Supplementary Information

Surfactant-assisted synthesis of titanium nanoMOFs for thin film fabrication

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S1. MATERIALS AND REAGENTS

2-aminoterephtalic acid (99%) was purchased from Alfa Aesar, $Ti(O^{i}Pr)_{4}$ (97%), *N*,*N*-dimethylformamide (99.8%) were purchased from Acros Organics, and dry methanol (99.9%) were purchased from Sigma-Aldrich. All reagents and solvents were used as received without further purification.

S2. SYNTHESIS OF MATERIALS AND EXPERIMENTAL DETAILS

Synthesis of MIL-125-NH₂ - 1 mmol of titanium isopropoxide $Ti(OiPr)_4$ (0.305 ml) (Acros Organics, 98%) and 1.0 or 1.5 mmol of 2-aminoterephtalic acid (183.0 mg or 274.5 mg, respectively) (Alfa Aesar, 99%) were dissolved in a solution of 20 mL of *N*,*N*-dimethylformamide (DMF, Acros Organics, extra-dry) and 2.2 mL of dry methanol (Aldrich, 99.9%). The mixture was stirred gently during 5 minutes at room temperature, then was introduced in a 25 ml bottles and then put into an oven at 120°C for 24 hours. After cooling back to room temperature, the yellow solid was separated by centrifugation and washed three times with DMF, twice with methanol and dried under vacuum at 80 °C overnight.

The solids were further purified by Soxhlet washing with hot methanol overnight.

Modulated synthesis of MIL-125-NH₂ - 1 mmol of titanium isopropoxide Ti(OiPr)₄ (0.305 mL) (Acros Organics, 98%) and 1.0 or 1.5 mmol of 2-aminoterephtalic acid (183.0 mg or 274.5 mg, respectively) (Alfa Aesar, 99%) were dissolved in a solution of 20 mL of *N*,*N*-dimethylformamide (DMF, Acros Organics, extra-dry) and 2.2 mL of dry methanol (Aldrich, 99.9%). To this solution, different amounts of dodecanoic acid as modulator (Mod) were added to achieve L:Mod ratios of 1:10, 1:20, 1:30, 1:40 and 1:50. The mixture was stirred gently during 5 minutes at room temperature, then was introduced in a 25 ml bottles and then put into an oven at 120°C for 24 hours. After cooling back to room temperature, the yellow solid was separated by centrifugation and washed three times with DMF, twice with methanol and dried under vacuum at 80 °C overnight. The solids were further purified by Soxhlet washing with hot methanol overnight.

	RATIO	METAL:I	JINKER
EQUIVALENTS OF	1:0.5	1:1	1:1.5
MODULATOR			
0	0.5_0	1_0	1.5_0
10	0.5_10	1_10	1.5_10
20	0.5 20	1_20	1.5 20
30	0.5_30	1_30	1.5_30
40	0.5_40	1_40	1.5_40
50	0.5 50	1 50	1.5 50

Table S1. Nomenclature for the experiments with ratios L:M 0.5, 1.0 and 1.5 and Mod:M 0-50.

PXRD measurements - glass capillaries (0.5 mm) were filled with polycrystalline samples of the as-synthesised compounds, mounted and aligned on an Empyrean PANalytical powder diffractometer, using Cu K α radiation ($\lambda = 1.54177$ Å) with a PIXcel detector, operating at 40 mA and 45 kV. Profiles were collected by using a Soller Slit of 0.04° and a divergence slit of ½ at room

temperature in the angular range $3^{\circ} < 2\theta < 40^{\circ}$ with a step size of 0.013°. LeBail refinements were carried out with the FULLPROF software package. Average particle size analysis was carried out by means of the Scherrer equation and Williamson-Hall analysis in order to account for the peak broadening due to lattice strain effects. The instrumental contribution to the peak broadening was determined by measuring a LaB₆ standard under the same conditions.

Scanning Electron Microscopy (SEM) - Particle morphologies and dimensions were studied with a Hitachi S-4800 scanning electron microscope at an accelerating voltage of 20 kV, over metalized samples with a mixture of gold and palladium for 90 seconds.

¹**H-NMR** - NMR spectra were recorded on a Bruker Advance III 400 MHz spectrometer using DMSO-d6 as solvent (Chemical shifts (H) are reported in ppm). The samples were prepared by digestion of the solids in a D_2SO_4 :d₆-DMSO mixture (1:6) under stirring at 80°C overnight. The analysis was carried out with the MestRenova software package.

Gas sorption - measurements were performed on MIL-125-NH₂ powders Soxhlet washed with methanol. Surface area, pore size and volume values were calculated from nitrogen adsorptiondesorption isotherms (77 K) recorded on a Micromeritics 3Flex apparatus. Samples were degassed overnight at 60 °C and 10⁻⁶ Torr prior to analysis. Brunauer-Emmett-Teller (BET) Surface area analysis were performed as recommended for microporous and mesoporous materials. Specific surface area was calculated by multi-point BET method. Pore size distributions (PSD) were estimated by NLDFT methods assuming an oxide surface model with cylindrical shaped pores, which provided a good fit to the experimental data.

Thermogravimetric analysis (TGA) - curves were recorded on Soxhlet washed samples at a ramp rate of 5 °C/min on a Mettler Toledo TGA/SDTA 851e/SF/1100 apparatus between 25 and 600 °C under synthetic air.

Fourier-transform Infrared - FT-IR spectra of Soxhlet washed MIL-125-NH₂ solids were collected in the range 4000-650 cm⁻¹ with an Agilent Cary 630 FTIR Spectrometer equipped with an ATR module.

Dispersion of the NPs- Suspensions of MIL-125-NH₂ (20 mg/10 mL) were either prepared in water/methanol mixture (1:3 v/v) ethanol, toluene, dichloromethane, DMF or chloroform. The mixtures were sonicated for 10 minutes and then sedimented by gravimetry. For the photographs in Figure 2e, the samples were centrifuged to eliminate the sedimentation.

High-resolution transmission electron microscopy (HR-TEM) – The sizes and shapes of Soxhlet washed NPs were characterized using a TECNAI G2 F20 S-TWIN HR microscope operating at 200 kV. Sample preparation was done placing a drop of the colloidal suspension containing the MIL-125-NH₂ NPs onto a carbon coated copper grid. Size estimation was manually performed using image-J software.¹

UV–Visible Absorption Spectroscopy - UV–vis absorption spectra were recorded on a Jasco V-670 spectrophotometer using transmission photometric mode on Soxhlet washed samples.

Dynamic light scattering (DLS) - measurements were performed on Soxhlet washed samples using a Zetasizer ZS (Malvern Instrument, UK) at room temperature.

Substrate Preparation - ITO substrates were washed with soap and Mili-Q water, and then with isopropanol, and finally dried under nitrogen. Next, the substrates were placed in an O_2 plasma current (MiniPCFlecto, Plasma Technology) and activated for 15 minutes.

Film Preparation – For all cases freshly prepared dispersions of MIL-125-NH₂ (20 mg/10 mL) in a water/methanol mixture (1:3, v/v) were used after sonicating for 10 minutes. Spin coated samples were prepared on ITO substrates (120 rpms in 10 s with 3 s of time-lapse). For the dip coating method, ITO substrates were immersed in the dispersion for 15 minutes and then dried under nitrogen. For the spray coating method, the same dispersion was spray deposited onto ITO substrates for a period of 20 sec using a Central Pneumatic airbrush model 47791.

Atomic force microscopy (AFM) - measurements were carried out with a Digital Instrument Veeco Nanoscope IVa microscope in tapping mode using silicon tips with natural resonance frequency of 300 kHz and with an equivalent constant force of 40 N. Topography images were processed using Gwyddion software.²

Kr sorption isotherms of thin film samples were measured at 77 K using a Micromeritics 3Flex apparatus. Before the measurement, samples were degassed overnight at 120° C under dynamic vacuum (10^{-2} mbar). The calculated Kr surface area of MIL-125-NH₂ was obtained by Monte Carlo (MC) sampling with the Zeo++ software package³, using a probe radius of 1.8 Å and 5000 MC samples per atom.

Thin film X-ray diffraction - Samples were measured in a PANalytical Empyrean diffractometer (Bragg-Brentano geometry) using copper radiation (Cu K α = 1.5418 Å) with an PIXcel detector, operating at 40 mA and 45 kV. Profiles were collected in Gonio mode by using a Soller Slit of 0.02° and a divergence slit of ½ at room temperature in the angular range 4° < 20 < 40° with a step size of 0.013°.

S3. POWDER X-RAY DIFFRACTION (PXRD)





Figure S1. XRD patterns of MIL-125-NH₂ samples with L:M a) 0.5, b) 1.0 and c) 1.5 and Mod:M 0-50.



Figure S2. Bragg peak widths of MIL-125-NH₂ samples with L:M a) 1.0 and b) 1.5 and Mod:M 0-50.

S4. PROFILE FITTING AND CRYSTAL SIZE



Figure S3. LeBail refinements of the XRD data of MIL-125-NH₂ samples synthesised with a L:M ratio of a) 1.0 and b) 1.5 and different Mod:M ratios ranging from 0 to 50.

L:M	Mod:M	a = b [Å]	c [Å]	V [Å ³]	R _{exp} [%]	R _p [%]	R _{wp} [%]	gof
1:1	0	18.7598	18.2240	6413	3.95	5.09	6.68	1.7
	10	18.7662	18.2390	6476	3.39	4.61	6.06	1.8
	20	18.7627	18.2429	6422	3.38	4.42	5.74	1.7
	30	18.7732	18.2505	6432	3.33	4.50	5.99	1.8
	40	18.7779	18.2504	6435	3.41	4.43	5.80	1.7
	50	18.7651	18.2358	6421	3.32	4.39	5.91	1.8
1.5:1	0	18.7551	18.1982	6401	3.54	5.21	7.16	2.0
	10	18.7583	18.2157	6409	3.56	5.74	7.77	2.2
	20	18.7712	18.2334	6424	3.55	4.60	6.06	1.8
	30	18.7838	18.2529	6440	3.57	4.60	6.13	1.8
	40	18.7858	18.2580	6443	3.81	4.11	5.33	1.4
	50	18.7758	18.2456	6435	3.46	4.47	5.92	1.7

Table S2. Summary of cell parameters and agreement factors obtained from the LeBail refinements. Crystal system: Tetragonal. Space group: I4/mmm.

Table S3. Comparison of crystal sizes of the L:M 1.0 and 1.5 series as function of the Mod:M ratio obtained from PXRD and SEM.

	L:M 1.0		
Mod:M	Average size by PXRD (nm)	Average size by SEM (nm)	
0	526 ± 6.63	850 ± 103	
10	138 ± 2.26	100 ± 21.34	
20	92 ± 1.97	90 ± 9.81	
30	63 ± 1.16	85 ± 4.75	
40	59 ± 1.12	70 ± 4.63	
50	95 ± 0.61	90 ± 9.52	

	L:N	1 1.5
Mod:M	Average size by PXRD (nm)	Average size by SEM (nm)
0	793 ± 12.17	700 ± 81.37
10	468 ± 6.32	200 ± 49.89
20	134 ± 2.74	90 ± 10.25
30	91 ± 0.97	80 ± 9.93
40	70 ± 0.85	80 ± 5.17
50	84 ± 0.43	70 ± 4.71

S5. SCANNING ELECTRON MICROSCOPY (SEM-EDX)



850 ± 103 nm





90 ± 9.8 nm

85 ± 4.7 nm



Figure S4. SEM images of MIL-125-NH₂ samples with L:M 1.0 and Mod:M of a) 0 b) 10 c) 20 d) 30 e) 40 and f) 50. Representative images of the L:M 1.5 set are shown in the main text. Size estimation was manually performed using image-J software.¹

S6. ¹H-NMR EXPERIMENTS



Figure S5. ¹H-NMR experiments of DA(blue), NPs as made (green) and MIL-125-NH₂ bulk (red).



Figure S6. a) N_2 adsorption isotherms and b) pore distribution for the L:M 1.5 series as function of the Mod:M ratio 0-50.



Mod:M ratio 0-50



Figure S8 - Pore distribution for the L:M 1 series as function of the Mod:M ratio 0-50.

	L:M 1.0		
Mod:M	$S_{BET} (m^2/g)$	Micro pores volume (cm ³ /g)	
0	1360.1	0.459	
10	1642.9	0.542	
20	1408.5	0.444	
30	1396.6	0.439	
40	1384.6	0.438	
50	824.1	0.268	
	L:M 1.5		
	L:	M 1.5	
Mod:M	L:1 S _{BET} (m ² /g)	M 1.5 Micro pores volume (cm ³ /g)	
Mod:M 0	L:M S _{BET} (m ² /g) 1509.7	M 1.5 Micro pores volume (cm ³ /g) 0.513	
Mod:M 0 10	L:N S _{BET} (m ² /g) 1509.7 1487.6	M 1.5 Micro pores volume (cm ³ /g) 0.513 0.501	
Mod:M 0 10 20	L:N S _{BET} (m ² /g) 1509.7 1487.6 1517.0	M 1.5 Micro pores volume (cm ³ /g) 0.513 0.501 0.499	
Mod:M 0 10 20 30	L:N S _{BET} (m ² /g) 1509.7 1487.6 1517.0 1390.5	M 1.5 Micro pores volume (cm ³ /g) 0.513 0.501 0.499 0.439	
Mod:M 0 10 20 30 40	L:N S _{BET} (m ² /g) 1509.7 1487.6 1517.0 1390.5 1442.6	M 1.5 Micro pores volume (cm ³ /g) 0.513 0.501 0.499 0.439 0.478	

Table S4. Comparison of BET surfaces areas and micro pores volume of the L:M 1.0 and 1.5 samples as function of the Mod:M ratio obtained from N_2 adsorption isotherms at 77K.



Figure S9. DLS distribution of NPs size for dispersion in MeOH.

S9. NP TRANSMISSION ELECTRON MICROSCOPY (TEM)



Figure S10. HR-TEM image of NPs.



Figure S11. Histogram of particle distribution from HR-TEM.

S10. UV-Vis



Figure S12. UV-Vis of the ethanol NPs dispersion after 24 to 72 hours.

S11. ATOMIC FORCE MICROSCOPY (AFM) OF THE FILMS



Figure S13. AFM image of a NPs film prepared using the dip coating method.



Figure S14. AFM image of a NPs film prepared using spray coating method.



Figure S15. AFM image of a NPs film prepared using the spin coating method.

S12. FILM PREPARATIOM USING BULK MIL-125-NH₂



Figure S16. AFM and optical images of the bulk film prepared using the spin coating method.

250 µm



Figure S17. Krypton physisorption isotherms of a spin coated film onto Si and a bare Si substrate for reference.

S13. REFERENCES

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