

Supporting Information

One-Step Rapid Fabrication of MOF@Polymer Core-shell Particles through Non-Solvent Induced Surface Deposition

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Other supporting materials for this manuscript include the following:

Video S1

Section S1. Materials

Zirconium(IV) chloride ($ZrCl_4$, Alfa Aesar, 98%), copper(II) nitrate hydrate ($Cu(NO_3)_2 \cdot 3H_2O$, Tokyo Chemical Industry, 98%), 2-aminoterephthalic acid (NH_2 -BDC, Tokyo Chemical Industry, 98%), 1,4-dicarboxybenzene (H_2 BDC, Aladdin, 99%), fumaric acid (FA, J&K, 98%), 1,3,5-benzenetricarboxylic acid (H_3 BTC, Alfa Aesar, 98%), 4,4'-biphenyldicarboxylic acid (H_2 bpdc, Aladdin, 97%), acetic anhydride (Ac_2O , SCRC, 98.5%), triethylamine (TEA, Aladdin, 99%), acetic acid glacial (HOAC, Greagent, 99.5%), formic acid ($HCOOH$, Alfa Aesar, 98%), hydrofluoric acid (HF, Aladdin, 40%), oleic acid (OA, Aladdin, 85%), sodium hydroxide (NaOH, Aladdin, 96%), N,N-dimethylformamide (DMF, Greagent, 99.5%), n-hexane (SCRC, 97%), dichloromethane (DCM, Greagent, 99.5%), cyclohexane (Adamas, 99%), petroleum ether (PE, Greagent, 60-90 °C) tetrahydrofuran (THF, SCRC, 99%), 1-methyl-2-pyrrolidinone (NMP, Aladdin, 99%), anhydrous methanol (Greagent, 99.5%), Polysulfone (SCRC, M.W ~80000, 98%) and *O,O'*-bis(2-aminopropyl) polypropylene glycol-block-polyethylene glycol-block-polypropylene glycol (Jeffamine ED-2003, Huntsman, 50% v/v) were purchased from the mentioned sources and used without further purification. 4,4'-Oxydiphthalic anhydride (ODPA, Aladdin, 97%) and 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA, Tokyo Chemical Industry were purified by recrystallization in acetic anhydride. 2,4,6-trimethyl-1,3-phenylenediamine (DAM, Adamas, 98%) and 2,3,5,6-tetramethyl-1,4-phenylenediamine (durene, Tokyo Chemical Industry, 98%) were purified by recrystallization in ethanol. 4,4'-diaminodiphenylsulfon (DDS) was purified by recrystallization in ethanol. 5,5'-Tetrahydroxy-3,3,3',3'-tetramethyl spirobisindane (TTSBI, Alfa Aesar, 97%) was purified from hot methanol by dichloromethane. Tetrafluoroterephthalonitrile (TFTPN, Aladdin, 99%) was recrystallized *via*

vacuum sublimation at 140 °C. Potassium carbonate (K_2CO_3 , Aladdin, 99.0%) was ground, heated under vacuum at 110 °C before use.

Section S2. Synthesis

Synthesis of 6FDA-durene ^[1]

Durene (2.354 g, 14.33 mmol) and NMP (26 mL) were added into a 250 mL flask equipped with a nitrogen inlet. The mixture was cooled to 0 °C and then 6FDA (6.364 g, 14.33 mmol) and NMP (26 mL) were added. The solution was stirred for 24 hours to form polyamic acid. Next, 2 mL of TEA, 5.4 mL of Ac_2O and NMP (10 mL) were added. The mixture was vigorously stirred for 20 hours to allow complete imidization. The polyimide product was precipitated in methanol (1 L), filtered, washed with methanol several times and dried under vacuum at 150 °C for 24 hours.

Synthesis of ODPA-DAM/6FDA-DAM

ODPA-DAM/6FDA-DAM was obtained following a previous method. ^[2] 2.152 g (14.33 mmol) DAM was dissolved in 15 mL NMP under a nitrogen atmosphere. Then, the reaction vessels were immersed in an ice-bath. 4.445/6.364 g (14.33 mmol) ODPA/6FDA and additional 15 mL NMP was added into the reaction solution. Then the mixture was stirred for 24 hours to form a viscous poly (amic acid) (PAA) solution. For the imidization, a solution of 2 mL triethylamine (TEA) and 5.4 mL of Ac_2O dissolved in 6 mL NMP was added. The mixture was stirred at room temperature for another 24 hours. The obtained mixture was added slowly into methanol to obtain white polyimide fibers. The as-synthesized polyimide was washed several times by anhydrous methanol before drying in a vacuum oven at 150 °C for 24 h.

Synthesis of 6FDA-DAM-co-Jeffamine ^[3]

1.722 g (11.46 mmol) DAM and 5.445 g (2.87 mmol) Jeffamine was dissolved in 15 mL NMP under a nitrogen atmosphere. Then, the reaction vessels were immersed in an ice-bath. 6.364 g (14.33 mmol) 6FDA and additional 15 mL NMP was added into the reaction solution. Then the mixture was stirred for 24 hours to form a viscous poly (amic acid) (PAA) solution. For the imidization, a solution of 2 mL triethylamine (TEA) and 5.4 mL of Ac₂O dissolved in 6 mL NMP was added. The mixture was stirred at room temperature for another 24 hours. The obtained mixture was added slowly into methanol to obtain white polyimide fibers. The as-synthesized polyimide was washed several times by anhydrous methanol before drying in a vacuum oven at 150 °C for 24 h.

Synthesis of 6FDA-DDS

6FDA-DDS polymer was synthesized following a previously reported method with slight modification. ^[2] Under a nitrogen atmosphere, 3.7245 g (15 mmol) DDS was dissolved in 15 mL anhydrous DMF. After the monomer was completely dissolved, the flask was then immersed in an ice-bath. 6.6636 g (15 mmol) 6FDA and additional 15 mL anhydrous DMF was added. Then the mixture was stirred for 24 hours to form a viscous poly (amic acid) (PAA) solution. For the imidization, a solution of 2.1 mL triethylamine (TEA) and 5.7 mL Ac₂O dissolved in 6 mL anhydrous DMF was added. The mixture was stirred at room temperature for another 24 hours. The obtained mixture was ejected slowly into methanol, yielding white polyimide fibers. The obtained polyimide was then washed several times by fresh methanol. The final product was dried in a vacuum oven at 150 °C for 24 hours.

Synthesis of PIM-1

PIM-1 was synthesized *via* low-temperature condensation between TTSBI and TFTPBN according to a reported protocol. ^[4] A mixture of TTSBI (10.213 g, 30 mmol), TFTPBN (6.003 g, 30 mmol), anhydrous K₂CO₃ (8.292 g, 60 mmol) and anhydrous DMF (200 mL) were stirred 15 minutes with a nitrogen inlet to ensure that all monomers were dissolved. Then the mixture was vigorously stirred for 23 hours at 55 °C. After cooling to room temperature, PIM-1 was precipitated in water. The crude product was then re-dissolved in chloroform and precipitated in methanol. The procedure was repeated for three times to ensure complete removal of impurities. Finally, the yellow powder was dried under vacuum at 150 °C for 24 hours.

Synthesis of MOF-801

MOF-801 was synthesized by dissolving ZrCl₄ (481.93 mg, 2.1 mmol) and fumaric acid (719.6 mg, 6.2 mmol) in 80 mL DMF. After mixing, 5.46 mL HCOOH was added. The mixture was heated in an oven at 120 °C for 24 hours. After cooling down to room temperature, the product was collected by centrifugation and washed by fresh DMF and anhydrous methanol three times respectively.

Synthesis of UiO-66

UiO-66 was synthesized by dissolving ZrCl₄ (583.6 mg, 2.5 mmol) and H₂BDC (413.6 mg, 3.56 mmol) in 100 mL DMF and 1 mL ethanol. After mixing, 9.14 mL acetic acid was added. The mixture was heated in an oven at 120 °C for 20 hours. After cooling down to room temperature, the product was collected by centrifugation and washed by fresh DMF and anhydrous methanol three times respectively.

Synthesis of UiO-66-NH₂

UiO-66-NH₂ was synthesized by dissolving ZrCl₄ (242.4 mg, 1.04 mmol) and NH₂-BDC (188 mg, 1.04 mmol) in 60 mL DMF. After mixing, 1.8 mL acetic acid was added. The mixture was heated in an oven at 120 °C for 20 hours. After cooling down to room temperature, the product was collected by centrifugation and washed by fresh DMF and anhydrous methanol three times respectively.

Synthesis of UiO-67

UiO-67 was synthesized by dissolving ZrCl₄ (30 mg, 0.13 mmol) and H₂bpdc (30 mg, 0.12 mmol) in 20 mL DMF. After mixing, 0.48 mL acetic acid was added. The mixture was heated in an oven at 120 °C for 24 hours. After cooling down to room temperature, the product was collected by centrifugation and washed by fresh DMF and anhydrous methanol three times respectively.

Synthesis of HKUST-1

HKUST-1 was synthesized following a previously reported method with slight modification. [5] First, 2.5 mL of NaOH aqueous solution (1 M) was added to a mixed solution of deionized water (17.5 mL), ethanol (30 mL), OA (10 mL) and n-hexane (4.25 mL) under stirring at 50 °C to obtain a thermostable microemulsion system. Then, 250 mg of Cu(NO₃)₂·3H₂O dissolved in 5 mL of deionized water. After stirring for 10 minutes, 250 mg of H₃BTC dissolved in a mixed solution deionized water (3.25 mL) and ethanol (4.25 mL) was added to the above solution. The mixture was heated to 70 °C for 2 hours with continuous stirring. The product was collected by centrifugation and washed by a mixture of cyclohexane and anhydrous ethanol for three times.

Synthesis of MOF@polymer

Firstly, the above synthesized 5 mg MOF was dispersed in 2.5 mL DCM, then add different content of the above synthesized polymer into the solution. After ultrasound for 10 min, 5 mL of petroleum ether was quickly poured into the mixture under stirring (600 rpm), the MOF and polymer quickly precipitate to form MOF@polymer in a matter of seconds. The product was collected by centrifugation and washed 3 times with petroleum ether. This synthesis can be scaled up to form the same product.

Synthesis of MOF-801/ODPA-DAM

Firstly, the above synthesized 5 mg MOF-801 was dispersed in 2.5 mL DCM, then 0.5 mg ODPA-DAM was dissolved in the mixture. After slow evaporation of solvent, the MOF-801/ODPA-DAM was obtained and dried overnight to remove residual solvent.

Compression procedure

Universal testing machines (INSTRON 5960) were used to compact the powders. A cylindrical die of 6 mm in diameter and close-fitting compression punch were used for this purpose. 30 mg powder were added into the die for compaction, and the speed of the punch is set at 1 mm/min during the compression until the targeted force is reached. The punch finally raises at 10 mm/min during the ascent. Finally, the tablets were taken down and stored at N₂ atmosphere.

Membrane preparation

To prepare MOF-801@6FDA-DAM-co-Jeffamine membrane, 20 mg as-synthesized MOF-801@6FDA-DAM-co-Jeffamine was dispersed in 0.5 mL dry DCM solution. Then, the mixture

was dropped onto a casting tray. The tray consisted of a glass ring attached to a leveled glass plate by epoxy sealant. After slow evaporation of solvent, the membrane was peeled off from the glass plate.

Section S3. Characterization

Transmission electron microscope (TEM) images were acquired on a JEM 1400 field-emission transmission electron microscope with voltage set at 120 kV. Selected area electron diffraction (SAED) patterns were acquired on a JEM-2100 Plus field-emission transmission electron microscope with voltage set at 200 kV. Scanning electron microscope (SEM) images were acquired on a JEOL JSM 7800F Prime SEM. Energy-dispersive X-ray spectroscopy (EDS) elemental mapping images and line scan were collected on a JEM 1400 plus (120 kV). Powder X-ray diffraction patterns (PXRD) were acquired on a Bruker D8 Advance diffractometer with Cu K α radiation. X-ray photoelectron spectroscopy (XPS) data of the samples was collected on an ESCALAB 250Xi X-ray photoelectron spectrometer. Inductively coupled plasma atomic emission spectroscopy (ICP-OES) data of the samples was collected on an Icap 7400 inductively coupled plasma atomic emission spectroscopy. TGA experiments were performed on a PerkinElmer TGA 8000. Samples were firstly heated to 150 °C and retained at that temperature for 30 minutes under N₂ atmosphere to remove residual solvent and then heated to 700 °C at a rate of 20 °C/min under oxygen (O₂) atmosphere, and then kept 700 °C for 10 min, and finally raised the temperature to 750 °C with rate of 20 °C/min at O₂. Gas adsorption analysis was performed on MicrotracBEL-Belsorp-MAXII volumetric gas adsorption analyzer. All samples were activated at 120 °C under vacuum for 6 h before measurement. The interparticle pore size distribution was measured on a

Quantachrome PoreMaster 33G mercury porosimeter. For argon ion slice, samples were cut by a Gatan Iliion II+ model 697 precision ion polishing mill, then the cross-sectional SEM images were acquired on a JEOL JSM 7800F Prime SEM. Zeta (ζ) potential measurements were performed using a Malvern zetasizer Nano ZS system from Malvern.

Dye adsorption experiment

5 mg as-synthesized MOF-801 or MOF-801@ODPA was dispersed in 0.5 mL ethanol. Then, 0.5 mL 0.5 mL/mg crystal violet ethanol solution was added. After 10 min of ultrasound, the product was collected by centrifugation and washed by deionized water for three times. Next, the obtained product was dispersed in 1 mL DMF. Finally, HF was added to etch the MOF for UV-Vis spectra measurement. The absorbance at 575 nm was used for quantification.

Dynamic vapor/gas sorption (DVS) measurements

DVS from Surface Measurement Systems (UK) is a gravimetric apparatus to measure the mass change of the sample using continuously and constant nitrogen flow to bring the vapor to the sample. By varying the flow rates of two mass flow controllers (one passing through the liquid and the other one does not), different relative humidity (from 0-95%) or vapor partial pressure can be achieved and maintained to measure the H₂O kinetics. The carrier gas can be changed to CO₂ (15%), N₂ mixture gas to measure the CO₂ kinetics. We further use the constant surface concentration model, also known as the Fickian diffusion model, to fit the kinetic CO₂ and H₂O uptake curves and calculate the value of D_s/r^2 which determines the characteristic rate of mass uptake, the form of Fickian diffusion model is: [6]

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \exp\left(-\frac{n^2 \pi^2 D_s t}{r^2}\right) \quad (1)$$

where M_t (mmol) and M_∞ (mmol) are moles adsorbed during time t and as $t \rightarrow \infty$, D_s (m²/s) is the diffusion coefficient, r (m) is the diffusion length. In the short time region, the kinetic uptake curve is essentially linear and approximated by:

$$\frac{M_t}{M_\infty} \approx \frac{6}{\sqrt{\pi}} \sqrt{\frac{D_s}{r^2}} \quad (2)$$

Section S4. Supplemental figures and tables

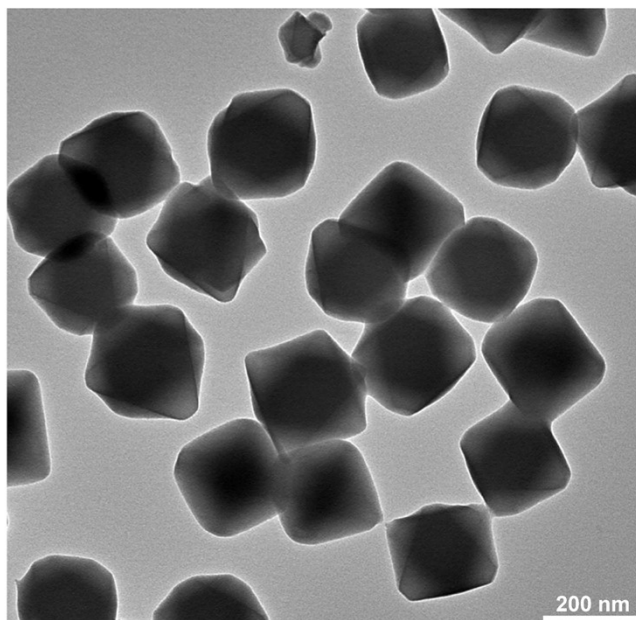


Figure S1. The TEM image of MOF-801.

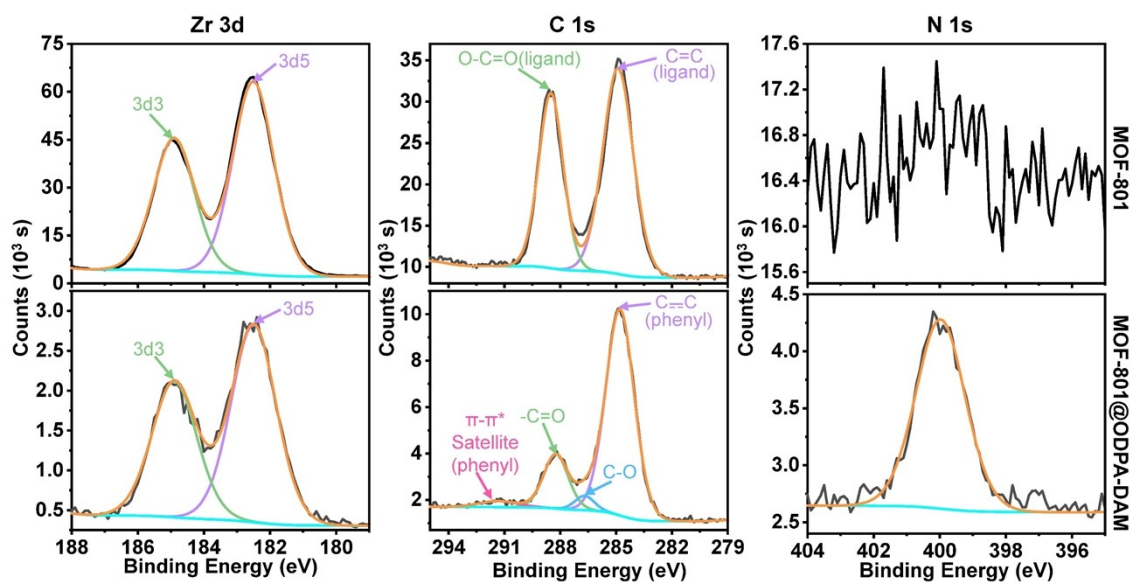


Figure S2. X-ray photoelectron spectroscopy patterns (XPS) of MOF-801 and MOF-801@ODPA-DAM.

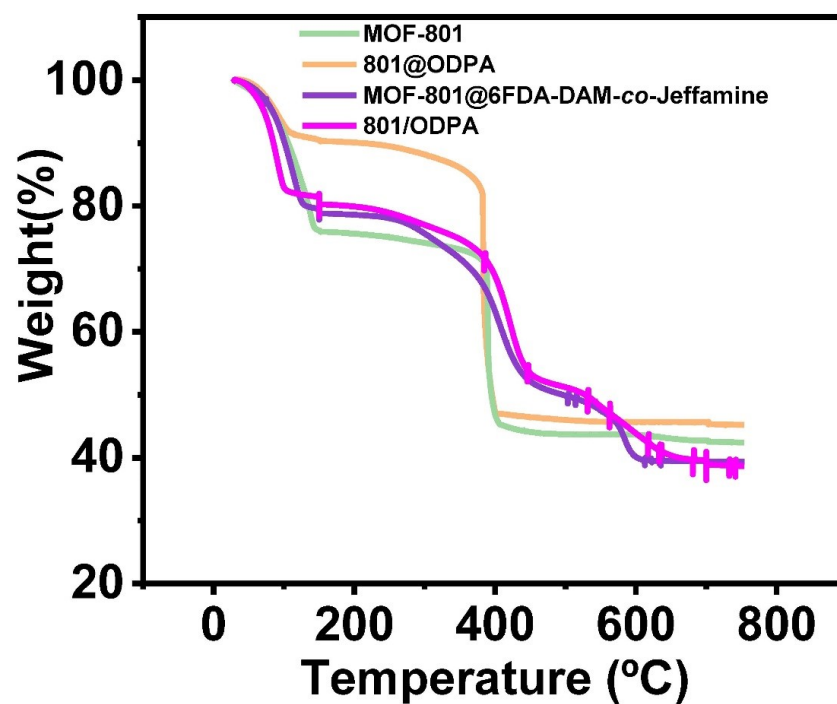


Figure S3. TGA profiles of MOF-801, 801@ODPA, MOF-801@6FDA-DAM-co-Jeffamine and 801/ODPA.

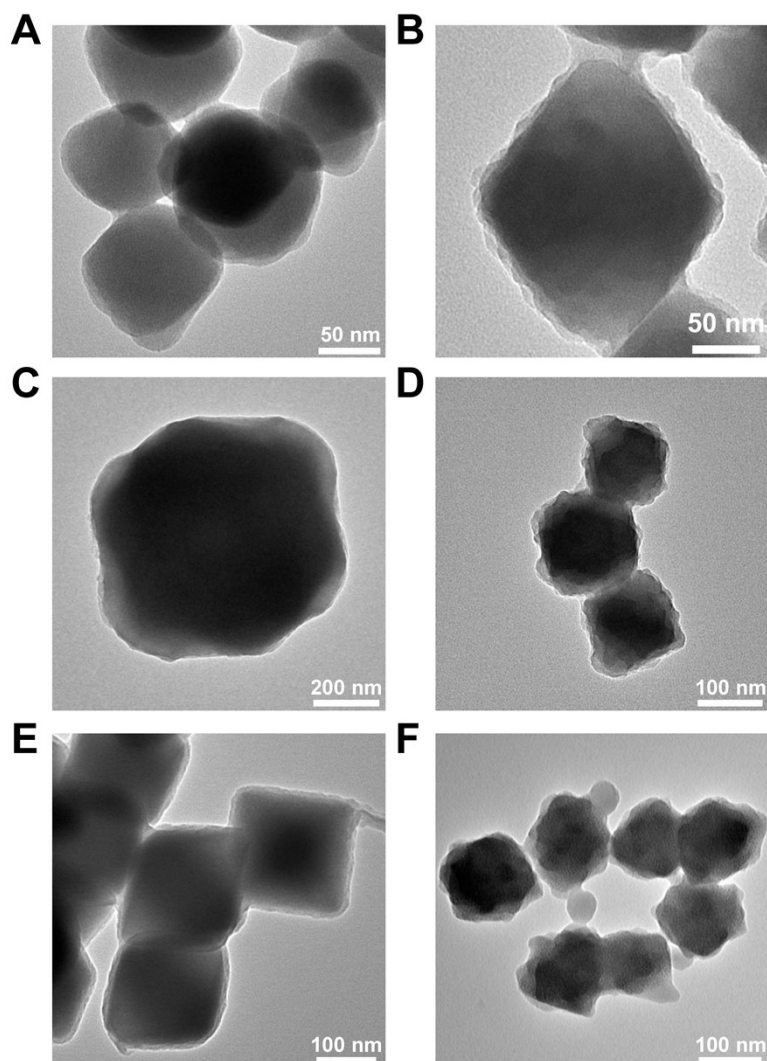


Figure S4. TEM images of UiO-66@ODPA-DAM (A), UiO-66-NH₂@6FDA-DDS (B), UiO-67@ODPA-DAM (C), UiO-66-NH₂@PIM-1 (D), MOF-801@6FDA-durene (E) and HKUST-1@ODPA-DAM (F). For all samples, polymer: MOF =1:10 (w/w).

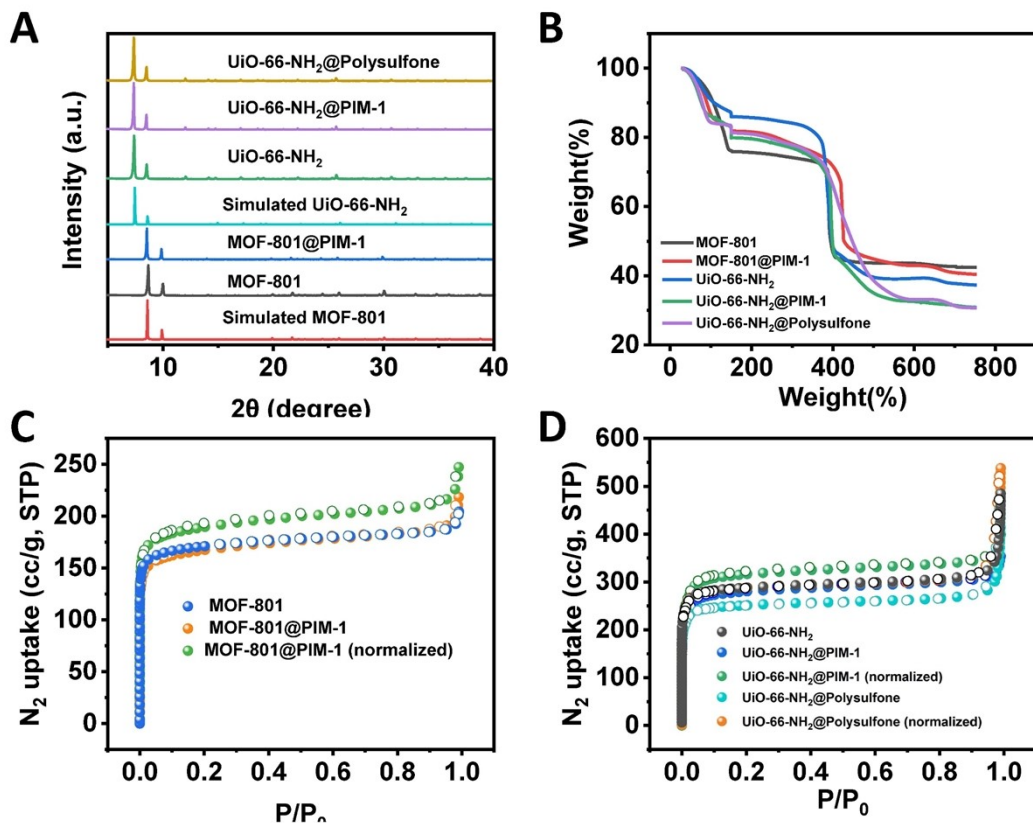


Figure S5. Experimental/theoretical PXRD patterns (A) and TGA profiles (B) of MOF-801 and UiO-66-NH₂ before and after coating with PIM-1 and polysulfone. (C) N₂ adsorption-desorption isotherms at 77 K of MOF-801, MOF-801@PIM-1, and the normalized isotherm of MOF-801@PIM-1 (Note that since a different batch of MOF-801 was used for PIM-1 coating and subsequent N₂ adsorption experiment, the uptake capacity is slightly lower compared to Figure 1D). (D) N₂ adsorption-desorption isotherms at 77 K of UiO-66-NH₂ before and after coating with PIM-1 and polysulfone.

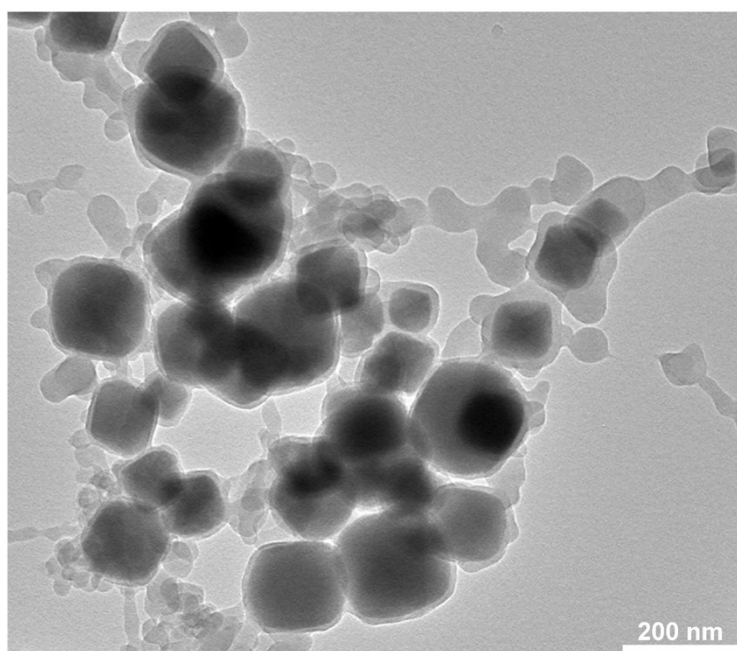


Figure S6. The TEM image of 801@ODPA sample with 20 wt% polymer loading.

Table S1. The relationship between compaction force and pressure during shaping.

Compaction force (kN)	Pressure (MPa)
0.02	0.71
0.1	3.54
0.4	14.15
1	35.39
3	106.16
5	176.93
7	247.70

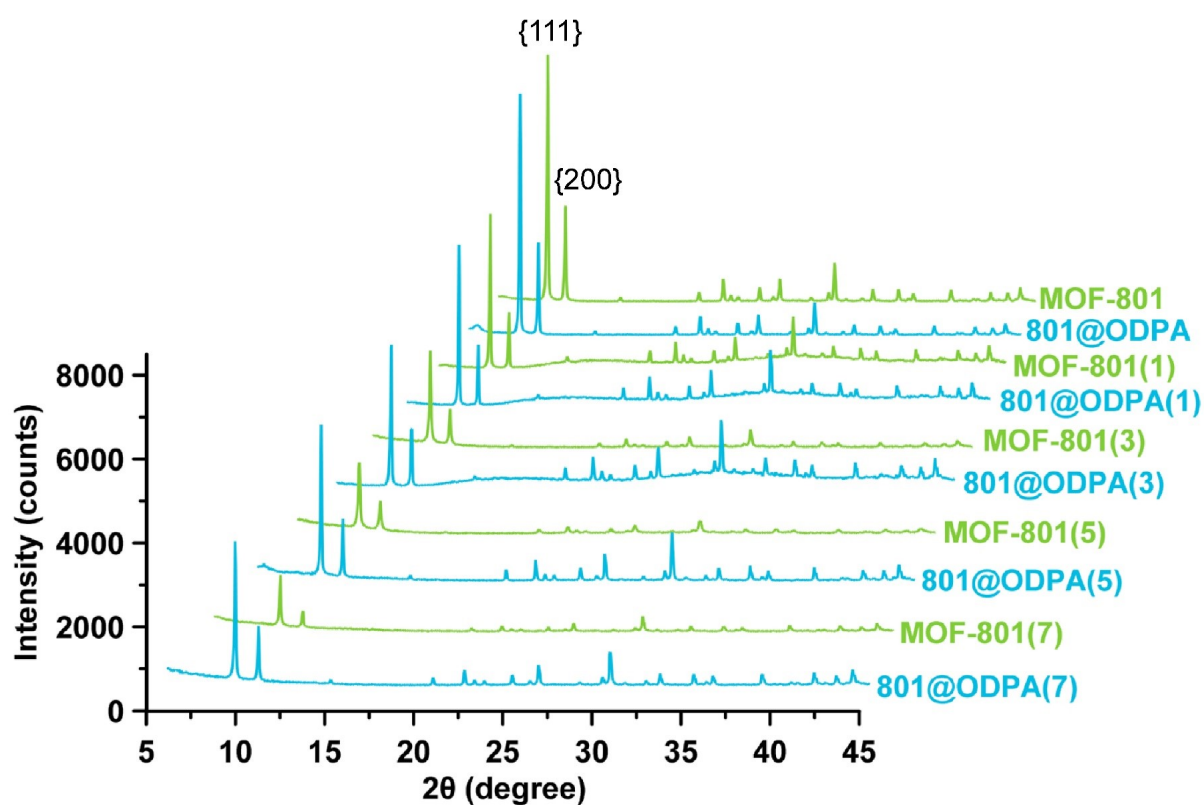


Figure S7. PXRD patterns of MOF-801(x) and 801@ODPA(x) obtained under various compaction force.

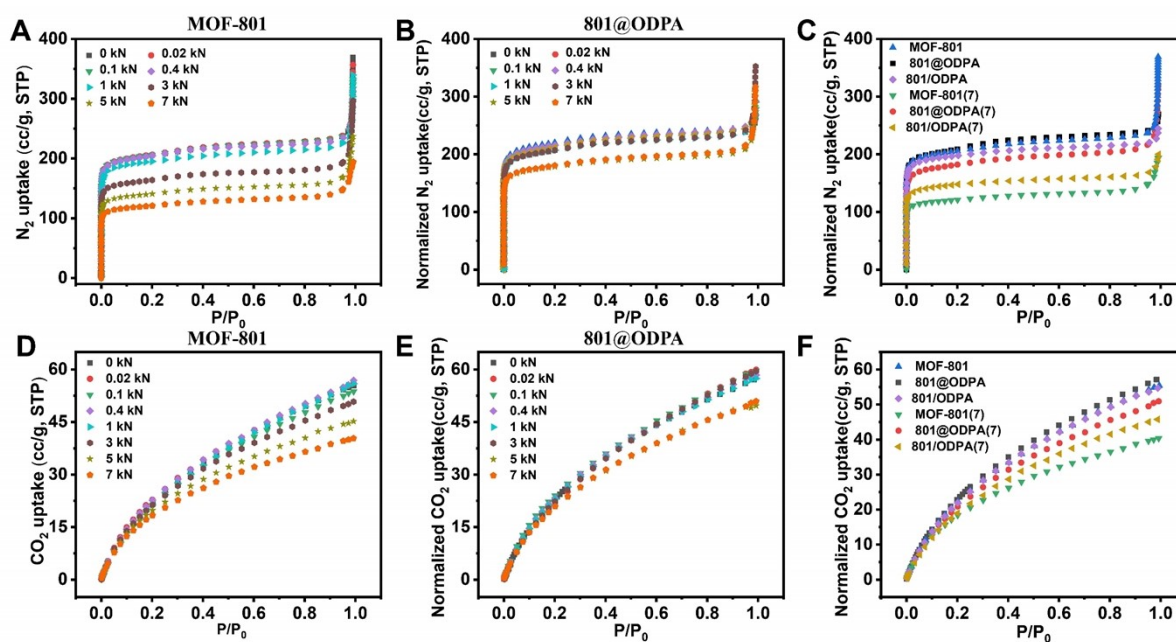


Figure S8. N_2 adsorption isotherms (77 K) of MOF-801 (A) and 801@ODPA pellets (B) obtained under various compaction force. (C) N_2 adsorption isotherms (77 K) of MOF-801, 801@ODPA, 801/ODPA, MOF-801(7), 801@ODPA(7) and 801/ODPA(7). CO_2 adsorption isotherms (298 K) of MOF-801 (D) and 801@ODPA pellets (E) obtained under various compaction force. (F) CO_2 adsorption isotherms (298 K) of MOF-801, 801@ODPA, 801/ODPA, MOF-801(7), 801@ODPA(7) and 801/ODPA(7). All the N_2 and CO_2 isotherms were normalized to the weight of MOF-801.

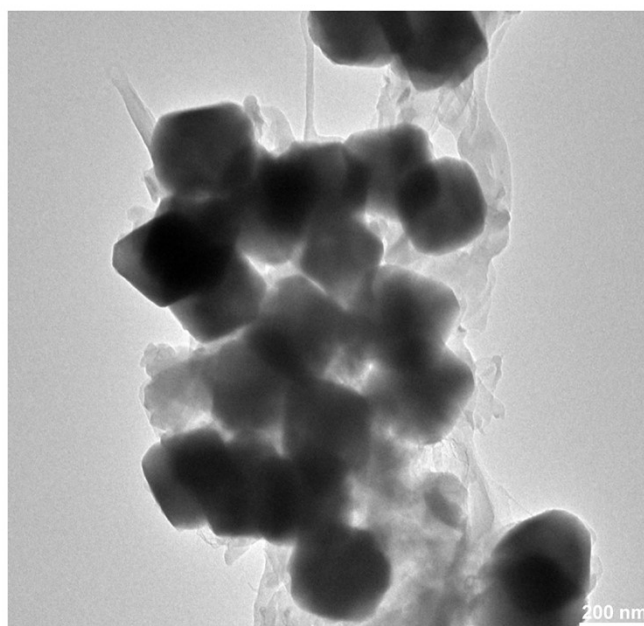


Figure S9. The TEM image of 801/ODPA.

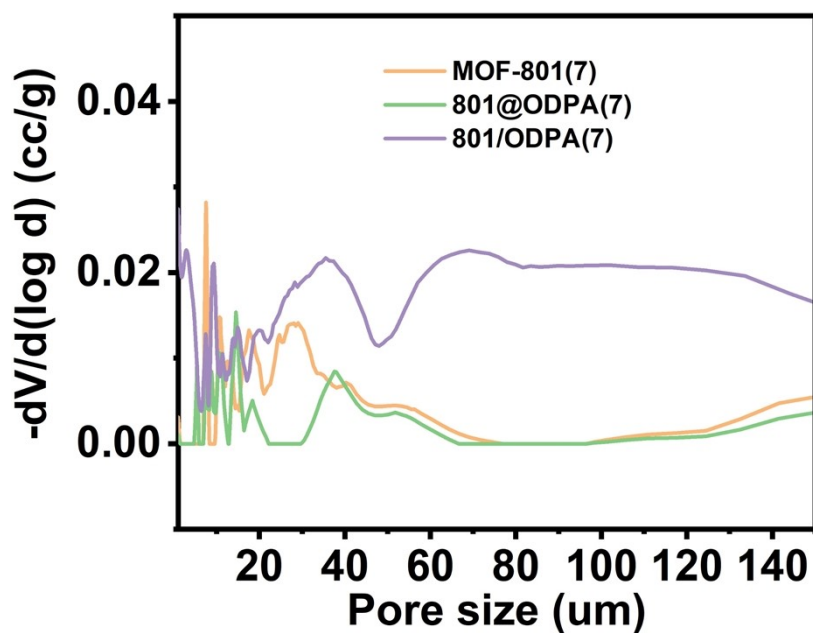


Figure S10. The interparticle pore size distribution of MOF-801(7), 801@ODPA(7) and 801/ODPA(7) based on mercury porosimetry data. The pore size range is set at above 1 μm to complement Figure 5D.

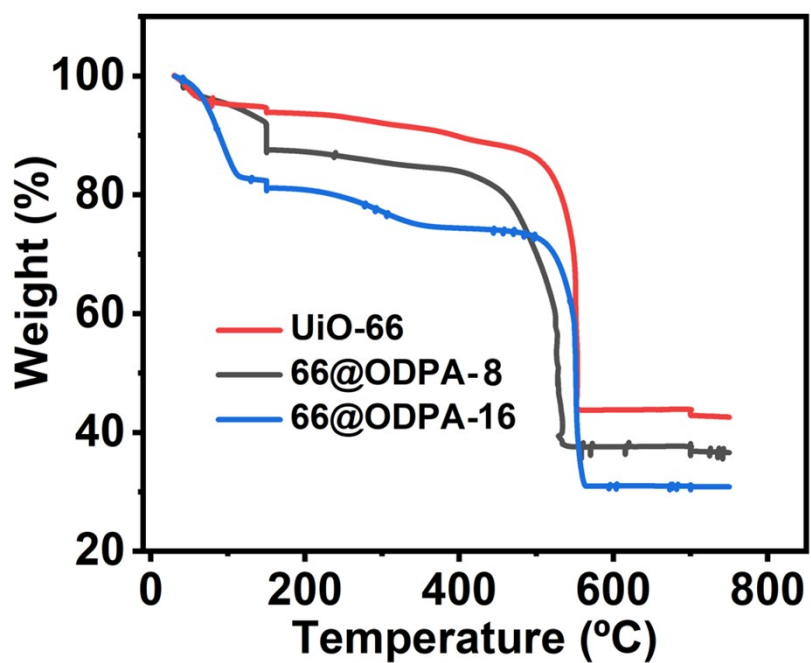


Figure S11. TGA profiles of UiO-66, 66@ODPA-8 and 66@ODPA-16.

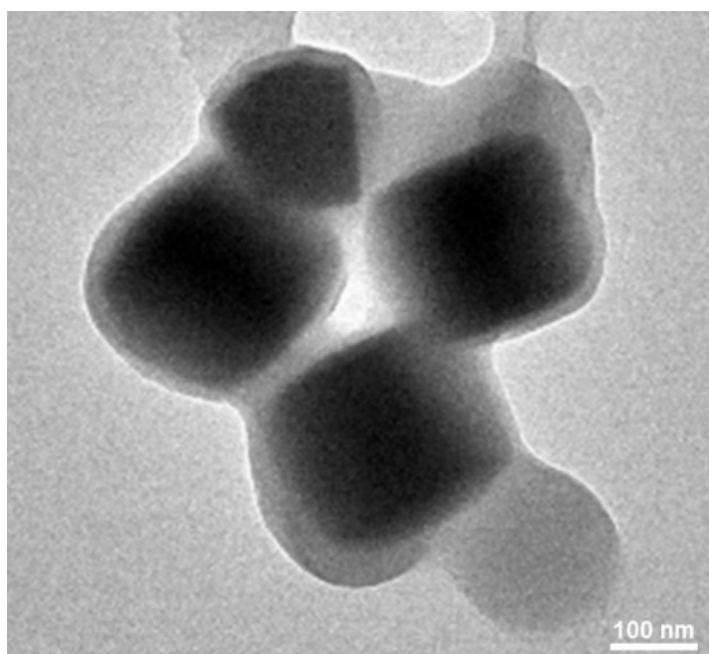


Figure S12. The TEM image of 66@ODPA-16.

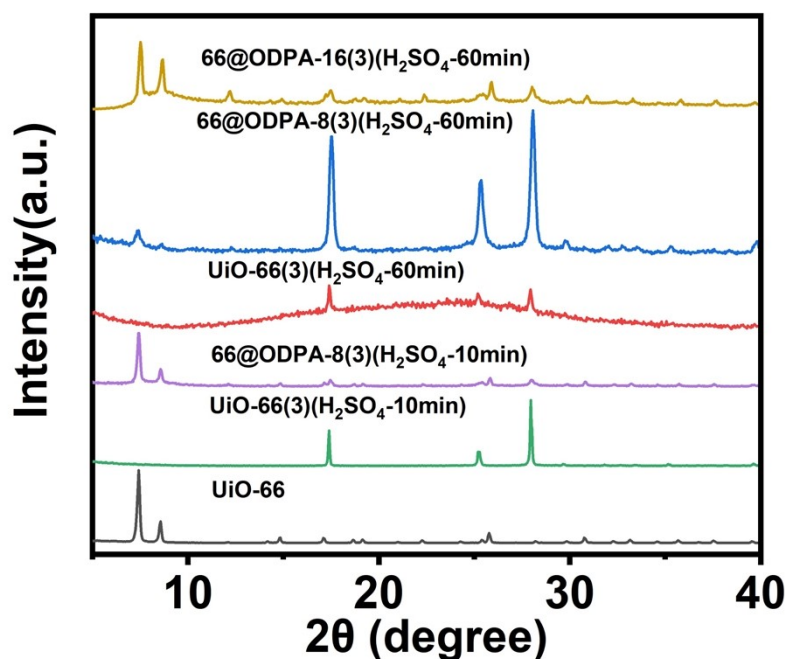


Figure S13. PXRD patterns of UiO-66(3), 66@ODPA-8(3) and 66@ODPA-16(3) after being treated with 1 M H_2SO_4 at room temperature with various time.

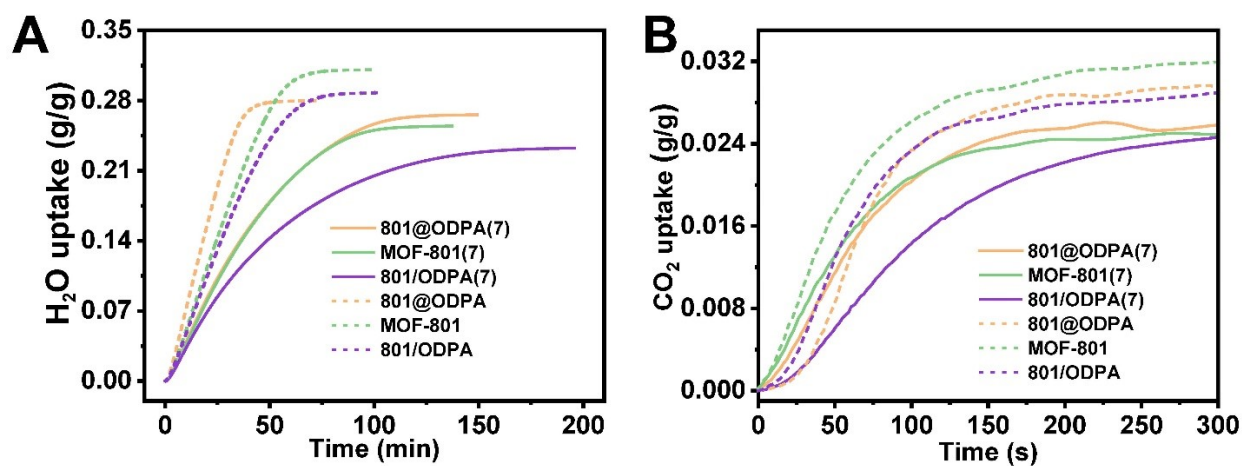


Figure S14. Time-dependent water adsorption profiles at 50% RH (in N_2) (A) and CO_2 (15% CO_2 and 85% N_2) adsorption profiles (B) using a dynamic vapor sorption (DVS) analyzer (298 K).

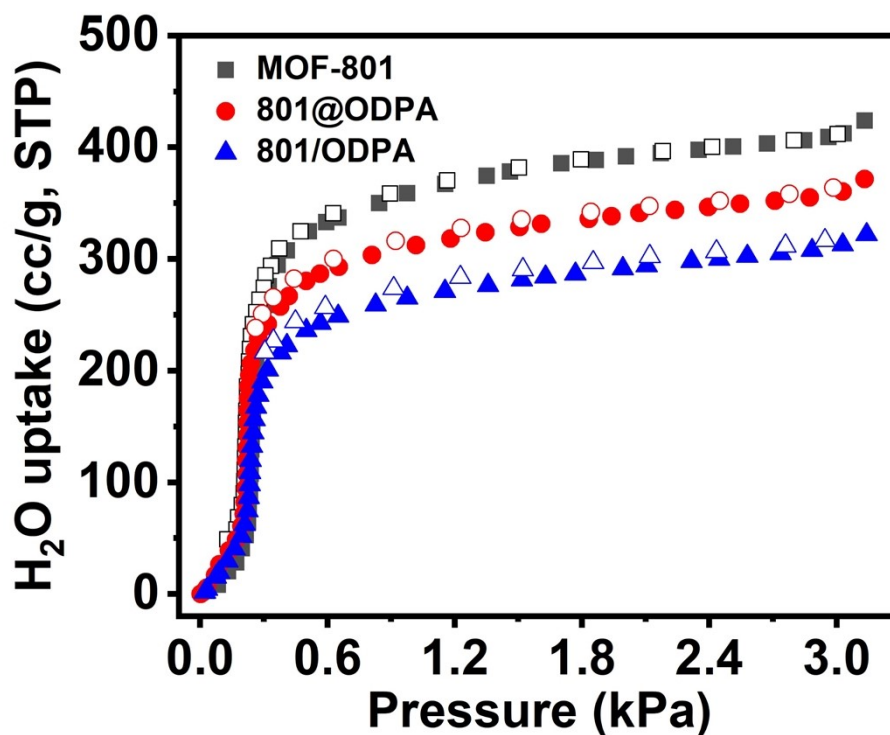


Figure S15. H₂O adsorption-desorption isotherms at 298 K of MOF-801, 801@ODPA and 801/ODPA.

Table S2. The gas adsorption capacity calculated from DVS and static gas adsorption isotherms.

Sample	H ₂ O (50% RH)		CO ₂ (0.15 P/P ₀)	
	q_d^a (cc/g)	q_s^b (cc/g)	q_d (cc/g)	q_s (cc/g)
MOF-801	382.3	385.8	16.29	18.47
801@ODPA	332.1	348.4	15.06	16.99
801/ODPA	284	350.9	14.74	15.591

^a q_d refers to the gas adsorption capacity calculated from DVS profiles at 298 K; ^b q_s refers to the gas adsorption capacity calculated from static gas adsorption isotherms at 298 K.

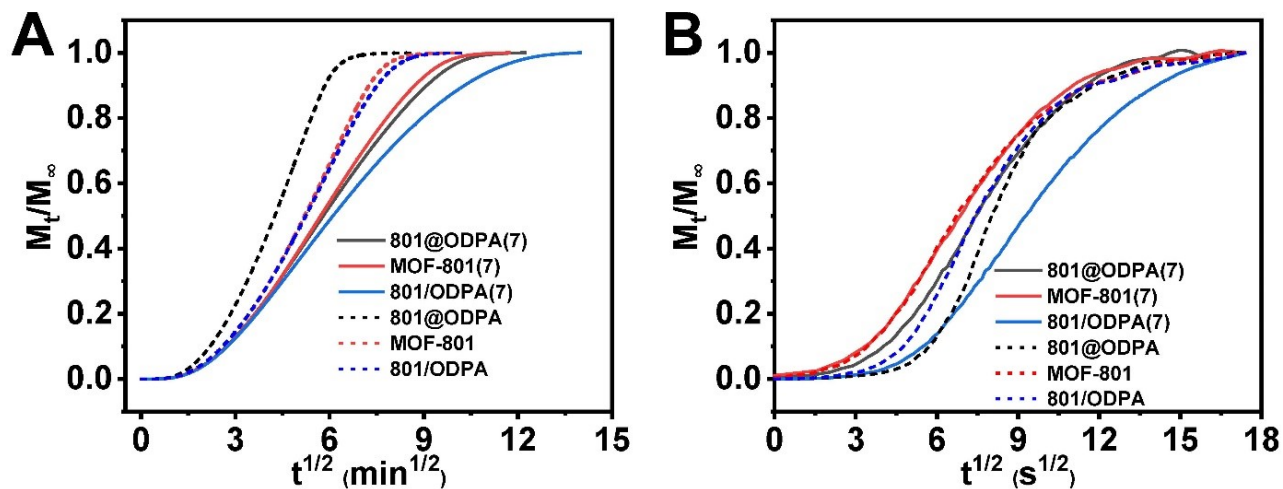


Figure S16. H₂O (50% RH) (A) and CO₂ (15%) (B) adsorption kinetics of MOF-801, 801@ODPA and 801/ODPA powder and pellet at 298 K obtained by dynamic vapor sorption.

Table S3. Values of the Fickian diffusion model parameters for H₂O (50% RH) and CO₂ (15%) adsorption at 298 K.

Sample	D_s/r^2		R^2 (regression coefficient)(%)	
	H ₂ O (P/P ₀ =0.5)(min ⁻¹)	CO ₂ (P/P ₀ =0.15)(s ⁻¹)	H ₂ O (P/P ₀ =0.5)	CO ₂ (P/P ₀ =0.15)
MOF-801	3.33×10^{-3}	1.49×10^{-3}	99.94	99.91
801@ODPA	5.47×10^{-3}	2.88×10^{-3}	99.99	99.82
801/ODPA	2.94×10^{-3}	2.02×10^{-3}	99.97	99.94
MOF-801(7)	1.82×10^{-3}	1.34×10^{-3}	99.92	99.72
801@ODPA(7)	1.72×10^{-3}	1.61×10^{-3}		
)			99.92	99.81
801/ODPA(7)	1.32×10^{-3}	1.10×10^{-3}	99.92	99.80

References

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