Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting information

Liquid phase epitaxial growth of heterostructured hierarchical MOF thin films

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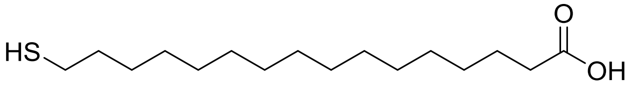
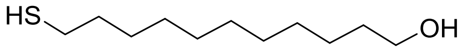
1. Materials and instrumentation

Starting materials: All starting materials for synthesis were purchased commercially and were used without further purification.

Self-Assembled Monolayers (SAM):



MHDA (16-Mercaptohexadecanoic acid)



MUD (11-Mercapto-1-undecanol)

SAM were purchased from Sigma Aldrich and used without further purifications.

Powder X-ray diffraction (PXRD) measurements were carried out at room temperature on a PANalytical X'Pert PRO diffractometer operating at 45kV, 40mA for CuKα (λ = 1.5418 Å). The data was recorded with a scan speed of 1.0° min^{-1} and a step size of 0.01° in the 2θ range of 4–40 degree.

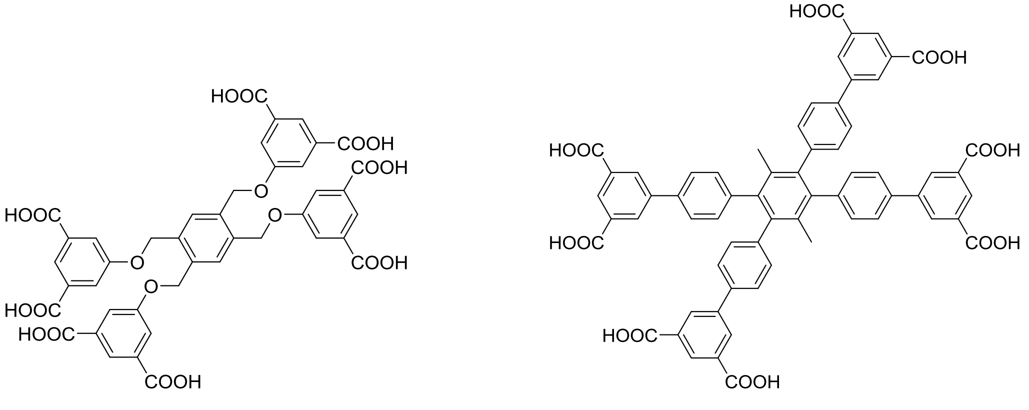
Scanning electron microscope (SEM) Quanta 600 was used to acquire top and cross-section SEM images of MOF-on-MOF films.

Quartz Crystal Microbalance (QCM) Q-Sense Inc. was used in this study. The instrument has a fundamental resonance frequency of 5 MHz, runs in pulsed mode and can measure up to seven different harmonics and their corresponding dissipation factors. The isothermal conditions in the Q-Sense system are achieved using Peltier temperature control cells (±0.02°C). QCM measurements were performed on a LabView-controlled system. The electrodes were purchased.

Fourier-transform infrared (FT-IR) spectra (4000–600 cm^{-1}) were collected in the solid state on a Nicolet 700 FT-IR spectrometer.

LbL robot: all MOF layer by layer films were prepared using a robotic dipping machine - nanoStrata StratoSequence IV.

2. Synthesis of the ligands



H_8L1 H_8L2

Fig. S1. Chemical structure of the ligands used in synthesis of **tbo-MOF-2** and **tbo-MOF-5**

Ligands were synthesized following previously reported procedures: H_8L1[1] and H_8L2[2]

(H_8L1): 5,5',5'',5'''-[1,2,4,5-phenyltetramethoxy] tetraisophthalate[1]

In a typical reaction, (12.7 g, 0.06 mol) of dimethyl 5-hydroxyisophthalate was dissolved in DMF (250 mL). A catalytic amount of KI (74.0 mg, 4.40 mol) was added to the solution followed by K_2CO_3 (26.0 g, 0.260 mol). The solution was then heated to 100°C for 1 hour. 1,2,4,5-tetrakis(bromomethyl)benzene (2.88 g, 0.008 mol) was dissolved in DMF (10 mL), added dropwise to the mixture and heated at 100°C for an additional hour and then cooled to room temperature. Approximately 800mL of water was added to the solution to produce a white precipitate which was filtered, washed thoroughly with ice cold water and air-dried (6.0 g, 96.9%). In a typical hydrolysis reaction, the tetramethyl ester was added to a round bottom flask containing methanol (250 mL). An aqueous NaOH solution (6 g in 60 mL H_2O) was added to this mixture and then refluxed at 50°C/12h. The solution was acidified to pH = 1 using concentrated HCl (15N). The precipitate was separated by filtration, washed with cold H_2O and air-dried. Yield = 5 g (91.4%).

Note: No further purification is required.

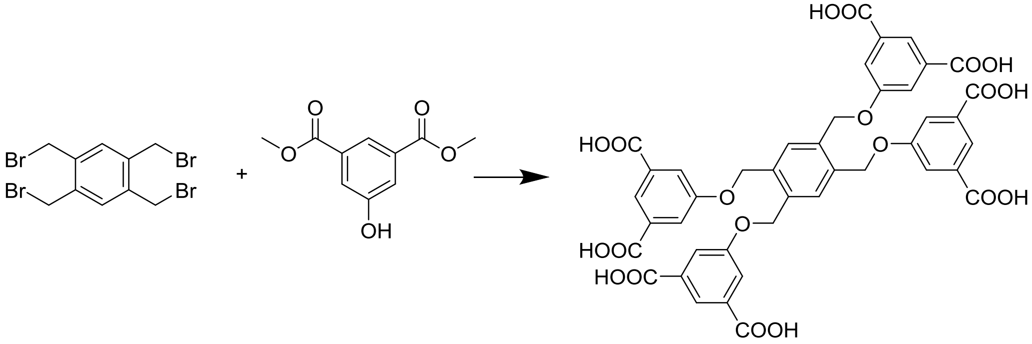


Fig. S2. Scheme of the synthesis of **tbo**-MOF-2 ligand

(H_8L2): 1,2,4,5-tetrakis [4 - (3',5'-dicarboxy-1,1'-biphenyl)] - 3,6 dimethylbenzene[2]

Compound (1): A stirred mixture of the dimer of 2,5-dimethyl-3,4-diphenylcyclopentadienone (2.00 g, 3.84 mmol) and diphenylacetylene (2.05 g, 11.5 mmol) in diphenyl ether (5 mL) was heated under reflux for 2 h. During this time, the mixture turned deep red and then faded to orange. Slow cooling yielded crystals after 24 h, which were collected by filtration and washed with hexane, giving 1,4-dimethyl-2,3,5,6-tetraphenylbenzene (2.54 g, 6.19 mmol, 81%) as a colorless solid. ^1H NMR (300 MHz, $CDCl_3$): 7.13 (m, 8H), 7.05 (m, 12H), 1.80 (s, 6H).

In a 25 mL round bottom flask 590 mg (1.44 mmol) of 1,4-dimethyl-2,3,5,6-tetraphenylbenzene was treated with 4 mL of neat Br_2 and the mixture was stirred at room temperature for 50 min. Then chilled ethanol (-20°C) was added and the flask was kept at -20°C for 16 h. The mixture was filtered and washed with chilled ethanol. Yield = 954 mg (91%), ^1H NMR (300 MHz, $CDCl_3$): 7.34 (d, J = 8.5 Hz, 8H), 6.90 (d, J = 8.5 Hz, 8H), 1.76 (s, 6H).

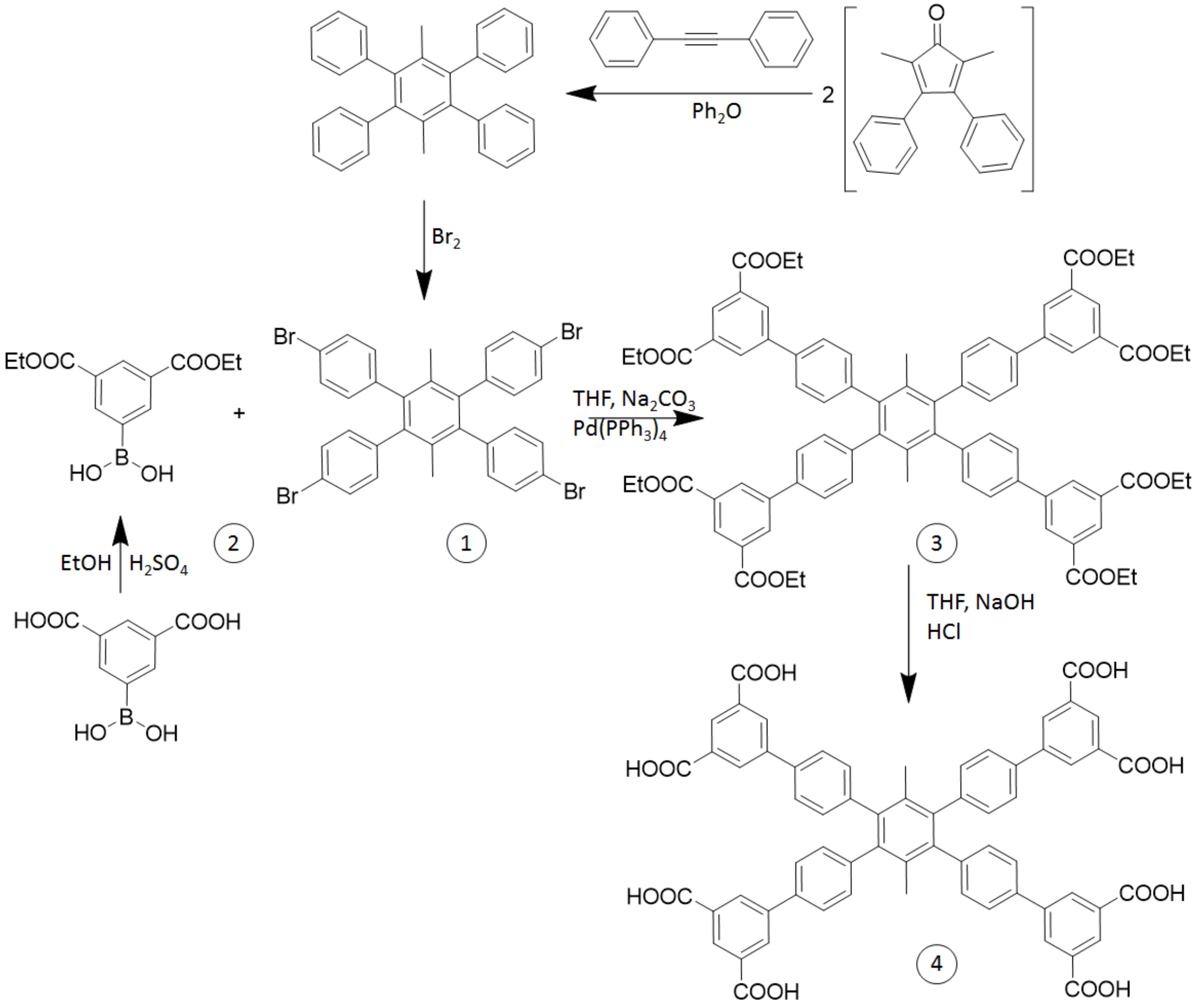


Fig. S3. Scheme of the synthesis of **tbo**-MOF-5 ligand

Compound (2). In a 50 mL round bottom flask, 20 mL EtOH, 0.4 g (1.905 mmol) 3,5-dicarboxyphenyl boronic acid and 0.4 mL c.H_2SO_4 were mixed, and the mixture was heated at 85^{o}C for 13 h. The solvent was removed under vacuum and the white solid was filtered and washed with water. Yield = 0.4 g (80%), ^{1}H NMR (500 MHz, DMSO-d_6): 8.63 (d, J = 1.5 Hz, 2H), 8.52 (br.s, 2H), 8.50 (t, J = 1.5 Hz, 1H), 4.36 (q, J = 7 Hz, 2H), 1.35 (t, J = 7 Hz, 3H). SSI-MS m/z $[M-H]^-$: 265.1.

Compounds (3) and (4). A 100 mL double neck round bottom flask was dried using a heat gun under nitrogen flow. Then 45 mL of dry THF, 0.9 g (1.24 mmol) of the bromide, 1.62 g (6.2 mmol) of boronic ester and 25 mL Na_2CO_3 2M were added and finally the catalyst, 85 mg (0.073 mmol) of $Pd(PPh_3)_4$, was added under nitrogen flow. The system was sealed with a balloon filled with nitrogen and refluxed at 85^{o}C for 7 days. Then the reaction mixture was extracted many times with THF and the THF was then removed under reduced pressure. To the resulting solid was added 20 mL MeOH, 20 mL NaOH 5 N and 20 mL THF. The mixture was refluxed at 85^{o}C overnight. The solvents were removed under reduced pressure. To the remaining reddish solid 15 mL HCl 3N was added. The solid was filtered and washed with water. Yield = 1.3 g (98%), ^{1}H NMR (500 MHz, DMSO-d_6): 13.31 (br.s 8H), 8.39 (s, 4H), 8.30 (s, 8H), 7.63 (d, J = 8 Hz, 8H), 7.32 (d, J = 8 Hz, 8H), 1.80 (s, 6H).

3. Cell parameters for tbo-MOF structures

The supermolecular building layer (SBL) pillaring strategy was used for **tbo** MOFs expansion. Following the SBL approach, substitution of the organic-inorganic pillar in HKUST-1 with H_8L1 and H_8L2 allowed construction of **tbo**-MOF-2 and **tbo**-MOF-5. The matching of (a x b) cell parameters in HKUST-1, **tbo**-MOF-2 and **tbo-**MOF-5 suggests the possibility to grow MOF-on-MOF heterostructural films.

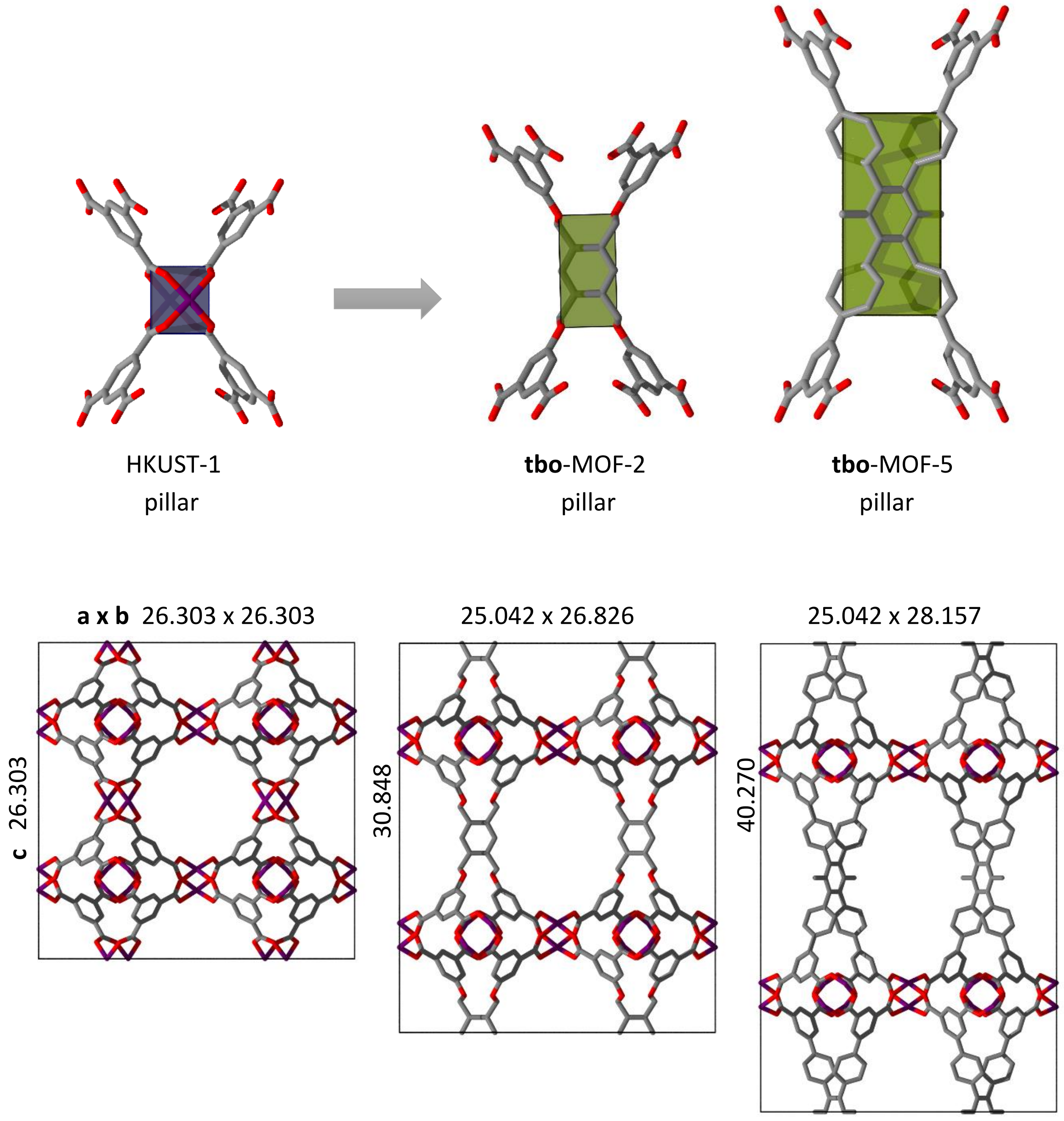


Fig. S4. Pillar expansion to access **tbo**-MOF-2 and **tbo**-MOF-5 structures and unit cell dimensions of original HKUST-1 MOF and expanded **tbo**-MOF-2 and **tbo**-MOF-5

4. MOF-on-MOF heteroepitaxial growth strategy

In order to obtain heterostructural MOF films, a denser structure was chosen as a first layer to provide better support and to navigate an orientated growth of a second MOF layer.

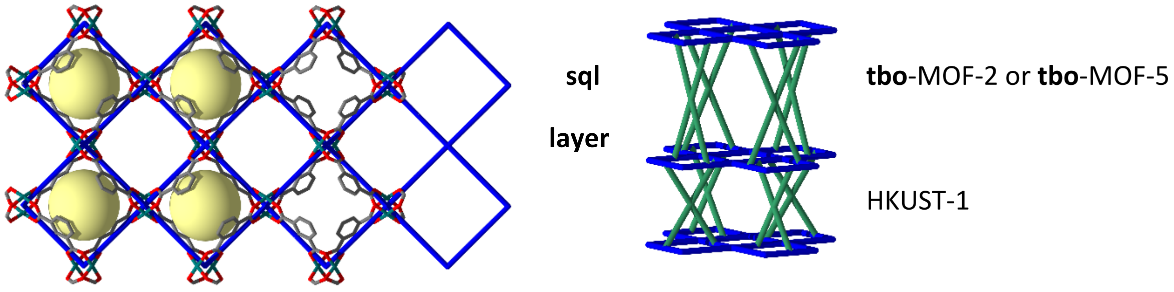


Fig. S5. Simplified view of **sql** layer and its pillaring in **tbo** structures

5. Layer by Layer tbo-MOF-2 on HKUST-1 growth

HKUST-1 oriented along [001] direction: MOF layer by layer films were prepared using a robotic dipping machine (nanoStrata StratoSequence IV). In a typical synthesis, the 0.7 x 0.7 cm sized gold substrates (200-nm Au/2-nm Ti evaporated on Si wafers) were first washed with water and ethanol, then dried at 150°C to remove any contaminants from the surface and then were functionalized with 16-Mercaptohexadecanoic acid (MHDA) as reported elsewhere[3]. The freshly-prepared substrates were then immersed subsequently in 100 ml of 0.25 mM of copper(II) acetate solution for 3 minutes, then soaked in 100 ml of ethanol for washing, then immersed in 100ml of 0.5 mM H_3BTC (1,*3*,5-benzenetricarboxylic acid) ethanol solution for 5 min and again soaked in 100 ml of ethanol for washing at room temperature. Copper(II) acetate – Ethanol - H_3BTC – Ethanol is considered as one cycle. This cycle was repeated until 100 layers were deposited. Note: to get better-quality, oriented film, copper(II) acetate and H_3BTC ethanolic solutions were heated in the oven at 85°C. Thus the first several layers, which dictate further orientation, were perfectly deposited. After 100 cycles, the sample was dried in air and PXRD was measured.

tbo**-MOF-2 growth on top of HKUST-1:** Many attempts were undertaken in order to obtain the second oriented layer of **tbo**-MOF-2 on top of first layer of HKUST-1 (varying concentration, solvents, metal precursor, time and temperature of LbL). However, attempts were unsuccessful, probably due to the flexibility of the ligand and possibility of all 8 carboxylic acids to coordinate to the metal **sql** layer.

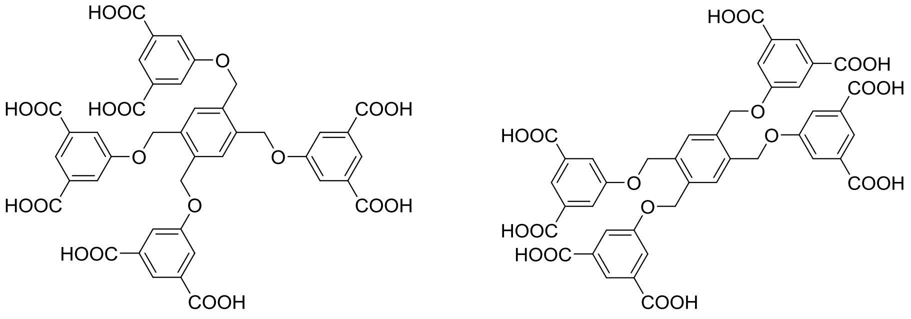


Fig. S6. Flexibility of H_8L2 ligand, two possible conformations as an example

6. Layer by Layer tbo-MOF-5 on HKUST-1 growth along [001] direction

HKUST-1 oriented along [001] direction: 100 layers of HKUST-1 were deposited on MHDA functionalized gold support as described in (5).

tbo**-MOF-5 growth on top of HKUST-1:** A more rigid H_8L2 ligand was chosen in order to avoid flexibility problems associated with the H_8L1 pillar. Freshly prepared HKUST-1 [001] film was immersed subsequently in 100 ml of 0.5 mM of copper(II) acetate solution for 5 minutes, then soaked in 100 ml of ethanol for washing, then immersed in 100ml of 0.25 mM H_8L ethanol solution (with addition of the same mole amount (as H_8L) of pyridine for better solubility of the ligand) for 10 min and again soaked in 100 ml of ethanol for washing at room temperature. Copper(II) acetate – Ethanol – H_8L2 – Ethanol is considered as one cycle. This cycle was repeated until 100 layers were deposited. After 100 cycles gold was dried and XRD patterns and SEM images were collected. No boundaries between two MOFs were seen.

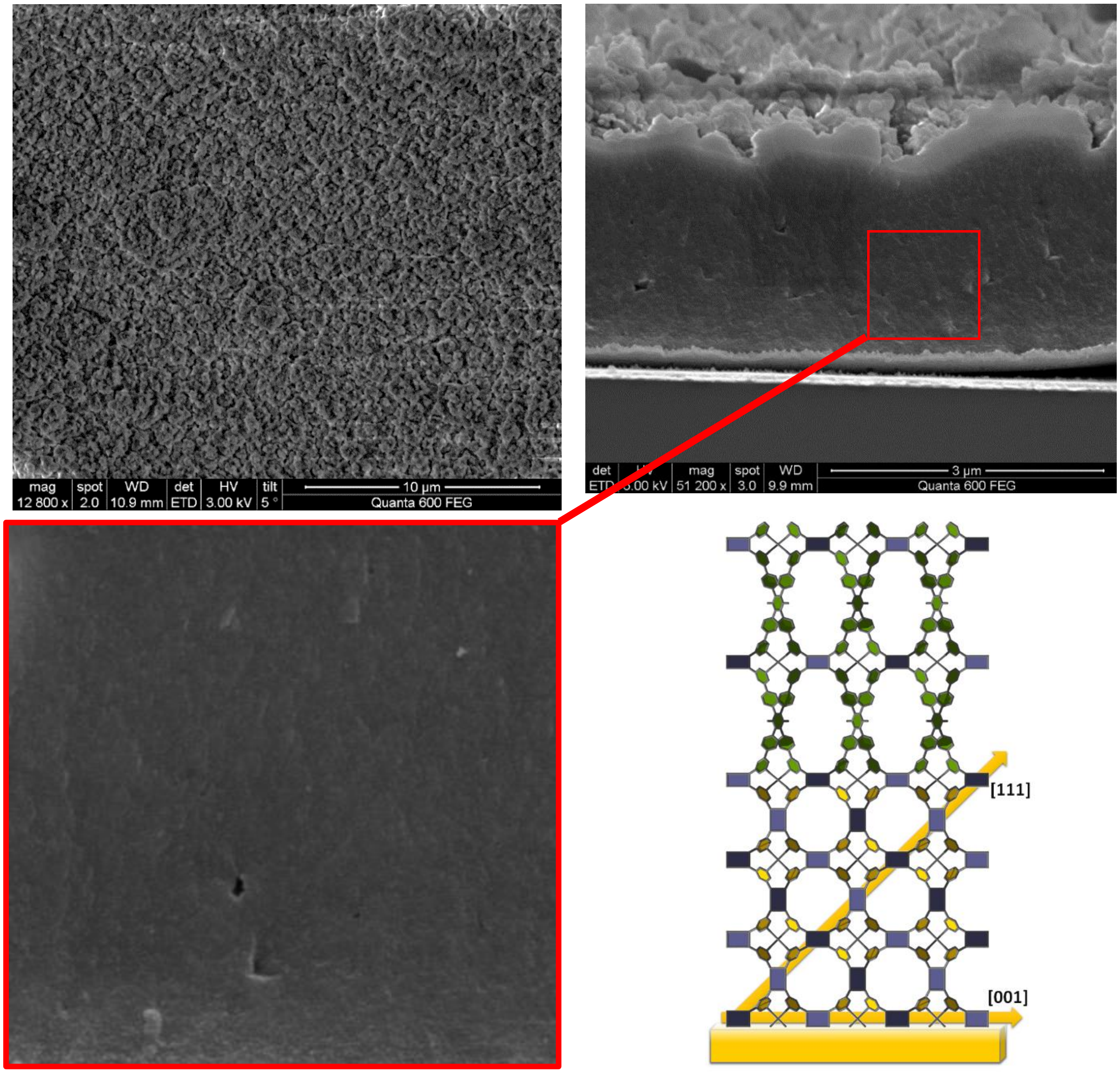


Fig. S7. Top and cross section SEM images of **tbo**-MOF-5 grown on top of HKUST-1 oriented along [001] direction. Schematic illustration of possible growth in a molecular level

7. Layer by Layer tbo-MOF-5 on HKUST-1 growth along [111] direction

HKUST-1 oriented along [111] direction: 100 layers of HKUST-1 were deposited on functionalized gold support as described in (5), except that instead of MHDA SAM, MUD SAM was used.

tbo**-MOF-5 growth on top of HKUST-1:** 100 layers of **tbo**-MOF-5 were deposited on top of HKUST-1 as described in (6). After 100 cycles, the sample was dried in air and XRD patterns and SEM images were collected. No noticeable boundaries between the two MOFs were seen, however there is a noticeable difference between heterostructures oriented along [001] and [111] direction in terms of roughness of the film, which can be explained by the lack of possibility to grow **tbo**-MOF-5 oriented along [111] due to the mismatch of cell parameters between HKUST-1 and **tbo**-MOF-5 along [111] direction.

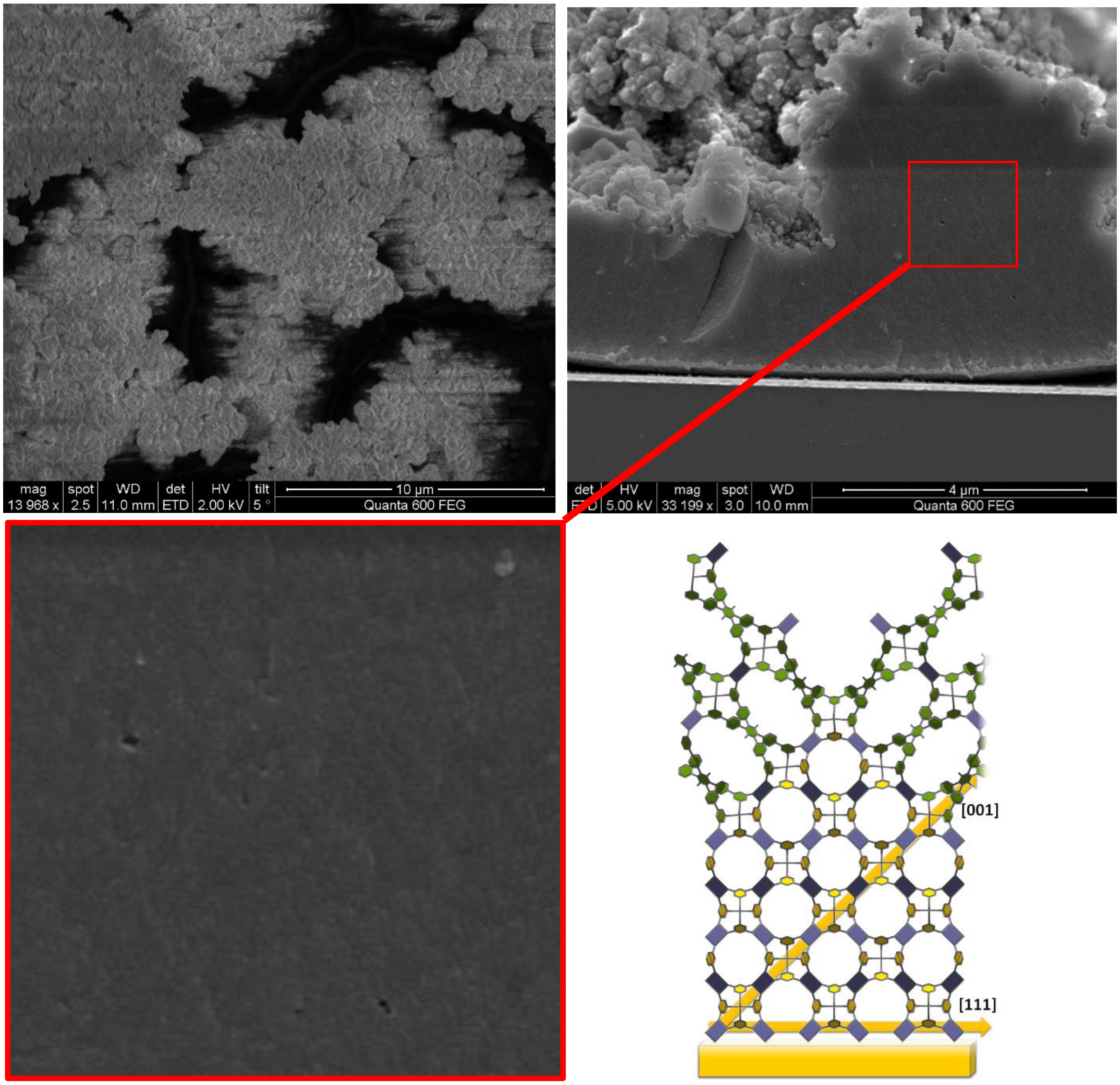


Fig. S8. Top and cross section SEM images of **tbo**-MOF-5 grown on top of HKUST-1 oriented along [111] direction. Schematic illustration of possible growth in a molecular level

8. References

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3. O. Shekhah, H. Wang, S. Kowarik, F. Schreiber, M. Paulus, M. Tolan, C. Sternemann, F. Evers, D. Zacher, R. A. Fischer and C. Woll, *Journal of the American Chemical Society*, 2007, **129**, 15118.