

In addition, adsorption isotherms of water were measured on various films (one day at 20 °C, 0–95% rel. humidity, Fig. S12, ESI<sup>‡</sup>). No or little differences in crystallinity and adsorption properties after the experiments were observed. This is an encouraging indication of good stability of these films toward moisture.

To sum up, the MOF thin film stepwise deposition concept was applied to a chemically very robust, MOF-5-analogue family. The obtained coatings on COOH-functionalized QCM substrates allowed the rapid screening and quantitative assessment of the adsorption properties of the various thin film materials. The selective adsorption of probe molecules depending on their size and/or hydrophobicity as a function of the linker functionalization of the MOF is demonstrated. From our data we conclude that  $[Zn_4O(dmcapz)_3]_n$  and its derivatives could be used as an active separating layer in applications such as gas chromatography or pervaporation.§ The well-controlled and facile stepwise deposition method, the robustness and compatibility of this type of MOF with a wide range of substrates open the way for integration into many functional devices.

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## Notes and references

§ Preliminary experiments (Fig. S4) showed that the growth is also possible on porous substrates. A detailed study will be published later.

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