

## Supporting Information

### **Complete Twin Suppression in Oriented NH<sub>2</sub>-MIL-125 Film via Facile Coordination Modulation**

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## 1. Experimental Procedures

### 1.1 Materials

Porous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> ceramic discs were purchased from Fraunhofer IKTS (Germany). 2-aminobenzene-1,4-dicarboxylic acid (NH<sub>2</sub>-BDC, 99.5%) was purchased from Alfa Aesar. Ti isopropoxide (TPOT, 99.9%) was purchased from Energy. N, N-dimethylformamide (DMF, 99.5%), methanol (MeOH, 99.5%) and acetic acid (AC, 99.5%) were purchased from Kermei. All chemicals were used as received without further purification. Various metal salts including copper nitrate (Cu(NO<sub>3</sub>)<sub>2</sub>, 99.5%), copper chloride (CuCl<sub>2</sub>, 99.5%), copper acetate (Cu(OAc)<sub>2</sub>, 99.9%), (Co(NO<sub>3</sub>)<sub>2</sub>, 99.9%), zinc nitrate (Zn(NO<sub>3</sub>)<sub>2</sub>, 99.9%), zirconium chloride (ZrCl<sub>4</sub>, 99.9%) and cuprous chloride (CuCl, 99.9%) were purchased from Macklin Chemical Reagent Co., Ltd.

### 1.2 Synthesis of NH<sub>2</sub>-MIL-125 seeds

0.56 g of NH<sub>2</sub>-BDC and 0.6 ml TPOT were dissolved in a solution containing 36 ml DMF and 4 ml dry MeOH with stirring. The mixture was then transferred to a 50 ml Teflon-lined autoclave and solvothermally treated at 150 °C under static conditions for 24 h. After cooling down, the solid product was centrifuged, washed with DMF and methanol, and finally dried in an oven at 60 °C overnight.

### 1.3 c-Oriented NH<sub>2</sub>-MIL-125 seed layer deposition

0.04 g NH<sub>2</sub>-MIL-125 microcrystals were mixed with 5 ml of ethanol and stirred in a cone-shaped bottle at room temperature for 6~30 days before use. First, the pre-cleaned  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> plate was placed onto a horizontal plane. Then the top of a needle was held at the air/water interface, seed solution was spread onto the water using an automatic injector at the speed of 2  $\mu$ l min<sup>-1</sup> until a continuous layer was formed at air-water interface. With controlled evaporation of the liquid layer, NH<sub>2</sub>-MIL-125 microcrystals self-assembled into a dense and highly c-oriented monolayer on the substrate. Identical procedures were employed to perform the self-assembly process on other substrates.

### 1.4 Epitaxial growth of c-oriented NH<sub>2</sub>-MIL-125(Ti) seed layer

#### 1.4.1 Acetic acid as the coordination modulator during epitaxial growth

0.28 g NH<sub>2</sub>-BDC was ultrasonically dissolved in a solution containing 27 ml DMF and 3 ml MeOH. Then, different amounts of acetic acid in the range of 0.003~0.03g was added to the above solution under ultrasonication following by the addition of 0.035 g TPOT. Subsequently, the precursor solution was poured into a 50 ml Teflon-lined autoclave in which a seeded support was placed vertically.

#### 1.4.2 Metal salts as coordination modulators during epitaxial growth

A mixture of 0.022 g Cu(NO<sub>3</sub>)<sub>2</sub> and 0.28 g NH<sub>2</sub>-BDC was ultrasonically dissolved in a solution containing 27 ml DMF and 3 ml MeOH. Then, 0.035 g TPOT was added to the above solution under ultrasonication. Subsequently, the precursor solution was poured into a 50 ml Teflon-lined autoclave in which a seeded support was placed vertically. Afterward, the vessel was sealed and heated at 150 °C in an oven for 3 h. After cooling, the membrane was washed with methanol and dried at room temperature overnight. Identical procedures were employed to prepare the membrane with diverse metal salts as coordination modulator.

#### 1.4.3 TiS<sub>2</sub> and TiS<sub>3</sub> as the metal precursor during epitaxial growth

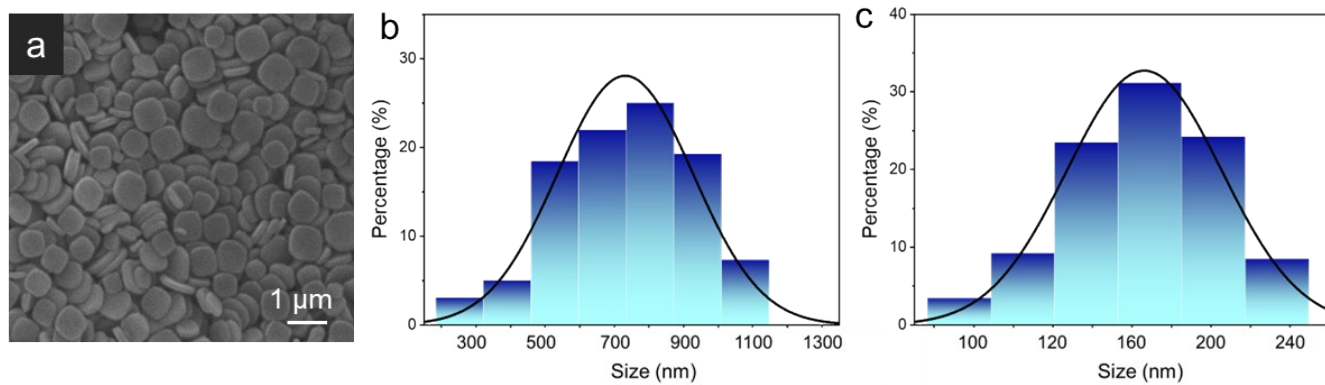
0.28 g of NH<sub>2</sub>-BDC and 0.009 g TiS<sub>3</sub> were dissolved in a solution containing 27 ml DMF and 3 ml MeOH. Subsequently, the precursor solution was poured into a 50 ml Teflon-lined autoclave in which a seeded support was placed vertically. Afterward, the vessel was sealed and heated at 150 °C in an oven for 3 h. After cooling, the membrane was washed with methanol and dried at room temperature overnight. Identical procedures were employed to prepare the membrane with TiS<sub>2</sub> as metal source during secondary growth process except that 0.007 g TiS<sub>2</sub> was used.

### 1.5 Characterization

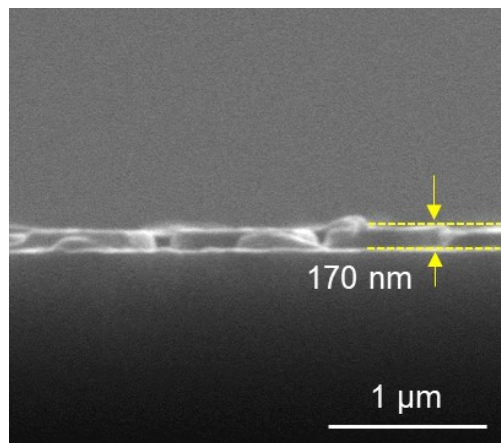
Powder X-ray diffraction (XRD) patterns were collected on a Rigaku SmartLab diffractometer with Cu K $\alpha$  radiation ( $\lambda$  = 0.15418 nm). SEM images were taken on a field mission scanning electron microscope (Hitachi FLEXSEM 1000). ATR-IR spectra were recorded using a Nicolet iN10 Infrared Microscope (Thermo Fisher, America).

## 2. Results and Discussion

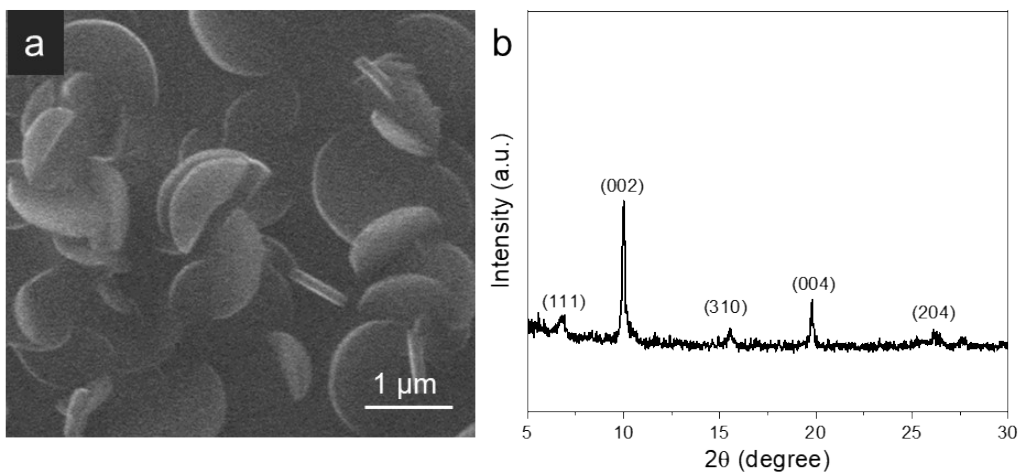
### 2.1 Supplementary Figures (Figure S1 to S8)



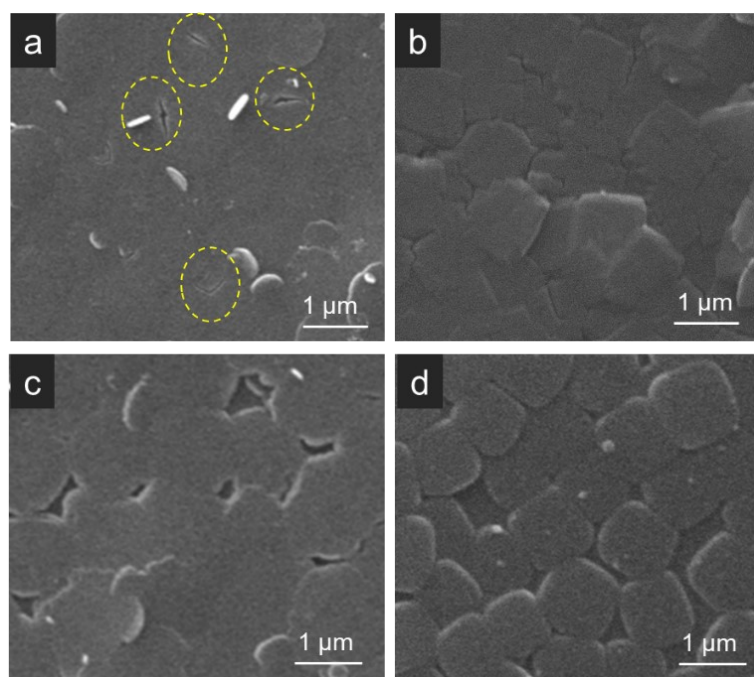
**Fig. S1** (a) SEM image of prepared NH<sub>2</sub>-MIL-125 seeds and size distributions of NH<sub>2</sub>-MIL-125 seeds (b) vertical to the *c*-axis direction and (c) in the *c*-axis direction.



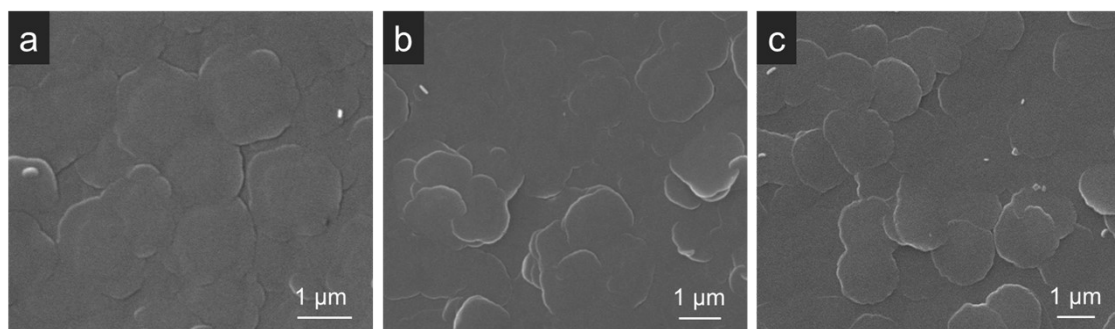
**Fig. S2** SEM image of cross-sectional views of the NH<sub>2</sub>-MIL-125 seed monolayer.



**Fig. S3** (a) SEM image and (b) XRD pattern of the  $\text{NH}_2\text{-MIL-125}$  film prepared in the absence of coordination modulators during epitaxial growth.

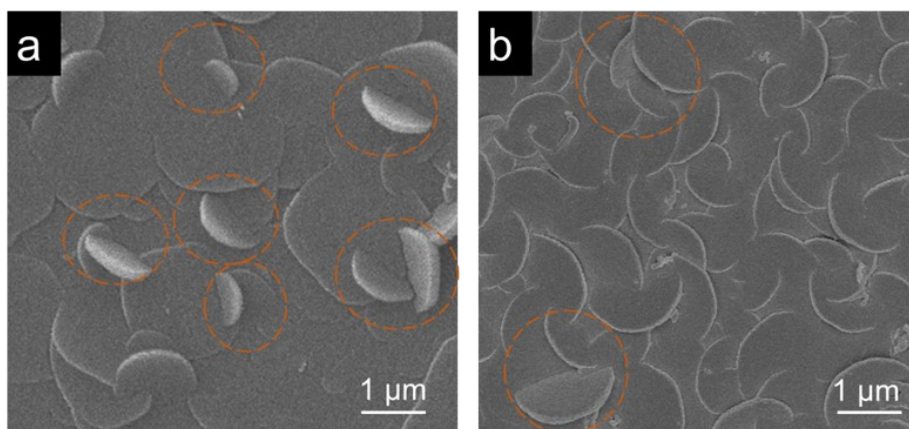


**Fig. S4** SEM images of NH<sub>2</sub>-MIL-125 films prepared with (a) 2 mM, (b) 4 mM, (c) 8 mM, and (d) 16 mM acetic acid as the growth modulator in the precursor solution.

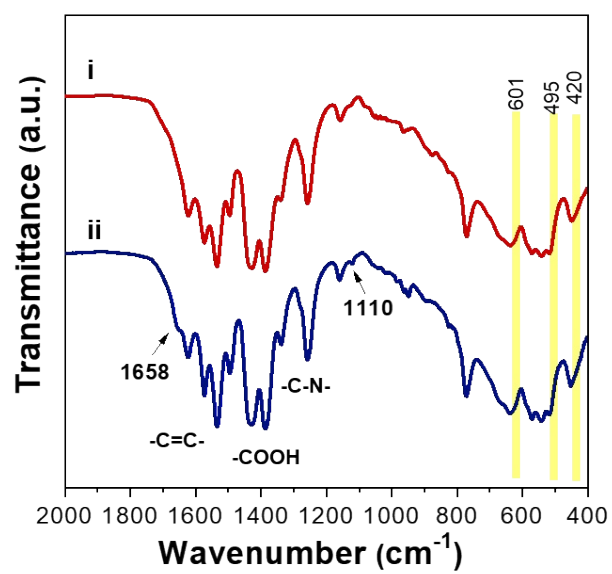


**Fig. S5** Low-magnification SEM images of the prepared NH<sub>2</sub>-MIL-125 film in the presence of Cu(NO<sub>3</sub>)<sub>2</sub> ([Cu<sup>2+</sup>]=4 mM).

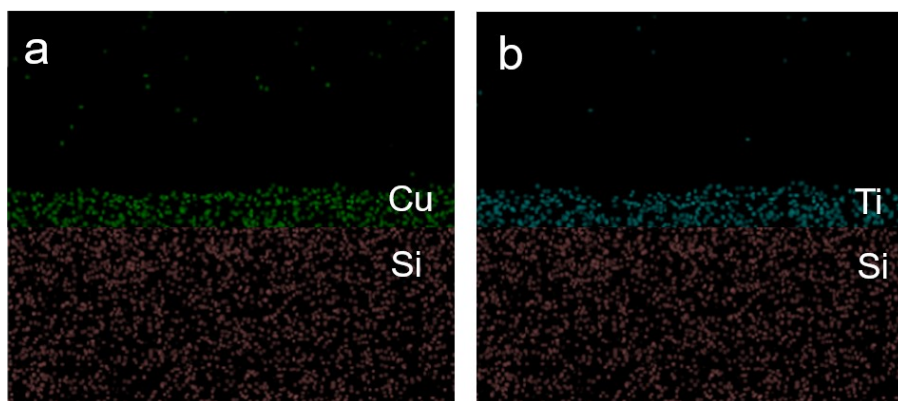




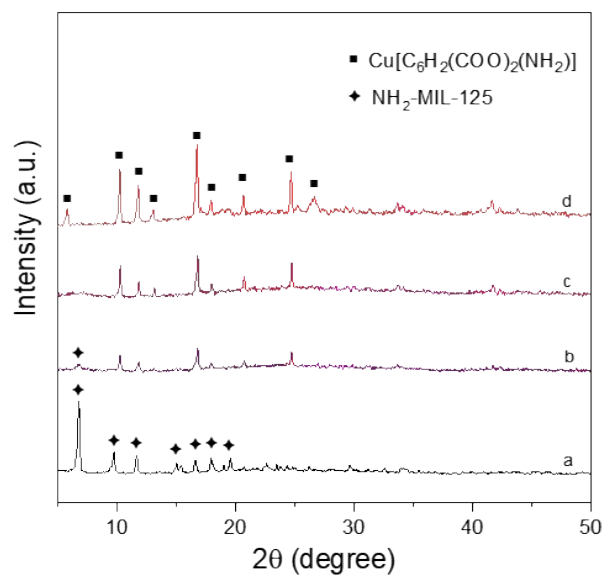
**Fig. S6** SEM images of NH<sub>2</sub>-MIL-125 films prepared with (a) TiS<sub>2</sub> and (b) TiS<sub>3</sub> as titanium sources using single-mode microwave heating during epitaxial growth.



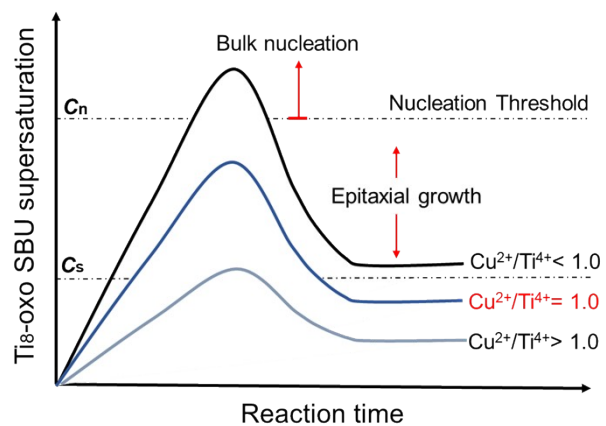
**Fig. S7** ATR-IR spectrum of NH<sub>2</sub>-MIL-125 films prepared in the presence of Cu(NO<sub>3</sub>)<sub>2</sub> (4 mM) (red) and in the absence of Cu(NO<sub>3</sub>)<sub>2</sub> as coordination modulator (green).



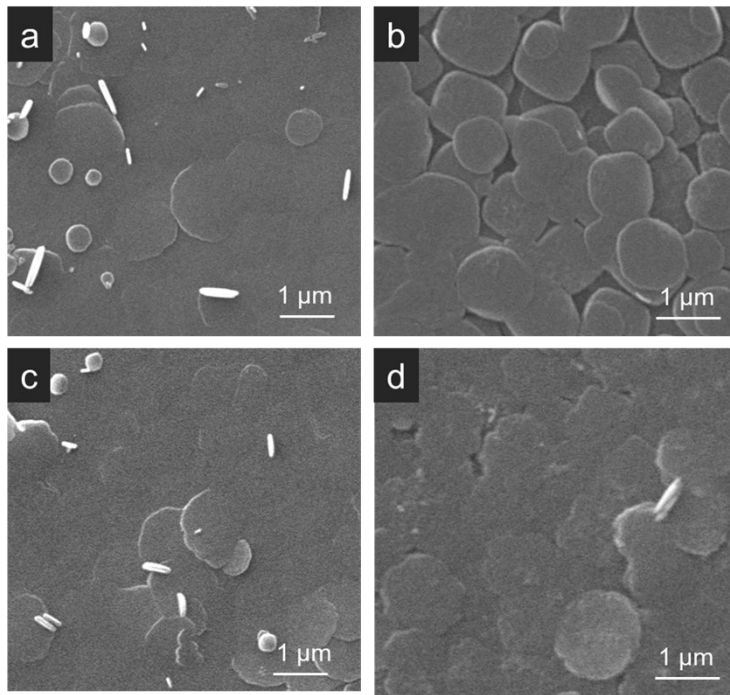
**Fig. S8** EDS mappings of (a) Cu and (b) Ti elements at the cross-section of prepared  $\text{NH}_2\text{-MIL-125}$  film in the presence of  $\text{Cu}(\text{NO}_3)_2$  ( $[\text{Cu}^{2+}] = 4 \text{ mM}$ ).



**Fig. S9** XRD patterns of precipitates sedimented from the bulk solution after epitaxial growth with  $[\text{Cu}^{2+}]$  of (a) 1 mM, (b) 2 mM, (c) 4 mM, and (d) 6 mM.

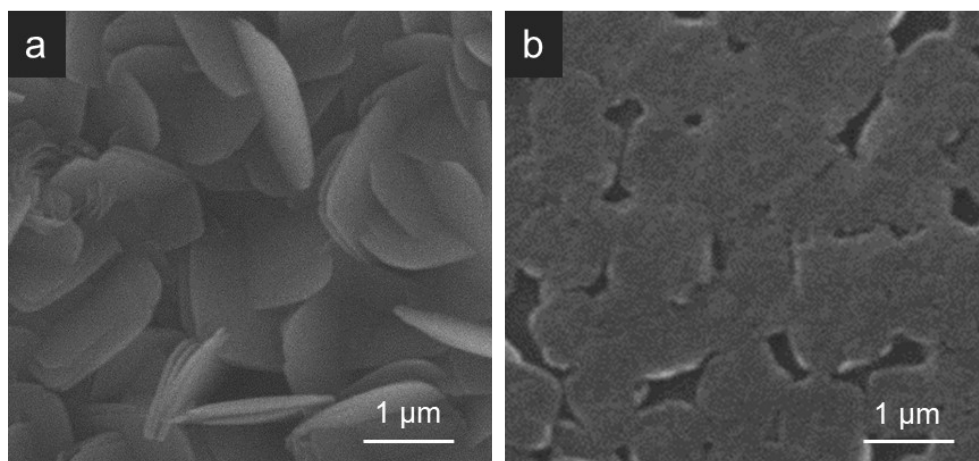


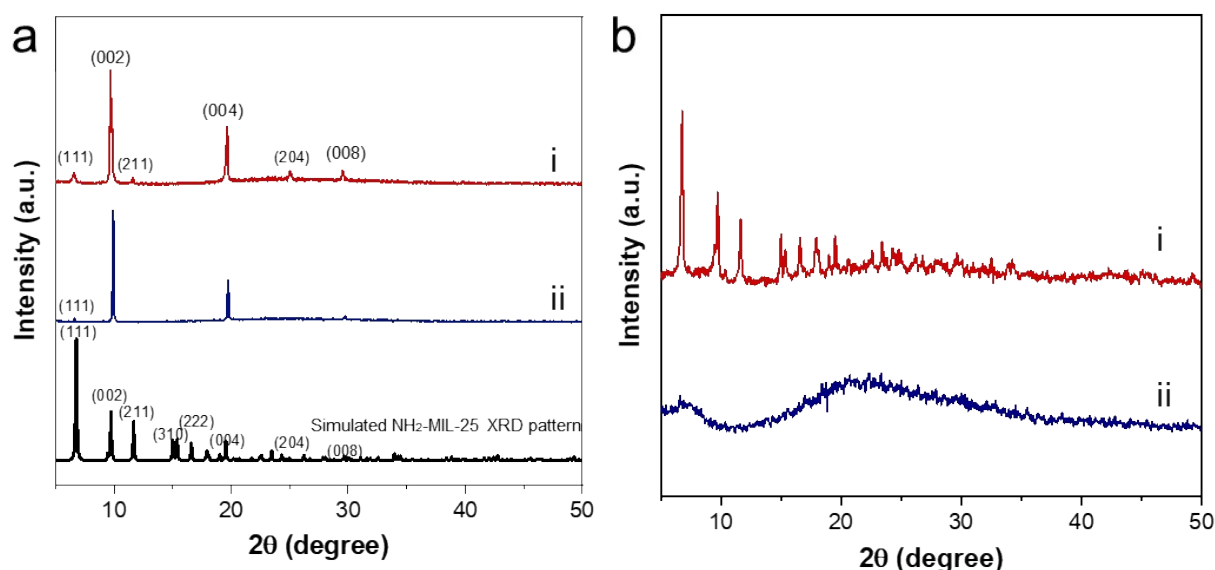
**Fig. S10** Schematic illustration of the change of  $Ti_8$ -oxo SBU supersaturation degree as a function of time in LaMer's model with various molar ratios of  $Cu^{2+}/Ti^{4+}$ .



**Fig. S11** SEM images of NH<sub>2</sub>-MIL-125 films prepared with (a) Co(NO<sub>3</sub>)<sub>2</sub> ([Co<sup>2+</sup>]= 2 mM), (b) Co(NO<sub>3</sub>)<sub>2</sub> ([Co<sup>2+</sup>]= 8 mM), (c) Zn(NO<sub>3</sub>)<sub>2</sub> ([Zn<sup>2+</sup>]= 2 mM), and (d) Zn(NO<sub>3</sub>)<sub>2</sub> ([Zn<sup>2+</sup>]= 8 mM) as growth modulators in the precursor solution.

**Fig. S12** SEM images of NH<sub>2</sub>-MIL-125 films prepared with (a) CuCl ([Cu<sup>+</sup>]= 4 mM) and (b) ZrCl<sub>4</sub> ([Zr<sup>4+</sup>]= 4 mM) as coordination modulators, respectively.





**Fig. S13** (a) XRD patterns of  $\text{NH}_2\text{-MIL-125}$  films prepared with (i)  $\text{CuCl}$  ( $[\text{Cu}^+] = 4 \text{ mM}$ ) and (ii)  $\text{ZrCl}_4$  ( $[\text{Zr}^{4+}] = 4 \text{ mM}$ ) as growth modulators. (b) XRD patterns of precipitates sedimented from the bulk solution after epitaxial growth with (i)  $\text{CuCl}$  ( $[\text{Cu}^+] = 4 \text{ mM}$ ) and (ii)  $\text{ZrCl}_4$  ( $[\text{Zr}^{4+}] = 4 \text{ mM}$ ).

As shown in Fig. S13a, no extra peaks except for characteristic peaks assigned to the  $\text{NH}_2\text{-MIL-125}$  phase could be discerned in the case that  $\text{Zr}^{4+}$  or  $\text{Cu}^+$  were used as the coordination modulator, thus confirming that no other crystalline phase was generated. It has been proven that  $\text{Zr}^{4+}$  ions, classified as a hard acid, enabled incorporation into the  $\text{NH}_2\text{-MIL-125}$  framework via substituting  $\text{Ti}^{4+}$  ions based on hard-hard interaction with  $\text{NH}_2\text{-BDC}$  ligands. Therefore, we deduced that  $\text{Zr}^{4+}$  ions were coordinated into the framework, resulting in the formation of mix-metal  $\text{NH}_2\text{-MIL-125}$  films. As a result, not only twin growth could not be completely suppressed as was convinced by the appearance of a weak diffraction peak assigned to the (111) plane of prepared  $\text{NH}_2\text{-MIL-125}(\text{Ti})$  film, but also substantial intercrystalline defects were simultaneously generated in the film (Fig. S12b).

In addition to  $\text{Zr}^{4+}$  ions, we further tried epitaxially growing  $\text{NH}_2\text{-MIL-125}(\text{Ti})$  films by using  $\text{Cu}^+$  ions, a soft acid, as the modulator (Fig. S12a). Nevertheless, characteristic peaks assigned to (111), (211), (204) planes of the  $\text{NH}_2\text{-MIL-125}$  phase could be clearly distinguished in the XRD pattern, indicating that crystal twinning could not be efficiently suppressed (Fig. S13a).

To further confirm the possible effect of hard and soft acids on twin suppression, precipitates sedimented from the bulk solution after epitaxial growth were collected and subjected to characterization. As confirmed by the XRD patterns (Fig. S13b), amorphous precipitates were formed in the bulk solution in the case that  $\text{Zr}^{4+}$  ions were used as the coordination modulator, indicating that incorporation of  $\text{Zr}^{4+}$  effectively inhibited the assembly of  $\text{NH}_2\text{-MIL-125}$  secondary building units ( $\text{Ti}_6\text{-oxo}$ ). Combining with excessive competition between  $\text{Zr}^{4+}$  and  $\text{Ti}^{4+}$  ions in terms of coordination with  $\text{NH}_2\text{-BDC}$  ligands, poorly intergrowth  $\text{NH}_2\text{-MIL-125}$  film containing nanosized twin crystals was finally formed. As for  $\text{Cu}^+$  ions, it was observed that substantial  $\text{NH}_2\text{-MIL-125}$  crystals were formed in the bulk solution during epitaxial growth. This could be ascribed to incompatible interaction of  $\text{Cu}^+$  ions with  $\text{NH}_2\text{-BDC}$  ligands, which exerted negligible influence on the strong ligand-metal ion interaction between  $\text{Ti}^{4+}$  ions and  $\text{NH}_2\text{-BDC}$  ligands.



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## 2.2 Supplementary table

**Table S1.** Calculation of relative lateral epitaxial growth rate of the seed layer during epitaxial growth with  $\text{Cu}(\text{NO}_3)_2$  as the coordination modulator.

	Lateral length (nm)	Vertical length (nm)	Relative lateral epitaxial growth rate
Seed layer	750	170	-
film	1300	195	-
Increment in the lateral direction and vertical direction	550	25	<b>22.0</b>

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