

## Electronic Supplementary Information

# An Organic Guest Molecule Induced Ultrafast Breathing of Epitaxially Grown Metal-Organic Framework on Self- Assembled Monolayer

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## 1. Synthesis

### 1.1 Materials

Zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) was purchased from Sigma Aldrich. 5-Aminoisophthalic acid (AIP) was purchased from Alfa Aesar. 4,4'-Bipyridine (BPY), Aminoethanethiol (AET), 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC), Mercaptoundecanoic acid (MUA), and 3-Aminopyridine were purchased from Tokyo Chemical Industry. Aminodecanethiol was purchased from LabNetWork, United States. *N,N*-dimethylformamide (DMF), Ethyl alcohol were purchased from a local Korean company, Samchun Chemical, Gyeonggi-Do, South Korea. All chemicals were used as received without further purification. PDMS stamps were prepared using SYLGARD™ 184 Silicone Elastomer Kit.

### 1.2 Preparation of MOF (compound 1)

Zinc nitrate hexahydrate (298 mg, 1.0 mmol), 5-aminoisophthalic acid (181 mg, 1.0 mmol), and 4,4'-bipyridine (78 mg, 0.50 mmol) were dissolved separately in 10 mL of DMF (3:3:4). Then, the individual solutions were sonicated until they dissolved. The solutions were mixed and transferred into a 20 ml glass vial. The glass vial was sealed and heated at 100 °C in an oven for 24 h at ambient pressure. After 24 h, the reaction yielded brown colored crystals of **1**, the crystals were collected by filtration and washed with fresh DMF and dichloromethane (10 mL × 3 times). The crystals were then dried at 100 °C under vacuum overnight to remove DMF molecules in the pores.

### 1.3 Fabrication of MOF thin films

#### Gold wafer preparation:

The gold wafer was prepared by evaporating 15 nm of Ti as an adhesion layer, followed by 200 nm Au on the silicon wafer. A gold wafer (1 cm × 3 cm) was cleaned using a freshly prepared piranha solution for 2 min. The wafer was rinsed with Millipore water and absolute ethanol, followed by drying under vacuum for 1 h.

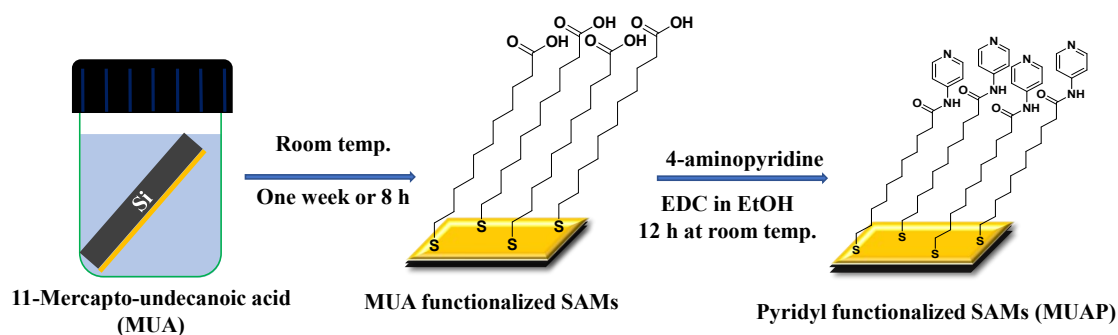
#### Step-1 Preparation amine-terminal of SAM on gold wafer:

The gold wafer was dipped into the 3 mL (1 mM in ethanol) aminoalkylthiol solution [Aminoethanethiol (film-AET) or Aminodecanethiol (film-ADT)] for 1 week or 8 hr at room

temperature. After the designated time, amine-terminal SAM on the Au wafer was taken out from the thiol solution, washed with ethanol, and dried using an N<sub>2</sub> gun.

### Preparation of pyridine-terminal SAM on Au

The gold wafer was dipped into 3 mL (1 mM in ethanol) of mercaptoundecanoic acid solution for 1 week or 8 hr at room temperature. After the designated time, the SAM wafer was taken out from the thiol solution, washed with ethanol, and dried using an N<sub>2</sub> gun. In addition, EDC coupling was conducted by dipping the wafer into the EDC solution (3 mL and 2 mM in ethanol) (EDC = 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide); after 30 min, 4-amino-pyridine (6 mg, 63.7 μmol) was added into the EDC solution. After 12 hr, the pyridine-terminal SAM on the Au wafer was taken out from the solution, washed with ethanol, and dried with an N<sub>2</sub> gun (Scheme S1).



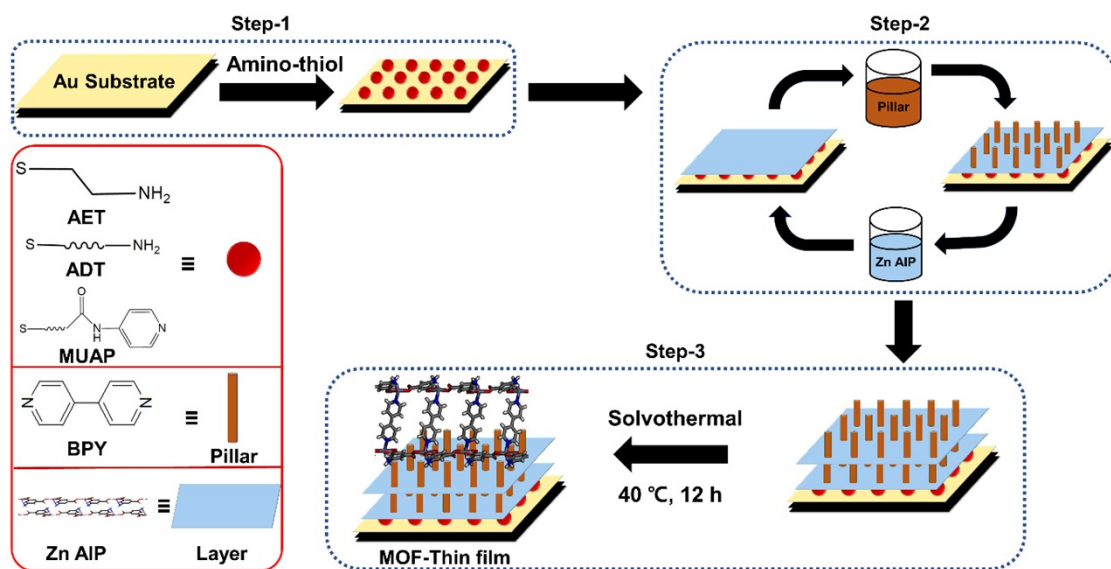
**Scheme S1.** Schematic illustration for the synthesis of pyridyl functionalized SAMs.

### Step-2 MOF seeding on SAMs (layer by layer MOF growth):

The prepared SAM wafer was soaked into the solution containing 3 mL (100 mM in DMF) of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and AIP for 30 min., then washed with ethanol and soaked again into the solution of 3 mL (100 mM in DMF) bpy for 30 min. For the formation of well-ordered MOF seeds on SAMs, the process was repeated 5 times.

### Step-3 MOF growth by the solvothermal method:

After the seed growth, the SAM wafer was soaked in a vial charged with 3 mL of 100 mM of MOF precursor solution ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , AIP, and bpy in DMF). Then, the vial was kept in the oven at 40 °C for 12 h to form a metal-organic porous material thin film on the surface.



**Scheme S2.** Stepwise fabrication of MOF thin films.

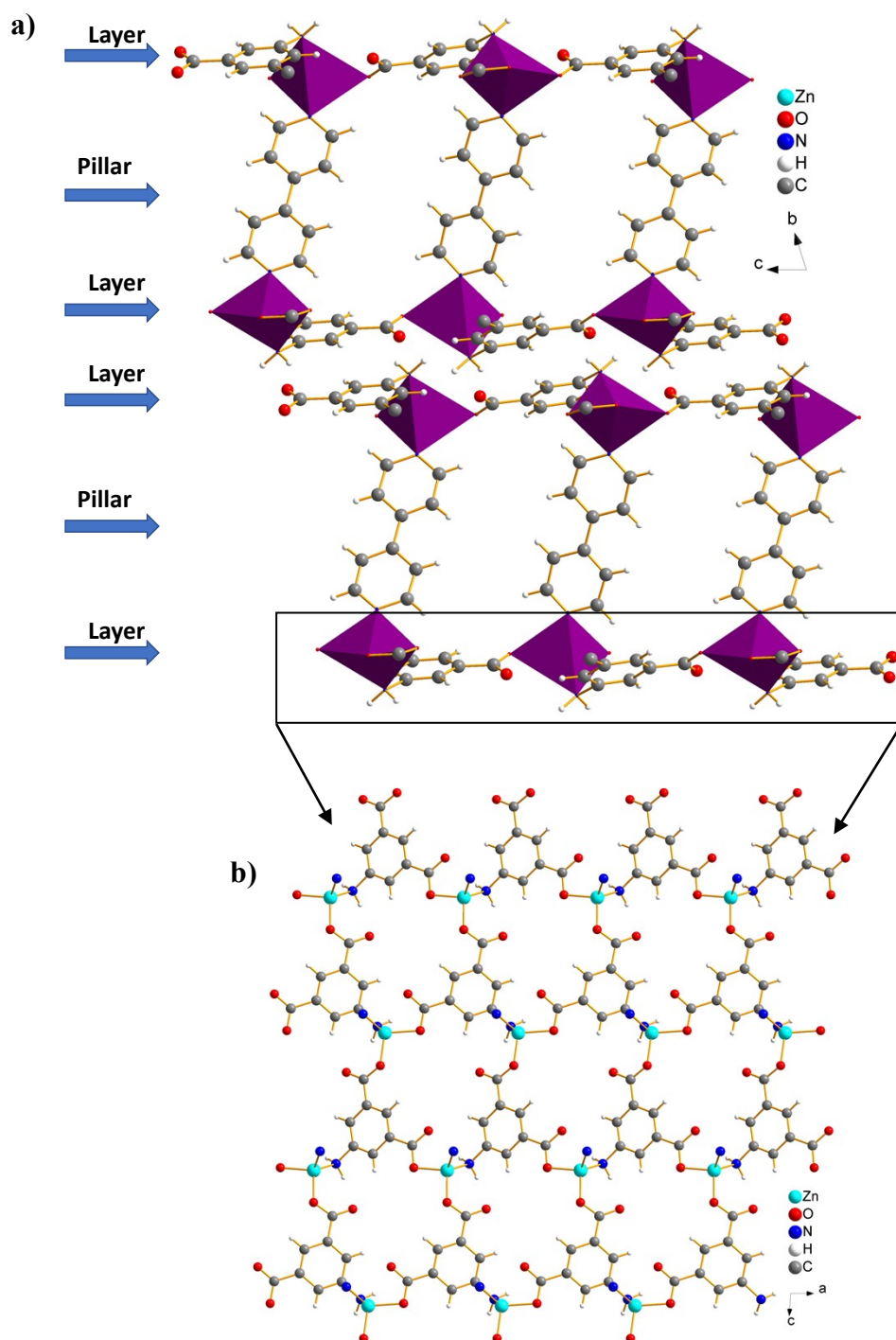
## 2. Characterization

### 2.1 Methods

The powder XRD diffractograms and out-of-plane XRD data were obtained on a Bruker D8 Advance system equipped with Cu sealed tube ( $\lambda = 1.54178 \text{ \AA}$ ). Following conditions were used: 40 kV, 40 mA, increment = 0.05°, scan speed = 3.0 deg/min. The in-plane and out-of-plane XRD data and rocking curve were obtained in the Pohang Accelerator Laboratory 10C HEXRS beamline ( $\lambda = 1.14 \text{ \AA}$ ). SEM image was collected on a JEOL JSM-7410F with 5kV acceleration voltage and 30 mA current.

#### Structural description of compound 1

Compound **1** is an unusual form of layered-pillared-layered structure, where the layers and pillars are repeated in two-dimensional manner. Also, these two layers are interconnected by the H-bonding interactions (N-H-O).



**Figure S1.** a)  
2D-pillared

layered structure of compound **1** (view through a-axis), b) Layered connectivity of aip linker with zinc metal centers in **1** (view through b-axis).

## 2.2 Breathing behavior of compound **1** (bulk sample)

After confirming the phase purity of compound **1**, the DMF molecules (present in the lattice) were removed by activating the sample at 100 °C under a dynamic vacuum. The activated compound **1'** was confirmed using single-crystal X-ray and PXRD analysis. In addition, the breathing behavior **1**, was confirmed through powder XRD analysis by redispersing the activated compound (**1'**) into the fresh DMF solvent for 24 h (Fig. S2).

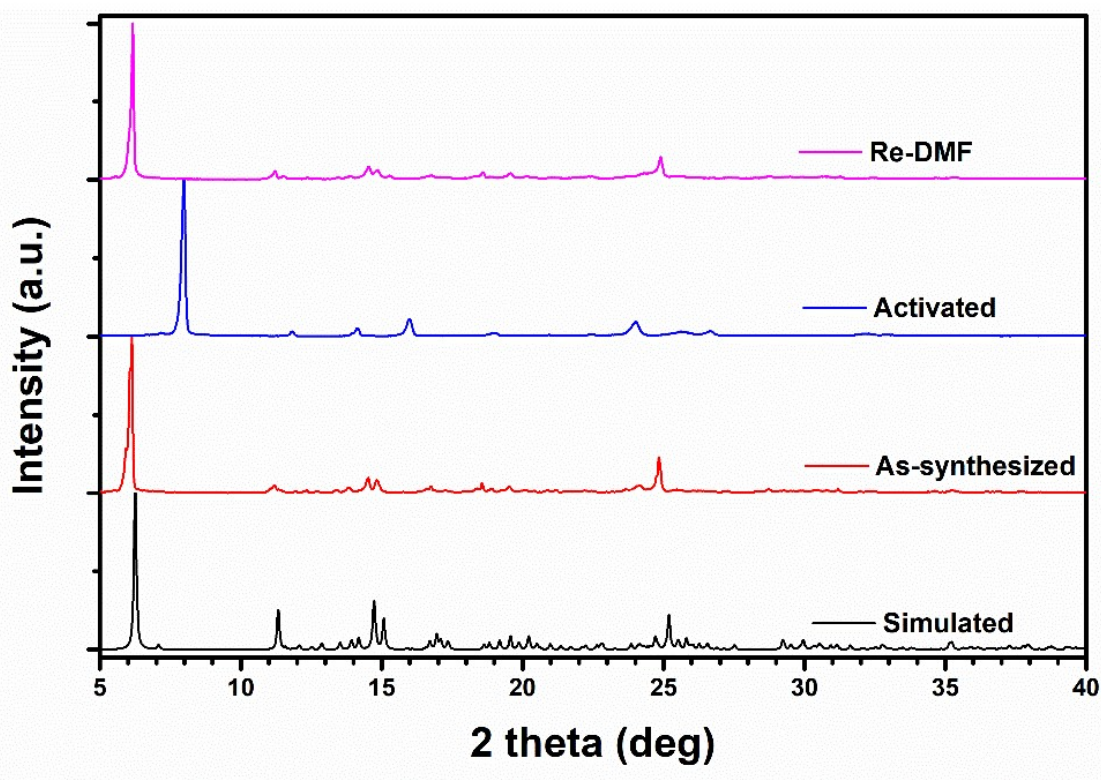
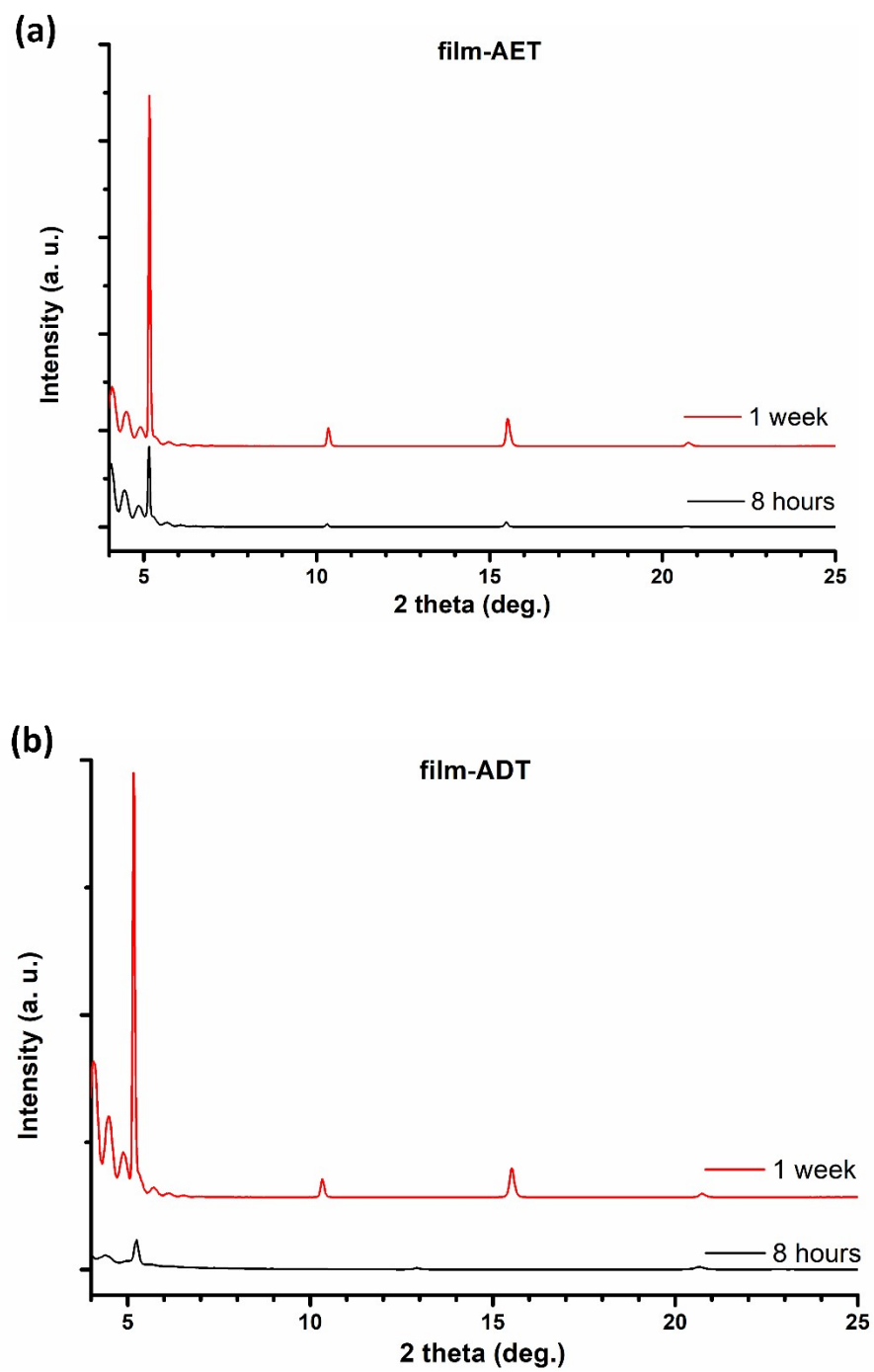
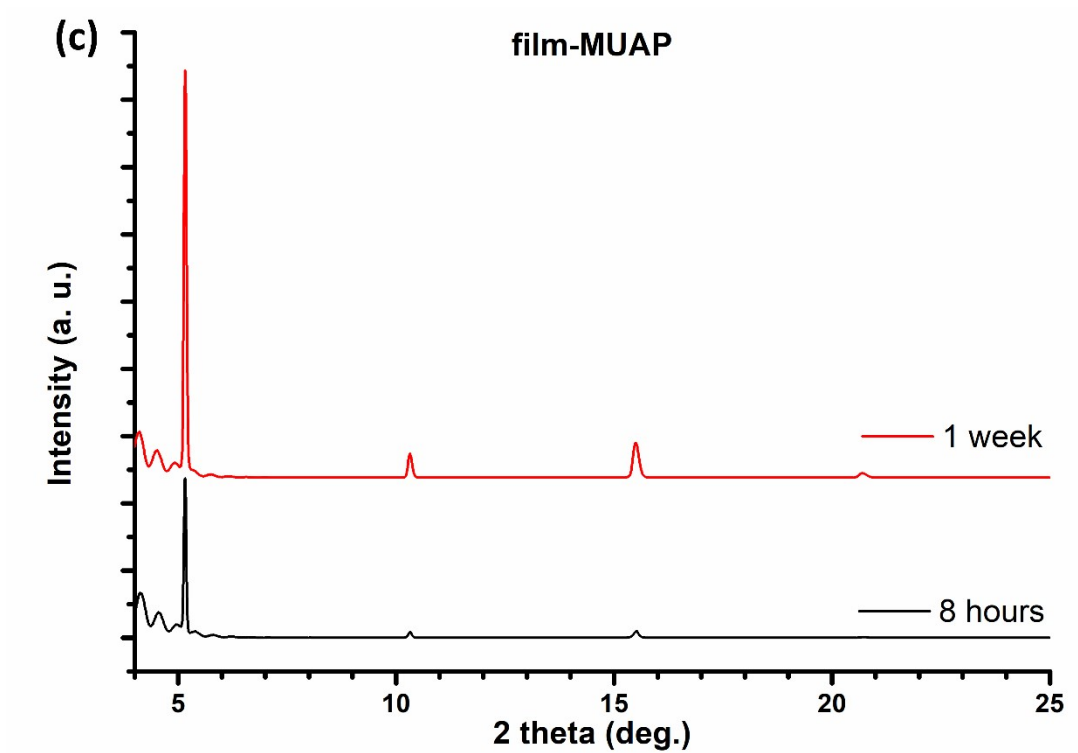


Figure S2. PXRD pattern of compound **1** (bulk state).

### 2.3 Out-of-plane synchrotron XRD measurements

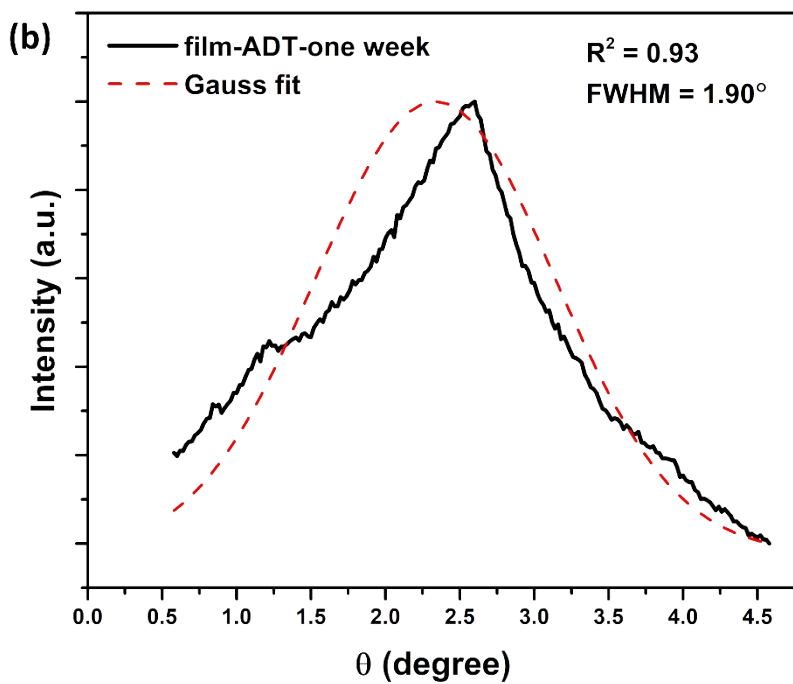
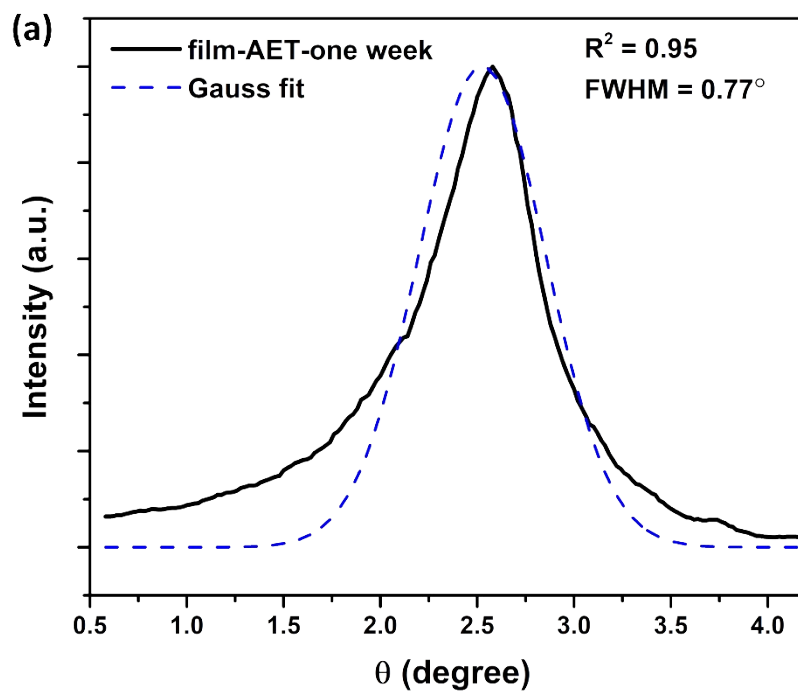


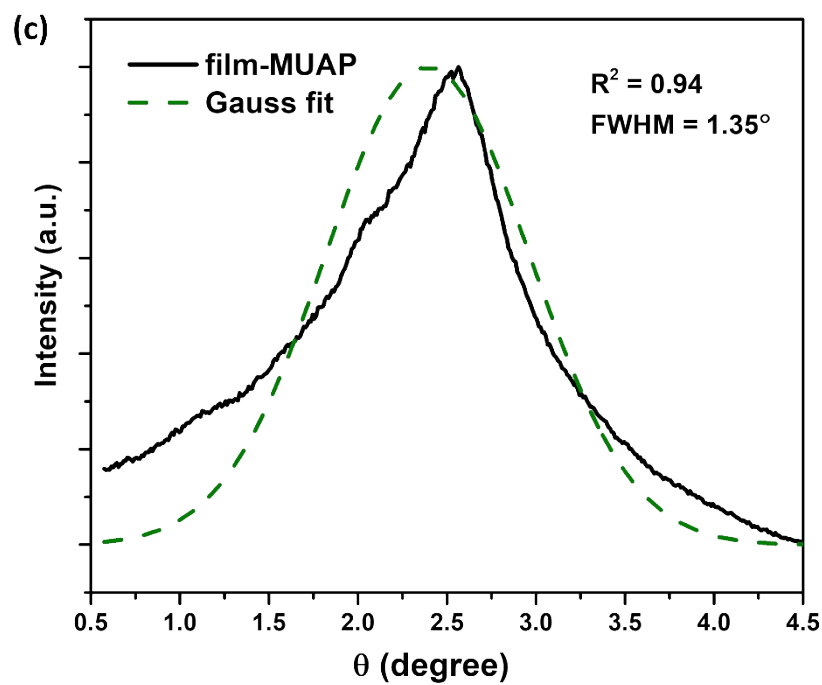




**Figure S3.** The out-of-plane ( $\theta$ - $2\theta$  mode) synchrotron XRD patterns of thin films (a) **film-AET**, (b) **film-ADT** and (c) **film-MUAP** at two-time intervals (8 h and 1 week).

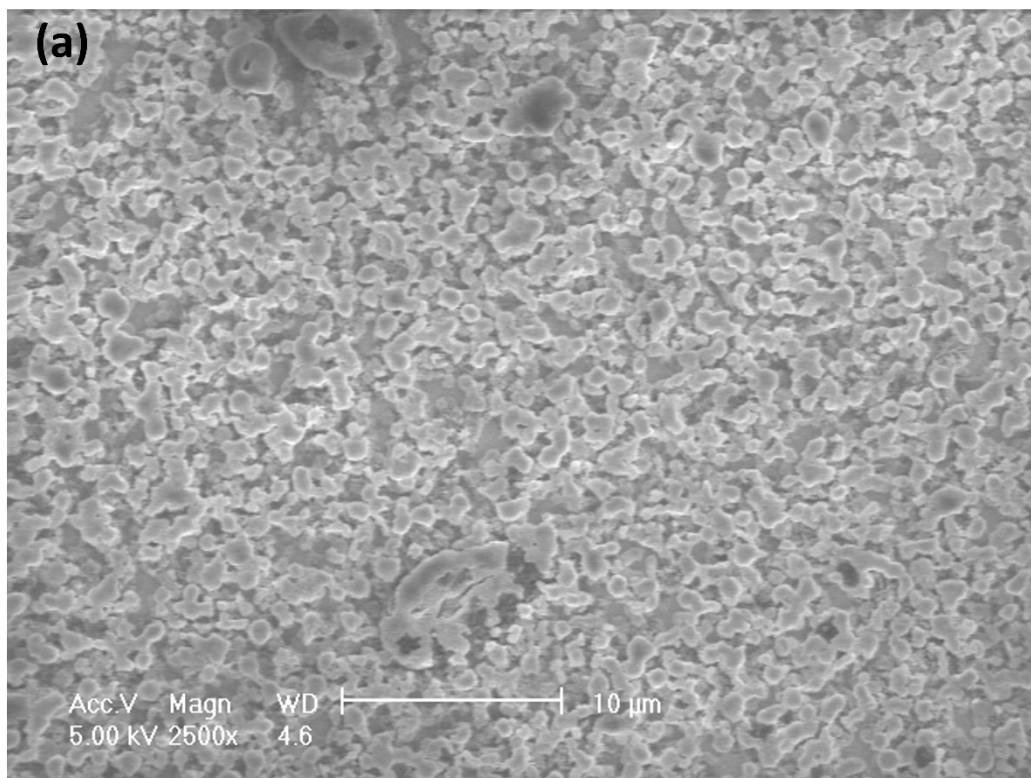
## 2.4 Rocking curve analysis



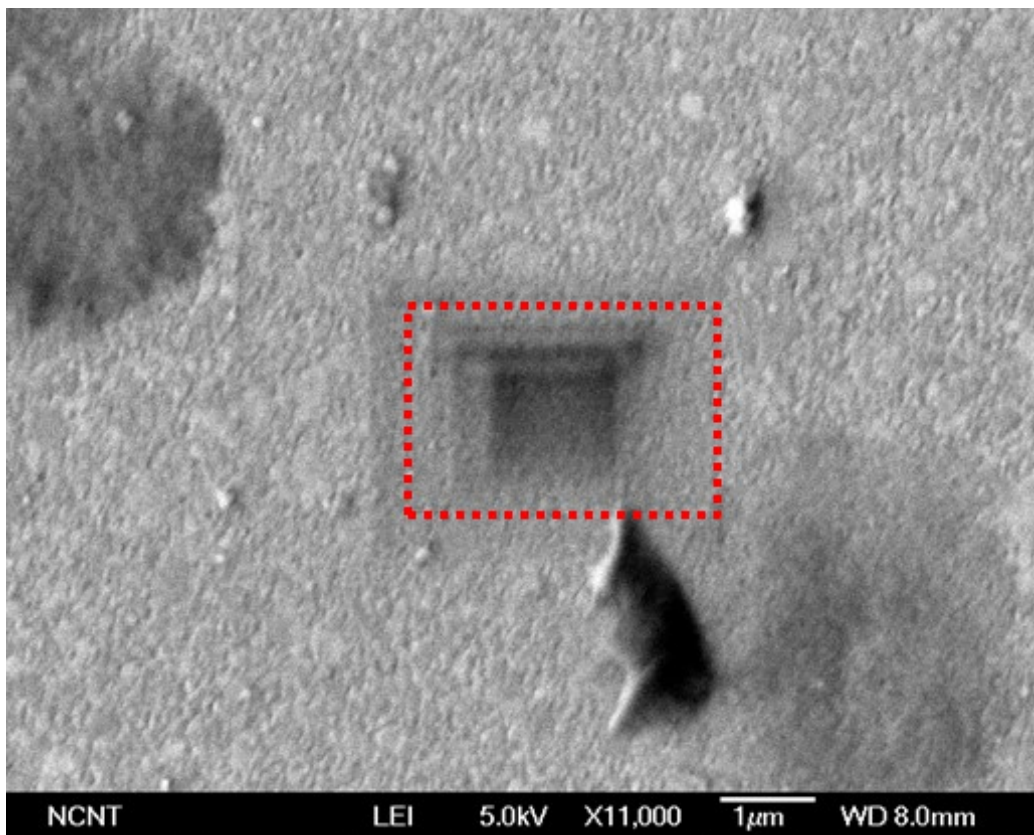


**Figure S4.** Rocking curves ( $\theta$ -scan) of (a) **film-AET**, (b) **film-ADT** and (c) **film-MUAP** at 010 peak position in the out-of-plane geometry. Inset:  $R^2$  = Coefficient of determination and FWHM = full-width at half-maximum.

## 2.5 Scanning electron microscopy (SEM) analysis



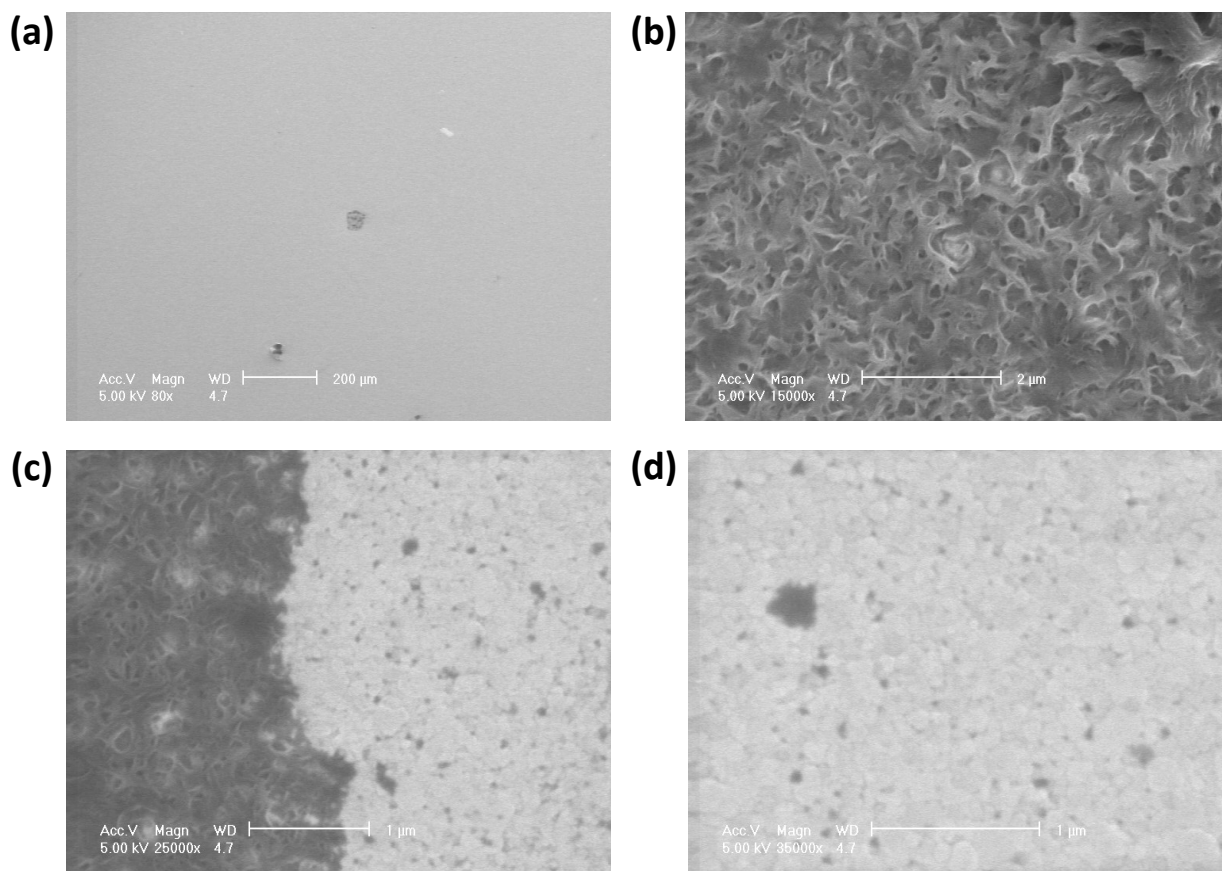
**Figure S5.** Morphology studies of **film-MUAP** analyzed using scanning electron microscopy.



**Figure S6.** Scanning electron microscopy image of **film-AET**, in which burn surface indicated in the figure with dotted red lines.

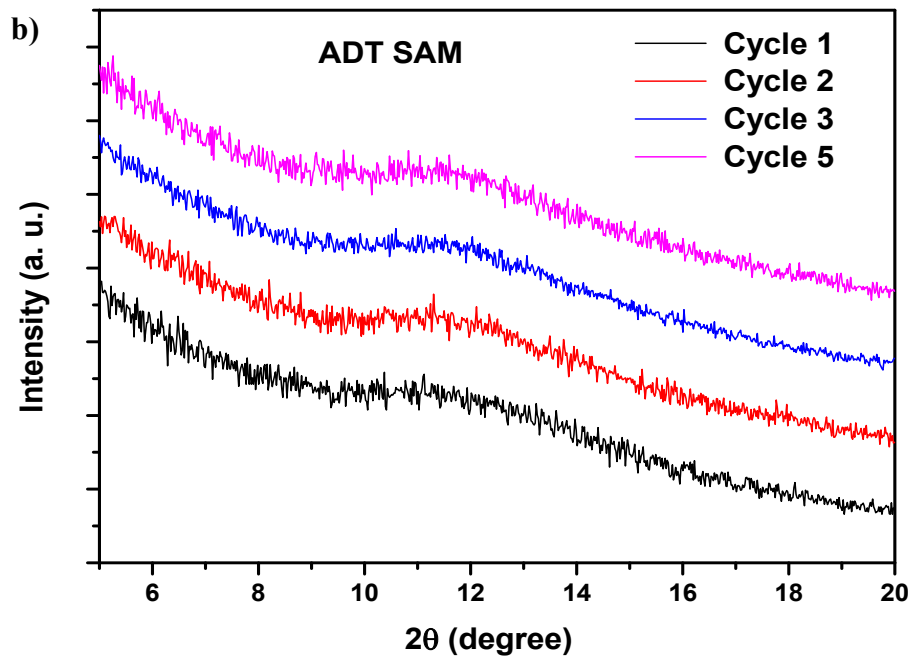
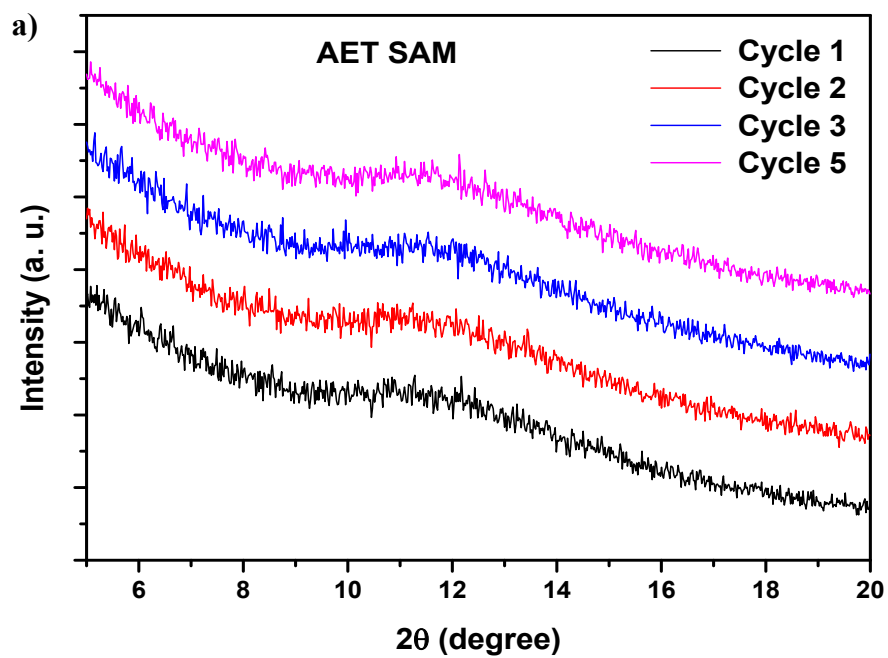
## Mechanistic studies of MOF thin film formation

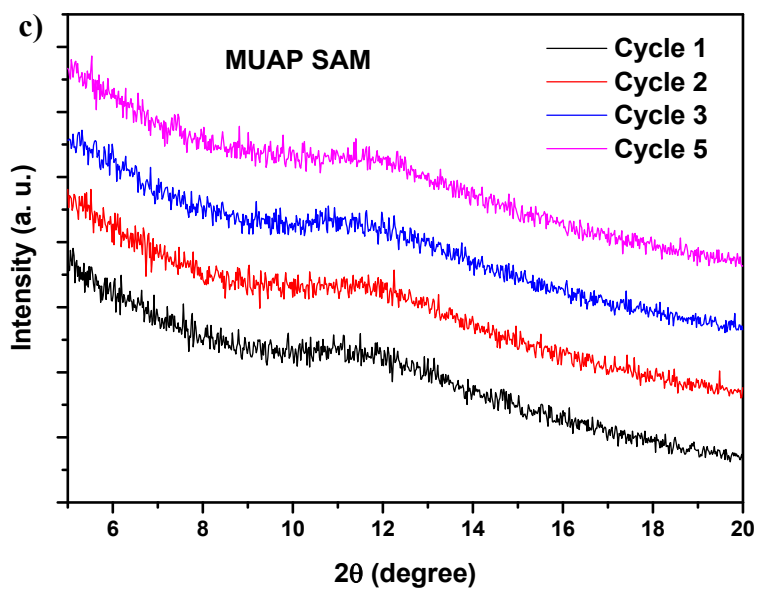
We conducted the SEM analysis in the followed sequential order: (1) bare Au-substrate, (2) self-assembled monolayers (SAMs) formation on Au-substrate, (3) conjunction of SAMs and MOF thin film, (4) completely grown MOF thin film. Based on the SEM images, we predicted the mechanism of thin film formation, in which the epitaxially grown MOF thin films are formed on Au-SAMs. Since the synthesis procedure is similar for all discussed MOF thin films, we focused on mechanism of **film-MUAP** formation.



**Figure S7.** Scanning electron microscopy (SEM) images of (a) bare Au-substrate, (b) self-assembled monolayer (**MUAP**) formation, (c) combination of **MUAP** and **film-MUAP**, (d) **film-MUAP**.

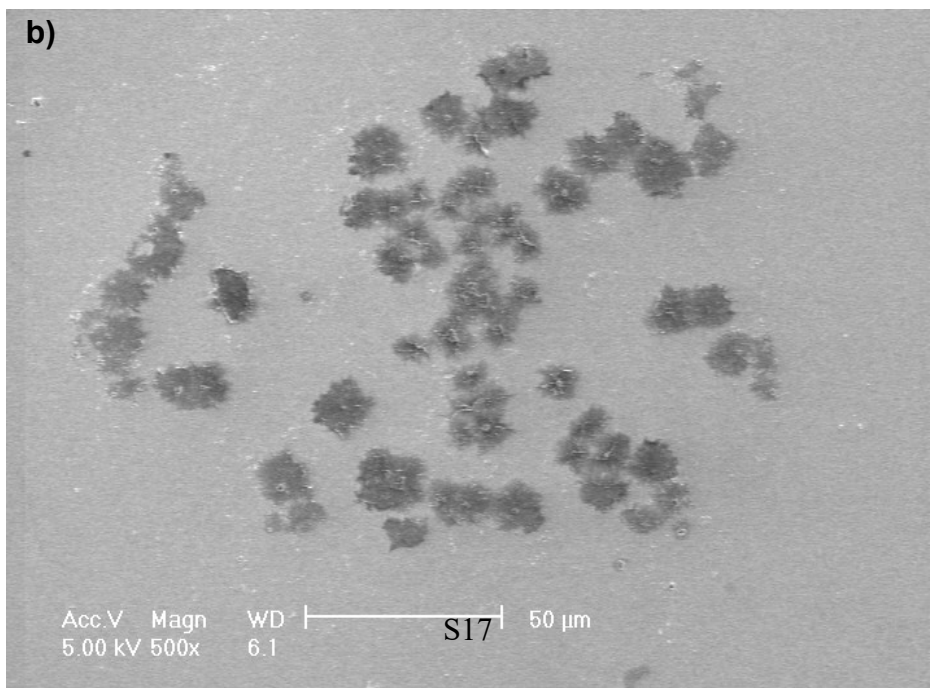
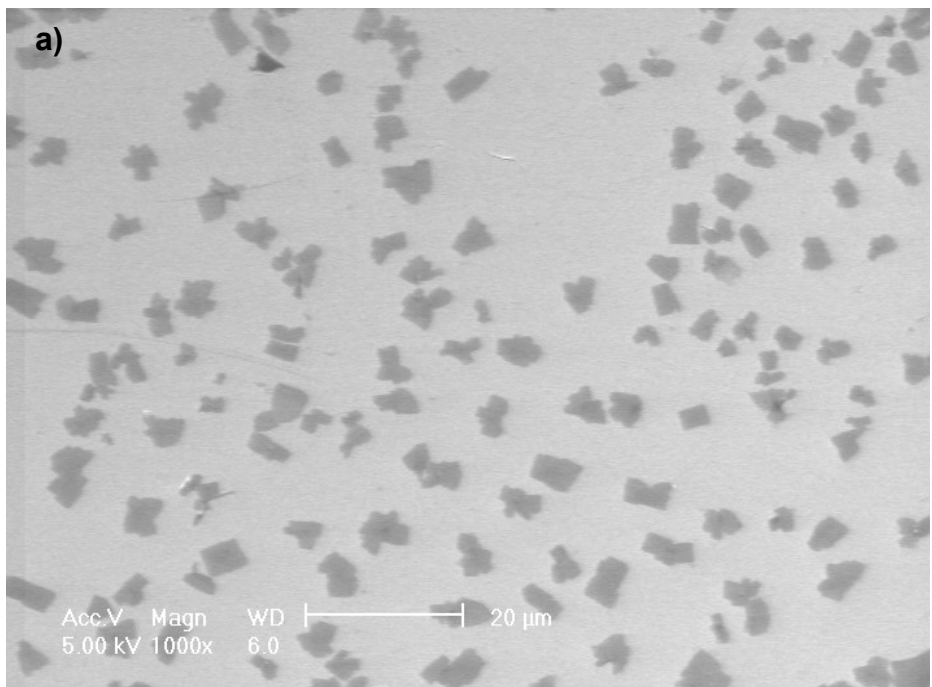
## 2.6 Control experiments for MOF thin films growth





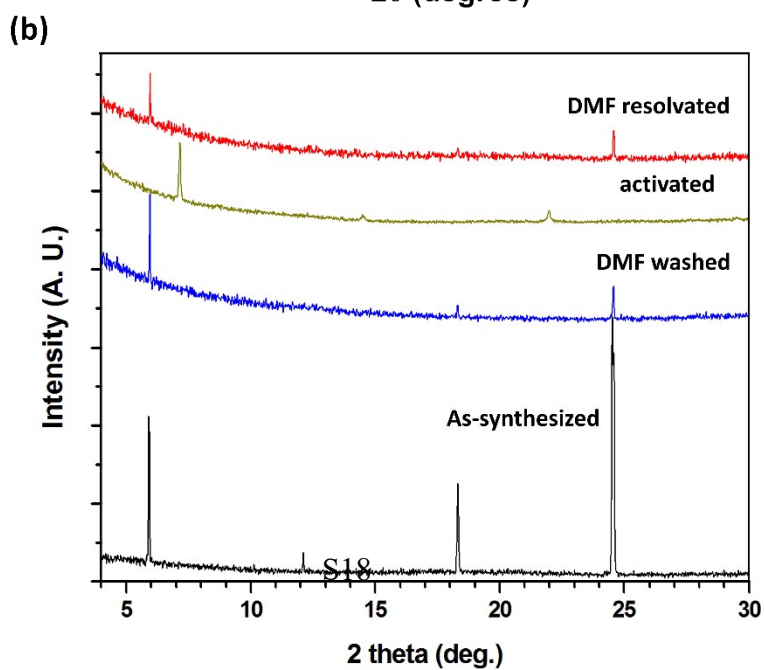
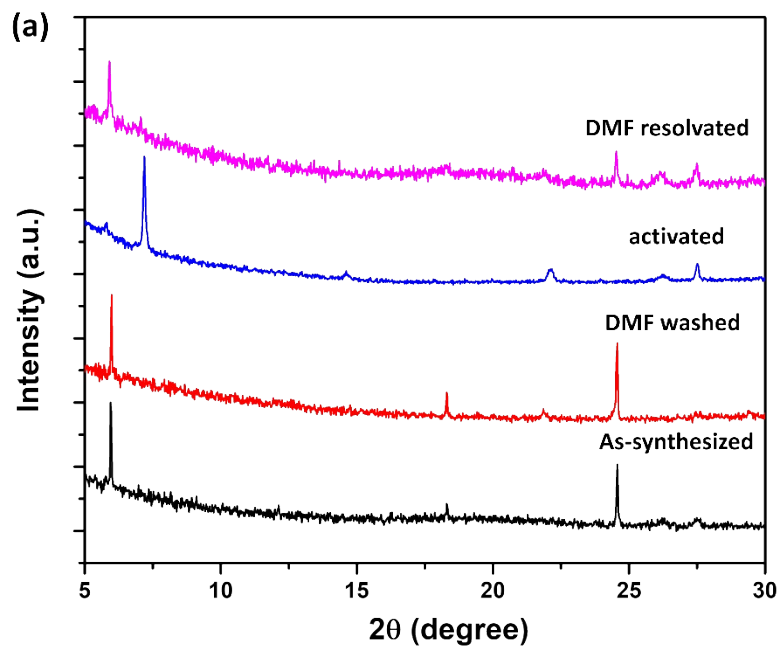
**Figure S8.** PXRD patterns (a), (b) and (c) are MOF seed grown substrates of AET-SAM, ADT-SAM, and MUAP, respectively.





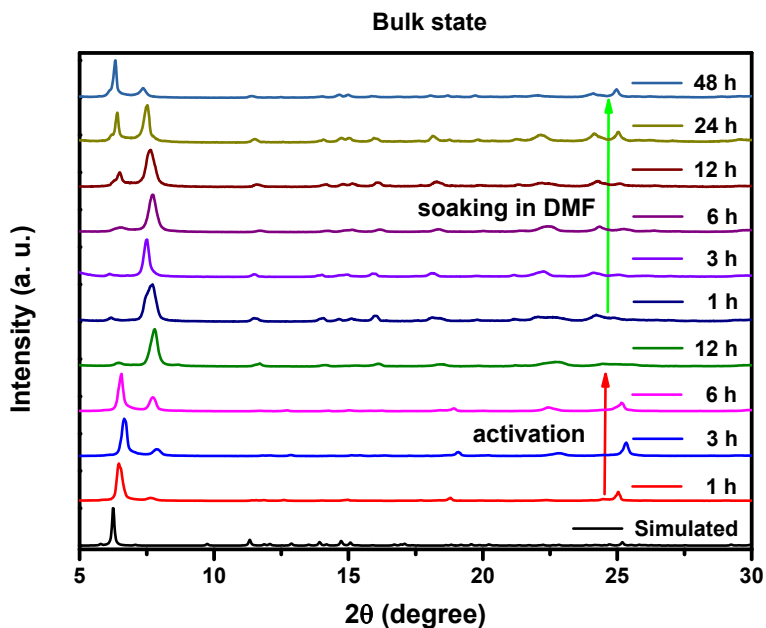
**Figure S9.** SEM images depicted the MOF growth at solvothermal conditions on different SAMs (a) AET-SAM and (b) ADT-SAM.

### 2.7 Breathing studies of MOF thin films

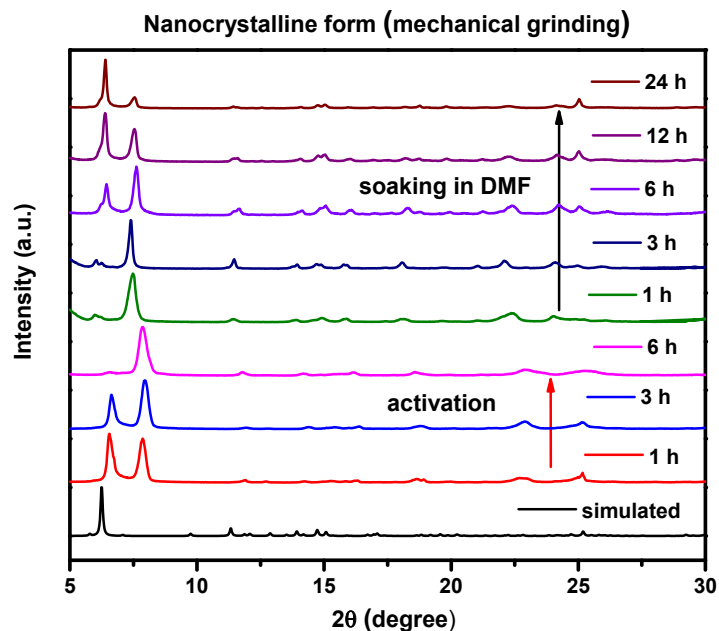


**Figure S10.** Powder X-ray diffraction patterns of breathing assisted structural flexibility in MOF thin films (a) **film-AET**, (b) **film-ADT** upon soaking and removal of DMF guest molecules.

## 2.8 Time dependent breathing studies



**Figure S11.** Time dependent PXRD patterns for guest (DMF solvent) responsive breathing behavior of MOF compound in the bulk state.



**Figure S12.** Time dependent PXRD patterns for guest (DMF solvent) responsive breathing behavior of MOF compound in the nanocrystalline state (after mechanical grinding).

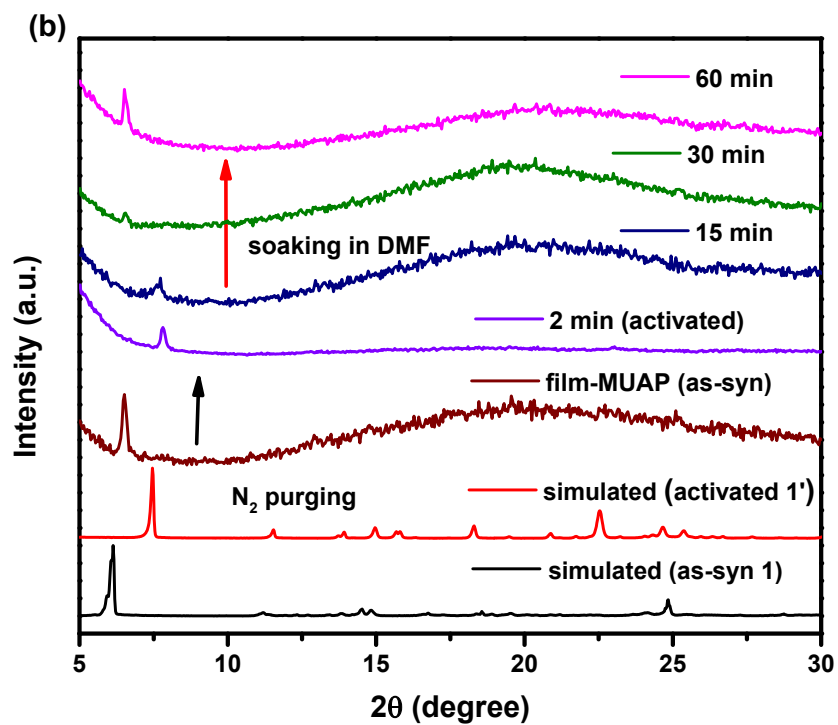
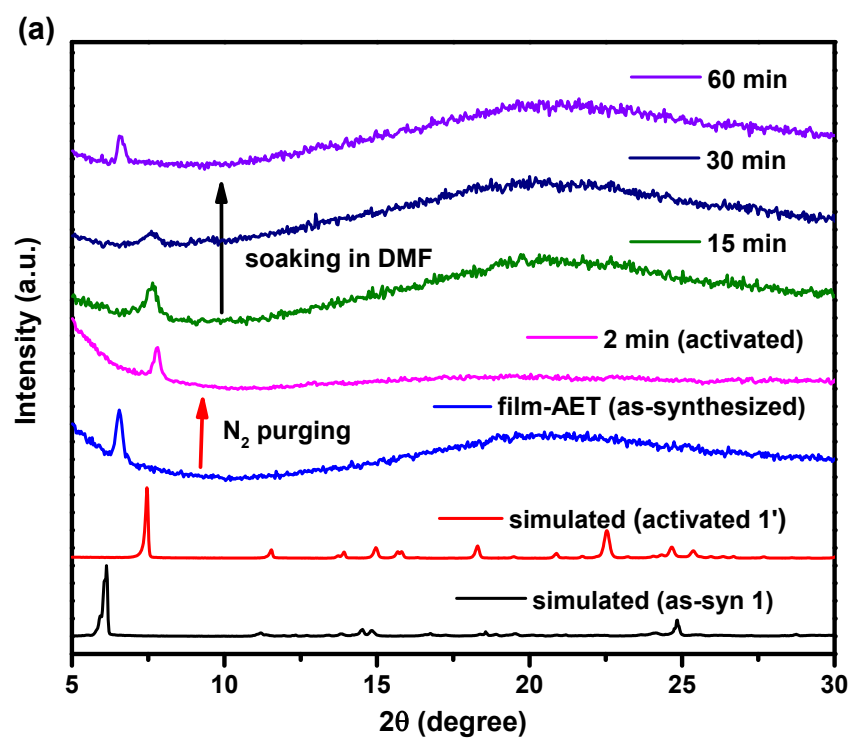


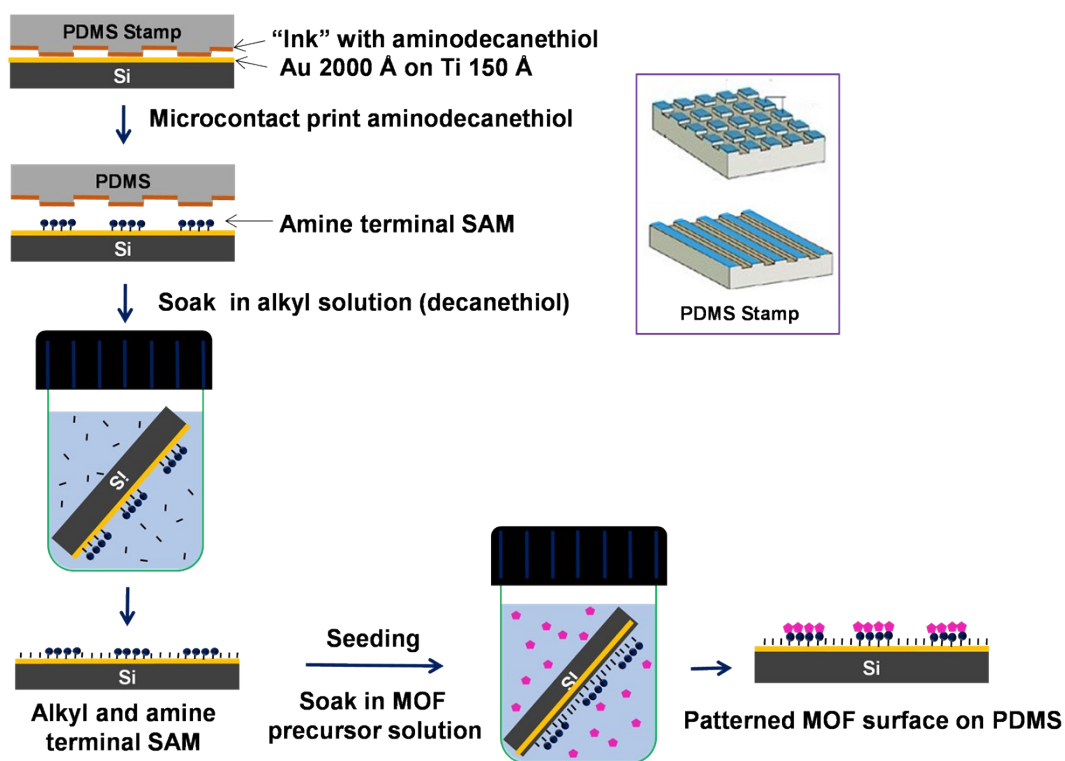
Figure S13.

Time  
dependent

PXRD patterns for guest (DMF solvent) responsive breathing behavior of MOF thin films (a) **film-AET**, (b) **film-MUAP**.

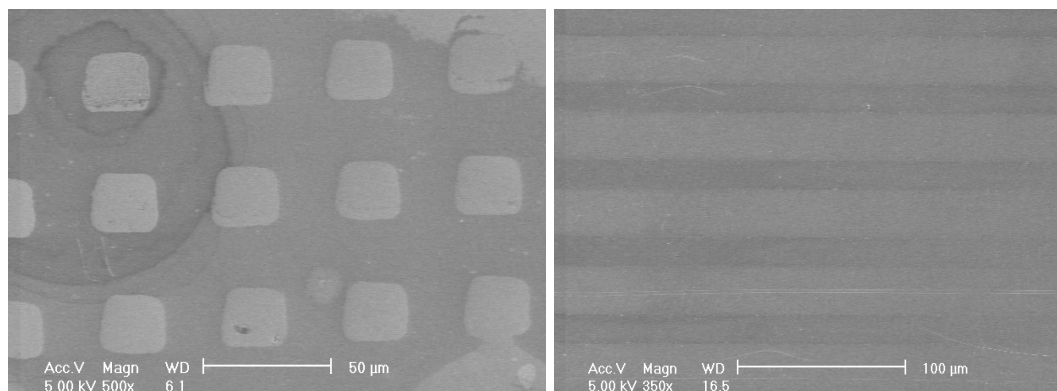
## 2.9 Procedure for MOF thin-film patterning

Aminodecanethiol (ADT) was patterned on a gold surface by a micro-contact printing ( $\mu$ -CP) using PDMS stamps (inked with 50 mM). The patterned surface was then immersed in decanethiol solution (50 mM in EtOH) to create the unreactive alternate layer (the area that was not functionalized by ADT). After that, the patterned substrate was immersed upside-down in a glass vessel containing MOF (100 mM) precursor solution for 12 hours. After the designated time, the substrate decorated with the patterned thin film was examined by scanning electron microscopy (SEM).

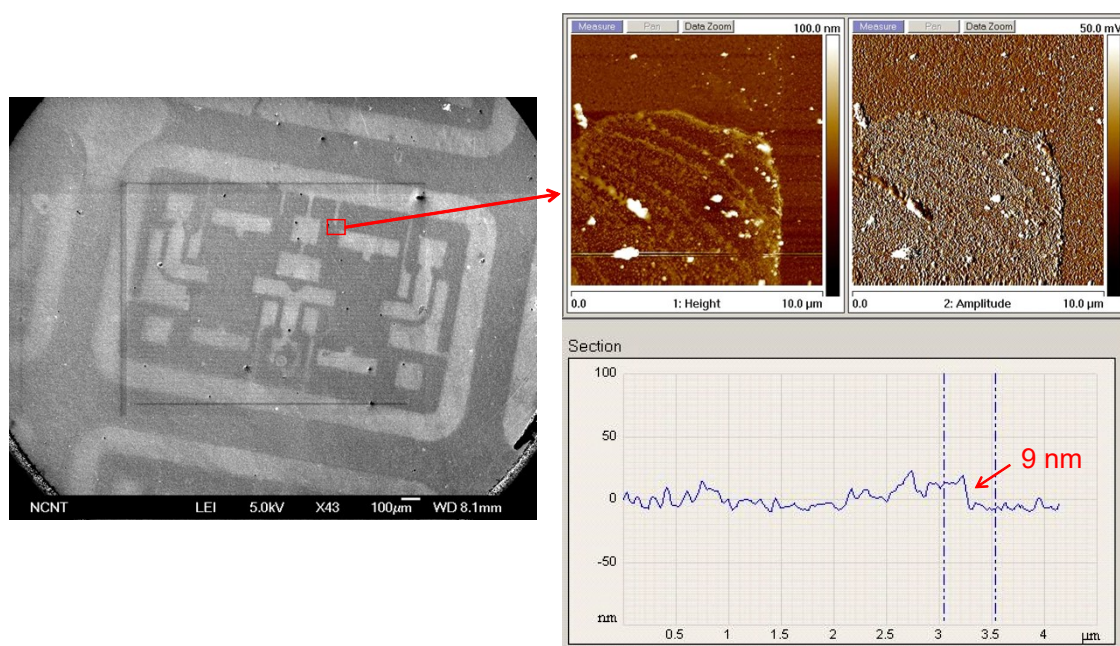


**Scheme S3.** A pictorial illustration of micropatterning of compound **1** on PDMS.

### 3. AFM and SEM analysis of Patterns



**Figure S14.** SEM images of micropatterned surfaces of **1**.



**Figure S15.** AFM images of micropatterned surfaces of **1** (without solvothermal synthesis)