Supplementary information

Heteroepitaxial growth of surface mounted metal-organic framework thin films with hybrid adsorption functionality

Min Tu and Roland A. Fischer*

Inorganic Chemistry II—Organometallics and Materials Chemistry, Ruhr-University Bochum, D-44870 Bochum, Germany.

1 General method

X-ray diffraction (XRD)

Out-of-plane XRD data of SURMOFs were collected by the X'Pert PRO PANanalytical equipment (Bragg-Brentano geometry with automatic divergence slits, position sensitive detector, continuous mode, room temperature, Cu-K α radiation, Ni filter, the range of $2\theta = 5-20^{\circ}$, at a step of 0.0197°, with accumulation time 550s per step). The powder samples were dropped onto a zero background silicon wafer.

Infrared Reflection Absorption Spectroscopy (IRRAS)

IRRAS measurements were done on a Biorad Excalibur FTIR spectrometer (FTS 3000) with 2 cm⁻¹ resolution at an angle of incidence of 80° relative to the surface normal and further processed by using boxcar apodization.

Thermal Gravimetric Analysis (TGA)

TGA measurements were performed on a Seiko TG/DTA 6300S11 instrument (sample weight approximately 10 mg) at a heating rate of 5 °C/min in the range from 30 to 500°C under nitrogen (99.999%).

Scanning Electron Microscopy (SEM)

SEM images were recorded on a LEO1530 Gemini FESEM to investigate the SURMOFs' morphologies.

Adsorption of organic vapors measured by a means of environment controlled quartz crystal microbalance (QCM)

The sorption properties of SURMOFs were measured by an environment controlled QCM instrument. As shown in Fig. S1, the relative vapor pressure of adsorbates could be controlled by four independent mass flow controllers (MFCs) in the range of 0-95%. Quantitative mass change of SURMOFs mounted on QCM substrate was obtained from the frequency change according to the Sauerbrey equation (shown in Eq. 1). At each relative pressure, the sorption amount could be obtained by Eq. 2.

$$\Delta M = -\frac{A\sqrt{\mu \times \rho}}{2F_0^2} \Delta F \tag{1}$$

F₀: Fundamental frequency, ΔM: Mass change A: Surface area of electrode μ : Shear stress of quartz (2.947×10¹⁰ kg/(m×s²)) ρ : Density of quartz (2648 kg/m³) ΔF: Frequency change

$$\frac{\Delta M}{M_0} = \frac{F - F_s}{F_s - F_0} \tag{2}$$

M₀: Initial weight of the measurement sample

F: Measuring frequency

Fs: Frequency after deposition and pretreatment of the sample

F₀: Fundamental frequency

Prior to sorption measurements of organic vapors, it is important to remove all solvent molecules from the pores to be able to compare the sorption data of different SURMOFs. The activation process was performed in two steps. Firstly, SURMOFs were soaked in pure CH₂Cl₂ overnight at room temperature and subsequently dried in an Ar stream. Additionally, they were placed into the QCM instrument cells and heated at 80 °C under He stream (99.999%, 100 sccm) for two hours. All the sorption measurements were performed at 293K. The equilibrium time was set as 30 min and the Δ F was set in the range of ± 3 Hz.

2 Synthetic procedures

Self-assembly monolayers (SAMs) functionalization

Pyridyl-terminated SAMs were obtained by immersing commercial Au covered QCM substrates in 20 μ M of PPMT (PPMT = (4,(4-pyridyl)phenyl)-methanethiol) in absolute ethanol solution for 12 hours at room temperature. After remove the substrates from solution, they were washed with ethanol and dried under argon.

Preparation of SURMOF A, B and B@A

A: [Cu₂ndc₂dabco], **B**: [Cu₃btc₂], (ndc: 1,4-naphtalene dicarboxylate, dabco: 1, 4-diazabicyclo (2.2.2) octane, btc: 1,3,5-benzene tricarboxylate).

As shown in Fig. S2, for preparation of SURMOF **A**, the reactant solutions were prepared as following: 0.5 mM Cu(II) acetate hydrate (Cu(Ac)₂) in absolute ethanol and an equimolar mixture (0.2 mM) of 1,4-ndc and dabco in absolute ethanol. The step-by-step growth of SURMOF **A** were carried out using the automated QCM instrument Q-Sense E4 Auto at 40 °C and at a flow rate of 100 μ L/min. The preparation started by exposing the pyridyl-terminated Au QCM substrates first to the Cu(Ac)₂ solution for 5 min and then equimolar mixture of linker 1,4-ndc/dabco for 10 min. Each subsequent step of dosing components was separated by a washing step of 5 min with absolute ethanol. After a few deposition cycles, crystalline SURMOF **A** could be obtained. In this work, a total 20 or 40 cycles were performed for fabrication of SURMOF A(20) and A(40). SURMOF **B** can be prepared following the same procedure except using 1mM Cu(Ac)₂ as metal precursor and 0.2 mM H₃btc as linker solution. In the case of hetero-SURMOF **B**@A, 20 cycles SURMOF **A** was deposited on pyridyl-terminated Au QCM substrate using the protocol described as above. Afterwards, another 20 cycles SURMOF **B** was deposited on top of SURMOF **A**(20) using the procedure for preparation of SURMOF **B**, giving the formation of hetero-SURMOF **B**(20)@A(20).

3 Supplementary figures



Fig. S1 Experimental setup for adsorption of organic vapors in SURMOFs deposited on QCM substrates.



Fig. S2 Schematic illustration of step-by-step liquid epitaxial growth of metal-organic frameworks on self-assembly monolayers (SAMs).



Fig. S3 QCM profiles of step-by-step liquid phase epitaxial growth of 40 cycles SURMOFs **A** and **B**. (a): stepwise deposition of 0.5mM Cu(Ac)₂ and a equimolar mixture (0.2mM) of H₂ndc and dabco on pyridyl-terminated Au QCM substrate. (b): stepwise deposition of 1mM Cu(Ac)₂ and 0.2mM H₃btc on pyridyl-terminated Au QCM substrate. Inset: sequential injection of metal ions, solvent and linkers in QCM cells.



Fig. S4 In situ QCM monitoring of 30 cycles stepwise deposition of 0.5mM Cu(Ac)₂ and an equimolar mixture (0.2mM) of H₂ndc and dabco on top of SURMOF **B**(40) on pyridyl-terminated Au QCM substrate.



Fig. S5 Out-of-plane XRD patterns of SURMOFs: a) A(40) and b) B(40) on pyridyl-terminated Au substrates in comparison of bulk patterns of MOF A and B, respectively.



Fig. S6 IRRAS spectra of SURMOF **A** (20) (black) and SURMOF **B**(20)@**A**(20) (blue) and IR(ATR) spectra of bulk MOF **A**(red) and **B**(cyan). In comparison with the spectrum of SURMOF **A**(20), a new band appears at the wavenumber of 1655 cm⁻¹ in the recorded spectrum of **B**(20)@**A**(20), corresponding to v_{as} (COO⁻) of H₃btc according to the IR spectrum of bulk MOF **B**.



Fig. S7 IRRAS spectra of 40 cycles SURMOF **A** (black)and **B** (blue) and IR(ATR) spectra of bulk MOF **A**(red) and **B**(cyan).



Fig. S8 SEM images of SURMOF A(40) (a, top view; b, cross-section) and B(40) (c, top view; d, cross-section).



Fig. S9 Adsorption isotherms of organic vapors ((a) hexane and (b) toluene) on SURMOFs A(40) (red cycle), B(40) (black square) and B(20)@A(20) (blue triangle) at 293K. The saturated vapor pressure P₀ of hexane and toluene at 293K are 121 and 22 mmHg, respectively.



Fig. S10 Methanol adsorption isotherms of SURMOF **B**(40) (black) and stepwise deposition of 40 cycles of Cu(Ac)₂ and H₂ndc/dabco on top of **B**(40), in the attempt of fabrication of an oriented **A**(40)@**B**(40) hetero-SURMOF (inverted structure of **B**(40)@**A**(40)). As shown in Fig. S3 and S4, the mass of **B**(40) and the additional layer (by stepwise deposition of 40 cycles of Cu(Ac)₂ and H₂ndc/dabco) on **B**(40) are similar, but the methanol uptake decreased significantly after growth of the additional layer. It suggests that the additional layer "**A**" is not porous or the porosity is quite low compared with **B**(40). Nevertheless "**A**" allows peneration of MeOH to the **B**(40).



Fig. S11 a) QCM monitoring of H_2 ndc/dabco dosing to SURMOF **B**(40). b) Methanol adsorption isotherms of SURMOF **B**(40) (black) before (black) and after (red) dosing H_2 ndc/dabco.



Fig. S12 Powder XRD patterns (left: $2\theta = 5-50^{\circ}$; right: $2\theta = 7-14^{\circ}$) of as-synthesized (**A**_as), activated (**A**_ht) and TIPB loaded (TIPB@**A**) bulk MOF **A**. The powder sample of MOF **A** was synthesized following the procedure reported elsewhere.¹ The as-synthesized **A** was activated under dynamic vacuum at 130 °C for 2 days. 100 mg activated sample (**A**_ht) was immersed into 5 mL TIPB for 1 day. Afterwards, the sample was isolated by centrifugation and dried at 100 °C for 2 days (denoted as TIPB@**A**). We can observe that the framework of **A** did not show any structural changes after activation. However, a slight shift of peak position at around 8.2° (100 reflection of **A**) could be observed after loading with TIPB molecules. Although we cannot correlate the shift of peak position with the detailed framework changes at the moment because of the difficulty of obtaining single crystal of **A** (no report for synthesis of single crystal of **A** up to now), according to the expansion of the pores of [Zn₂bdc₂dabco] after guest inclusion² we surmise that the introduction of TIPB molecules into the channels of **A** does not affect the porous nature of the structure but induces a small amount of lattice expansion compared with the activated one.



Fig. S13 TGA profiles of activated (A_ht) and TIPB loaded (TIPB@A) bulk MOF A. A flat plateau to 300 °C in TGA profile of A_ht indicates the entire guest molecules were removed completely during the activation and A is thermal stable as high as 300 °C. However, an obvious weight loss could be observed up to 300 °C corresponding to the removal of TIPB from the host framework.

References:

- 1 R. Heck, O. Shekhah, O. Zybaylo, P. G. Weidler, F. Friedrich, R. Maul, W. Wenzel, C. Wöll, *Polymers*, 2011, **3**, 1565.
- 2 D. N. Dybtsev, H. Chun, K. Kim, Angew. Chem., Int. Ed., 2004, 43, 5033.