

Supplementary information

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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1) General methods

X-ray Diffraction (XRD): The X-ray diffraction data of the samples were collected on an X'Pert PRO PANalytical equipment (Bragg–Brentano geometry with automatical divergence slits, position sensitive detector, continuous mode, room temperature, Cu-K α radiation, Ni-filter, step size 0.02°). The powders were dispersed in cyclopentane and dropped on a silicon wafer (zero background substrate).

Scanning Electron Microscopy (SEM) images were taken using a LEO 1530 Gemini Scanning Electron Microscope.

Nuclear magnetic resonance (NMR) spectroscopy was performed on a DPX 200 (Bruker) instrument.

Environment-controlled quartz crystal microbalance (QCM) measurement: The measurements were carried out on a BEL-QCM-4 equipment provided by BEL Japan. The relative vapor pressure in helium was controlled by three independent mass flow controllers (MFC) in the range of 0.0 – 95.0 %; A vapor saturated carrier gas was generated by passing through the solvent (301 K) and cooling to 298 K. The vapor saturated gas was then mixed with the dry helium in a certain amount to obtain the desired relative pressure.

The mass change of the film (ΔM) owing to adsorption can be estimated from the change of resonance frequency (ΔF) using the Sauerbrey equation as followed;

$$\Delta F = -\frac{2F_0^2}{A\sqrt{\mu \cdot \rho}} \cdot \Delta M \quad (1)$$

where F_0 : fundamental frequency, A : Area of the electrode,
 μ : Shear stress of quartz (2.947×10^{10} kg/m \cdot s 2) and ρ : density of quartz (2648 kg/m 3).

Consequently, the adsorption amount can be derived as shown in equation (2).

$$\text{Adsorption amount (g/g): } \frac{\Delta M}{M_0} = \frac{F - F_s}{F_s - F_0} \quad (2)$$

where M_0 : weight of the film after pretreatment, F : current frequency and
 F_s : frequency after deposition and pretreatment of the sample.

2) Synthetic procedures

3-cyclopropylpyrazole-4-carboxylic acid and 3-isopropylpyrazole-4-carboxylic acid were purchased from Sigma Aldrich. All reagents were used as received. 3,5-dimethyl-4-carboxypyrazole ($H_2dmcapz$) was synthesized according to the published procedure.¹

Synthesis of basic zinc acetate: The synthesis was inspired by published procedures² but simplified. Zinc acetate dehydrate (5g) was loaded in a schlenk fitted with a sublimation apparatus and slowly heated to 280°C under vacuum ($\sim 1.10^{-3}$ torr) in a sand bath; the cold finger was cooled by tap water. The product sublimes quickly and forms crystals both on the cold finger and on the walls of the schlenk. After crushing of the crystals, 3.2 g of white powder (yield 87.7% based on zinc) was harvested and its purity assessed by XRD.

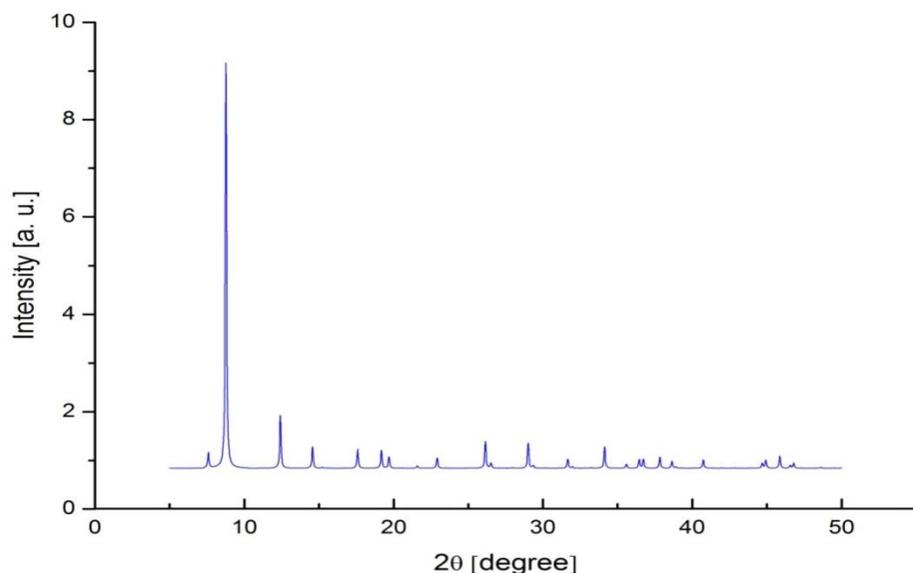
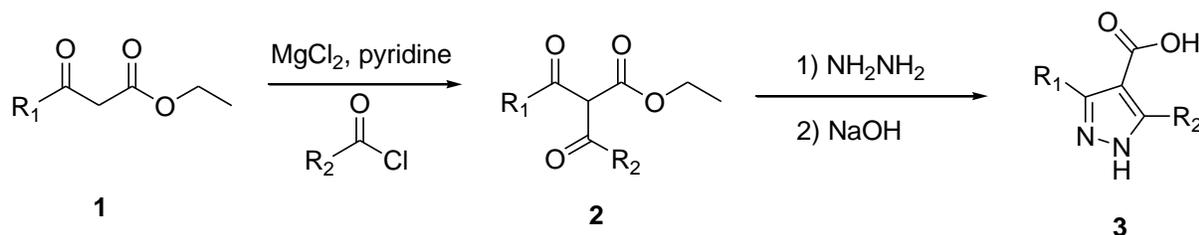


Figure S 1: XRD pattern of basic zinc acetate obtained by sublimation.

Synthesis of the functionalized ligands:



The reaction from **1** to **2** was performed according to the method reported by Rathke and Cowan³. Briefly, 25 mmol of dry magnesium chloride was added to a 100mL round bottom flask. The flask was closed with a septum. Under argon atmosphere, dry methylene chloride (25 mL) was added to the flask. To the resulting heterogeneous mixture, 25 mmol of **1** was added. After cooling to 0 °C, 50 mmol (4 mL) of pyridine was added via the septum inlet. After the solution was stirred for 15 min, 25 mmol of acid chloride was added. The resulting mixture was stirred 15 min at 0 °C and 1 h at room temperature. After being cooled again to 0 °C, 15mL of HCl 6M were added. The resulting solution was washed three times with 20 mL of diethyl ether. The combined ether extracts were dried over MgSO₄. The ether was removed, and the residue was chromatographed with 2-4% of ethyl acetate in hexane to afford the pure product **2**.

The reaction from **2** to **3** was performed following the same procedure than the cyclization of 3,5-dimethyl-4-carboxypyrazole, with some modifications. To a solution of 15 mmol of **2** in 25 mL methanol was added 16 mmol of hydrazine monohydrochloride. The solution was refluxed 2 h (up to 15 h for bulky R groups) and then concentrated in vacuum. Subsequently, 5 mL of water were added to the solution and then 16 mmol of NaOH dissolved in 10mL of water, until the pH reached the range 7-9. A yellow oil formed but was not separated from the water (this is the ester of **3**). 18 mmol of solid NaOH together with 15 mL of methanol were then added to the flask and the mixture was refluxed overnight. The methanol was evaporated and approx. 15 mL of water was added. The insoluble impurities were filtrated and the clear solution was acidified with HCl 37% up to pH 4-5. Compound **3** precipitated in the form of a white solid.

R₁ = methyl, R₂ = ethyl:

Ethyl 2-acetyl-3-oxopentanoate was prepared from ethyl acetoacetate and propionyl chloride (yield 90%): ¹H NMR (200MHz, CDCl₃) δ 4.19 (2H, q), 2.62 (2H, q), 2.25 (3H, s), 1.24 (3H, t), 1.07 (3H, t); ¹³C NMR (50MHz, CDCl₃) δ 200.1, 194.8, 167.1, 108.2, 60.5, 31.3, 25.1, 14.0, 9.3.

5-methyl-3-ethyl-4-carboxypyrazole was prepared from ethyl 2-acetyl-3-oxopentanoate (yield 71%): ¹H NMR (200MHz, MeOD) δ 2.78 (2H, q), 2.32 (3H, s), 1.12 (3H, t); ¹³C NMR (50MHz, MeOD) δ 167.5, 155.4, 149.9, 109.0, 21.0, 13.9, 12.9.

R₁ = methyl, R₂ = n-propyl:

ethyl 2-acetyl-3-oxohexanoate was prepared from ethyl acetoacetate and butyryl chloride (yield 75%): ¹H NMR (200MHz, CDCl₃) δ 4.19 (2H, q), 2.56 (2H, t), 2.25 (3H, s), 1.59 (2H, sex), 1.24 (3H, t), 0.88 (3H, t); ¹³C NMR (50MHz, CDCl₃) δ 198.4, 195.8, 167.2, 108.6, 60.56, 39.5, 25.4, 19.1, 14.0, 13.7.

5-methyl-3-propyl-4-carboxypyrazole was prepared from ethyl 2-acetyl-3-oxohexanoate (yield 63%): ¹H NMR (200MHz, MeOD) δ 2.74 (2H, t), 2.32 (3H, s), 1.57 (2H, sex), 0.84 (3H, t). ¹³C NMR (50MHz, MeOD) δ 167.7, 153.8, 150.2, 109.3, 29.7, 23.4, 14.2, 13.2.

R₁ = methyl, R₂ = isopropyl:

ethyl 2-acetyl-4-methyl-3-oxopentanoate was prepared from ethyl acetoacetate and isobutyryl chloride (yield 70%): ¹H NMR (200MHz, CDCl₃) δ 4.20 (2H, q), 3.10 (1H, sep), 2.23 (3H, s), 1.27 (3H, t), 1.8 (6H, d); ¹³C NMR (50MHz, CDCl₃) δ 202.0, 195.1, 167.4, 108.0, 60.8, 34.6, 25.1, 19.3, 14.0.

5-methyl-3-isopropyl-4-carboxypyrazole was prepared from ethyl 2-acetyl-4-methyl-3-oxopentanoate (yield 74%): ¹H NMR (200MHz, DMSO-d₆) δ 3.55 (1H, sep), 2.23 (3H, s), 1.19 (6H, d); ¹³C NMR (50MHz, DMSO-d₆) δ 156.4, 146.7, 106.9, 25.6, 21.8, 12.7.

Synthesis of the MOFs by controlled SBU approach:

The 0.5 mmol of SBU was dissolved in a 1:1 v/v mixture of technical ethanol and DMF or in technical ethanol (20 mL), and 1.5 mmol of ligand was dissolved in 15 mL 2:1 v/v of ethanol/water. The precursor and ligand solutions were mixed at ambient temperature. Precipitation occurred immediately when the SBU and ligand solutions were mixed. Consequently, the mixtures were left in oven at 50 °C for 1 h to allow full crystallisation and then stored overnight at room temperature for sedimentation. The synthesised powders were recovered by filtrations or centrifugation, sequentially washed with deionised water, ethanol and ether, and dried in air. The powders were activated at 110 °C for 3 days under vacuum.

Synthesis of MOF thin films:

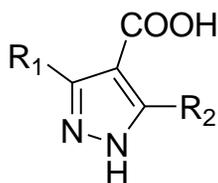
Gold substrates (100 nm on silicon wafers) were immersed 24 h in a 20 μM solution of 16-mercaptohexadecanoic acid in absolute ethanol/acetic acid (5%). The substrates were then abundantly rinsed and stored under air for further use. The same procedure was applied for 11-mercaptoundecanol and [4-(4-pyridyl)phenyl]methanethiol except that the solvent was pure ethanol.

[Zn₄O(dmcapz)₃]_n film: The reactant solutions were prepared as followed; 1 mM of basic zinc acetate in tech. ethanol, 0.5 mM of H₂dmcapz in 3:1 v/v of ethanol/water. The substrate was placed in a glass cell heated at 50°C. Every cycle, the substrate was immersed alternatively in the basic zinc acetate solution, in pure technical ethanol, in the H₂dmcapz solution and finally in pure technical ethanol thanks to a set of peristaltic pumps. Each immersion step lasted 5 min, and

a total of 30 cycles was performed. After being taken out, the film was rinsed with ethanol and dried. Prior to each adsorption measurement, the films were activated by immersion in dichloromethane for minimum one night, followed by a treatment at 80°C under a dry helium flow.

The films with the other linkers were grown using a similar method, however with some modifications which are summarized in Table S1. The XRD patterns are given on Figure S 7 and Figure S 9.

Table S1: Experimental conditions for the growth of $[\text{Zn}_4\text{O}(\text{L})_3]_n$ as films, where L =



R₁	R₂	Modifications
methyl	ethyl	Solution 1mM of the organic ligand in 3:1 v/v of ethanol/water
methyl	n-propyl	1 cycle of $[\text{Zn}_4\text{O}(\text{dmcapz})_3]_n$ was deposited as seeding layer Solution 1 mM of the organic ligand in 3:1 v/v of ethanol/water Immersion steps of 10 min, no intermediate washings
methyl	isopropyl	1 cycle of $[\text{Zn}_4\text{O}(\text{dmcapz})_3]_n$ was deposited as seeding layer Solution 1 mM of the organic ligand in 3:1 v/v of ethanol/water Immersion steps of 10 min, no intermediate washings
H	isopropyl	Solution 0.5 mM of the organic ligand in 4:1 v/v of ethanol/water
H	cyclopropyl	none

3) Supplementary figures

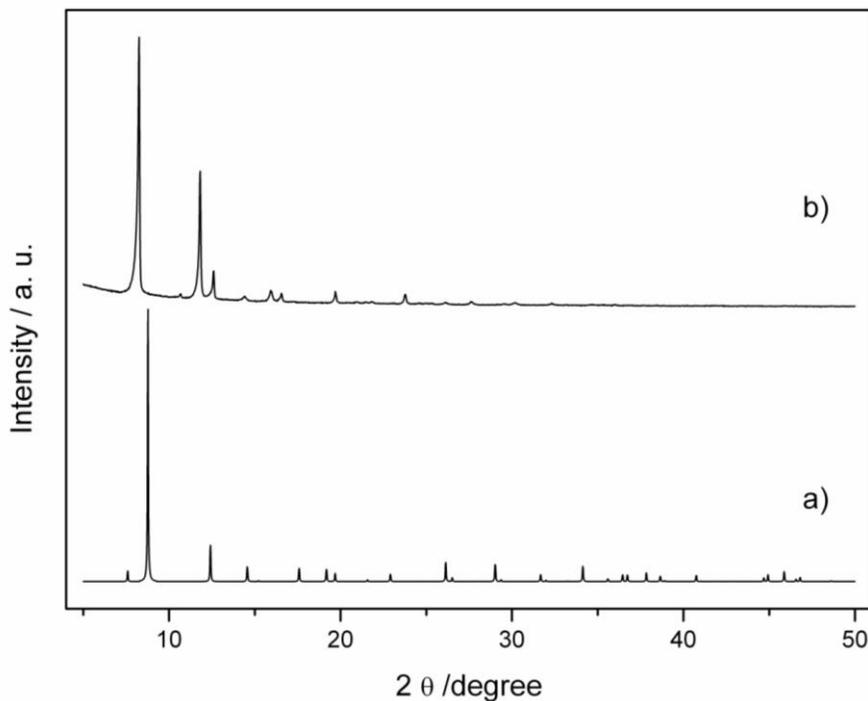


Figure S 2: X-ray diffractograms of a) $[\text{Zn}_4\text{O}(\text{dmcapz})_3]_n$ MOF phase simulated compared to b) the powder obtained by mixing $[\text{Zn}_4\text{O}(\text{OAc})_6]$ with H_2dmcapz in ethanol in the absence of water. The pattern b) can be indexed in an orthorhombic space group with cell parameters: $a = 16.52 \text{ \AA}$, $b = 14.03 \text{ \AA}$, $c = 7.49 \text{ \AA}$. The exact structure is yet unknown.

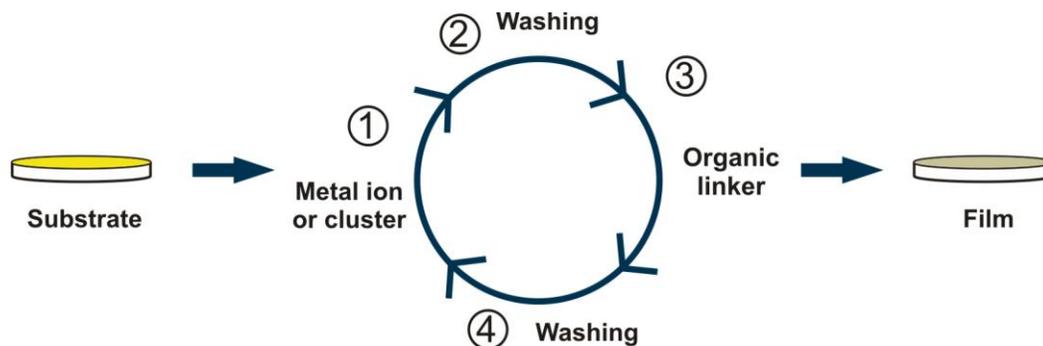


Figure S 3: Scheme of the stepwise deposition procedure.

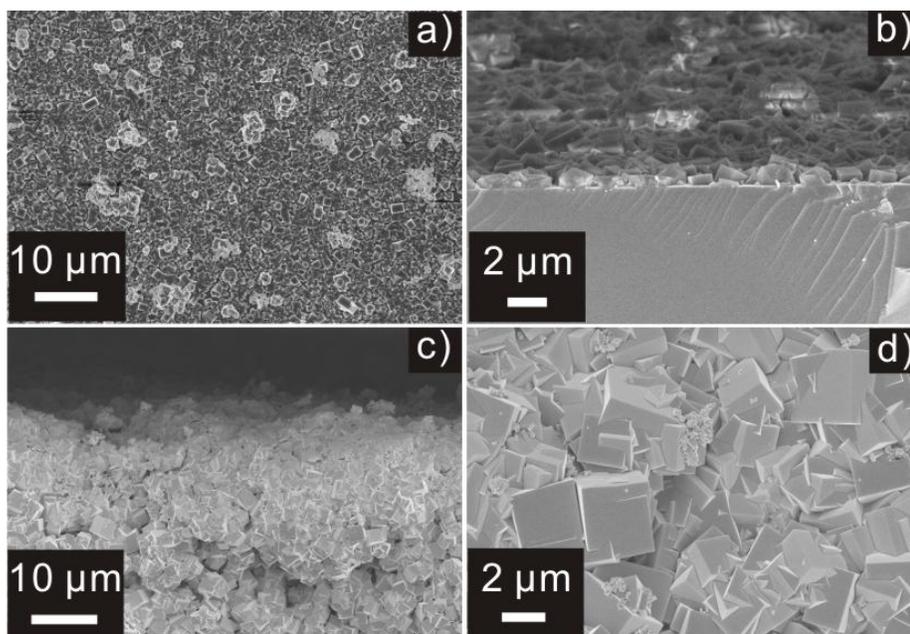


Figure S 4: Scanning electron microscopy images of $[\text{Zn}_4\text{O}(\text{dmcapz})_3]_n$ on a) silica surface, b) alumina surface, and c), d) on porous alumina.

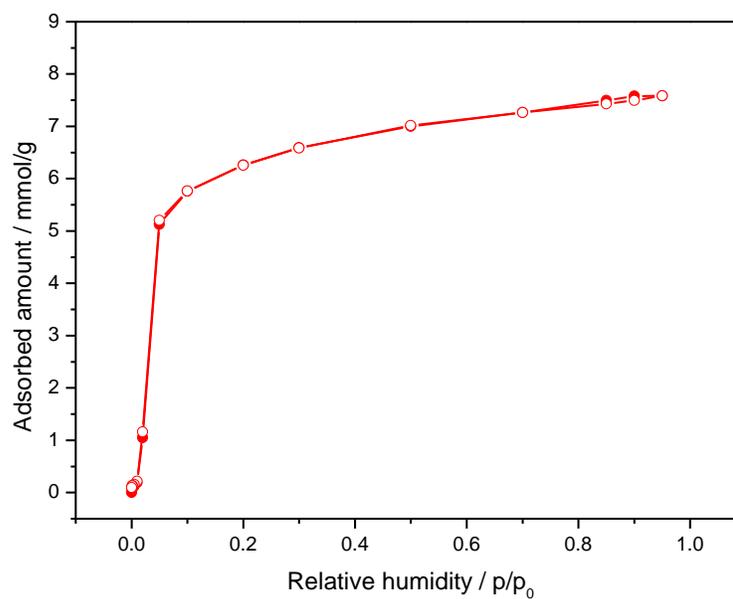


Figure S 5: Methanol adsorption isotherm at 20°C for a film of $[\text{Zn}_4\text{O}(\text{dmcapz})_3]_n$ (30 cycles on a COOH-functionalized gold substrate).

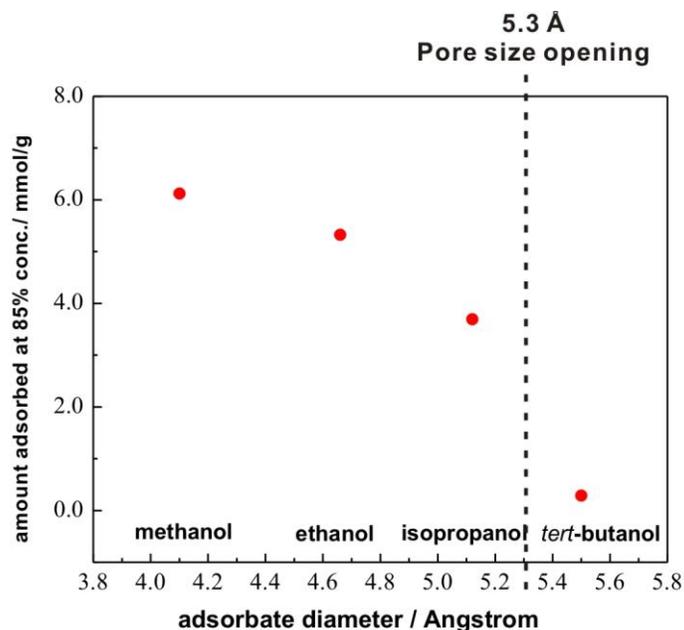


Figure S 6: Uptake of alkanol analyte at saturation (or after 90 min) upon exposure to a flow with relative humidity p/p_0 0.85.

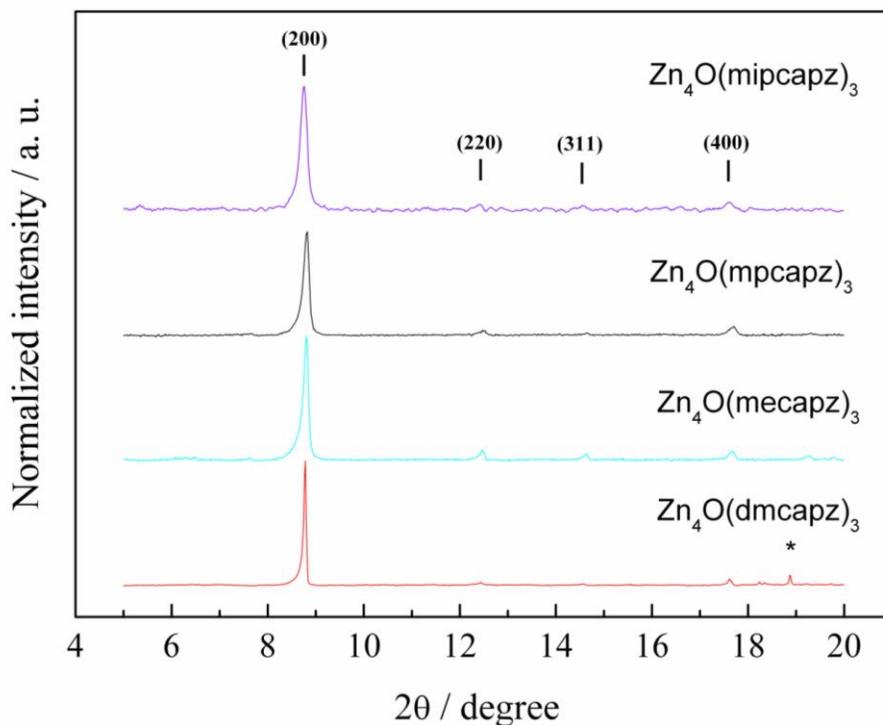


Figure S 7: XRD patterns of MOF thin films on COOH-functionalized gold substrates obtained after 30 deposition cycles. dm: $R_1=R_2=$ Me; me: $R_1=$ Me, $R_2=$ ethyl; mp: $R_1=$ Me, $R_2=$ *n*-propyl; mip: $R_1=$ Me, $R_2=$ isopropyl. The asterisk indicates a signal from the substrate.

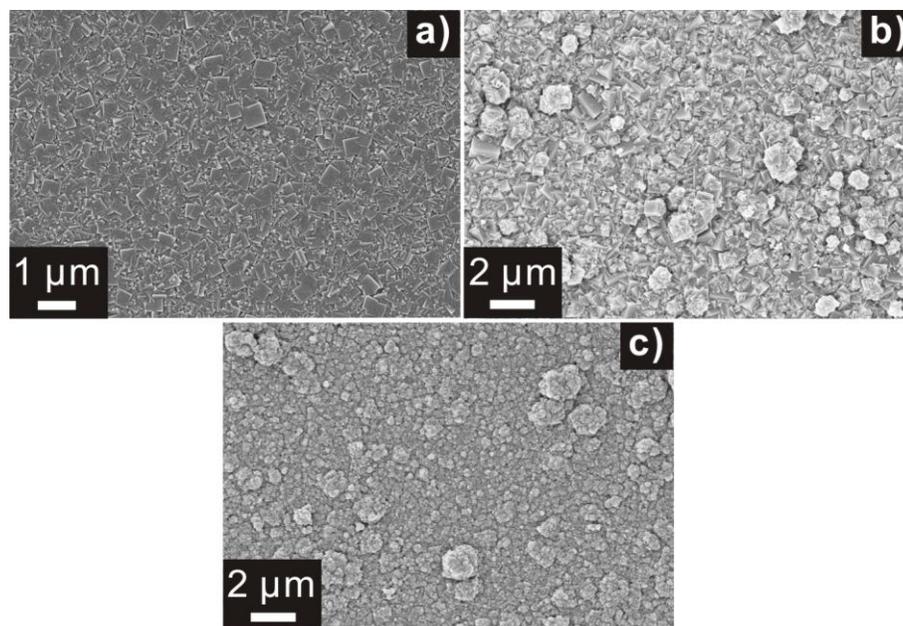


Figure S 8: Scanning electron microscopy images of films of a) $[\text{Zn}_4\text{O}(\text{mecapz})_3]_n$, b) $[\text{Zn}_4\text{O}(\text{mpcapz})_3]_n$, c) $[\text{Zn}_4\text{O}(\text{mipcapz})_3]_n$ (30 cycles on a COOH-functionalized gold substrate).

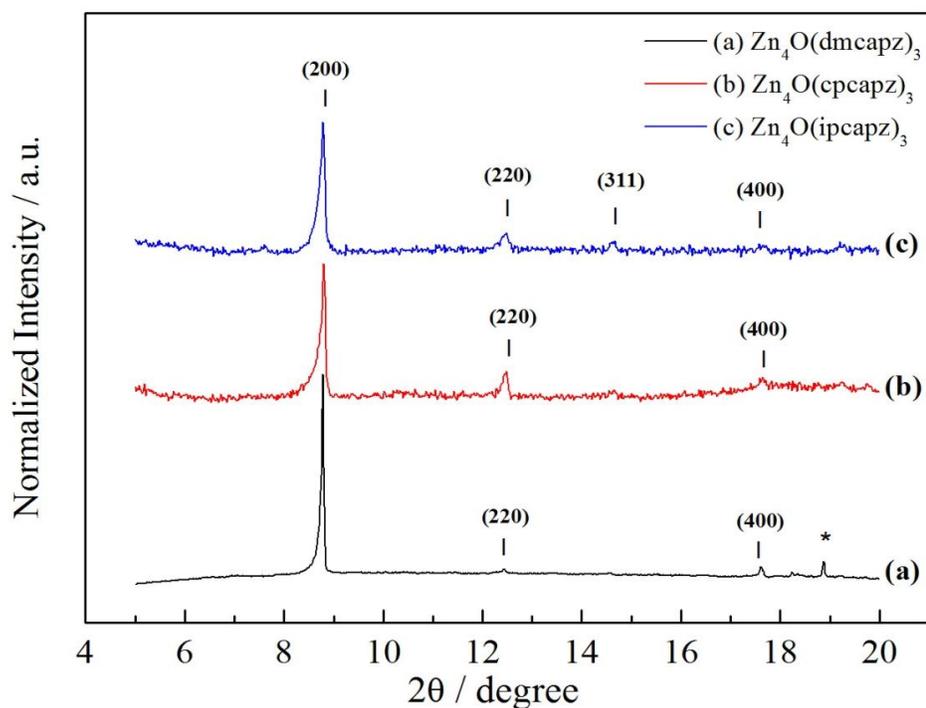


Figure S 9: XRD patterns of the MOF thin films on COOH-functionalized gold substrates obtained after 30 deposition cycles. dm: $R_1=R_2= \text{Me}$; cp: $R_1=\text{H}$, $R_2=\text{cyclopropyl}$; ip: $R_1=\text{H}$, $R_2=\text{isopropyl}$. The asterisk indicates a signal from the substrate.

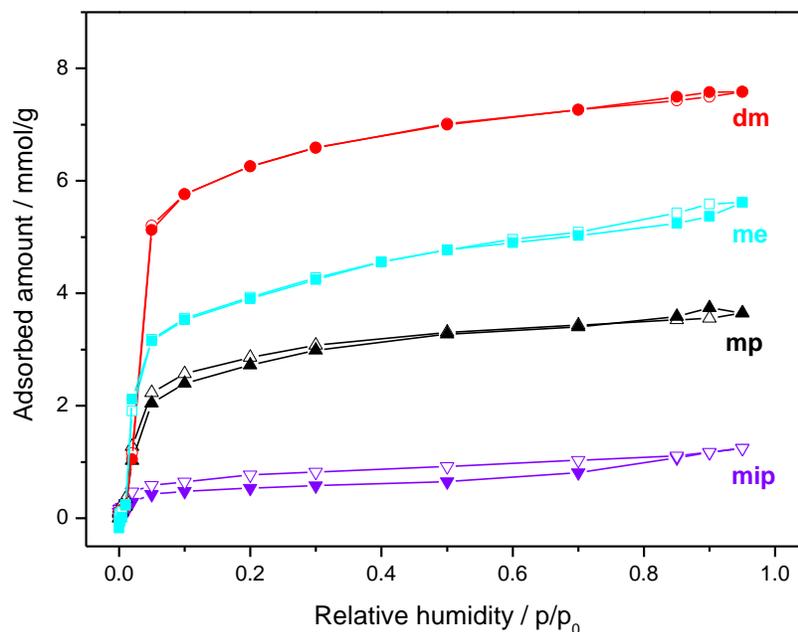


Figure S 10: Methanol adsorption isotherms at 20°C of a series of films (30 cycles on COOH-functionalized gold substrates) with increasing substituent length. dm: $R_1=R_2= \text{Me}$; me: $R_1=\text{Me}$, $R_2=\text{ethyl}$; mp: $R_1=\text{Me}$, $R_2=n\text{-propyl}$; mip: $R_1=\text{Me}$, $R_2=\text{isopropyl}$. Close symbols stand for the adsorption branch, open ones for the desorption branch.

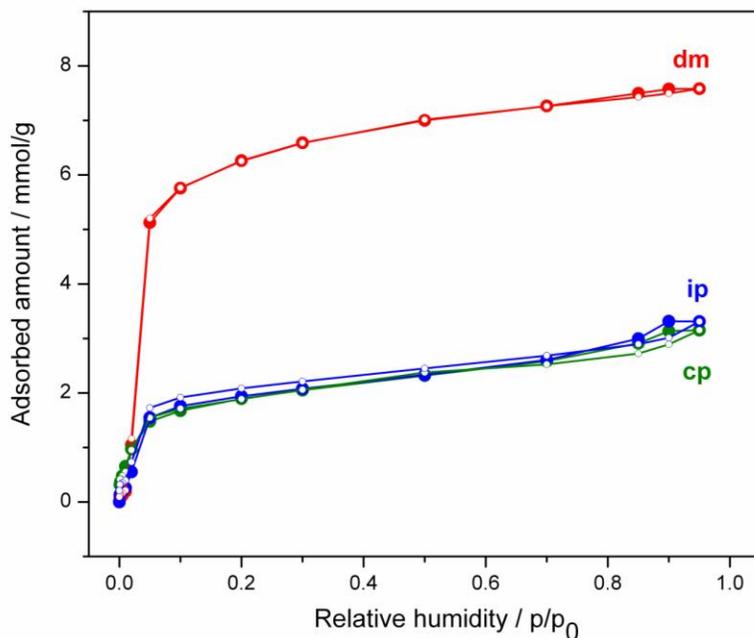
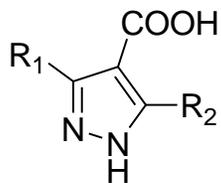


Figure S 11: Methanol adsorption isotherms at 20°C of a series of films (30 cycles on COOH-functionalized gold substrates) with different substituents. dm: $R_1=R_2= \text{Me}$; cp: $R_1=\text{H}$, $R_2=\text{cyclopropyl}$; ip: $R_1=\text{H}$, $R_2=\text{isopropyl}$. Close symbols stand for the adsorption branch, open ones for the desorption branch.

Table S2: Accessible pore volume calculated from methanol isotherms as a function of the substituents on the linker:



R ₁	R ₂	Accessible pore volume (cm ³ /g)
methyl	methyl	0.32
methyl	ethyl	0.23
methyl	n-propyl	0.15
methyl	isopropyl	0.052
H	isopropyl	0.14
H	cyclopropyl	0.13

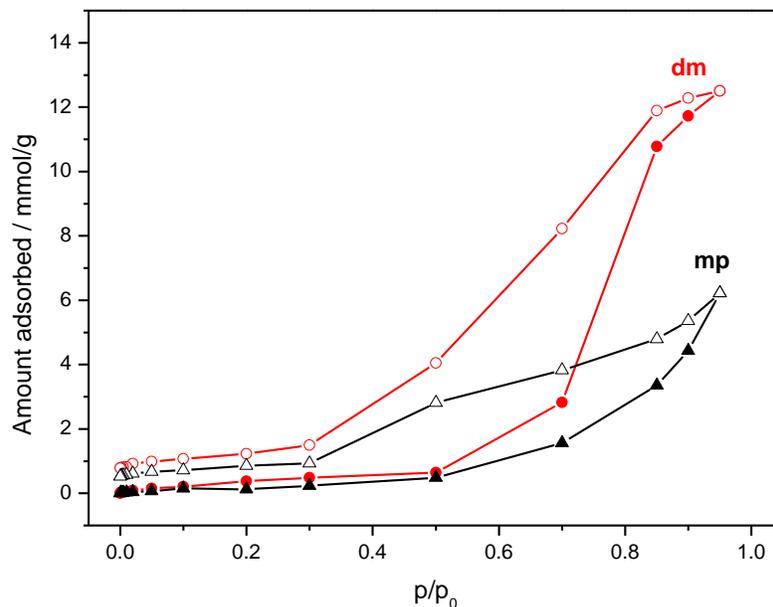


Figure S 12: Water adsorption isotherms at 20°C of two films (30 cycles on COOH-functionalized gold substrates). dm: R₁=R₂= Me; mp: R₁=Me, R₂=*n*-propyl. Close symbols stand for the adsorption branch, open ones for the desorption branch.

References:

1. C. Montoro, F. t. Linares, E. Quartapelle Procopio, I. Senkowska, S. Kaskel, S. Galli, N. Masciocchi, E. Barea and J. A. R. Navarro, *J. Am. Chem. Soc.*, 2011, **133**, 11888.
2. S. Hausdorf, F. Baitalow, T. Böhle, D. Rafaja and F. O. R. L. Mertens, *J. Am. Chem. Soc.*, 2010, **132**, 10978.
3. M. W. Rathke and P. J. Cowan, *J. Org. Chem.*, 1985, **50**, 2622.