

## Supporting Information

# **A Facile and General Coating Approach to Moisture/Water- Resistant Metal-Organic Frameworks with Intact Porosity**

Wang Zhang,<sup>†</sup> Yingli Hu,<sup>†</sup> Jin Ge, Hai-Long Jiang,<sup>\*</sup> and Shu-Hong Yu<sup>\*</sup>

*Division of Nanomaterials and Chemistry, Hefei National Laboratory for Physical Sciences at Microscale, Collaborative Innovation Center of Suzhou Nano Science and Technology, Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China*

<sup>†</sup> W.Z. and Y.H. contributed equally to this work.

<sup>\*</sup> Corresponding author. E-mail: [shyu@ustc.edu.cn](mailto:shyu@ustc.edu.cn) (S.H.Y.); [jianglab@ustc.edu.cn](mailto:jianglab@ustc.edu.cn) (H.L.J.)

## Methods

**Materials:** All chemical reagents were purchased and used without any further purification.

**Synthesis of MOF-5:** MOF-5 crystals were synthesized in *N,N*-Dimethylformamide (DMF) at room temperature by previous report.<sup>[S1]</sup> Typically, terephthalic acid (0.507 g) and triethylamine (0.85 mL) were dissolved in 40 mL of DMF. Then zinc acetate dihydrate (1.699 g) was dissolved in 50 mL DMF and was slowly added into the above solution under magnetic stirring at room temperature for 2.5 h. The precipitate was collected by centrifugation (8000 rpm, 5 min) and then washed several times with DMF and CHCl<sub>3</sub>.

**Synthesis of HKUST-1:** HKUST-1 crystals were synthesized as reported previously.<sup>[S2]</sup> Briefly, 1,3,5-benzenetricarboxylic acid (2.0 g) was dissolved in 30 mL DMF and 30 mL ethanol to give a solution. Copper nitrate trihydrate (4.154 g) was dissolved in 30 mL water. Then, the two solutions were mixed directly. After magnetic stirring for 15 min, the final solution was transferred into a 100 mL Teflon-lined stainless steel autoclave, which was closed and maintained at 100 °C for 10 h. After cooling down to room temperature, the resulting product was centrifuged (4000 rpm, 5 min) and washed several times with DMF and methanol.

**Synthesis of [Zn(bdc)(ted)<sub>0.5</sub>]:** ZnBT single crystals were grown in solvothermal reactions.<sup>[S3]</sup> Zinc nitrate hexahydrate (0.78 g), terephthalic acid (0.51 g) and triethylenediamine (0.18 g) were dissolved in 75 mL DMF. After magnetic stirring for 15 min, the final solution was transferred into a 100 mL Teflon-lined stainless steel autoclave, which was closed and maintained at 120 °C for 48 h. After cooling down to room temperature, the resulting product was centrifuged (6000 rpm, 5 min) and washed several times with DMF and CHCl<sub>3</sub>.

**PDMS coating of the MOFs:** The PDMS coating of the MOFs was carried out by a simple vapor deposition technique.<sup>[S4]</sup> Typically, a certain amount of MOF powder (spreading to layer as thin as possible) was flat on glass dish, which was placed in a sealed glass container with some fresh PDMS stamp. The glass container was maintained at 235 °C for 6 h in a digital-temperature-controlled oven and then allowed to cool to room temperature naturally to give PDMS-coated MOFs. (*Note:* 1, Both MOF-5 and ZnBT are very moisture sensitive. Keep them away from water/air as far as possible before PDMS coating. 2, For moisture/water resistant/treatment experiments of MOFs after PDMS coating, the coated MOF-5 and ZnBT samples on glass dish without perturbation were directly transferred into the constant temperature humidity incubator/chamber, while the coated HKUST-1 sample was collected and exposed to water.).

**Catalytic activity over pristine HKUST-1 and coated HKUST-1:** The as-prepared samples were activated in vacuum at 120 °C for 12 h. Then, the degassed 20 mg pristine HKUST-1 and coated HKUST-1 were exposed in the saturated water steam at room temperature for two minutes. After that, the samples were transferred into a flask, and 80 uL benzaldehyde (0.79 mmol), 220 uL trimethylsilylcyanide (TMSCN, 1.65 mmol), 4 mL heptane was added. The mixture was allowed to react at 60 °C for 48 h with stirring and the products were analyzed by GC. [Benzaldehyde (Aladdin Industrial Inc., 99.5%, GC), trimethylsilylcyanide (Energy Chemical, 97%, AR), heptane (Sinopharm Chemical Reagent Co. Ltd., 97%, AR)].

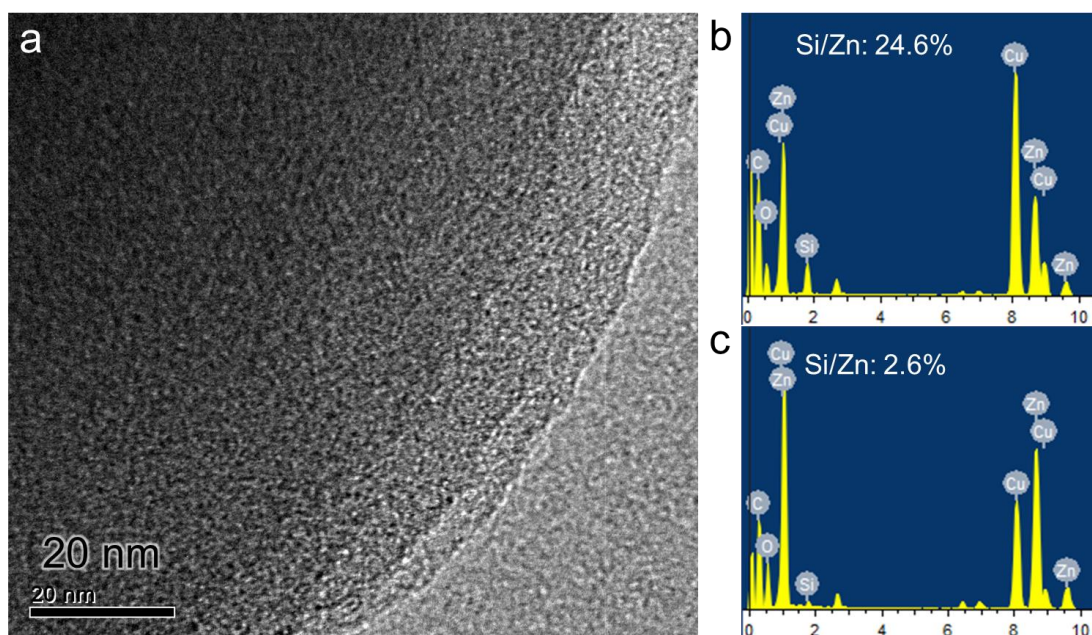
**Characterization:** Power X-ray diffraction (XRD) data were recorded from a Philips X'Pert PRO SUPER X-ray diffractometer equipped with graphite mono-chromatized Cu K $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ). Scanning electron microscopy (SEM) was carried out on a Zeiss Supra 40

field-emission scanning microscope operating at 5 kV. Transmission electron microscopy (TEM) image was obtained at 120 kV from Hitachi H7650 transmission electron microscope. HRTEM image and EDS were carried out on a JEOL JEM-2100F field-emission transmission electron microscope operated at 200 kV. Composition line-scan profile was obtained at 200 kV from JEM-ARM 200F. Water contact angle measurement was carried out on OCA 40 optical contact angle meter at ambient conditions. Nitrogen and carbon dioxide sorption was conducted using Micromeritics ASAP 2020 at different temperatures. Water sorption was investigated by using Quantachrome Autosorb-IQ2 at 298 K. Catalytic reaction products were analyzed and identified by gas chromatography (GC, Shimadzu 2010 Plus with a 0.25 mm  $\times$  30 m Rtx®-5 capillary column). GC-MS samples were recorded on a Shimadzu QP-5050 GC-MS system. X-ray photoelectron spectroscopy (XPS) was determined by an X-ray photoelectron spectrometer (ESCALab MKII) with an excitation source of Mg K $\alpha$  radiation (1253.6 eV). An Ar<sup>+</sup> sputter beam (150 s) was used for depth profiling of coated HKUST-1 after the initial data were collected.

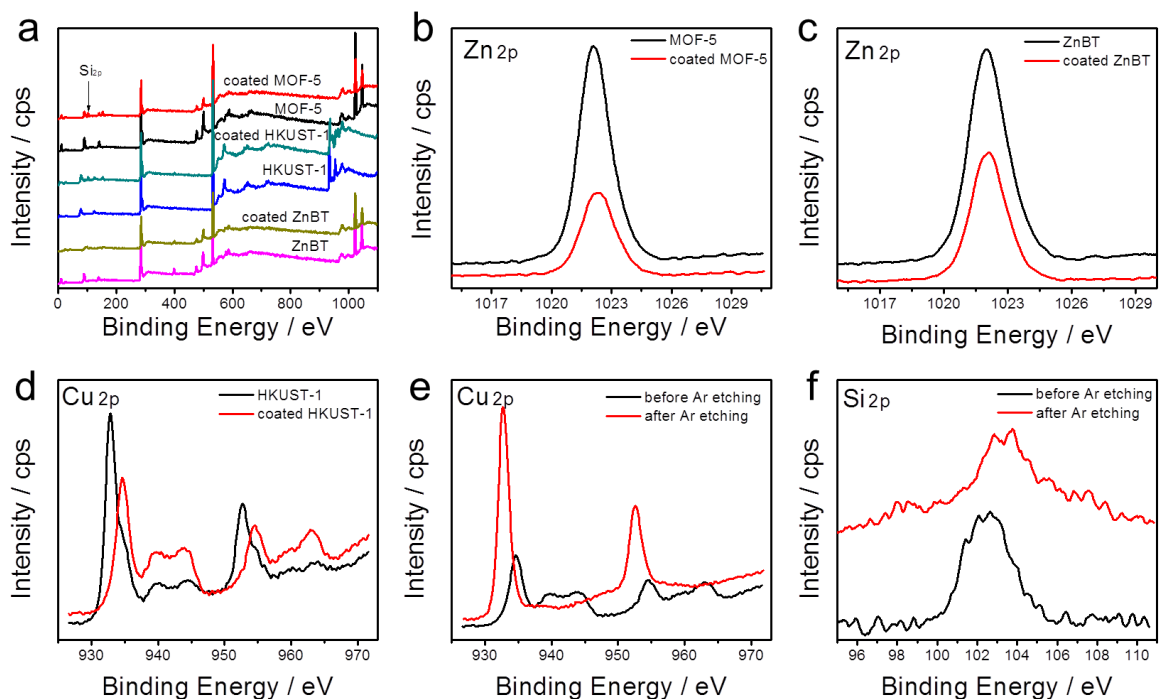


**Figure S1.** Digital photographs of HKUST-1 and coated HKUST-1 in water after different time.

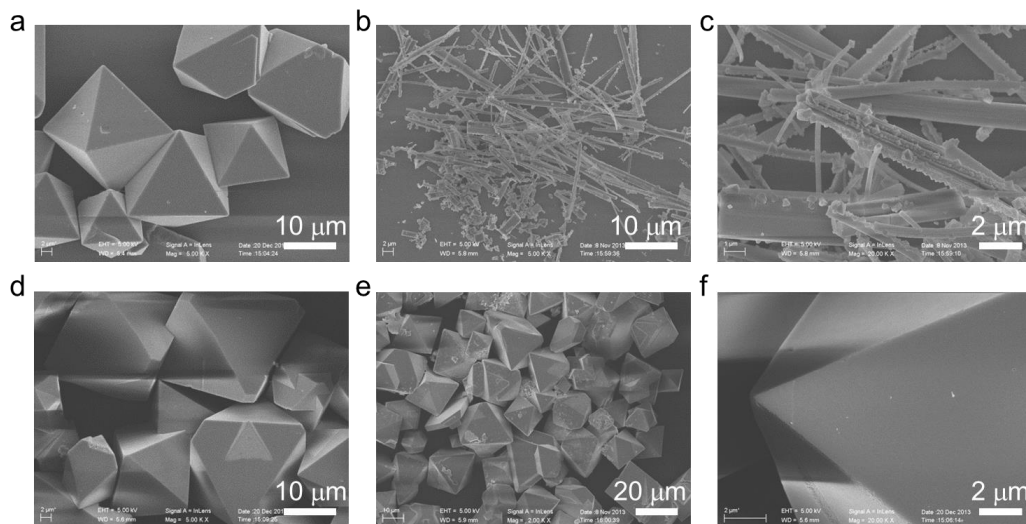
The PDMS-coated HKUST-1 exhibits hydrophobic behavior even after 3 months.



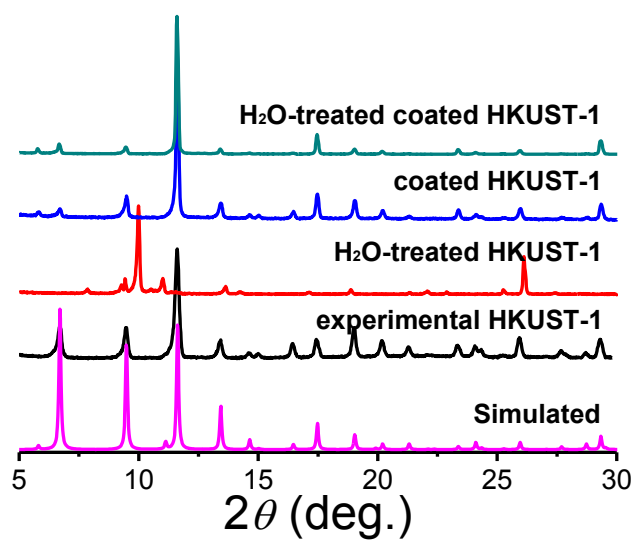
**Figure S2.** a) HRTEM image of coated MOF-5, and EDS results taken from (b) edge and (c) the area away from the edge.



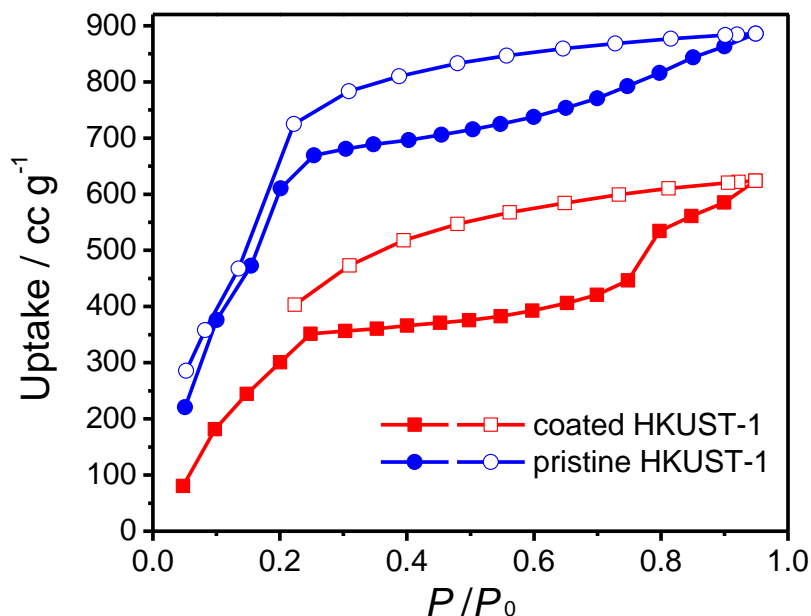
**Figure S3.** a) XPS survey spectra and b-d) high-resolution XPS spectra for Zn 2p and Cu 2p in MOF-5, ZnBT and HKUST-1. Unlike Cu 2p in HKUST-1, the binding energy of element Zn in MOF-5 and ZnBT remains before and after PDMS coating. It is assumed that the volatile short PDMS chains form a conformal layer on the surface of MOF-5 and ZnBT, and subsequently crosslink during the process of heat treatment, resulting in PDMS layer simply covered on the MOFs based on the previous report.<sup>[S4]</sup> e-f) XPS spectra of Cu 2p and Si 2p spectra for coated HKUST-1 before and after Ar etching for 150 s.



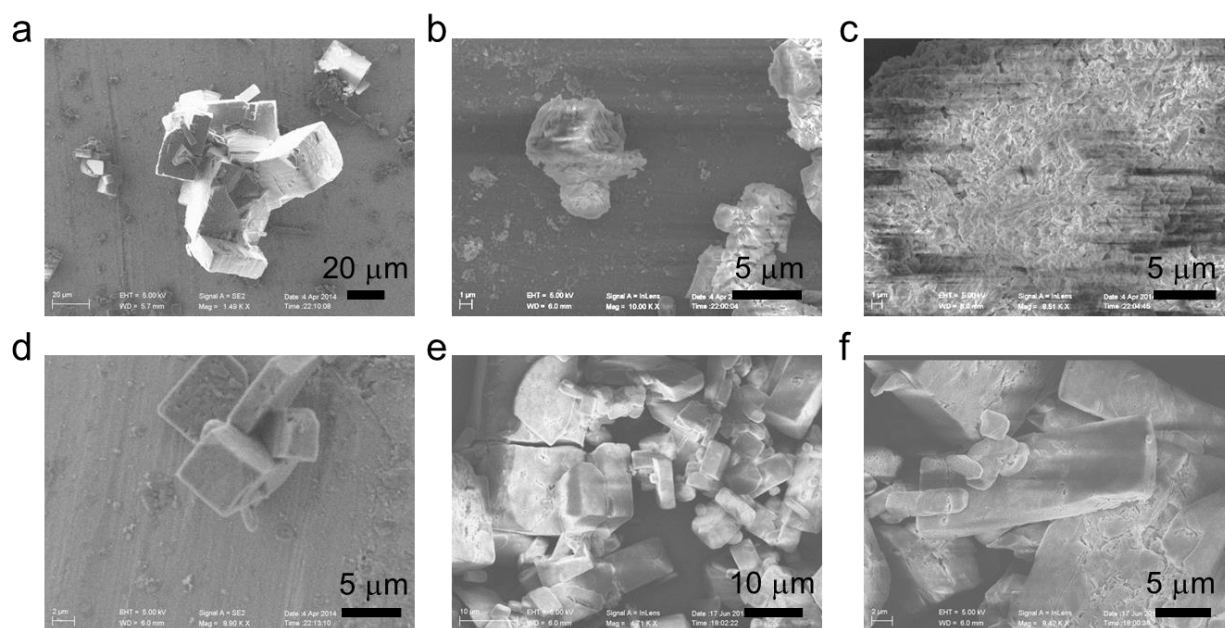
**Figure S4.** a-c) SEM images of pristine HKUST-1 (a) before and (b-c) after submersion in water for 3 days. d-f) SEM images of PDMS-coated HKUST-1 (d) before and (e-f) after water treatment for 3 days.



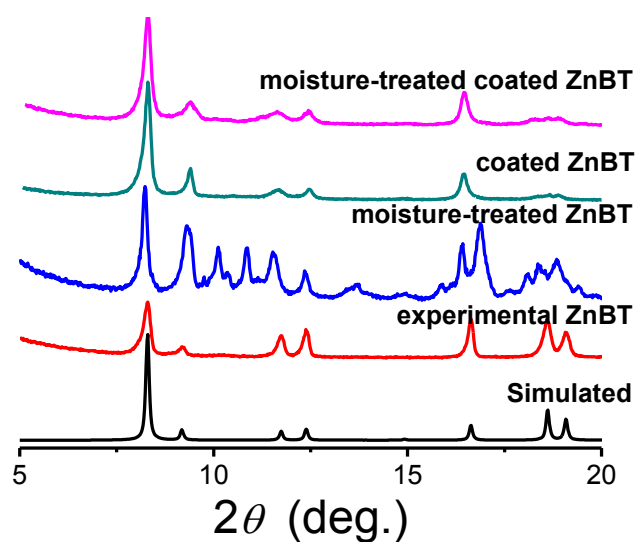
**Figure S5.** Power XRD patterns of pristine HKUST-1 and PDMS-coated HKUST-1 before and after water treatment for 3 days.



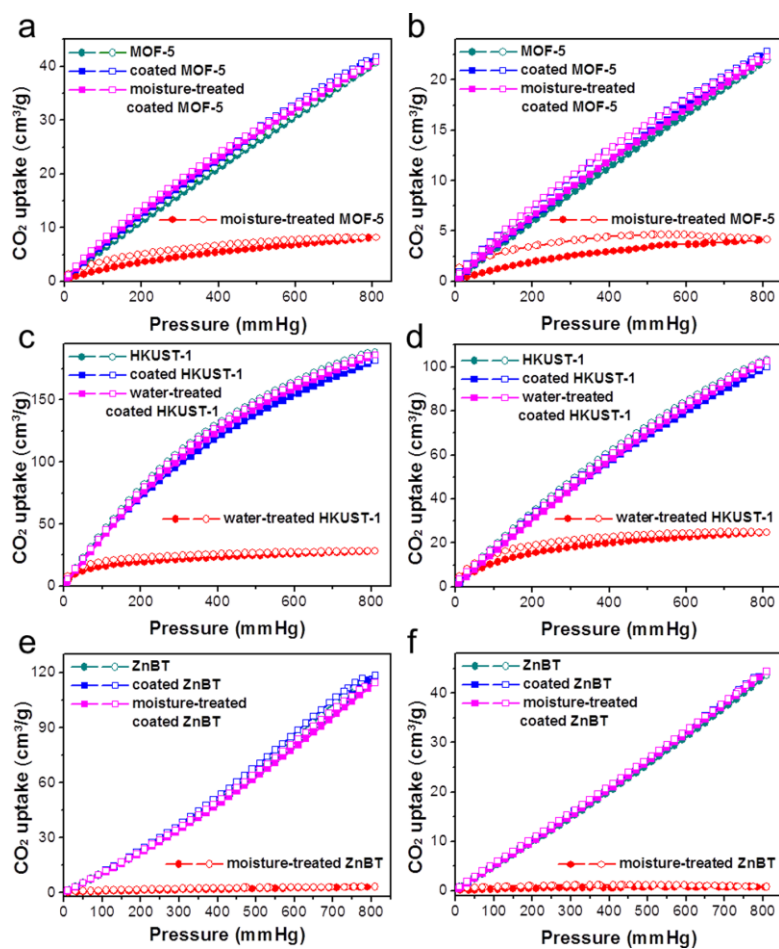
**Figure S6.** Water sorption isotherms for pristine and PDMS-coated HKUST-1 at 298 K. The water sorption capacity of coated HKUST-1 is much lower than that of HKUST-1, especially at low  $P/P_0$ , revealing the lower affinity of water to the hydrophobic surface of coated HKUST-1. A certain extent of water adsorption at low pressure could be understandable as free Cu(II) coordination sites are available for H<sub>2</sub>O to readily interact with. The water sorption for pristine HKUST-1 can be accomplished within 24 hours while coated HKUST-1 takes more than 48 hours. The significantly slower sorption kinetics of coated HKUST-1 could be attributed to the difficult penetration of water molecules through the outer PDMS coatings with high hydrophobicity.



**Figure S7.** (a-c) SEM images of pristine ZnBT (a) before and (b-c) after exposure to air at 55% relative humidity for 1 day. (d-f) SEM images of PDMS-coated ZnBT (d) before and (e-f) after exposure to air at 55% relative humidity for 1 day.



**Figure S8.** Power XRD patterns of pristine and PDMS-coated ZnBT before and after moisture treatment for 1 day.



**Figure S9.** CO<sub>2</sub> sorption isotherms for pristine and coated MOFs before and after moisture or water treatment (MOF-5 and ZnBT were treated in air at 55% relative humidity for 1 d; HKUST-1 was treated in water for 3 d) at (a, c, e) 273 K and (b, d, f) 298 K

**Table S1.** Porosity comparison of all samples with different modified methods before and after moisture/water treatment in this work and corresponding reported results in the literatures.

Samples	Modified method	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	Treated condition	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ ) after different treated time	References
<i>MOF-5</i>	PDMS-coating	3118	in air at 55%	2532 (2h), 0 (1d)	this Work
<i>Coated MOF-5</i>		3159	relative humidity	3158 (1d), 2871 (3d)	
<i>HKUST-1</i>		1547	in water	0 (3d)	
<i>Coated HKUST-1</i>		1544		1515 (3d)	
<i>ZnBT</i>		1950	in air at 55%	0 (1d)	
<i>Coated ZnBT</i>		1845	relative humidity	1808 (1d), 1417 (3d)	
<i>IRMOF-3</i>	postsynthetic modification with long alkyl chain inside the pores		no data		[S5]
<i>MIL-53(Al)</i>					
<i>MOF-5</i>	methyl modified	2750	in air with a relative humidity of 32-37%	no data	[S6]
<i>CH<sub>3</sub>MOF-5</i>		2537			
<i>DiCH<sub>3</sub>MOF-5</i>		1927			
<i>IRMOF-1</i>	thermally treated with carbon coatings	3450	exposed to ambient air (34% relative humidity)	1850 (5d), 960 (14d)	[S7]
<i>480N</i>		3130		2860 (5d), 2700 (14d)	
<i>510N</i>		2680		2430 (14d)	
<i>530N</i>		1740		1720 (14d)	
<i>550N</i>		520		no data	
<i>Cu-BTC</i>	PECVD of perfluorohexane	1468	exposure to 80-90% relative humidity at 25 °C	no data	[S8]
<i>Cu-BTC plasma</i>		1088			

**Table S2.** Carbon dioxide uptake capacities for pristine and coated MOFs before and after water/moisture-treatment (MOF-5 and ZnBT were treated in air at 55% relative humidity for 1 day; HKUST-1 was treated in water for 3 days) at 273 and 298 K under 760 mmHg.

Samples	Capacity before treatment at 273K (cm <sup>3</sup> /g)	Capacity after treatment at 273K (cm <sup>3</sup> /g)	Capacity before treatment at 298K (cm <sup>3</sup> /g)	Capacity after treatment at 298K (cm <sup>3</sup> /g)
<i>MOF-5</i>	38.2	8.1	20.7	4.3
<i>Coated MOF-5</i>	39.5	38.8	21.5	21.1
<i>HKUST-1</i>	182.2	27.4	98.4	24.6
<i>Coated HKUST-1</i>	175.3	180.1	95.2	97.7
<i>ZnBT</i>	107.6	3.1	40.6	0.85
<i>Coated ZnBT</i>	109.9	106.1	41.5	41.3

## References

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