Supporting Information

Advanced fabrication method for the preparation of MOF thin films: Liquid-phase epitaxy approach meets spin coating method.

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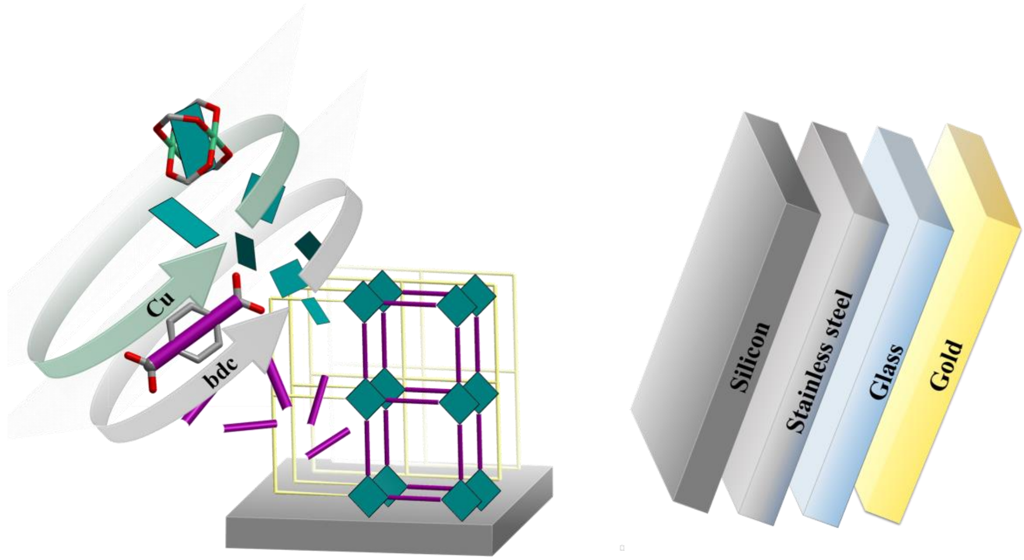
1. $Cu_2(bdc)_2 \cdot x\ H_2O$ SURMOF growth on different substrates

In order to proof the aplicability of the spin coating method for MOF thin film grows the $Cu_2(bdc)_2 \cdot xH_2O$ SURMOF was grown on different substrates including glass, functionalized Au (with –COOH groups), silicon wafer and stainless steel (fig. S1). The 2.5-3 cm in a size supports were first washed with water and ethanol and, then dried at 150°C to remove any contaminants from the surface, and then gold was functionalized with 16-Mercaptohexadecanoic acid (MHDA) as reported elsewhere. [1] These substrates were then placed (one at the time) on a vacuum chuck and subsequently spin coated with 50 µl of a 0.1 mM of $Cu(NO_3)_2 \cdot 6H_2O$ ethanol solution for 5 seconds and then with a 0.1 mM of terephthalic acid solution for 8 seconds at room temperature. Between each step, the substrates were rinsed with 50 µl of solvent for 5 seconds. Spin coating speed used is 500 rpm. Uniform coating was observed with naked eye (Fig. S1); i) the substrates gain blue color corresponding to the MOF coatings, (ii) reflections from the surfaces are despaired after deposition. In total, time spent for growth of 50 cycles of MOF by this method is less than 20 minutes and amount of solvent used is 10 ml. After a given number of cycles, samples were characterized with X-ray diffraction (XRD), results are presented of Fig. S2-S4.

(1)



(2)

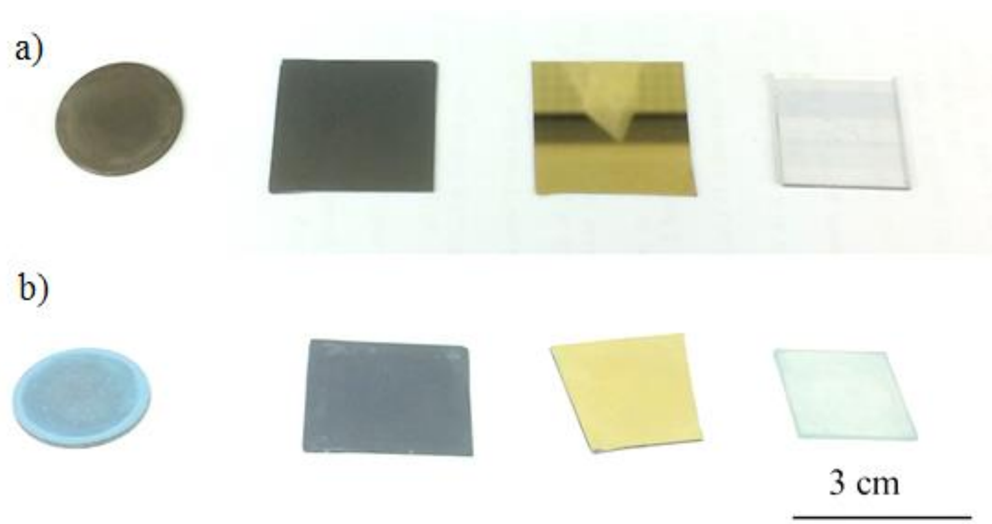


Figure S1. (1) Schematic representation of the $Cu_2(bdc)_2 \bullet xH_2O$ MOF thin film grown on different substrates using the spin coating approach. (2) Optical images of different substrates (stainless steel, silicon wafer, functionalized Au, and glass) before (a) and after (b) $Cu_2(bdc)_2 \bullet xH_2O$ MOF thin film grown on them.

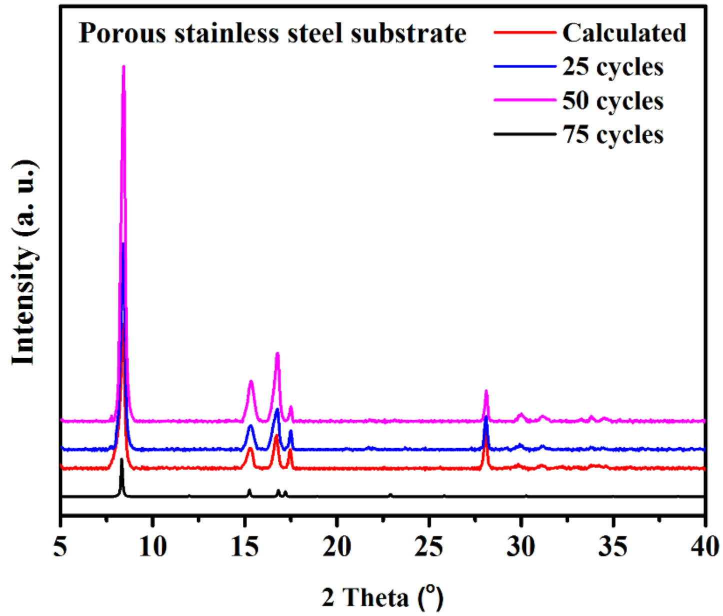


Figure S2. Out-of-plane XRD patterns (background-corrected) of porous stainless steel substrate after different cycles of $Cu_2(bdc)_2 \bullet xH_2O$ SURMOF growth.

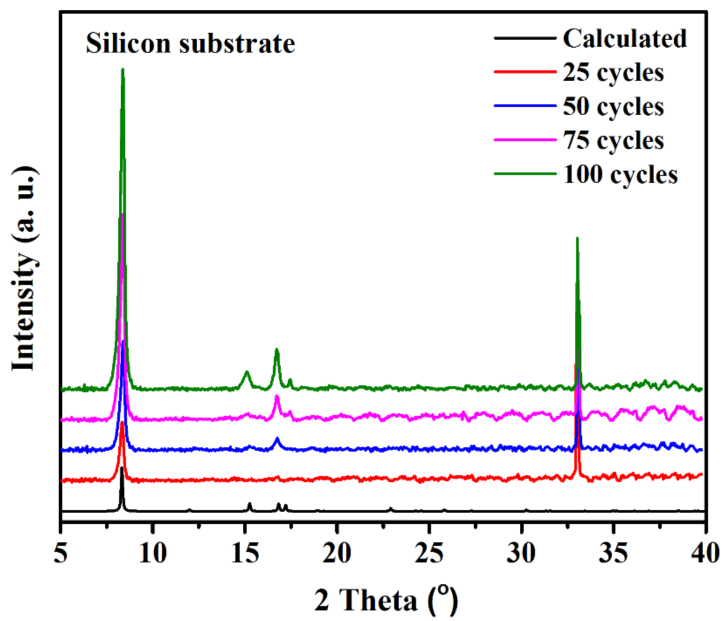


Figure S3. Out-of-plane XRD patterns (background-corrected) of silicon substrate after different cycles of $Cu_2(bdc)_2 \bullet xH_2O$ SURMOF growth.

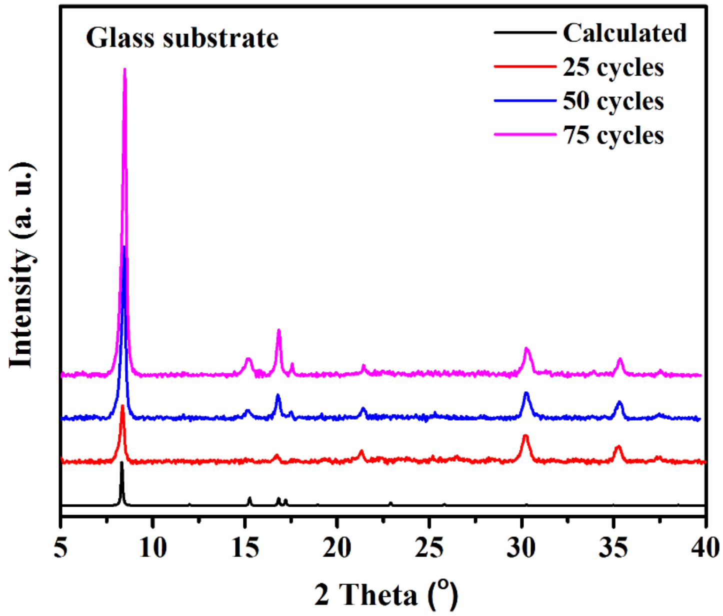


Figure S4. Out-of-plane XRD patterns (background-corrected) on glass substrate and after different cycles of $Cu_2(bdc)_2$•*x* H_2O SURMOF growth.

2. Growth of micrometers thick thin films of different MOFs

2.1 Growth of $Cu_2(bdc)_2 \cdot xH_2O$ MOF on functionalized gold substrate

$Cu_2(bdc)_2 \cdot xH_2O$ SURMOF was grown using the same way as described in section 1. The 1.5 µm thick film wes obtained after 150 cycles. After a given number of cycles, the sample was characterized with XRD and SEM. Results are shown on fig. S5 and fig. S6.

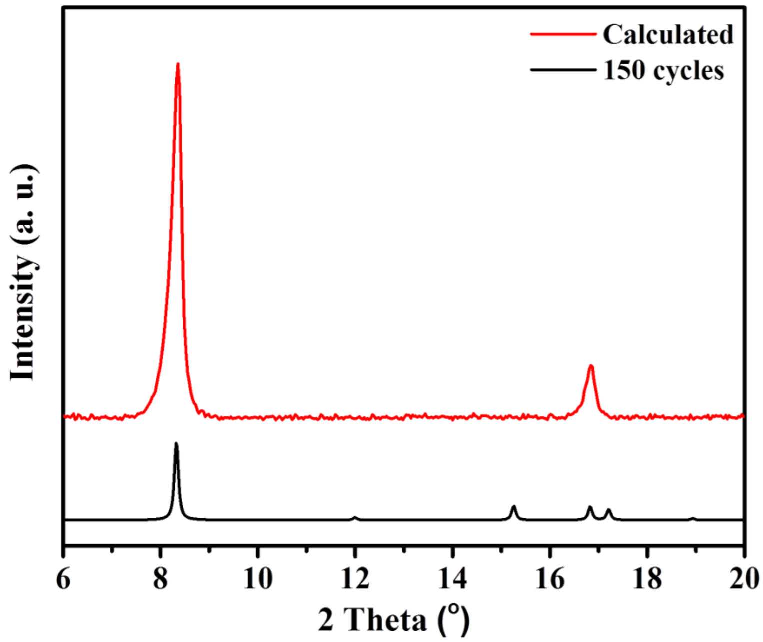


Figure S5. Out-of-plane XRD pattern (background-corrected) of $Cu_2(bdc)_2 \cdot xH_2O$ SURMOF grown on a gold substrate functionalized with -COOH groups.

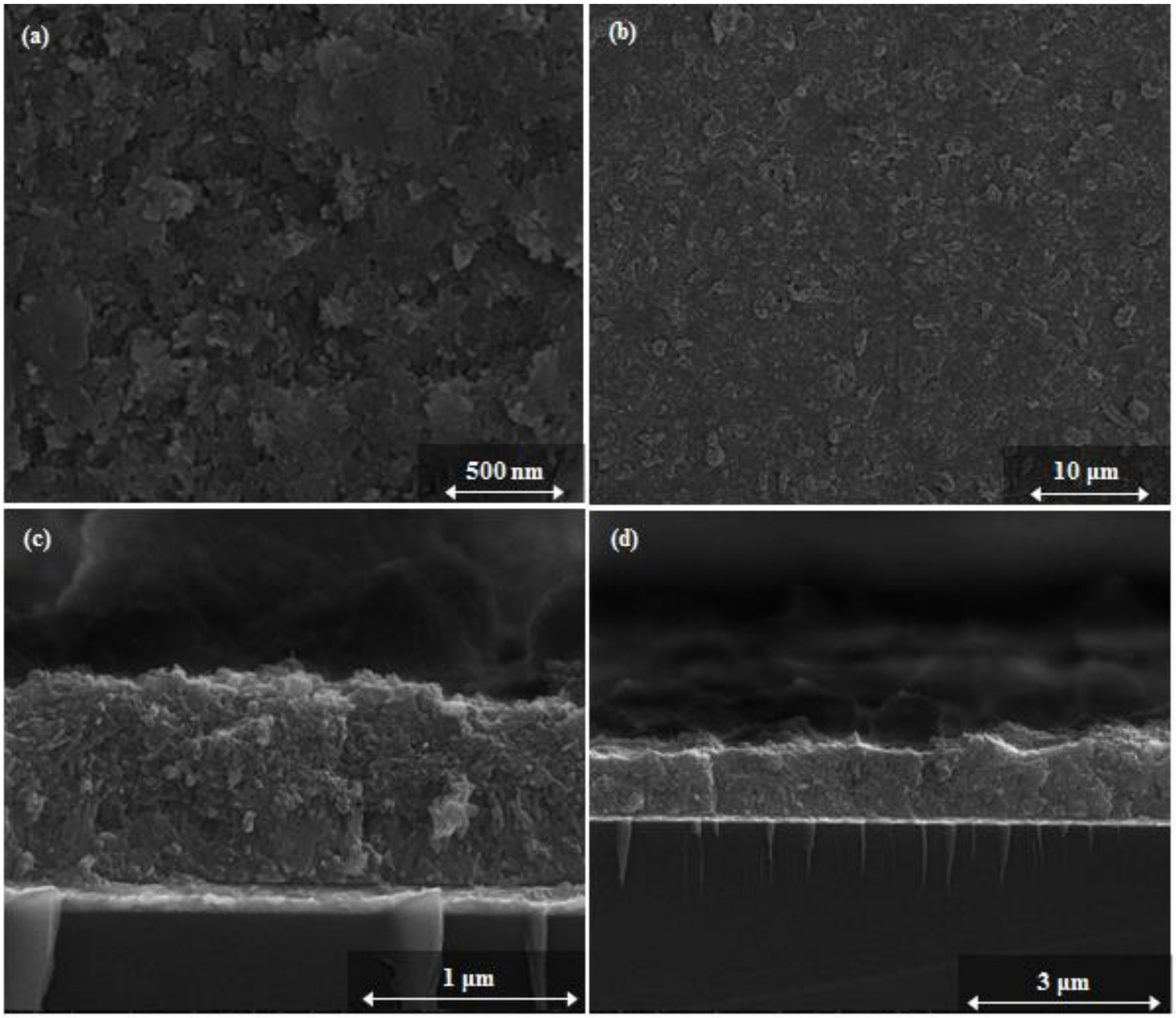


Figure S6. (a,b) Top-view and (c,d) cross-section SEM images of $Cu_2(bdc)_2$•*x* H_2O SURMOF grown on a gold substrate functionalized with -COOH groups with different magnification(150 cycles).

2.2 Growth of $Zn_2(bdc)_2.xH_2O$ MOF on functionalized gold support

$Zn_2(bdc)_2•xH_2O$ SURMOF was grown using the same way as described in section 1, ethanol solution of $Zn(CH_3COO)_2.6H_2O$ were used instead of $Cu(NO_3)_2.6H_2O$. 3 μm film was obtained after 200 cycles. After a given number of cycles, the sample was characterized with XRD and SEM, which are shown in Fig.S7 and Fig.S8.

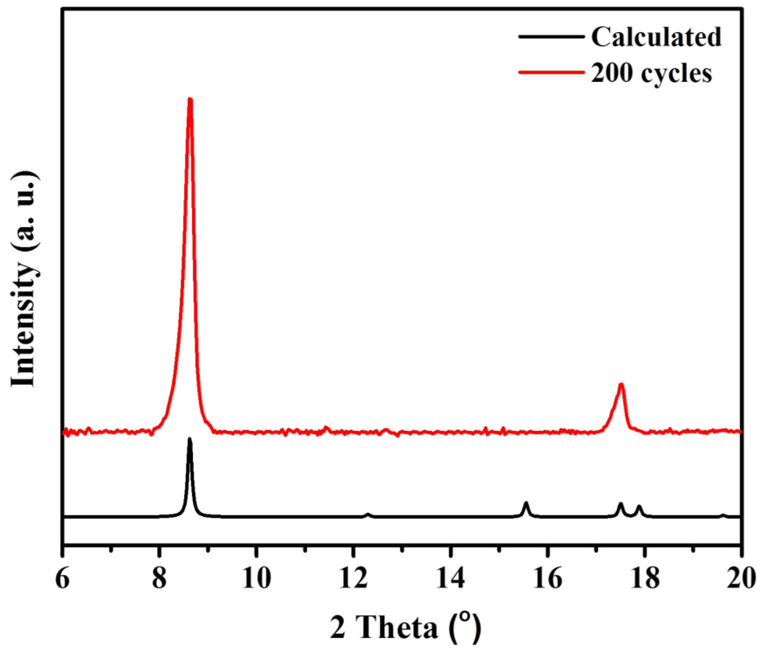


Figure S7. Out-of-plane XRD pattern (background-corrected) of $Zn_2(bdc)_2•xH_2O$ SURMOF grown on a gold substrate functionalized with -COOH groups.

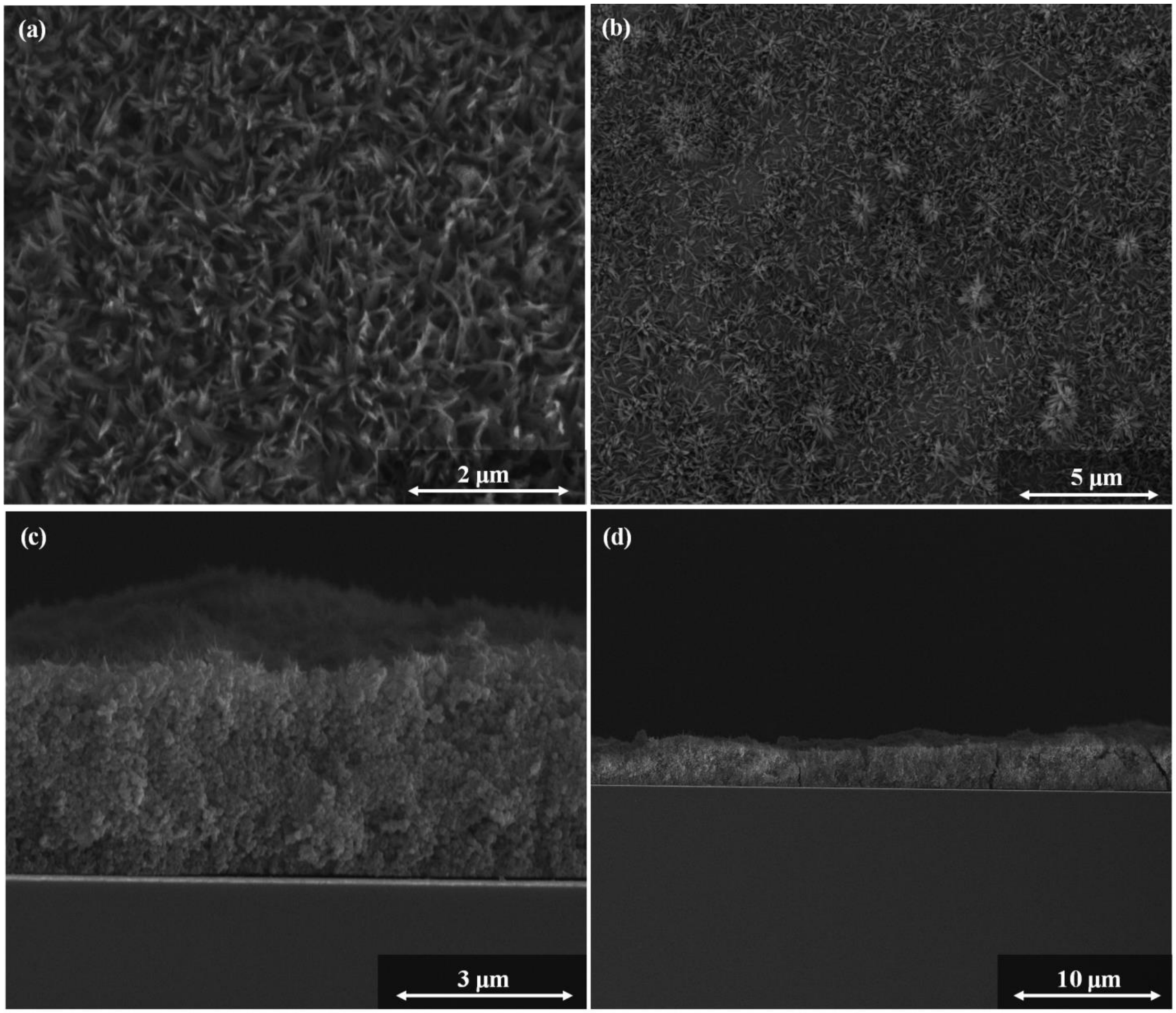


Figure S8. (a,b) Top-view and (c,d) cross-section SEM images of $Zn_2(bdc)_2 \cdot xH_2O$ SURMOF grown on a gold substrate functionalized with -COOH groups with different magnification (200 cycles).

2.3 Growth of ZIF-8 MOF on alumina oxide

The ZIF-8 MOF was grown on highly porous Al_2O_3 substrate (Cobra Technologies BV). The substrate was first washed with water and ethanol, and then dried at 150°C to remove any contaminants from the surface. This substrate was then placed on a vacuum chuck and subsequently spin coated with 50 µl of a 0.2 mM of $Zn(NO_3)_2•6H_2O$ methanol solution for 5 seconds and then with a 0.4 mM of 2-methylimidazole solution for 8 seconds at room temperature. Between each step the substrates were washed with solvent 50 µl for 5 seconds. The spin coating speed was 500 rpm. After a given number of cycles, the samples were characterized with XRD and Scanning electron microscope (SEM). In total, time spent for synthesis of 200 cycles of MOF by this method is less than 80 minutes and amount of solvent used is 40 ml. In a typical procedure for layer-by-layer growth of ZIF-8 by dip coating, [2] the thickness of ~2.5 µm membrane were achieved after 300 cycles, which took 25 hours (the speed is 5 min/cycle).

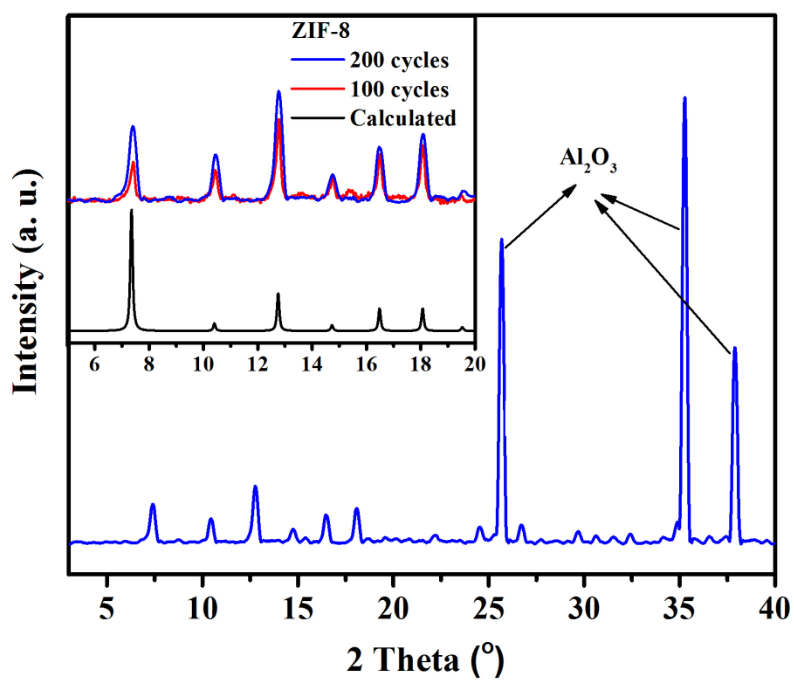


Figure S9. Out-of-plane XRD patterns (background-corrected) of ZIF-8 MOF membrane grown on an alumina substrate after different cycles.

2.4 Growth of HKUST-1 MOF on alumina oxide

The HKUST-1 MOF was grown on highly porous Al_2O_3 substrate (Cobra Technologies BV). The substrate prepared in the same way as described for ZIF-8 MOF membrane. The substrate was then placed on a vacuum chuck and subsequently spin coated with 50 μl of a 1.5 mM of $Cu_2(CH_3COO)_4{\cdot}H_2O$ ethanol solution for 5 seconds and then with a 3 mM of trimesic acid solution for 10 seconds at room temperature. Between each step, the substrates were washed with solvent 50 μl for 10 seconds. The spin coating speed was 500 rpm. After a given number of cycles, the samples were characterized with XRD and SEM. Results are presented of fig. S10 and fig. S11. 3 μm film were obtained after 150 cycles. Note that thickness depends also on the concentration precursors used for the synthesis.

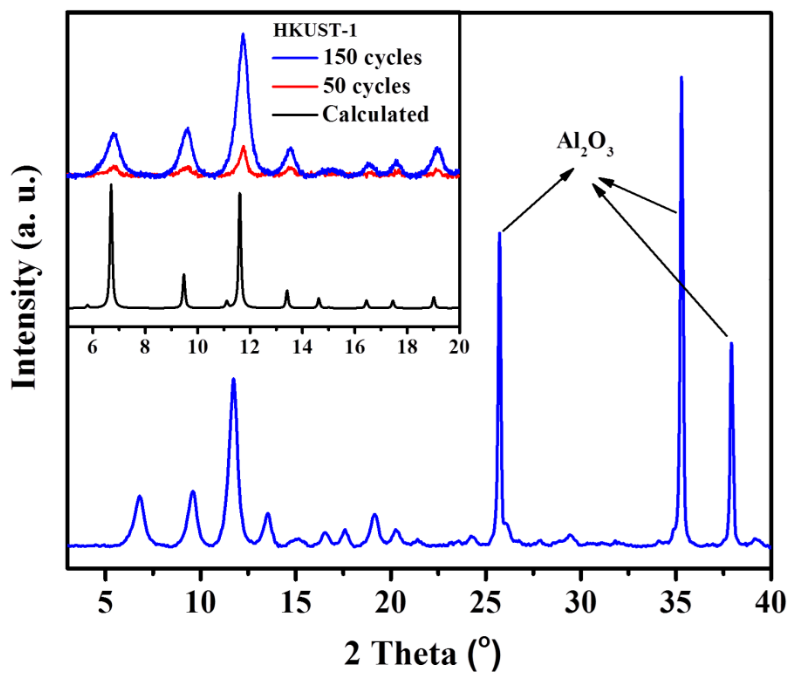


Figure S10. Out-of-plane XRD pattern (background-corrected) of an HKUST-1 MOF thin film grown on an alumina substrate after different cycles.

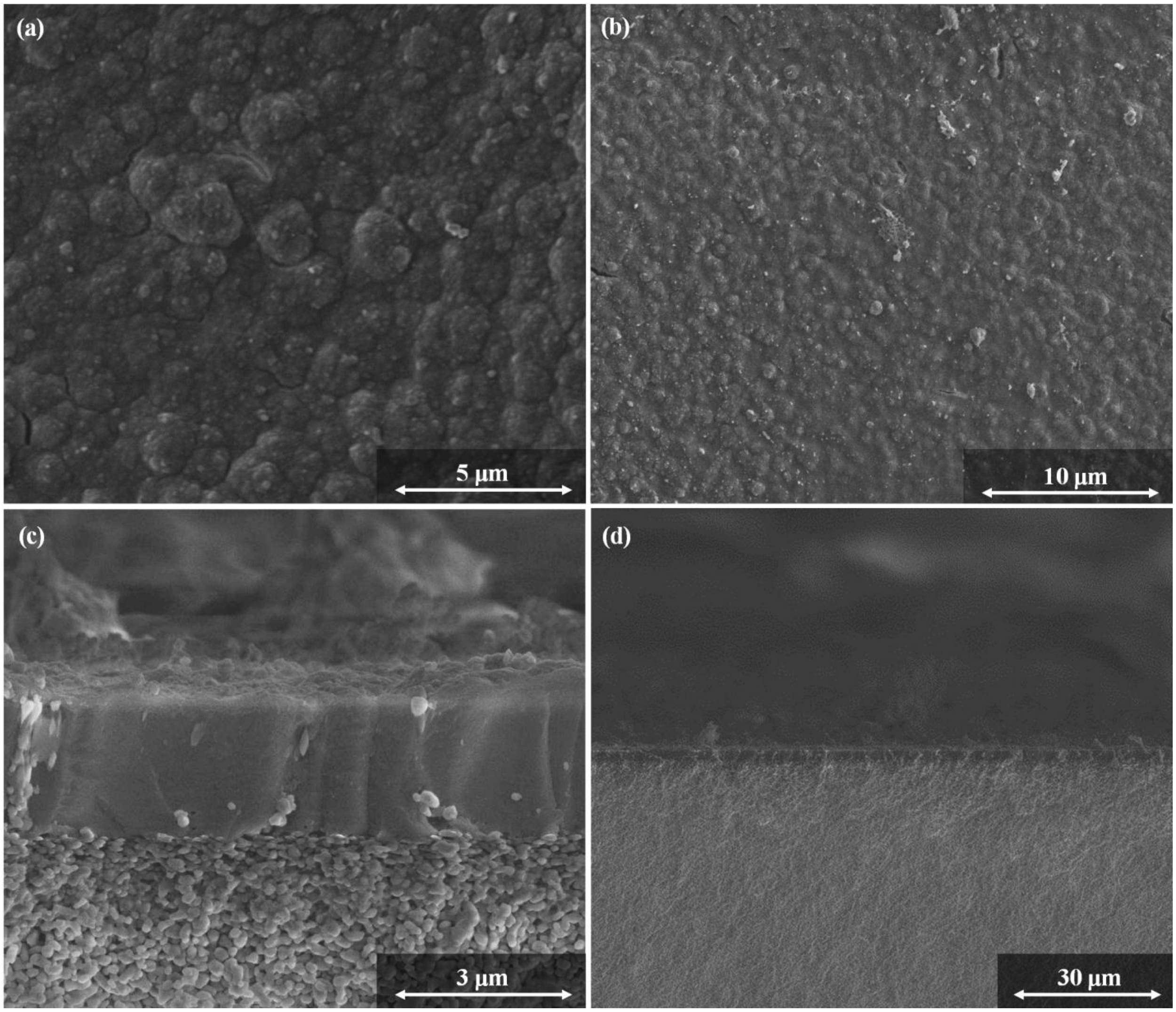


Figure S11. (a,b) Top-view and (c,d) cross-section SEM images of HKUST-1 grown on a Al_2O_3 substrate with different magnification.

3. Spin coating

The spin coating experiments were done on the "Laurell WS-650Mz-8NPPB- UD-3-UD-3b(x3) all four with μL Dispense" spin coater. PC controls switching "off and on" of four dispensers, time and rotation speed. Complex procedures can be programmed and the pressure in the syringe, time of dispersion and the size of the needle define the amount and speed of reagent added.

4. Mixed-gas permeation measurements.

Variable pressure-continuous permeate composition analysis technique using mass spectrometry: The VP-continuous permeate composition analysis technique developed in our group is a sample method used to test membrane in almost close conditions to application. [2] The permeate gas composition is monitored continuously until the occurrence of the stead state. In a typical experiment for ZIF-8 membrane, helium is supplied upstream while monitoring the gas composition in the permeate side. The helium flux during this preparation step was maintained to 5-10 cc/min until the establishment of the baseline (only presence of helium). Then, the binary gas mixture with composition a_{up}, b_{up} of interest is applied upstream with a maintained flux at 40-50 cc/min while monitoring the composition of the permeate downstream composition adown, b_{down}. The system was considered in a steady state when no change in the signal of the MS is observed. The permeselectivity was calculated using the following equation:

$$\alpha = \frac{a_{up}/b_{up}}{a_{down}/b_{down}}$$

5. References

(1) Shekhah, O.; Roques, N.; Mugnaini, V.; Munuera, C.; Ocal, C.; Veciana, J.; Wöll C. Grafting of Monocarboxylic Substituted Polychlorotriphenylmethyl Radicals onto a COOH-Functionalized Self-assembled Monolayer Through Copper (II) Metal Ions. *Langmuir* **2008**, *24*, 6640-6648.

(2) Shekhah, O.; Swaidan, R.; Belmabkhout, Y.; du Plessis, M.; Jacobs, T.; Barbour, L. J.; Pinnau, I.; Eddaoudi. M. The Liquid Phase Epitaxy Approach for the Successful Construction of Ultra-thin and Defect-free ZIF-8 Membranes: Pure and Mixed Gas Transport Study. *Chem. Comm*. **2014**, *17,* 2089-2092.