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Porphyrin based metal-organic framework films: nucleation and growth

Zhenyu Zhou,[a] Soumya Mukherjee,[a] Julien Warnan,[a] Weijin Li,*[a] Suttipong Wannapaiboon,[b] Shujin Hou,[c] Katia Rodewald,[d] Bernhard Rieger,[d] Peter G. Weidler,[e] Christof Wöll,[e] Roland A. Fischer*[a]

[a] *Chair of Inorganic and Metal-organic Chemistry, Catalysis Research Center, Ernst-Otto-Fischer Straße 1 and Department of Chemistry, Technical University of Munich, Lichtenbergstraße 4, 85748 Garching b. München, Germany*

[b] *Synchrotron Light Research Institute (Public Organization), Nakhon Ratchasima 30000, Thailand*

[c] *Physics of Energy Conversion and Storage, Department of Physics, James-Franck-Straße 1 and Catalysis Research Center, Otto-Fischer Straße 1, 85748, Garching b. München, Germany*

[d] *Wacker-Chair of Macromolecular Chemistry, Catalysis Research Center, Ernst-Otto-Fischer Straße 1 and Department of Chemistry, Technical University of Munich, Lichtenbergstraße 4, 85747 Garching b. München, Germany*

[e] *Institut für Funktionelle Grenzflächen, IFG, Karlsruher Institut für Technologie (KIT), 76021 Karlsruhe, Germany*

*Corresponding author: R. A. Fischer (roland.fischer@tum.de) and W.J. Li (wj.li@tum.de)

Contents

1. Characterisations

X-ray diffraction measurement: The crystalline phase and crystal orientation of the obtained MOF thin films were identified by powder X-ray diffraction (PXRD, X' Pert Pan Analytical instrument, Bragg-Brentano geometry, Cu Ka radiation, 2thera 2-25°, scan step size of 0.01°) and grazing incidence XRD (GIXRD, PANalytical Empyrean instrument, grazing incidence mode, room temperature, Cu-Ka radiation, a range of 2thera 5-25° for $Zn_2(ZnTCPP)$ and 2-15° for 3D PP-MOF, a step of 0.01313°, an accumulation time of 1.5 s per step); meanwhile, the in-plane XRD patterns of $Zn_2(ZnTCPP)$ thin films were measured with a Bruker D8 Discover with Cu $K_{\alpha1,2}$ radiation with an in-plane geometry, over a 2θ range ~ 5 to 23° using a scan-time of 2 seconds per 0.025°.

Scanning electron microscopy (SEM) analysis: Top and cross-sectional view images were taken by using an environmental scanning electron microscope (ESEM, FEI ESEM Dual Beam™ Quanta 3D FEG) in order to investigate the surface morphology and surface coverage of the MOF films.

Infrared spectroscopy and ultraviolet-visible spectroscopy analysis: Attenuated total reflectance infrared (ATR-IR) spectra of samples were performed using a PerkinElmer instrument with an ATR sampling accessory. Ultraviolet–visible spectroscopy (UV-Vis) were carried out on a UV-visible spectrophotometer (PerkinElmer Lambda 650 S UV/VIS spectrometer) with a slit of 2.0 nm, data interval 1.0 nm, the scan speed of 600.00 nm/min, and a scan range of 800.00 nm to 350.00 nm. For the measurements of digested MOF films, a small piece of the MOF thin film was dissolved in 1.0 M NaOH aqueous solution. The obtained solution was then added into a quartz cell (1.0 cm) for UV-visible measurement.

Surface profiles analysis: Surface profiles of the films were characterised using a profilometer (DektakXT, BRUKER, Germany) with a diamond stylus in order to investigate their surface roughness.

Methanol vapor sorption: was carried out at a controlled temperature of 25 °C on an environmental-controlled quartz crystal microbalance (BELQCM-4 instrument, BEL Japan). Prior to sorption measurements, the PP-MOFs films were activated by soaking them in pure CH_2Cl_2 for 24 hours at room temperature and subsequently dried in a pure N_2 stream. Additionally, the samples were placed into the BEL-QCM instrument cells and in situ heated at 50 °C under a He stream (99.999%, 100 sccm) for two hours. After the activation process, the QCM frequency was recorded when the frequency change was stable within ±5 Hz over 30 min. Afterwards, methanol sorption isotherms were collected by varying the relative vapor pressure (P/P_0) of the saturated vapor of probe molecules in a He gas stream at 25 °C ranging from 0.0 to 95.0 %. The mass of the PP-MOFs films and adsorption amounts were calculated from the difference of the read QCM frequency and the fundamental frequency of the bare QCM substrate according to Sauerbrey's equation.

2. Chemicals and materials

All reagents and solvents were purchased from commercial sources and used without further purification unless otherwise stated: zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}8H_2O$, ⩾99%)， zinc acetate dihydrate ($Zn(OAC)_2{\cdot}2H_2O$, 98%), copper(II) chloride dihydrate ($CuCl_2{\cdot}2H_2O$，99%) were purchased from ACROS; zirconium(IV) oxychloride octahydrate ($ZrOCl_2{\cdot}8H_2O$, ⩾99.5%), methacrylic acid (99%), acetic acid (reagent grade, ⩾99.5%), methanol (anhydrous, 99.8%), Methyl 4-formylbenzoate (⩾96.0%) were purchased from Sigma Aldrich; meso-tetra(4-

carboxyphenyl)porphine (H_2TCPP, TCI); N,N-dimethylformamide (DMF; spectrophotometric grade, VWR); ethanol(absolute, Th. Geyer); zirconium(IV) n-propoxide (70% w/v in n-propanol, Alfa Aesar); gold substrate (Angstrom Engineering); silicon substrate (Siegert Wafer); ITO glass(Adrafruit).

3. Ligand synthesis

The tetrakis(4-carboxyphenyl)porphyrin (H_2TCPP) ligand was purchased from TCI. Copper-involved TCPP (Cu-TCPP) ligand was synthesized based on previous reports.[1] Typically, we obtained it by three steps as follows:

1) 5,10,15,20-Tetrakis(4-methoxycarbonylphenyl)porphyrin (TPPCOOMe).

To refluxed propionic acid (100 mL) in a 500-mL three necked flask were added pyrrole (3.0, 0.043 mol) and methyl p-formylbenzoate (6.9 g, 0.042 mol), and the solution was refluxed for 12h in darkness. After the reaction mixture was cooled to room temperature, crystals were collected by suction-filtration to afford purple crystals (1.4g). 1 H NMR (300 MHz, $CDCl_3$): δ 8.81 (s, 8H), 8.43 (d, 8H), 8.28 (d, 8H), 4.11 (s, 12H), -2.83 (s, 2H).

2) [5,10,15,20-Tetrakis(4-methoxycarbonylphenyl)porphyrinato]-Cu(II) (CuTPPCOOMe).

A solution of TPPCOOMe 0.854 g (1.0 mmol) and $CuCl_2 \cdot 2H_2O$ (2.2g, 12.8 mmol) in 100 mL of DMF was refluxed for 6 h. After the mixture was cooled to room temperature, 150 mL of H_2O was added. The resultant precipitate was filtered and washed with 50 mL of H_2O for two times. The obtained solid was dissolved in $CHCl_3$, followed by washing three times with water. The organic layer was dried over anhydrous magnesium sulfate and evaporated to afford quantitative dark red crystals.

3) [5,10,15,20-Tetrakis(4-carboxyphenyl)porphyrinato]-Cu(II) (Cu-TCPP).

The obtained ester (0.75 g) was stirred in THF (25 mL) and MeOH (25 mL) mixed solvent, to which a solution of KOH (2.63 g, 46.95 mmol) in H_2O (25 mL) was introduced. This mixture was refluxed for 12 h. After cooling down to room temperature, THF and MeOH were evaporated. Additional water was added to the resulting water phase and the mixture was heated until the solid was fully dissolved, then the homogeneous solution was acidified with 1M HCl until no further precipitate was detected. The dark red was collected by filtration, washed with water and dried in vacuum. 1 H NMR (300 MHz, DMSO-d_6): δ 8.80 (s, 8H), 8.37 (d, 8H), 8.28 (d, 8H).

4. Synthesis of $Zr_6O_4(OH)_4(OMc)_{12}$

$Zr_6O_4(OH)_4(OMc)_{12}$ (Hexazirconium-tetraoxy-tetrahydroxy-dodecamethacrylate) is known as a precursor to the metal secondary building unit (SBU) of zirconium-based PP-MOFs. The compound was synthesized according to the adapted procedure from Kickelbick and Schubert. In a large Schlenk flask, 1 mL of 70% w/v $Zr(OPr)_4$ (3.1 mmol) in n-propanol was mixed at room temperature with 1 mL of methacrylic acid (McOH; 11.8 mmol, 5.3 equiv) under inert gas atmosphere (Ar). After 2 weeks, the colorless crystals were collected by filtration and washing with small quantities of n-propanol. The product was dried in vacuum for 12 h and yielded the desired sample.

5. Preparation of PP-MOF films

1) Substrate pretreatment.

Au substrates (1 cm x 1 cm), Au-coated QCM substrates (AT cut type, Au electrode, diameter

14 mm, thickness 0.3 mm, and fundamental frequency ca. 4.95 MHz) were cleaned by soaking them in the mixed solution of water/H_2O_2/ammonia with a ratio of 5/1/1 at 75 °C for 15 min. Afterwards, the substrates were functionalised by immersing them into a solution of 16-mercaptohexadecanoic acid (MHDA, 20 μM) in ethanol with acetic acid (5% v/v) or in a solution of 1-mercaptoundecanol (MUD, 20 μM) in ethanol for at least 24 h at room temperature in order to obtain the –COOH or –OH terminated surface via self-assembled monolayers formation (SAM) and subsequently rinsed with pure ethanol and dried with N_2 before the use.

The silicon-wafers (1 cm x 1 cm), ITO glass substrates (1 cm x 1 cm) were cleaned in ethanol for about 10 min in an ultrasonic bath, and then activated under UV light for 60 min in order to in order to clean and generate a surface with hydroxyl groups. The substrates were used immediately for the growth of PP-MOFs films after UV light treatment.

2) Synthesis of 2D PP-MOF films.

Zn2(ZnTCPP) film growth via VAC. For the film growth using VAC, a 20 mL glass vial with a cap equipped was used. A Raschig-ring was placed on the bottom of the vial to offer an elevated flat platform for the substrate. $Zn(NO_3)_2{\cdot}6H_2O$ (4.5 mg, 0.015 mmol), TCPP (4 mg, 0.005 mmol), acetic acid (10 μL, 1M in DMF solution) and pyrazine (0.8 mg, 0.01 mmol) were dissolved in a mixed solution DMF (1.5 mL) and ethanol (0.5 mL) as the precursor solution. A mixture of 1mL DMF/ethanol (v/v, 3/1) and 5 μL acetic acid was filled into the vial as vapour source. Afterwards, the pre-treated Au/Silicon/ITO substrates (1 cm x 1 cm) was placed on top of the Raschig-ring and fully coated with 40 μL freshly prepared MOF precursor solution. The vial was closed and was transferred into a preheated 80 °C oven where it was kept for the specified time (details in table S1). Afterwards the vial was removed from the oven and allowed to cool down for 10 min before the Zn_2(ZnTCPP) film was removed. The film was immersed in fresh DMF and ethanol several times and then dried under vacuum.

The Zn_2(ZnTCPP) film grew without acetic acid in precursor solution and vapour source also conducted in same procedure only without acetic acid in precursor solution and vapour source.

Zn2(ZnTCPP) film growth via solvothermal method. $Zn(NO_3)_2{\cdot}6H_2O$ (4.5 mg, 0.015 mmol), TCPP (4 mg, 0.005 mmol), acetic acid (10 μL, 1M in DMF solution) and pyrazine (0.8 mg, 0.01 mmol) were dissolved in a mixed solution DMF (1.5 mL) and ethanol (0.5 mL) at room temperature and then the mixture were sonicated for 10 min. The –COOH functionalised Au substrate was then placed into the vial (with the activated side facing down to the bottom). Then, the reaction precursors were heated to 80 °C and kept for one day. After cooling down to room temperature, the obtained Zn_2(ZnTCPP) thin film was removed from the reaction mixture, rinsed with fresh DMF and ethanol, and dried at 50 °C under vacuum.

Zn2(ZnTCPP) film preparation via Modular Assembly. Firstly, $Zn(NO_3)_2{\cdot}6H_2O$ (4.5 mg, 0.015 mmol), TCPP (4 mg, 0.005 mmol), acetic acid (10 μL, 1M in DMF solution) and pyrazine (0.8 mg, 0.01 mmol) were dissolved in a mixed solution DMF (1.5 mL) and ethanol (0.5 mL) at room temperature. The reaction mixtures were sonicated for 10 min and then heated to 80 °C and kept for one day. After slowly cooled to room temperature, the synthesized red powder was washed with ethanol and collected by centrifuging.

Secondly, the as-synthesized Zn_2(ZnTCPP) nanosheets were dispersed in ethanol by ultra-sonication to get a colloidal suspension (1.0 mg/cm^3); The suspension was placed dropwise onto the surface of water in a beaker, and due to the hydrophobic property of the Zn_2(ZnTCPP), they spread out to form a thin film; The thin film was easily transferred to a –COOH functionalised Au substrate by stamping. The film was immersed in pure water to remove un-deposited Zn_2(ZnTCPP) nanosheets and the water on the substrate was blown away. Additional nanosheets could be repeatedly stacked in a layer-bylayer (LBL) growth fashion to create a Zn_2(ZnTCPP) thin film with the desired thickness.

Zn2(ZnTCPP) film growth via LPE on pump system. Synthesis of Zn_2(ZnTCPP) thin films was conducted on a double-walled reaction vessel, which was heated with a silicon-oil thermostat. The solutions were pumped in and out by peristaltic pumps which were controlled by LAB view (National Instruments) on computer. For the growth of Zn_2(ZnTCPP), the –COOH functionalised Au substrate was placed in the reaction vessel (with the activated side facing down to the bottom) and alternatively treated with a 0.3 mM $Zn(OAC)_2$ in DMF/ethanol (v/v, 3/1) and 0.1 mM H_2TCPP in DMF/ethanol (v/v, 3/1) solution. The substrate was immersed into each solution for 10 min. In between these reactive steps, the substrate was rinsed with pure ethanol for 2 min. These deposition cycles were repeated 30 times (30 cycles) at 70 °C to fabricated the oriented crystalline Zn_2(ZnTCPP) thin films.

3) 3D PP-MOF films preparation.

a) PCN-222 films growth.

PCN-222 film growth via VAC. For the film growth using VAC, a 20 mL glass vial with a cap equipped was used. A Raschig-ring was placed on the bottom of the vial to offer an elevated flat platform for the substrate. A mixture of 1 mL DMF and 0.2 mL acetic acid was filled into the vial as vapour source. Afterwards, the pre-treated Au/Silicon/ITO substrates (1 cm x 1 cm) was placed on top of the Raschig-rings and fully coated with a drop of a freshly prepared MOF precursor solution. The vial was closed and was transferred into a preheated 100 °C oven where it was kept for the specified time (details in table S2). Afterwards the vial was removed from the oven and allowed to cool down for 10 min before the PCN-222 film was removed. The film was immersed in fresh DMF and ethanol several times and then dried under vacuum.

PCN-222 film growth via solvothermal method. $ZrOCl_2\cdot 8H_2O$ (1.9 mg, 0.006 mmol), CuTCPP (1.7 mg, 0.002 mmol), acetic acid (75 μL) were dissolved in 1 mL DMF at room temperature and then the mixture was sonicated for 10 min. The –COOH functionalised Au substrate was then placed into the vial (with the activated side facing down to the bottom). Then, the reaction precursors were heated to 100 °C and kept for one day. After cooling down to room temperature, the obtained PCN-222 film was removed from the reaction mixture, rinsed with fresh DMF and ethanol, and dried under vacuum.

PCN-222 film preparation via Modular Assembly. Firstly, the PCN-222 nanoparticles were synthesized using a solvothermal reaction. $ZrOCl_2\cdot 8H_2O$ (5.7 mg, 0.006 mmol), CuTCPP (5.1 mg, 0.006 mmol), acetic acid (225 μL) were dissolved in 3 mL DMF at room temperature and then the mixture were sonicated for 10 min. Then, the reaction precursors were heated to 100 °C and kept for one day. After slowly cooled to room temperature, the synthesized red powder was washed with fresh DMF and ethanol and collected by centrifuging.

Secondly, the as-synthesized PCN-222 nanoparticles were dispersed in ethanol by ultra-sonication to get a colloidal suspension (1.0 mg/cm^3); The suspension was placed dropwise onto the surface of water in a beaker, and due to the hydrophobic property of PCN-222, they spread out to form a thin film; The thin film was easily transferred to a –COOH functionalised Au substrate by stamping. The film was immersed in pure water to remove un-deposited PCN-222 and the water on the substrate was blown away. Additional cycles could be repeatedly stacked in a layer-by-layer

(LBL) growth fashion to create a PCN-222 film with the desired thickness.

PCN-222 film growth via LPE on pump system. The synthesis of PCN-222 film was conducted on a double-walled reaction vessel, which was heated with a silicon-oil thermostat. The solutions were pumped in and out by peristaltic pumps which were controlled by LAB view (National Instruments) on computer. For the growth of PCN-222, 30 μM $Zr_6O_4(OH)_4(OMc)_{12}$ solution (mixed with acetic acid, 50 and 100 eq.) and 60 μM CuTCPP linker solution were prepared in DMF. The –COOH functionalised Au substrate was placed in the reaction vessel (with the activated side facing down to the bottom) and alternatively treated with a $Zr_6O_4(OH)_4(OMc)_{12}$ solution for 10 min and then CuTCPP linker solution for 10 min. The substrate was immersed into each solution for 10 min. Each subsequent step of dosing components was separated by a washing step of 2 min with absolute ethanol. These deposition cycles were repeated 30 times (30 cycles) at 100 °C to fabricate the PCN-222 films.

b) PCN-224 films growth.

PCN-224 film growth via VAC. For the film growth using VAC, a 20 mL glass vial with a cap equipped was used. A Raschig-ring was placed on the bottom of the bottle to offer an elevated flat platform for the substrate. A mixture of 1 mL DMF and 0.2 mL acetic acid was filled into the bottle as vapour source. Afterwards, the pre-treated Au/Silicon substrates (1 cm x 1 cm) was placed on top of the Raschig-ring and fully coated with a drop of a freshly prepared MOF precursor solution. The bottle was closed and was transferred into a preheated 70 °C oven where it was kept for the specified time (details in table S3). Afterwards the bottle was removed from the oven and allowed to cool down for 10 min before the PCN-224 film was removed. The film was immersed in fresh DMF and ethanol several times and then dried under vacuum.

c) MOF-525 films growth

MOF-525 film growth via VAC. For the film growth using VAC, a 20 mL glass vial with a cap equipped was used. A Raschig-ring was placed on the bottom of the bottle to offer an elevated flat platform for the substrate. A mixture of 1mL DMF and 0.2 mL acetic acid was filled into the bottle as vapour source. Afterwards, the pre-treated Au/Silicon/ITO substrates (1 cm x 1 cm) was placed on top of the Raschig-ring and fully coated with a drop of a freshly prepared MOF precursor solution. The bottle was closed and was transferred into a preheated 80 °C oven where it was kept for the specified time (details in table S4). Afterwards the bottle was removed from the oven and allowed to cool down for 10 min before the MOF-525 film was removed. The film was immersed in fresh DMF and ethanol several times and then dried under vacuum.

6. Supporting Figures

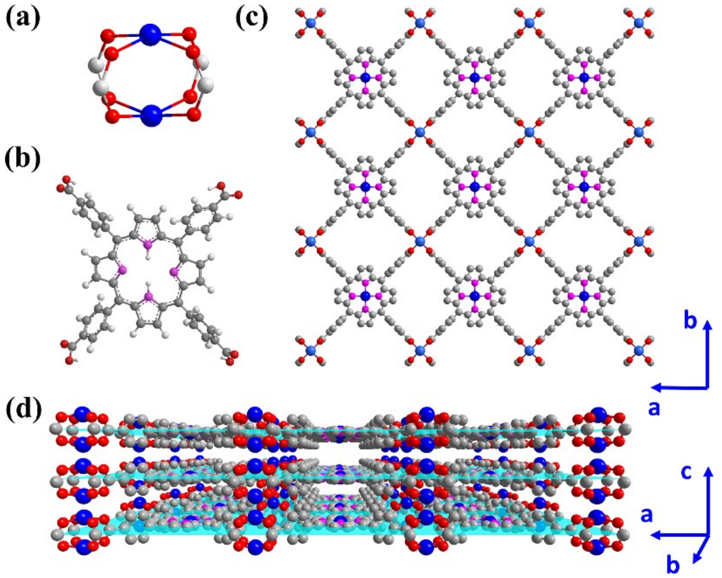

Fig. S1 Structures of the building units a) $Zn_2(COO)_4$ paddlewheel metal node, b) TCPP ligand for 2D Zn_2(ZnTCPP) nanosheets; 2D "checkerboard" structure of Zn_2(ZnTCPP) nanosheets c) view along [001] direction of one layer of Zn_2(ZnTCPP); d) the layered structure of 2D Zn_2(ZnTCPP) nanosheets stacked in an AA packing pattern, planes were inserted in each layer. H atoms have been omitted for clarity. Colour scheme: C, grey; O, red; N, pink and Zn, blue.

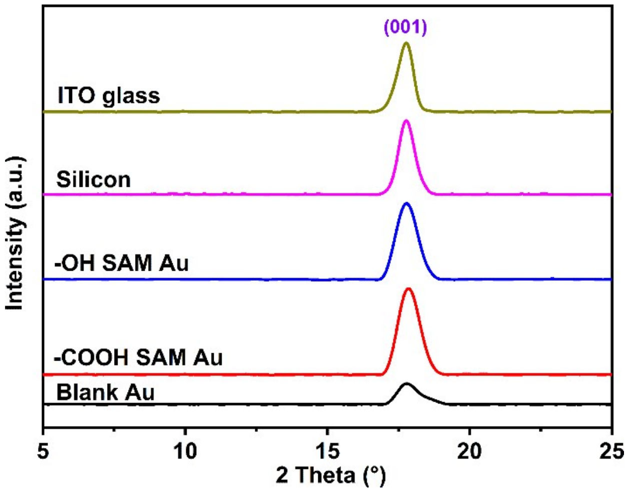

Fig. S2 GIXRD patterns of Zn_2(ZnTCPP) films grown by VAC method on different substrates: blank gold, –COOH SAM gold, –OH SAM gold, silicon and ITO glass.

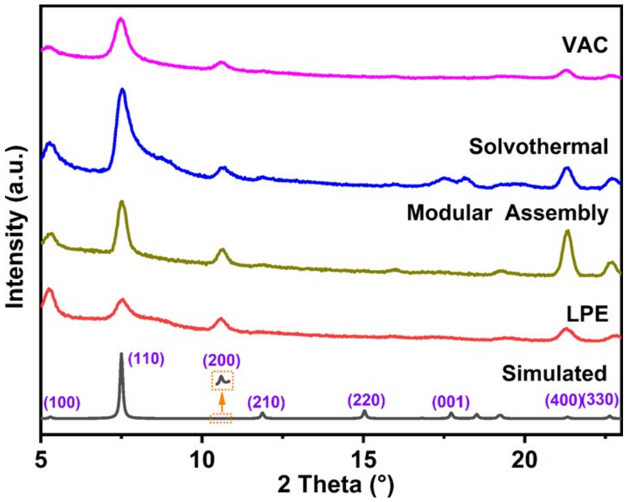

Fig. S3 In-plane PXRD patterns of $Zn_2(ZnTCPP)$ films fabricated by VAC, solvothermal, modular assembly and LPE methods. The insert was the magnified (200) peak.

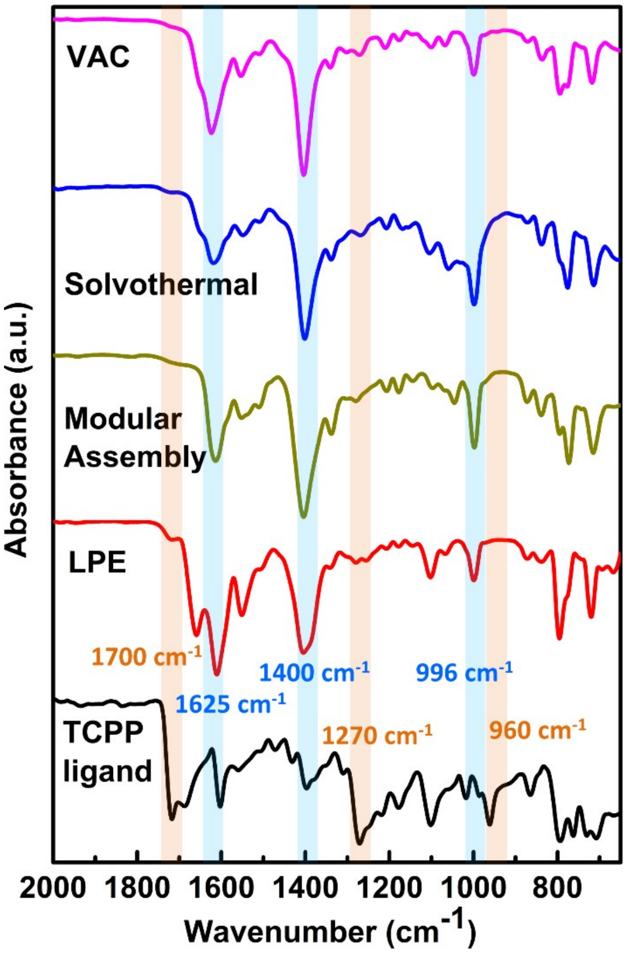

Fig. S4 ATR-IR spectra of TCPP ligand and $Zn_2(ZnTCPP)$ films fabricated on –COOH terminated gold substrates by different methods.

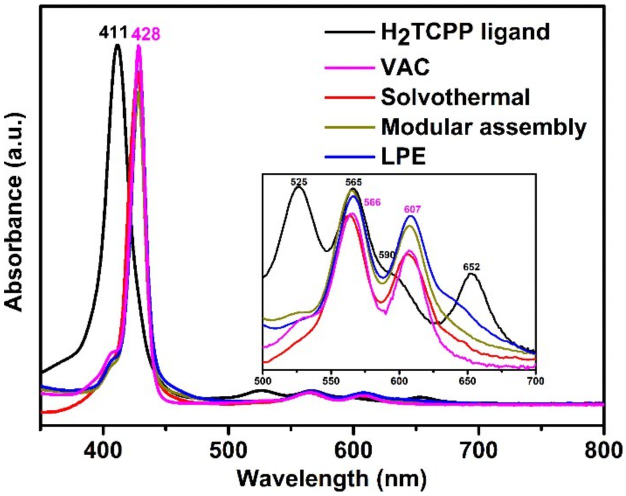

Fig. S5 UV-Vis spectra of TCPP ligand and $Zn_2(ZnTCPP)$ films fabricated on –COOH terminated gold substrates by different methods: VAC, solvothermal, modular assembly and LPE. Note that enlarged Q-band region is inserted.

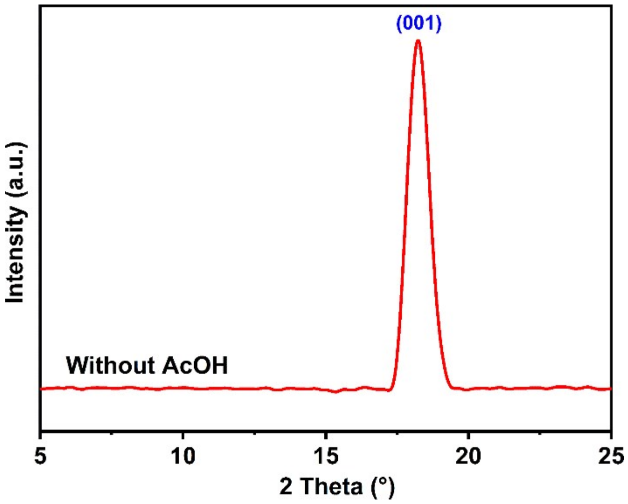

Fig. S6 GIXRD patterns of $Zn_2(ZnTCPP)$ film grown by VAC method on –COOH terminated gold substrate without acetic acid as modulator.

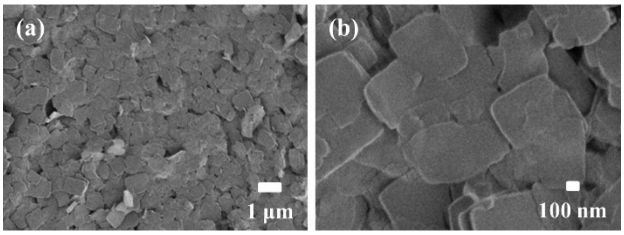

Fig. S7 SEM images of $Zn_2(ZnTCPP)$ film grown by VAC method on –COOH terminated gold substrate without acetic acid as modulator.

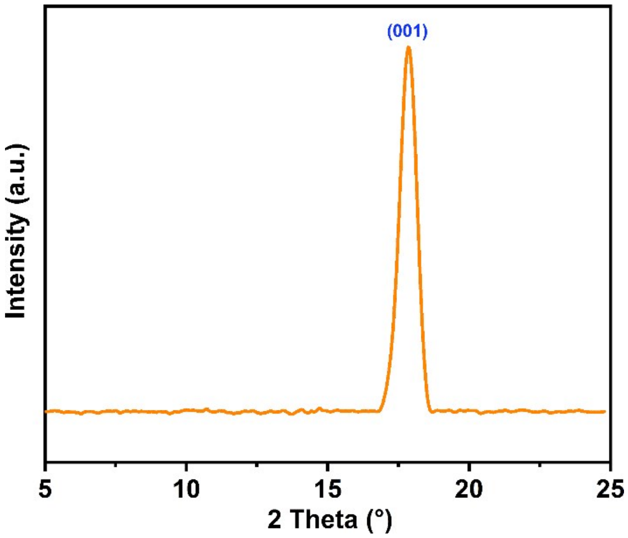

Fig. S8 GIXRD patterns of Zn_2(ZnTCPP) film grown by VAC method on –COOH terminated gold substrate without acetic acid and DMF.

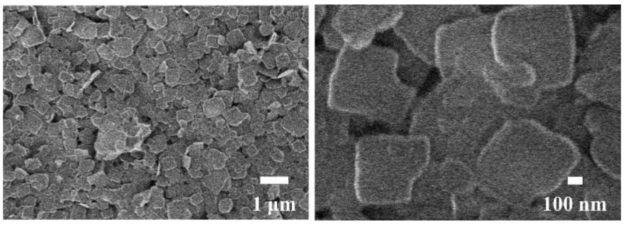

Fig. S9 SEM images of Zn_2(ZnTCPP) film grown by VAC method on –COOH terminated gold substrate without acetic acid and DMF.

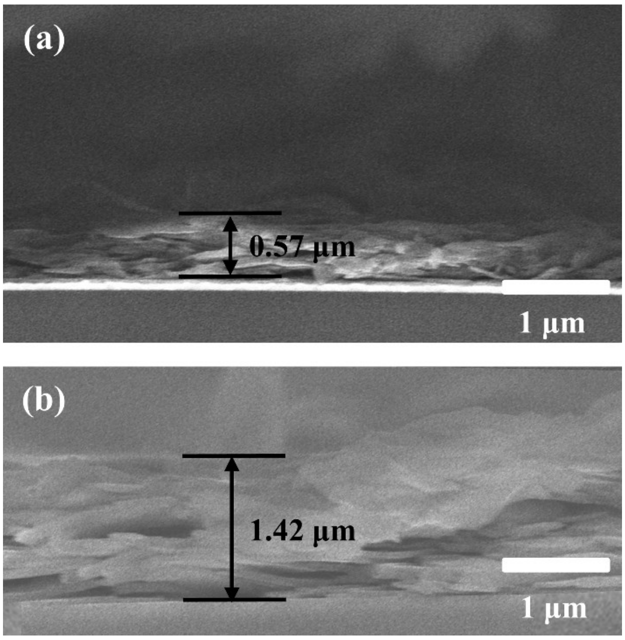

Fig. S10 Cross-section SEM images of Zn_2(ZnTCPP) films grown by VAC method on –COOH terminated gold substrate with (a) 30 μL and (b) 60 μL of precursor solution

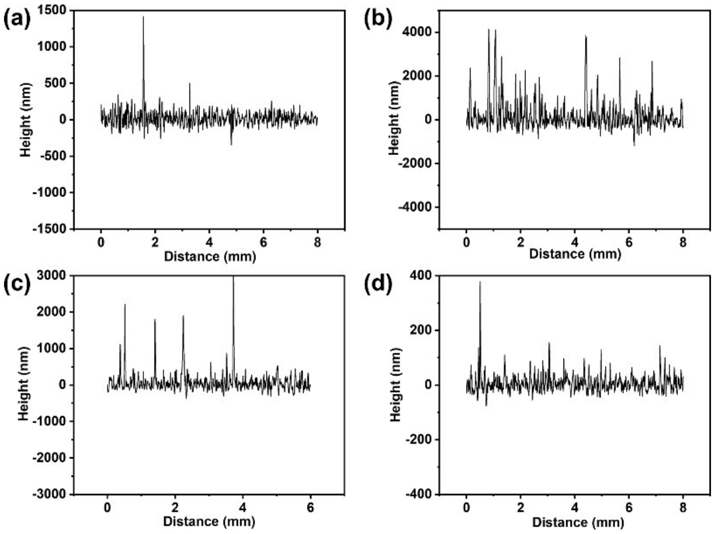

Fig. S11 Roughness profiles of $Zn_2(ZnTCPP)$ films fabricated on –COOH terminated gold substrates by (a) VAC, (b) solvothermal, (c) modular assembly and (d) LPE methods.

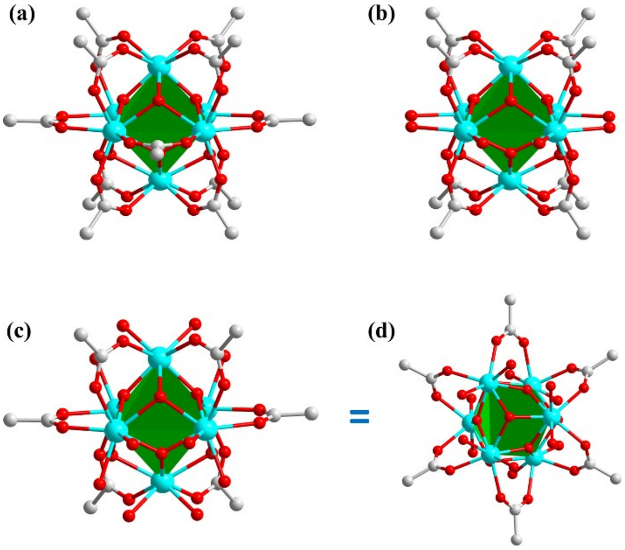

Fig. S12 Different connectivities of Zr_6 clusters in the structures of Zirconium-based porphyrinic MOFs: (a) 12-connected Zr_6 cluster for MOF-525; (b) 8-connected Zr_6 cluster for PCN-222; (c-d) 6-connected Zr_6 cluster for PCN-224 ((c): side view; (d): top view). Colour scheme: C, grey; O, red, and Zr, aqua. The green polyhedron represent the octahedral geometry of the Zr_6 cluster.

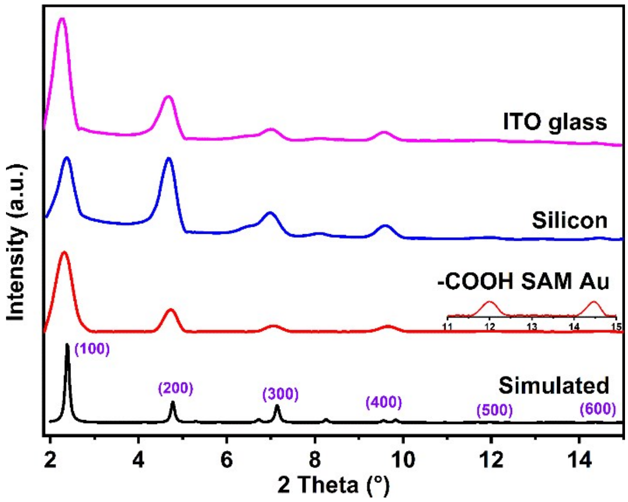

Fig. S13 GIXRD patterns of PCN-222 films grown by VAC technique on different functionalised substrates: –COOH SAM gold, silicon, ITO glass. Note that VAC deposition was conducted using 30 μL freshly prepared MOF precursor solution with the acetic acid as modulator ($r_M = 219$) at 100 °C for 3 h.

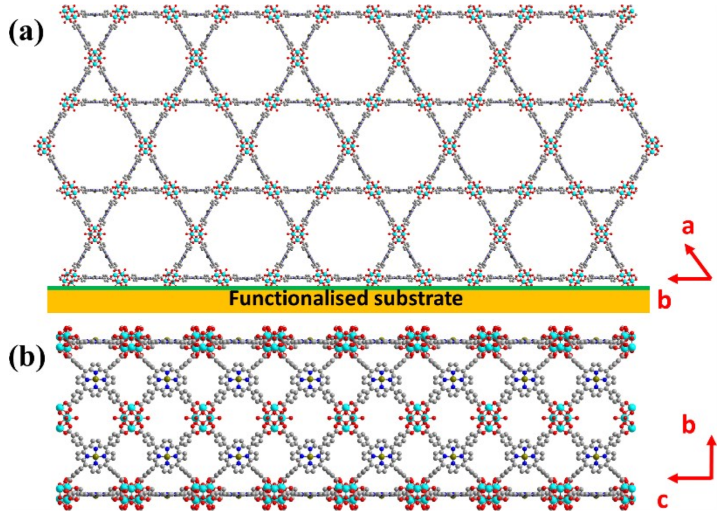

Fig. S14 (a) Side-view scheme (the *ab* plane) of the PCN-222 film grown upon functionalised substrate along *a* axis ([100] direction), in which the channels are parallel to the plane of the substrate; (b) the *bc* plane of PCN-222 film which nucleated on the substrate surface.

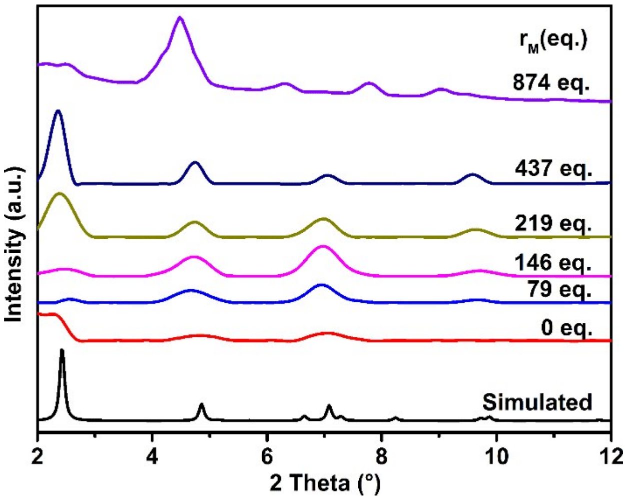

Fig. S15 GIXRD patterns of PCN-222 films grown on –COOH terminated gold substrates by VAC method with different modulator to metal ratios (r_M).

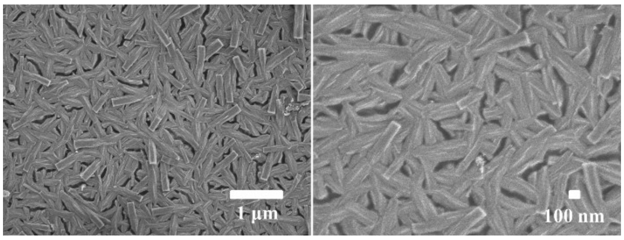

Fig. S16 SEM images of PCN-222 film grown on –COOH terminated gold substrate by VAC method with r_M at 437

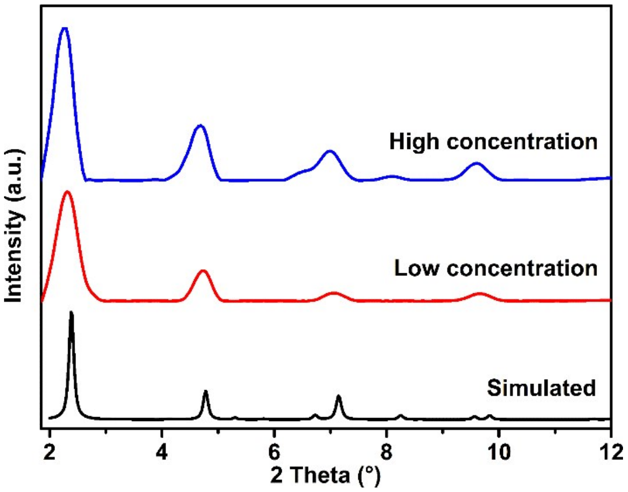

Fig. S17 GIXRD patterns of PCN-222 films grown by VAC method on –COOH terminated gold substrate with low and high precursor concentrations.

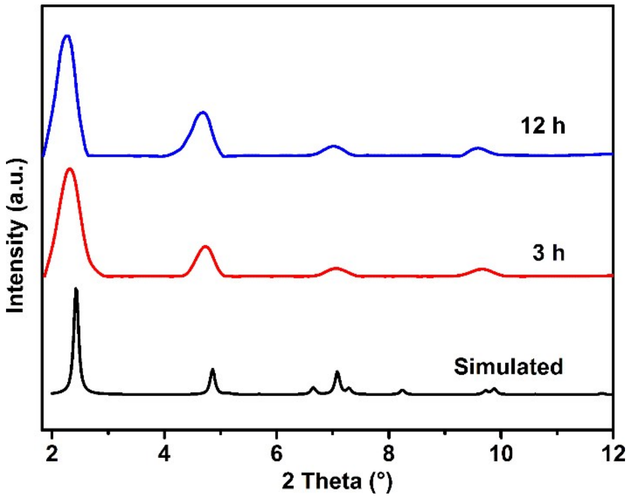

Fig. S18 GIXRD patterns of PCN-222 films grown on –COOH terminated gold substrates by VAC method using different reaction time.

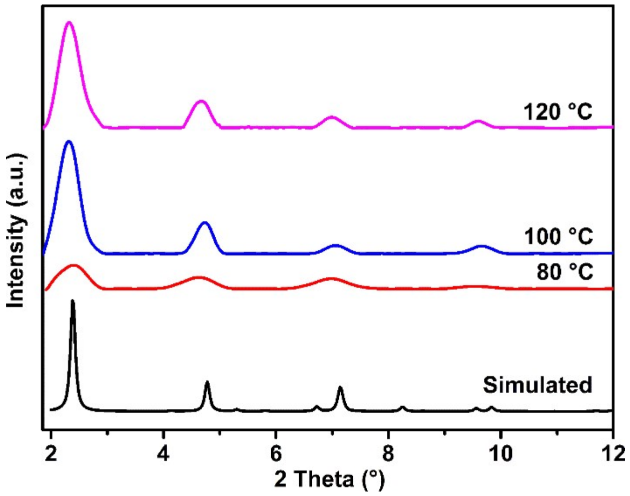

Fig. S19 GIXRD patterns of PCN-222 films grown on –COOH terminated gold substrates by VAC method on different reaction temperatures.

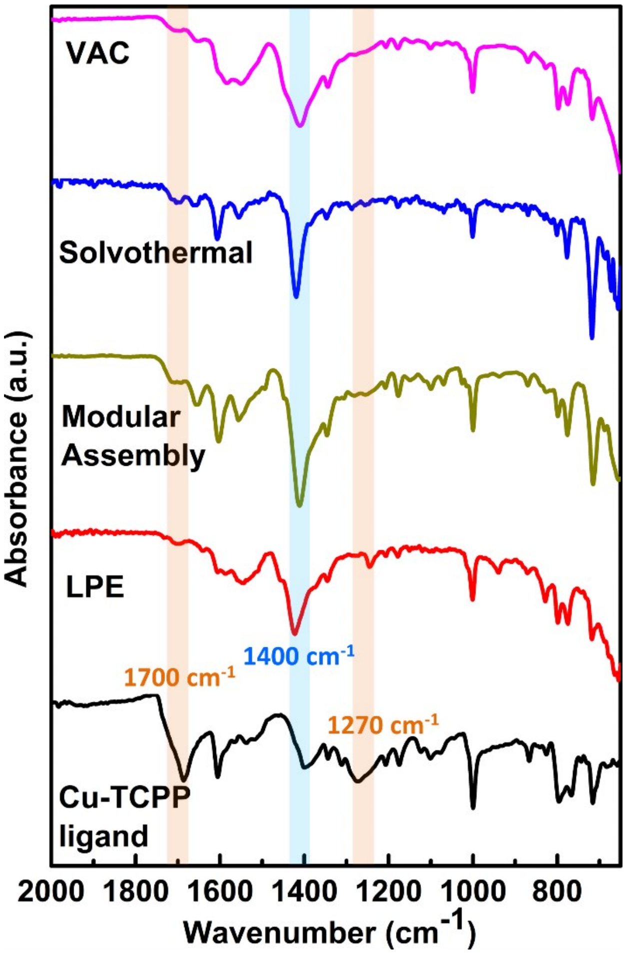

Fig. S20 ATR-IR spectra of CuTCPP ligand and PCN-222 films fabricated on –COOH terminated gold substrates by VAC, solvothermal, modular assembly and LPE methods.

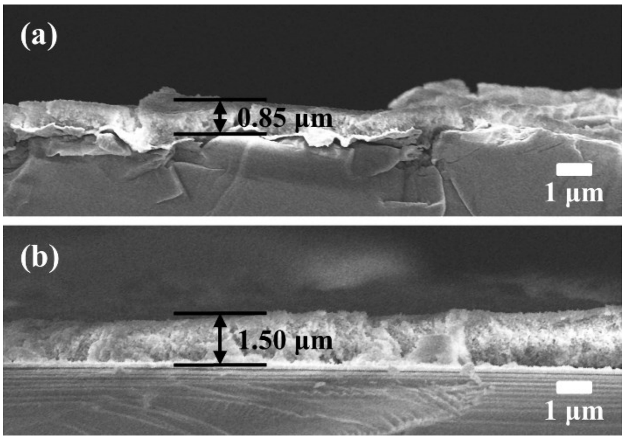

Fig. S21 Cross-section SEM images of PCN-222 films grown by VAC method on –COOH terminated gold substrate with (a) 30 μL and (b) 60 μL of precursor solution.

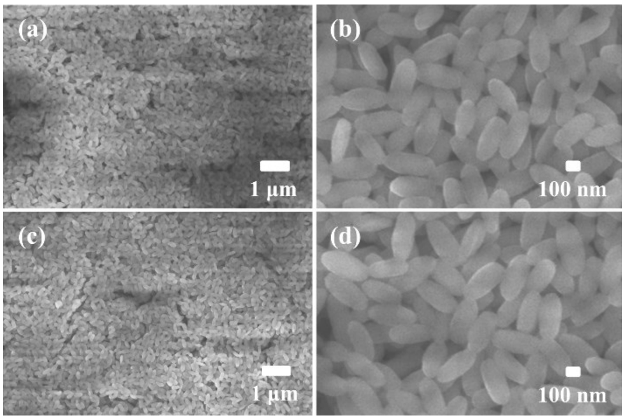

Fig. S22 SEM images of PCN-222 film grown on silicon (a-b) and ITO (c-d) by VAC.

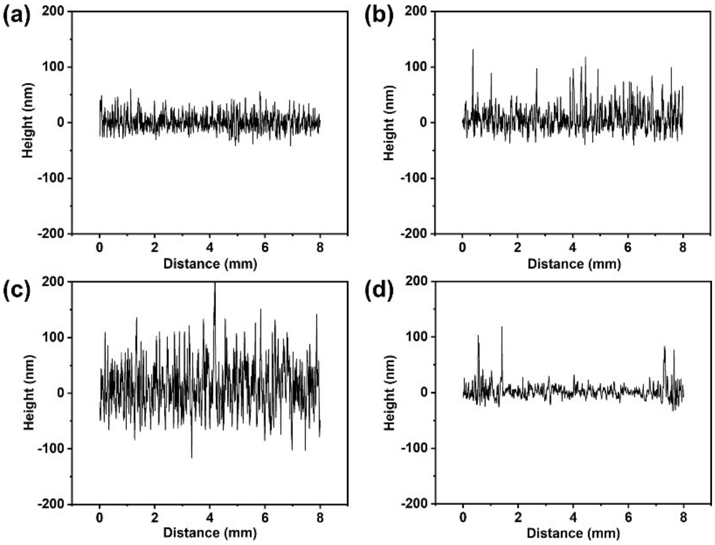

Fig. S23 Roughness profiles of PCN-222 films fabricated on –COOH terminated gold substrates by (a) VAC, (b) solvothermal, (c) modular assembly and (d) LPE methods.

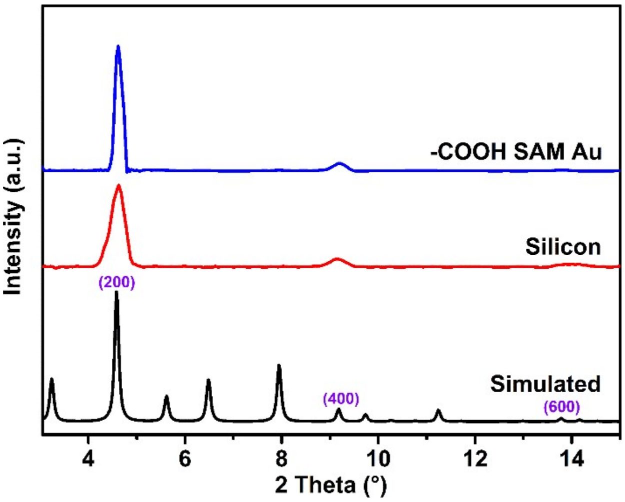

Fig. S24 GIXRD patterns of PCN-224 films grown by VAC method on different functionalised substrates.

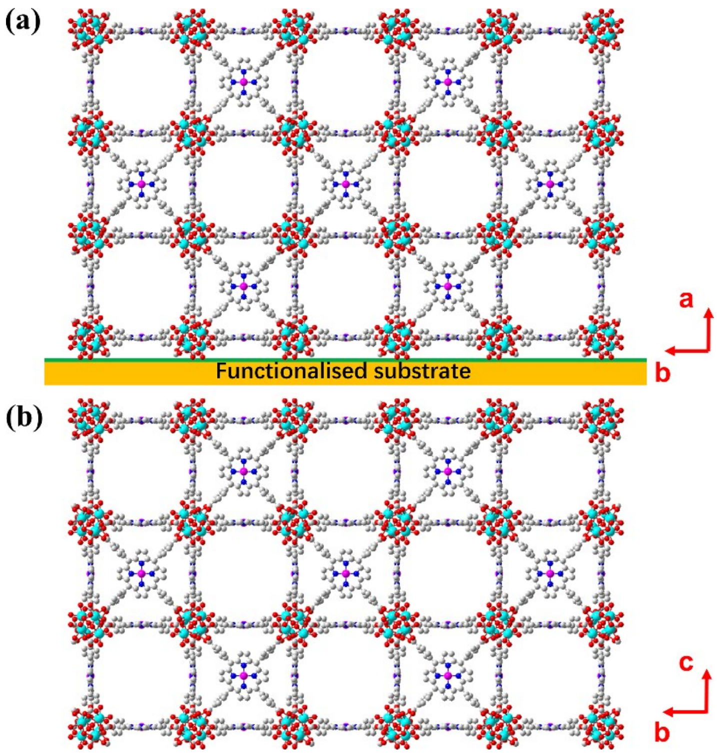

Fig. S25 (a) Side-view scheme (*ab* plane) of PCN-224 film grown upon functionalised substrate along *a* axis ([200] direction); (b) the *bc* plane of PCN-224 film which nucleated on the substrate surface.

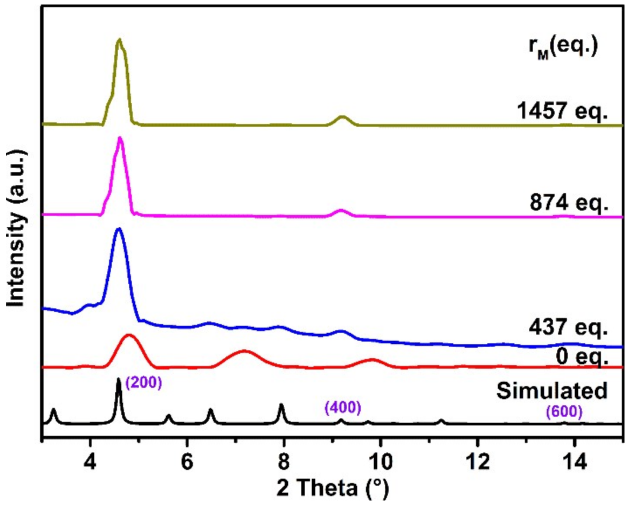

Fig. S26 GIXRD patterns of PCN-224 films grown on –COOH terminated gold substrates via VAC method with different modulator to metal ratios (r_M).

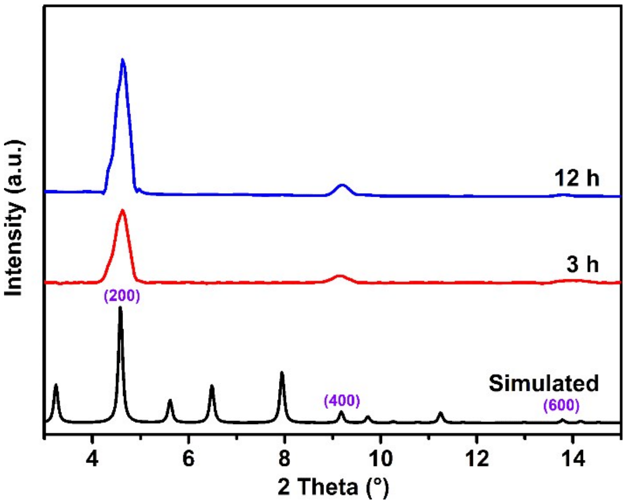

Fig. S27 GIXRD patterns of PCN-224 films grown on –COOH terminated gold substrates via VAC method using different reaction time.

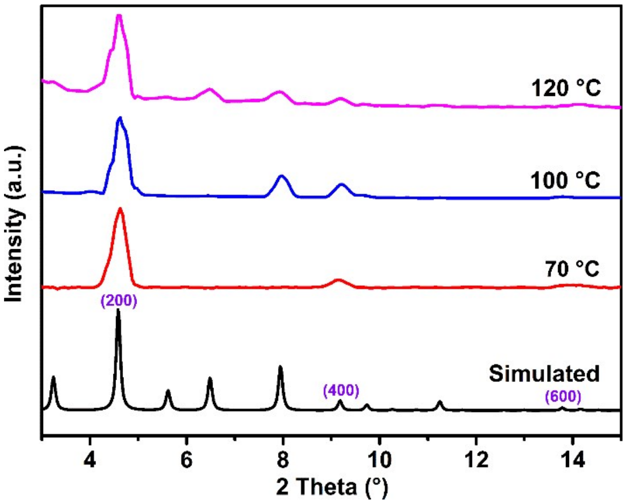

Fig. S28 GIXRD patterns of PCN-224 films grown on –COOH terminated gold substrates via VAC method on different reaction temperatures.

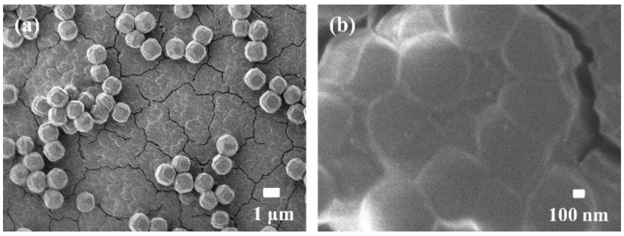

Fig. S29 SEM images of PCN-224 film grown on –COOH terminated gold substrate via VAC method; note that in the VAC deposition method, 30 μL freshly prepared MOF precursor solution is used with acetic acid as modulator (r_M = 1457) at 70 °C for 3 h.

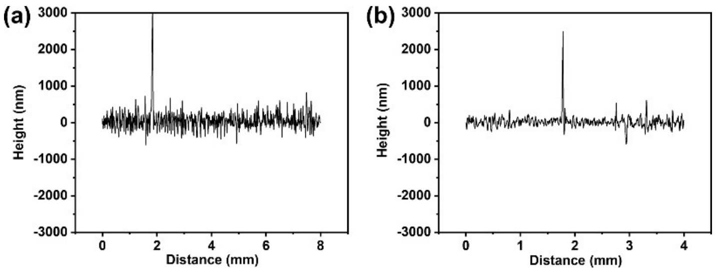

Fig. S30 Roughness profiles of (a) PCN-224 and (b) MOF-525 films fabricated on –COOH terminated gold substrates by VAC method.

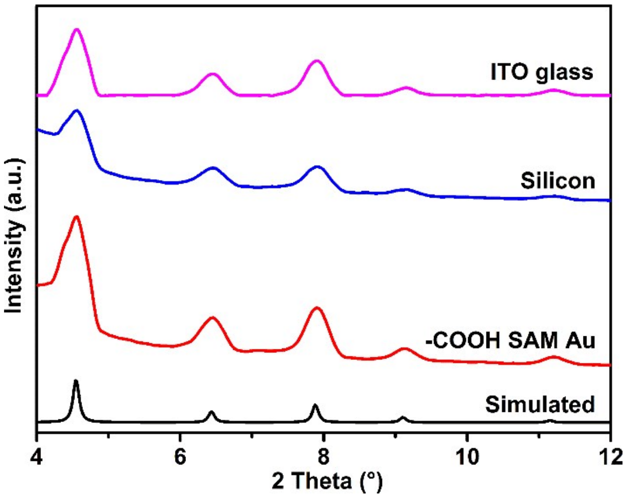

Fig. S31 GIXRD patterns of MOF-525 films grown by VAC method on different functionalised substrates.

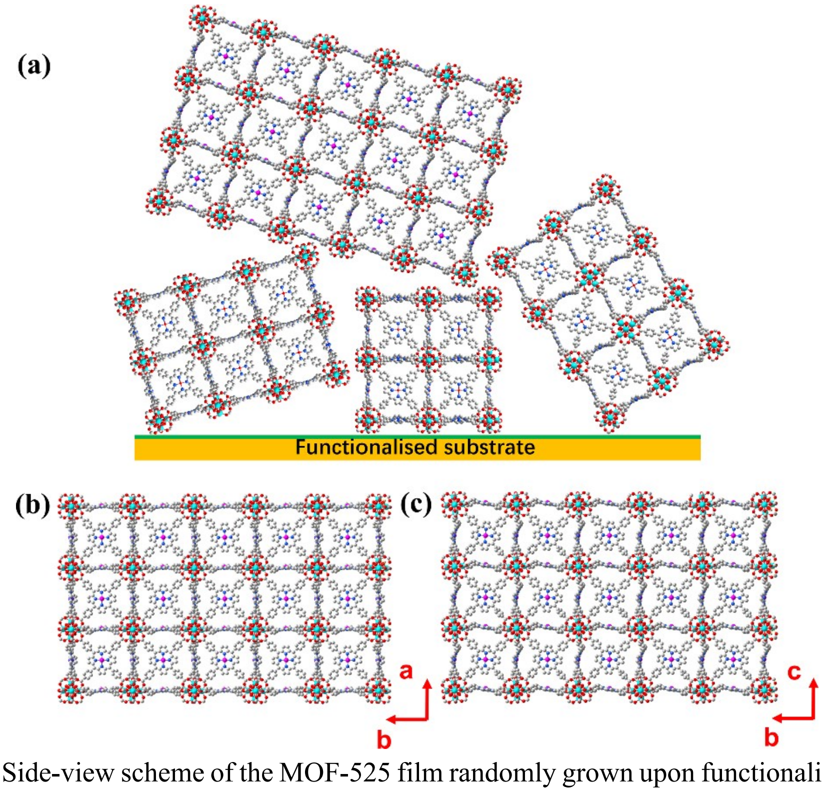

Fig. S32 (a) Side-view scheme of the MOF-525 film randomly grown upon functionalised substrate; (b) the *ab* plane and (c) *bc* plane of MOF-525.

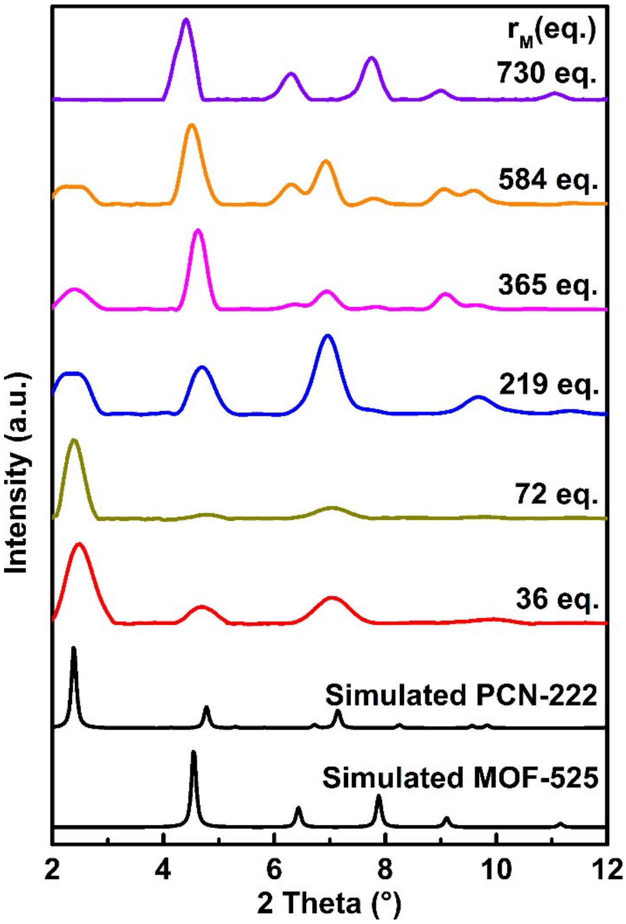

Fig. S33 GIXRD patterns of MOF-525 films grown on –COOH terminated gold substrates via VAC method with different modulator to metal ratios (r_M)

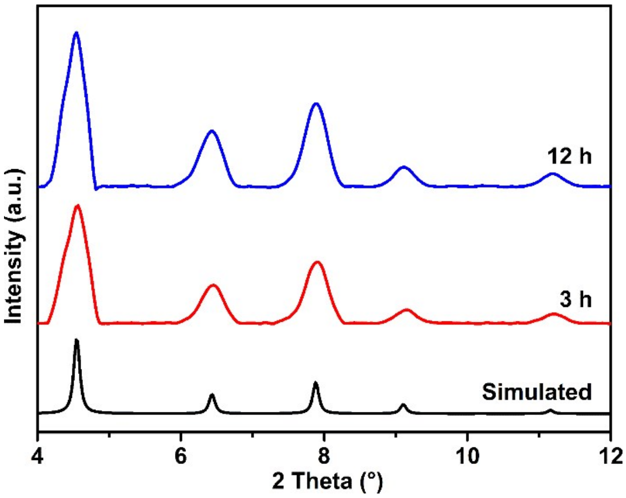

Fig. S34 GIXRD patterns of MOF-525 films grown on –COOH terminated gold substrates via VAC method using different reaction times.

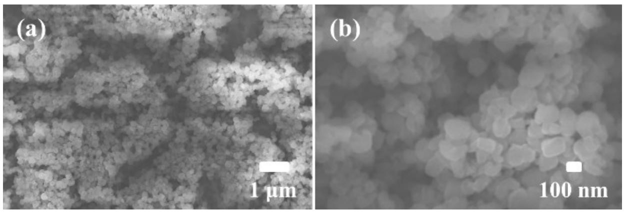

Fig. S35 SEM images of MOF-525 film grown on –COOH terminated gold substrate via VAC method; note that during VAC deposition, 30 μL freshly prepared MOF precursor solution is used with acetic acid as modulator (r_M = 730) at 80 °C for 3 h.

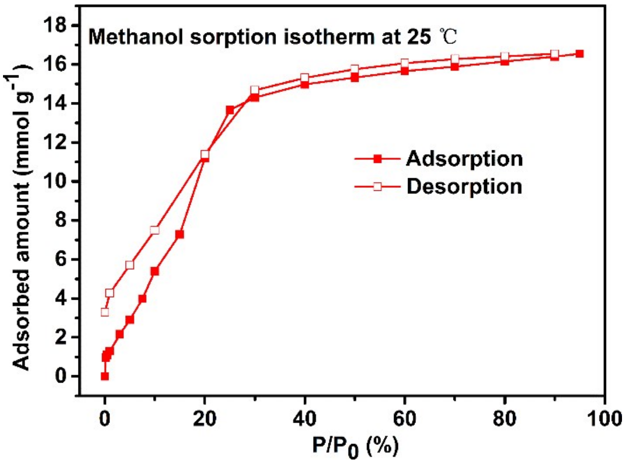

Fig.S36 Methanol sorption isotherms at ambient temperature (25 °C) of PCN-224 film fabricated by VAC method on the –COOH terminated Au-coated QCM substrate.

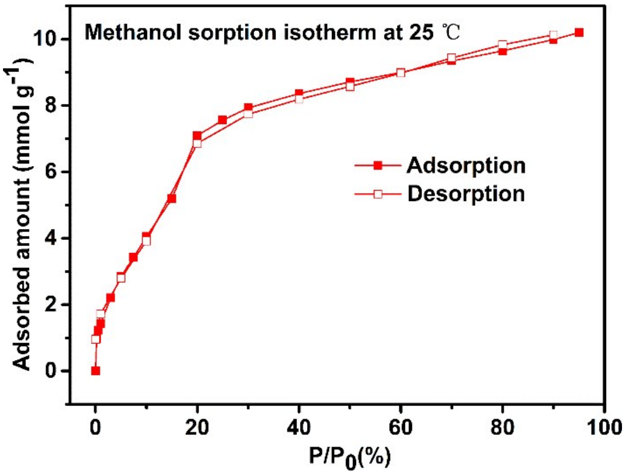

Fig.S37 Methanol sorption isotherms at ambient temperature (25 °C) of MOF-525 film fabricated by VAC method on the –COOH terminated Au-coated QCM substrate.

7. Supporting Tables

Table S1. List of atomic coordinates for the simulated structure of Zn_2(ZnTCPP) films.

Atoms	**x**	**y**	**z**	**Atoms**	**x**	**y**	**z**
Zn1	0	0	0	C7	-0.0653	0.1694	0
Zn2	0.5	0.5	0.2929	C8	-0.0404	0.2517	0
O1	0.41519	0.41519	0.22326	H8	-0.0736	0.2965	0
N1	0.1205	0	0	N1	0	-0.1205	0
C1	0.39255	0.39255	0	C7	0.0653	-0.1694	0
C2	0.3271	0.3271	0	C8	0.0404	-0.2517	0
C3	0.29735	0.29735	0.2334	H8	0.0736	-0.2965	0
H1	0.3169	0.3169	0.39482	O1	-0.41519	-0.41519	-0.22326
C4	0.2387	0.2387	0.23537	C1	-0.39255	-0.39255	0
H2	0.21935	0.21935	0.39718	C2	-0.3271	-0.3271	0
C5	0.2089	0.2089	0	C3	-0.29735	-0.29735	-0.2334
C6	0.14505	0.14505	0	H1	-0.3169	-0.3169	-0.39482
C7	0.1694	0.0653	0	C4	-0.2387	-0.2387	-0.23537
C8	0.2517	0.0404	0	H2	-0.21935	-0.21935	-0.39718
H8	0.2965	0.0736	0	C5	-0.2089	-0.2089	0
O1	0.41519	-0.41519	-0.22326	C6	-0.14505	-0.14505	0
C1	0.39255	-0.39255	0	C7	-0.0653	-0.1694	0
C2	0.3271	-0.3271	0	C8	-0.0404	-0.2517	0
C3	0.29735	-0.29735	-0.2334	H8	-0.0736	-0.2965	0
H1	0.3169	-0.3169	-0.39482	O1	-0.41519	0.41519	-0.22326
C4	0.2387	-0.2387	-0.23537	C3	-0.29735	0.29735	-0.2334
H2	0.21935	-0.21935	-0.39718	H1	-0.3169	0.3169	-0.39482

C5	0.2089	-0.2089	0	C4	-0.2387	0.2387	-0.23537
C6	0.14505	-0.14505	0	H2	-0.21935	0.21935	-0.39718
C7	0.1694	-0.0653	0	O1	-0.41519	-0.41519	0.22326
C8	0.2517	-0.0404	0	C3	-0.29735	-0.29735	0.2334
H8	0.2965	-0.0736	0	H1	-0.3169	-0.3169	0.39482
O1	0.41519	0.41519	-0.22326	C4	-0.2387	-0.2387	0.23537
N1	0	0.1205	0	H2	-0.21935	-0.21935	0.39718
C3	0.29735	0.29735	-0.2334	N1	-0.1205	0	0
H1	0.3169	0.3169	-0.39482	C7	-0.1694	-0.0653	0
C4	0.2387	0.2387	-0.23537	C8	-0.2517	-0.0404	0
H2	0.21935	0.21935	-0.39718	H8	-0.2965	-0.0736	0
C7	0.0653	0.1694	0	C7	-0.1694	0.0653	0
C8	0.0404	0.2517	0	C8	-0.2517	0.0404	0
H8	0.0736	0.2965	0	H8	-0.2965	0.0736	0
O1	0.41519	-0.41519	0.22326	Zn2	0.5	0.5	-0.2929
C3	0.29735	-0.29735	0.2334	Zn2	-0.5	-0.5	0.2929
H1	0.3169	-0.3169	0.39482	Zn2	-0.5	0.5	0.2929
C4	0.2387	-0.2387	0.23537	Zn2	0.5	-0.5	0.2929
H2	0.21935	-0.21935	0.39718	Zn2	-0.5	-0.5	-0.2929
O1	-0.41519	0.41519	0.22326	Zn2	-0.5	0.5	-0.2929
C1	-0.39255	0.39255	0	Zn2	0.5	-0.5	-0.2929
C2	-0.3271	0.3271	0	O1	0.58481	0.41519	0.22326
C3	-0.29735	0.29735	0.2334	O1	0.58481	0.58481	0.22326
H1	-0.3169	0.3169	0.39482	O1	0.41519	0.58481	0.22326
C4	-0.2387	0.2387	0.23537	O1	0.41519	0.58481	-0.22326

H2	-0.21935	0.21935	0.39718	O1	0.58481	0.41519	-0.22326
C5	-0.2089	0.2089	0	O1	0.58481	0.58481	-0.22326
C6	-0.14505	0.14505	0				

Table S2. Recipes for the fabrication of Zn_2(ZnTCPP) films by VAC.

	EXP.	**Precursor solution**						**Droplet volume**	**Substrate**	**Temper-ature**	**Reaction time**	**Vapour source**		
		$Zn(NO_3)_2 \cdot 6H_2O$	TCPP	pyrazine	acetic acid (1M in DMF)	DMF	EtOH					DMF	EtOH	Acetic acid
Variation of modulator conentration	1	4.5 mg 7.5 mmol/L	4.0 mg 2.5 mmol/L	0.8 mg 5 mmol/L	0 μl 0 mmol/L	1.5 mL	0.5 mL	30 μL	-COOH SAM gold	80 °C	3 h	1 mL	0 mL	0 μL
	2	4.5 mg 7.5 mmol/L	4.0 mg 2.5 mmol/L	0.8 mg 5 mmol/L	10 μl 5 mmol/L	1.5 mL	0.5 mL	30 μL	-COOH SAM gold	80 °C	3 h	1 mL	0 mL	5 μL
Variation of substrate type	3	4.5 mg 7.5 mmol/L	4.0 mg 2.5 mmol/L	0.8 mg 5 mmol/L	10 μl 5 mmol/L	1.5 mL	0.5 mL	30 μL	Blank gold	80 °C	3 h	1 mL	0 mL	5 μL
	4	4.5 mg 7.5 mmol/L	4.0 mg 2.5 mmol/L	0.8 mg 5 mmol/L	10 μl 5 mmol/L	1.5 mL	0.5 mL	30 μL	-OH SAM gold	80 °C	3 h	1 mL	0 mL	5 μL
	5	4.5 mg 7.5 mmol/L	4.0 mg 2.5 mmol/L	0.8 mg 5 mmol/L	10 μl 5 mmol/L	1.5 mL	0.5 mL	30 μL	Silicon wafer	80 °C	3 h	1 mL	0 mL	5 μL
	6	4.5 mg 7.5 mmol/L	4.0 mg 2.5 mmol/L	0.8 mg 5 mmol/L	10 μl 5 mmol/L	1.5 mL	0.5 mL	30 μL	ITO glass	80 °C	3 h	1 mL	0 mL	5 μL
	7	4.5 mg 7.5 mmol/L	4.0 mg 2.5 mmol/L	0.8 mg 5 mmol/L	10 μl 5 mmol/L	1.5 mL	0.5 mL	30 μL	-COOH SAM Au QCM	80 °C	3 h	1 mL	0 mL	5 μL
variation of droplet volume	8	4.5 mg 7.5 mmol/L	4.0 mg 2.5 mmol/L	0.8 mg 5 mmol/L	10 μl 5 mmol/L	1.5 mL	0.5 mL	60 μL	-COOH SAM gold	80 °C	3 h	1 mL	0 mL	5 μL

variation of solvent	9	4.5 mg 7.5 mmol/L	4.0 mg 2.5 mmol/L	0.8 mg 5 mmol/L	10 μl 5 mmol/L	0 mL	2.0 mL	30 μL	-COOH SAM gold	80 °C	3 h	0 mL	1 mL	0 μL

Table S3. Surface roughness of Zn_2(ZnTCPP) films fabricated via different methods.

Methods	**R_a (nm)**	**R_q (nm)**
VAC	4.5	6.1
Solvothermal	54.1	61.2
Modular assembly	8.1	10.4
LPE	2.9	3.1

Table S4. Recipes for the fabrication of PCN-222 films by VAC.

	EXP.	**Precursor solution**				**Droplet volume**	**Substrate**	**Temperature**	**Reaction time**	**Vapour source**	
		$ZrOCl_2 \cdot 8H_2O$	CuTCPP	acetic acid	DMF					DMF	Acetic acid
Variation of modulator conentration	9	1.9 mg 6 mmol/L	1.7 mg 2 mmol/L	0 μL 0 mmol/L	1 mL	30 μL	-COOH SAM gold	100 °C	3 h	1 mL	0.2 mL
	10	1.9 mg 6 mmol/L	1.7 mg 2 mmol/L	25 μL 438 mmol/L	1mL	30 μL	-COOH SAM gold	100 °C	3 h	1 mL	0.2 mL
	11	1.9 mg 6 mmol/L	1.7 mg 2 mmol/L	50 μL 875 mmol/L	1 mL	30 μL	-COOH SAM gold	100 °C	3 h	1 mL	0.2 mL
	12	1.9 mg 6 mmol/L	1.7 mg 2 mmol/L	75 μL 1314 mmol/L	1 mL	30 μL	-COOH SAM gold	100 °C	3 h	1 mL	0.2 mL
	13	1.9 mg 6 mmol/L	1.7 mg 2 mmol/L	150 μL 2625 mmol/L	1 mL	30 μL	-COOH SAM gold	100 °C	3 h	1 mL	0.2 mL
	14	1.9 mg 6 mmol/L	1.7 mg 2 mmol/L	300 μL 5250 mmol/L	1 mL	30 μL	-COOH SAM gold	100 °C	3 h	1 mL	0.2 mL

Variation of precursor conentration	15	5.7 mg 18 mmol/L	5.1 mg 6 mmol/L	225 μL 3942 mmol/L	1 mL	30 μL	-COOH SAM gold	100 °C	3 h	1 mL	0.2 mL
Variation of substrate type	16	1.9 mg 6 mmol/L	1.7 mg 2 mmol/L	75 μL 1314 mmol/L	1 mL	30 μL	Silicon wafer	100 °C	3 h	1 mL	0.2 mL
	17	1.9 mg 6 mmol/L	1.7 mg 2 mmol/L	75 μL 1314 mmol/L	1mL	30 μL	ITO glass	100 °C	3 h	1 mL	0.2 mL
	18	1.9 mg 6 mmol/L	1.7 mg 2 mmol/L	75 μL 1314 mmol/L	1mL	30 μL	-COOH SAM Au QCM	100 °C	3 h	1 mL	0.2 mL
variation of droplet volume	19	1.9 mg 6 mmol/L	1.7 mg 2 mmol/L	75 μL 1314 mmol/L	1 mL	60 μL	-COOH SAM gold	100 °C	3 h	1 mL	0.2 mL
Variation of reaction time	20	1.9 mg 6 mmol/L	1.7 mg 2 mmol/L	75 μL 1314 mmol/L	1mL	30 μL	-COOH SAM gold	100 °C	12 h	1 mL	0.2 mL
Variation of reaction temperature	21	1.9 mg 6 mmol/L	1.7 mg 2 mmol/L	75 μL 1314 mmol/L	1 mL	30 μL	-COOH SAM gold	80 °C	3 h	1 mL	0.2 mL
	22	1.9 mg 6 mmol/L	1.7 mg 2 mmol/L	75 μL 1314 mmol/L	1 mL	30 μL	-COOH SAM gold	120 °C	3 h	1 mL	0.2 mL

Table S5. Surface roughness of PCN-222 films fabricated via different methods.

Methods	**R_a (nm)**	**R_q (nm)**
VAC	2.2	2.7
Solvothermal	3.6	4.6
Modular assembly	5.5	6.9
LPE	4.0	4.7

Table S6. Recipes for the fabrication of PCN-224 films by VAC.

	EXP.	Precursor solution				Droplet volume	Substrate	Temperature	Reaction time	Vapour source	
		$ZrOCl_2 \cdot 8H_2O$	CuTCPP	acetic acid	DMF					DMF	Acetic acid
Variation of modulator conentration	23	1.9 mg 6 mmol/L	1.3 mg 1.5 mmol/L	0 μL 0 mmol/L	1 mL	30 μL	-COOH SAM gold	70 °C	3 h	1 mL	0.2 mL
	24	1.9 mg 6 mmol/L	1.3 mg 1.5 mmol/L	150 μL 2625 mmol/L	1 mL	30 μL	-COOH SAM gold	70 °C	3 h	1 mL	0.2 mL
	25	1.9 mg 6 mmol/L	1.3 mg 1.5 mmol/L	300 μL 5250 mmol/L	1 mL	30 μL	-COOH SAM gold	70 °C	3 h	1 mL	0.2 mL
	26	1.9 mg 6 mmol/L	1.3 mg 1.5 mmol/L	500 μL 8720 mmol/L	1 mL	30 μL	-COOH SAM gold	70 °C	3 h	1 mL	0.2 mL
Variation of substrate type	27	1.9 mg 6 mmol/L	1.3 mg 1.5 mmol/L	500 μL 8720 mmol/L	1 mL	30 μL	Silicon wafer	70 °C	3 h	1 mL	0.2 mL
	28	1.9 mg 6 mmol/L	1.3 mg 1.5 mmol/L	500 μL 8720 mmol/L	1 mL	30 μL	-COOH SAM Au QCM	70 °C	3 h	1 mL	0.2 mL
Variation of reaction time	29	1.9 mg 6 mmol/L	1.3 mg 1.5 mmol/L	500 μL 8720 mmol/L	1 mL	30 μL	-COOH SAM gold	70 °C	12 h	1 mL	0.2 mL
Variation of reaction temperature	30	1.9 mg 6 mmol/L	1.3 mg 1.5 mmol/L	500 μL 8720 mmol/L	1 mL	30 μL	-COOH SAM gold	100 °C	3 h	1 mL	0.2 mL
	31	1.9 mg 6 mmol/L	1.3 mg 1.5 mmol/L	500 μL 8720 mmol/L	1 mL	30 μL	-COOH SAM gold	120 °C	3 h	1 mL	0.2 mL

Table S7. Recipes for the fabrication of MOF-525 films by VAC.

	EXP.	Precursor solution				Droplet volume	Substrate	Temperature	Reaction time	Vapour source	
		$ZrOCl_2 \cdot 8H_2O$	CuTCPP	acetic acid	DMF					DMF	Acetic acid

Variation of modulator concentration	32	1.9 mg 6 mmol/L	2.6 mg 3 mmol/L	12.5 μL 219 mmol/L	1 mL	30 μL	-COOH SAM gold	80 °C	3 h	1 mL	0.2 mL
	33	1.9 mg 6 mmol/L	2.6 mg 3 mmol/L	25 μL 438 mmol/L	1 mL	30 μL	-COOH SAM gold	80 °C	3 h	1 mL	0.2 mL
	34	1.9 mg 6 mmol/L	2.6 mg 3 mmol/L	75 μL 1313 mmol/L	1 mL	30 μL	-COOH SAM gold	80 °C	3 h	1 mL	0.2 mL
	35	1.9 mg 6 mmol/L	2.6 mg 3 mmol/L	125 μL 2188 mmol/L	1 mL	30 μL	-COOH SAM gold	80 °C	3 h	1 mL	0.2 mL
	36	1.9 mg 6 mmol/L	2.6 mg 3 mmol/L	200 μL 3500 mmol/L	1 mL	30 μL	-COOH SAM gold	80 °C	3 h	1 mL	0.2 mL
	37	1.9 mg 6 mmol/L	2.6 mg 3 mmol/L	250 μL 4375 mmol/L	1 mL	30 μL	-COOH SAM gold	80 °C	3 h	1 mL	0.2 mL
Variation of substrate type	38	1.9 mg 6 mmol/L	2.6 mg 3 mmol/L	250 μL 4375 mmol/L	1 mL	30 μL	Silicon wafer	80 °C	3 h	1 mL	0.2 mL
	39	1.9 mg 6 mmol/L	2.6 mg 3 mmol/L	250 μL 4375 mmol/L	1 mL	30 μL	ITO glass	80 °C	3 h	1 mL	0.2 mL
	40	1.9 mg 6 mmol/L	2.6 mg 3 mmol/L	250 μL 4375 mmol/L	1 mL	30 μL	-COOH SAM Au QCM	80 °C	3 h	1 mL	0.2 mL
Variation of reaction time	41	1.9 mg 6 mmol/L	2.6 mg 3 mmol/L	250 μL 4375 mmol/L	1 mL	30 μL	-COOH SAM gold	80 °C	12 h	1 mL	0.2 mL

Table S8. Surface roughness of PCN-224 and MOF-525 films fabricated by VAC.

MOFs	**R_a (nm)**	**R_q (nm)**
PCN-224	13.1	16.5
MOF-525	8.5	10.3

Reference

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