# Supporting Information†

# Systematical evaluation of water adsorption in isoreticular UiOtype metal–organic frameworks

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## Supplementary Experimental section

#### 1.1 General materials and test methods

All used chemicals and solvents were purchased from commercial companies and used without further purification. Among them, zirconium chloride (ZrCl4, CAS: 10026-11-6), zirconyl chloride octahydrate (ZrOCl<sub>2</sub>·8H<sub>2</sub>O, CAS: 13520-92-8), and benzoic acid (CAS: 65-85-0) were purchased from Aladdin, terephthalic acid (H2BDC, CAS: 100-21-0), 2,5-pyridinedicarboxylic acid (H2BDC-N, CAS: 100-26-5), 2-hydroxyterephthalic acid (H2BDC-OH, CAS: 636-94-2), and 2-aminoterephthalic acid (H<sub>2</sub>BDC-NH<sub>2</sub>, CAS: 10312-55-7) were purchased from Energy acid (H2BDC-NO2, CAS: 610-29-7), 2-methyl-1,4-Chemical. 2-nitroterephthalic benzenedicarboxylic acid (H2BDC-CH3, CAS: 5156-01-4), and 2,5-dihydroxyterephthalic acid (H2BDC-(OH)2, CAS: 610-92-4) were purchased from Macklin, 2-chloroterephthalic acid (H2BDC-Cl, CAS: 1967-31-3), 2-bromoterephthalic acid (H2BDC-Br, CAS: 586-35-6), 2,6naphthalenedicarboxylic acid (H2NDC, CAS: 1141-38-4), and 4,4'-biphenyldicarboxylic acid (H2BPDC, CAS: 787-70-2) were purchased from Bidepharm, 2,2'-diamino-[1,1'-Biphenyl]-4,4'-dicarboxylic acid (H<sub>2</sub>BPDC-2NH<sub>2</sub>, CAS: 41738-56-1) and 3,3'-dihydroxy-[1,1'-Biphenyl]-4,4'-dicarboxylic acid (H<sub>2</sub>BPDC-(OH)<sub>2</sub>, CAS: 861533-46-2) were purchased from Extension Company (China), and all the used solvents were purchased from Sinopharm. Powder X-ray diffraction (PXRD) patterns were collected in the  $2\theta = 2-45^{\circ}$  on an X'Pert PRO diffractometer with Cu K $\alpha$  ( $\lambda$  = 1.542 Å) radiation at room temperature. Element analysis (EA) was measured by a Vario Micro instrument (Elenemtar Analysensysteme GmbH). Thermogravimetric analyses (TGA) were examined by using a thermal gravimetric analyzer (TGA, SDT 650, TA Instruments) under a nitrogen atmosphere with a heating rate of 10 K min<sup>-1</sup>. Attenuated total reflectance Fourier transform infrared (ATR-FT-IR) spectra were recorded on a Thermo Fisher Nicolet Is10 FT-IR spectrometer equipped with a single reflection diamond ATR module. The static water contact angles of these UiO-type MOFs were measured by a JY-82B Kruss DSA instrument.

#### Nitrogen adsorption measurements

The as-synthesized sample (50–100 mg) should be solvent-exchanged with DMF at least three times within one day and then with dry methanol at least eight times within three days to completely remove the guest solvent molecules in the channels before the gas sorption measurement. The solvent-exchanged sample was evacuated at room temperature for 12 hours and further at 393 K for 12 hours until the outgas rate was 4  $\mu$ mHg min<sup>-1</sup>. N<sub>2</sub> sorption isotherms were measured by the Micromeritics ASAP 2460 surface area analyzer and the measurement was taken at 77 K maintained by liquid nitrogen.

#### 1.2 Synthesis methods

#### Synthesis of UiO-66

UiO-66 was synthesized according to the previously reported literature procedures with slight modification.<sup>1,2</sup> ZrCl<sub>4</sub> (0.54 mmol) was totally dissolved in the mixture of DMF (5 mL) and concentrated HCl (1 mL) by sonication. After that, H<sub>2</sub>BDC (0.74 mmol) and DMF (10 mL) were added and the mixture was sonicated for an additional 15 minutes. The resulting solution was transferred to a Teflon-lined autoclave and placed into the oven (105 °C) for 24 hours. Then, the resulting white crystalline powder was filtered and washed with DMF and anhydrous methanol at least three times, respectively. EA for the activated sample of UiO-66 exposed in air: Calcd for Zr<sub>6</sub>C<sub>48</sub>H<sub>56</sub>O<sub>46</sub> = Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(BDC)<sub>6</sub>·14H<sub>2</sub>O: C, 30.09; H, 2.95%. Found: C, 31.68; H, 3.28%. TGA data for loss of 14 H<sub>2</sub>O (Figure S5): Calcd: 13.16%, found: 13.10%. IR (neat, cm<sup>-1</sup>): 1589, 1395 (COO<sup>-</sup>); 1507 (C–C).

#### Synthesis of UiO-66-N

UiO-66-N was synthesized according to the previously reported literature with slight modification.<sup>3</sup> ZrCl<sub>4</sub> (1.0 mmol) and H<sub>2</sub>BDC-N (1.0 mmol) were dissolved in the mixture of acetic acid (4 mL), deionized water (6 mL) and ethanol (1 mL) by sonication for 30 minutes. The resulting solution was then transferred to a Teflon-lined autoclave and placed into the oven (100 °C) for 24 hours. Then, the resulting white crystalline powder was filtered and washed with DMF and anhydrous methanol at least three times, respectively. EA for the activated sample of UiO-66-N exposed in air: Calcd for Zr<sub>6</sub>C<sub>42</sub>H<sub>50</sub>N<sub>6</sub>O<sub>46</sub> = Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(BDC-N)<sub>6</sub>·14H<sub>2</sub>O:

C, 26.24; H, 2.62; N, 4.40%. Found: C, 28.76; H, 3.28; N, 5.12%. TGA data for loss of 14 H<sub>2</sub>O: Calcd: 13.12%, found: 12.81%. IR (neat, cm<sup>-1</sup>): 1287 (C–N).

### Synthesis of UiO-66-OH, UiO-66-NH<sub>2</sub>, UiO-66-CH<sub>3</sub>, and UiO-66-NO<sub>2</sub>

UiO-66-OH was synthesized according to the previously reported literature procedures with slight modification.<sup>2,4</sup> ZrCl<sub>4</sub> (0.54 mmol) was dissolved in the mixture of DMF (5 mL) and concentrated HCl (1 mL) by sonication for 10 minutes. H2BDC-OH (0.74 mmol) and DMF (10 mL) were then added and the mixture was sonicated until totally dissolved. The resulting solution was then transferred to a Teflon-lined autoclave and placed into the oven (80 °C) for 24 hours. Then, the resulting crystalline powder was filtered and washed with DMF and anhydrous methanol at least three times each. UiO-66-NH2, UiO-66-CH3, and UiO-66-NO2 were synthesized analogously by replacing H<sub>2</sub>BDC-OH with the equivalent molar amounts of H2BDC-NH2, H2BDC-CH3, and H2BDC-NO2, respectively. EA for the activated sample of UiO-66-OH exposed in air: Calcd for  $Zr_6C_{48}H_{60}O_{54} = Zr_6O_4(OH)_4(BDC-OH)_6 \cdot 16H_2O: C, 28.15;$ H, 2.95%. Found: C, 30.88; H, 3.44%. TGA data for loss of 16 H<sub>2</sub>O: Calcd: 14.07%, found: 12.78%. IR (neat, cm<sup>-1</sup>): 1245 (C–O). EA for the activated sample of UiO-66-NH<sub>2</sub> exposed in air: Calcd for Zr<sub>6</sub>C<sub>48</sub>H<sub>58</sub>N<sub>6</sub>O<sub>44</sub> = Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(BDC-NH<sub>2</sub>)<sub>6</sub>·12H<sub>2</sub>O: C, 29.27; H, 2.97; N, 4.27%. Found: C, 30.18; H, 3.24; N, 4.27%. TGA data for loss of 12 H<sub>2</sub>O: Calcd: 10.97%, found: 11.56%. IR (neat, cm<sup>-1</sup>): 1258 (C–N), 3480, 3368 (N–H). EA for the activated sample of UiO-66-CH<sub>3</sub> exposed in air: Calcd for  $Zr_6C_{54}H_{66}O_{45} = Zr_6O_4(OH)_4(BDC-CH_3)_6 \cdot 13H_2O: C, 32.72;$ H, 3.36%. Found: C, 34.23; H, 3.51%. TGA data for loss of 13 H<sub>2</sub>O: Calcd: 11.82%, found: 11.94%. IR (neat, cm<sup>-1</sup>): 2967, 2930 (C-H). EA for the activated sample of UiO-66-NO<sub>2</sub> exposed in air: Calcd for  $Zr_6C_{48}H_{46}N_6O_{56} = Zr_6O_4(OH)_4(BDC-NO_2)_6 \cdot 12H_2O: C, 26.81; H, 2.16;$ N, 3.91%. Found: C, 29.40; H, 2.81; N, 4.75%. TGA data for loss of 12 H<sub>2</sub>O: Calcd: 10.05%, found: 10.17%. IR (neat, cm<sup>-1</sup>): 1540, 1307 (N–O).

#### Synthesis of UiO-66-(OH)<sub>2</sub>

UiO-66-(OH)<sub>2</sub> was synthesized according to the previously reported literature procedures.<sup>5</sup> ZrOCl<sub>2</sub>·8H<sub>2</sub>O (0.2 mmol) and H<sub>2</sub>BDC-(OH)<sub>2</sub> (0.2 mmol) were dissolved in the mixture of deionized DMF (10 mL) and formic acid (4 mL) by sonication for 10 minutes. The resulting solution was then transferred to a Teflon-lined autoclave and placed into the oven (120 °C) for 24 hours. Then, the resulting crystalline powder was filtered and washed with DMF and anhydrous methanol at least three times each. EA for the activated sample of UiO-66-(OH)<sub>2</sub> exposed in air: Calcd for  $Zr_6C_{48}H_{68}O_{64} = Zr_6O_4(OH)_4(BDC-(OH)_2)_6 \cdot 20H_2O$ : C, 26.12; H, 3.10%. Found: C, 30.33; H, 3.69%. TGA data for loss of 20 H<sub>2</sub>O: Calcd: 11.38%, found: 11.74%. IR (neat, cm<sup>-1</sup>): 1235 (C–O).

#### Synthesis of UiO-66-Cl and UiO-66-Br

UiO-66-Cl was synthesized according to the previously reported literature procedures.<sup>6</sup> ZrCl<sub>4</sub> (0.26 mmol) and H<sub>2</sub>BDC-Cl (0.26 mmol) were dissolved in the mixture of DMF (15 mL) and acetic acid (0.45 mL) under ultrasonication. The resulting solution was then transferred to a Teflon-lined autoclave and placed into the oven (120 °C) for 24 hours. Then, the resulting crystalline powder was filtered and washed with DMF and anhydrous methanol at least three times each. For UiO-66-Br, the synthesis procedure is the same as the UiO-66-Cl, except the 2-chloroterephthalic acid is replaced by H<sub>2</sub>BDC-Br. ATR-FT-IR for UiO-66-Cl, IR (neat, cm<sup>-1</sup>): 766 (C–Cl). ATR-FT-IR for UiO-66-Br, IR (neat, cm<sup>-1</sup>): 682 (C–Br).

### **Synthesis of DUT-52**

DUT-52 was synthesized according to the previously reported literature with slight modification.<sup>7</sup> ZrCl4 (1.03 mmol) was totally dissolved in DMF (15 mL) under sonication. H<sub>2</sub>NDC (1.0 mmol) was dissolved in the resulting solution in the same way. Acetic acid (3 mL) was then added in the mixture solution and sonicated for an additional 10 minutes. The mixture was then transferred to a Teflon-lined autoclave and placed into the oven (120 °C) for 24 hours. Then, the resulting crystalline powder was filtered and washed with DMF and anhydrous methanol at least three times each. EA for the activated sample of DUT-52 exposed in air: Calcd for Zr<sub>6</sub>C<sub>67.2</sub>H<sub>60.8</sub>O<sub>42.2</sub> = Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(NDC)<sub>5.6</sub>(OH)<sub>0.4</sub>(H<sub>2</sub>O)<sub>0.4</sub>·11H<sub>2</sub>O: C, 38.61; H, 2.91%. Found: C, 38.60; H, 2.77%. TGA data for loss of 11 H<sub>2</sub>O: Calcd: 9.48%, found: 8.45%. IR (neat, cm<sup>-1</sup>): 1654 (NDC characteristic peak).

#### Synthesis of UiO-67

UiO-67 was synthesized according to the previously reported literature procedures with slight modification.<sup>8</sup> ZrCl<sub>4</sub> (0.4 mmol) was dissolved in the mixture of DMF (5 mL) and concentrated HCl (0.5 mL) under sonication. H<sub>2</sub>BPDC (0.4 mmol) and DMF (10 mL) were then added and

the mixture was sonicated for an additional 15 minutes. The resulting solution was then transferred to a Teflon-lined autoclave and placed into the oven (80 °C) for 24 hours. Then, the resulting white crystalline powder was filtered and washed with DMF and anhydrous methanol at least three times, respectively. EA for the activated sample of UiO-67 exposed in air: Calcd for  $Zr_6C_{70}H_{69}O_{41} = Zr_6O_4(OH)_4(BPDC)_5(OH)_1(H_2O)_1 \cdot 11H_2O$ : C, 39.78; H, 3.29%. Found: C, 38.89; H 3.33%. TGA data for loss of 11 H<sub>2</sub>O: Calcd: 9.37%, found: 9.08%. IR (neat, cm<sup>-1</sup>): 1178 (BPDC characteristic peak).

#### Synthesis of UiO-67-(NH<sub>2</sub>)<sub>2</sub>

UiO-67-(NH<sub>2</sub>)<sub>2</sub> was synthesized according to the previously reported literature procedures with slight modification.<sup>9,10</sup> ZrCl<sub>4</sub> (0.35 mmol), H<sub>2</sub>BPDC-2NH<sub>2</sub> (0.35 mmol), and benzoic acid (7.0 mmol) were dissolved in DMF (20 mL) under sonication. The resulting solution was then transferred to a Teflon-lined autoclave and placed into the oven (120 °C) for 48 hours. Then, the resulting crystalline powder was filtered and washed with DMF and anhydrous methanol at least three times each.

#### Synthesis of UiO-67-(OH)<sub>2</sub>

UiO-67-(OH)<sub>2</sub> was synthesized according to the previously reported literature procedures.<sup>5</sup> ZrOCl<sub>2</sub>·8H<sub>2</sub>O (0.1 mmol) and H<sub>2</sub>BPDC-(OH)<sub>2</sub> (0.050 mmol) were dissolved in the mixture of DMF (10 mL) and formic acid (2 mL) under sonication. The resulting solution was then transferred to a Teflon-lined autoclave and placed into the oven (120 °C) for 48 hours. Then, the resulting crystalline powder was filtered and washed with DMF and anhydrous methanol at least three times each.

### Synthesis of MIP-200, MIL-160, MOF-303, and KMF-1

MIP-200, MIL-160, MOF-303, and KMF-1 were synthesized according to the previously reported literature procedures.<sup>11–14</sup>

#### **1.3 Characterized methods**

#### Water sorption measurement

To completely remove the guest solvent molecules in the channel, the fresh sample (20-50 mg) should be first solvent-exchanged with DMF and then with dry methanol at least eight times in the three days prior to the sorption test. The solvent-exchanged sample was evacuated for 12 hours at room temperature and then for 12 hours at 393 K (the activation temperature should be adjusted according to the specific samples) under high vacuum (< 0.2 Pa). Volumetric water sorption isotherms were measured by the BELSORP-max instrument (BeL-Japan). All water analyses were performed using water baths held at a constant temperature with a recirculating chiller.

#### Kinetic measurement

Together with a humidity generator, a thermal gravimetric analyzer (TGA, SDT 650, TA Instruments) was utilized to measure the water adsorption/desorption kinetics. The schematic diagram of this kinetic measurement instrument is shown in Figure S17. Two N<sub>2</sub> purge gases make up the humidification system: one circulates inside liquid water, carrying water vapor (at 100% relative humidity, RH), and the other is dry N<sub>2</sub>, which is subsequently combined in a humidifier-mixer. Before the mixture gas entered the thermogravimetric balance, its humidity was measured using a highly accurate humidity sensor. The humidity of the mixture gas can be changed between 0% and 100% RH by adjusting the proportion of these two purge gases. For kinetic adsorption measurements, all the UiO-type MOFs (~ 10 mg) were activated prior to each adsorption measurement, and the adsorption profiles were obtained at 298 K in humid nitrogen with 20% RH and 40% RH, respectively. For kinetic desorption measurements, all the UiO-type MOFs were equilibrated at 298 K and 40% RH to ensure comparability between the measurements prior to each desorption measurement, and the desorption profiles were collected at 338 K and 358 K in dry nitrogen with 0% RH, respectively. Since the results of kinetic measurement are influenced by the experimental equipment and test procedures, four benchmark MOFs: MIL-160, MOF-303, KMF-1, and MIP-200 were synthesized according to the reported literature<sup>11-14</sup> and then measured kinetic adsorption performances at 298 K and 20% RH to make the kinetic experimental data comparable.

#### Calculation of the experimental isosteric heat of water adsorption

The experimental isosteric heat  $(-\Delta_{ads}H)$  of water adsorption was calculated by applying the Clausius–Clapeyron equation<sup>15</sup>:

$$\Delta_{\rm ads} H_W = R \left( \frac{\partial \ln P}{\partial (\frac{1}{T})} \right) w \tag{1}$$

where  $\Delta_{ads}H_W$ , *R*, *P*, *T*, and *W* represent the isosteric enthalpy of adsorption (kJ mol<sup>-1</sup>), universal gas constant (kJ mol<sup>-1</sup> K<sup>-1</sup>), pressure (bar), temperature (K), and volume liquid adsorbed (mL(liq) g<sup>-1</sup>), respectively.

#### Calculation of the initial adsorption rate $(R_0)$ for UiO-type MOFs

The calculation of  $R_0$  was based on the previously reported literature.<sup>13</sup> The adsorption kinetic curve shows a clear mono-exponential behavior with time under the water adsorption process of MOF, so we can use the mono-exponential fit to reflect the adsorption kinetic properties of the corresponding MOF. The mono-exponential model was used to fit the water adsorption kinetic curve:

$$y = y_0 + A e^{-x/t}$$
<sup>(2)</sup>

And the  $R_0$  was identified as:

$$R_0 = A/t \tag{3}$$

#### **Grand Canonical Monte Carlo simulations**

The adsorption sites of water molecules in the pores of UiO-type MOFs were identified using Grand Canonical Monte Carlo (GCMC) simulations. The GCMC simulations were carried out using the Sorption program in BIOVIA Material studio 8.0. In this work, the crystal structures of these MOFs were selected for related simulations without additional geometry optimization. The interaction energy between water molecules and framework were computed through the Coulomb and Lennard-Jones 12–6 (LJ) potentials. A cutoff radius of 12.5 Å was used to handle

the nonbonding interactions, and the Ewald & Group summation method was applied to calculate the long-range electrostatic interactions. Any MOF frameworks of these UiO-type MOFs were treated as rigid structures by fixing atoms at their crystallographic positions, and the simulation box was made of 12 ( $2 \times 2 \times 3$ ) unit cells. A mixed set of UFF<sup>16</sup> and DREIDING force field<sup>17</sup> parameters were adopted to describe the LJ parameters for the atoms in the MOF framework. Partial charges for atoms of guest-free MOF were derived from QEq method and QEq\_neutral1.0 parameter. Water molecules were described by the TIP4P/2005 potential model.<sup>18</sup> The Lorentz-Berthelot combining rules were employed to calculate cross interactions. The loading steps and the equilibration steps were  $1 \times 10^7$ , the production steps were  $1 \times 10^7$ .

#### Calculation of the coefficient of performance for cooling of UiO-66 and UiO-66-N

A thorough scheme of the thermodynamic cycle exhibited between an adsorbent and the adsorbate water was depicted in Figure S31. The whole thermodynamic cycle consists of four parts: I–II (isosteric heating), II–III (isobaric desorption), III–IV (isosteric cooling), and IV–I (isobaric adsorption). The energy efficiency of the heat chiller cycle can be demonstrated by the coefficient of performance for cooling (COPc), which is a ratio of useful cooling energy output ( $Q_{ev}$ ) delivered to the required energy input ( $Q_{reg}$ ). COP<sub>C</sub> are calculated by thermodynamic models applied at various boundary temperature conditions for water evaporation ( $T_{ev}$ ), condensation ( $T_{con}$ ), adsorption ( $T_{ads}$ ), and desorption/regeneration ( $T_{des}$ ). We here use the standard refrigeration 2 boundary temperature conditions ( $T_{ev} = 5$  °C and  $T_{ads} = 30$  °C) to calculate the COPc value of UiO-66 and UiO-66-N.<sup>11,19</sup>

First, we need to transform the water adsorption isotherms to the characteristic curves. The characteristic curve is used to make the loading dependent on only one free variable ("energy") rather than two (P, T). The energy parameter employed is the adsorption potential (A), which is the inverse sign of the Gibbs free energy of adsorption:

$$A = -\Delta G = RT \ln(\frac{P_0(T)}{P})$$
(4)

 $P_0$  represents the saturation vapor pressure of the working fluid at the measurement temperature,

P represents the pressure at each loading value, R represents the ideal gas constant, and T represents the analysis temperature. The characteristic curves of UiO-66 and UiO-66-N calculated by equation 4 were shown in Figure S33 and S34.

The Dubinin model is used to represent the adsorption equilibrium, or the loading of the adsorbent W as a function of temperature T and pressure P. The volume occupied by the adsorbed phase in terms of the amount adsorbed is defined as:

$$W = \frac{q(P,T)}{\rho_{\text{liq}}^{\text{wr}}(T)}$$
(5)

The working capacity,  $\Delta W (\Delta W = W_{\text{max}} - W_{\text{min}})$ , is the difference in working fluid at adsorption (IV–I) and desorption stages (II–III).

An express method relies on De Lange et al. is used to calculate the thermodynamics of adsorption chiller cycles. From a thermodynamic standpoint, the COP<sub>C</sub> is used to represent the energy efficiency of the heat chiller cycle.

$$COP_{C} = \frac{Q_{ev}}{Q_{reg}}$$
(6)

The energy absorbed in the evaporator  $(Q_{ev})$  can be calculated using the concept of enthalpy of evaporation:

$$Q_{\rm ev} = -\frac{\Delta_{\rm vap} H(T_{\rm ev}) \,\rho_{\rm liq}^{\rm wf} \,\mathrm{m}_{\rm sorbent} \,\Delta W}{M_{\rm W}} \tag{7}$$

The energy required for I-II and II-III is the energy necessary for desorption ( $Q_{reg}$ ):

$$Q_{\text{reg}} = Q_{\text{I-II}} + Q_{\text{II-III}}$$

$$Q_{\text{I-II}} = \int_{T_{\text{ads}}}^{T_2} c_{\text{P}}^{\text{eff}}(T) \, \mathrm{d}T + \int_{T_{\text{ads}}}^{T_2} \rho_{\text{liq}}^{\text{wf}} W_{\text{max}} \, c_{\text{P}}^{\text{wf}}(T) \, \mathrm{d}T$$
(8)

$$Q_{\text{II-III}} = \int_{T_2}^{T_{\text{des}}} c_{\text{P}}^{\text{eff}}(T) \, \mathrm{d}T + \int_{T_2}^{T_{\text{des}}} \rho_{\text{liq}}^{\text{wf}} \frac{W_{\text{max}} + W_{\text{min}}}{2} \, c_{\text{p}}^{\text{wf}}(T) \, \mathrm{d}T - Q_{\text{sorption}}$$
(9)

The effective heat capacity  $(c_P^{eff})$  is considered to be the same as the heat capacity of sorbent  $(c_P^{sorbent})$ .

The energy released during adsorption of the working fluid ( $Q_{\text{sorption}}$ ) can be written as:

$$Q_{\text{sorption}} = \frac{1}{M_{\text{W}}} \int_{W_{\text{min}}}^{W_{\text{max}}} \rho_{\text{liq}}^{\text{wf}} \Delta_{\text{ads}} H(W) \, \mathrm{d}W$$

(10)

# **Supplementary Figures**



**Figure S1.** The PXRD patterns of as-synthesized group 1 UiO-type MOFs compared with the simulated XRD patterns from the structures of UiO-66.



**Figure S2.** The PXRD patterns of as-synthesized group 2 UiO-type MOFs compared with the simulated XRD patterns from the structures of UiO-66.



**Figure S3.** The PXRD patterns of as-synthesized DUT-52 and UiO-67 compared with the simulated XRD patterns from their crystal structures.



**Figure S4.** The PXRD patterns of as-synthesized UiO-67, UiO-67-(NH<sub>2</sub>)<sub>2</sub> and UiO-67-(OH)<sub>2</sub> compared with the simulated XRD patterns from the UiO-67 crystal structures.



**Figure S5.** TGA curves of (a) UiO-66, (b) group 1 UiO-type MOFs, (c) group 2 UiO-type MOFs, and (d) group 3 UiO-type MOFs. Prior to measurement, all samples were activated and then exposed in air until fully hydrated. And ATR-FT-IR spectra of (e) UiO-66, (f) group 1 UiO-type MOFs, (g) group 2 UiO-type MOFs, and (h) group 3 UiO-type MOFs.<sup>20</sup>



**Figure S6.** The static water contact angles of (a) UiO-66, (b) group 1 UiO-type MOFs, (c) group 2 UiO-type MOFs, and (d) group 3 UiO-type MOFs.



**Figure S7.** N<sub>2</sub> sorption isotherms at 77 K (filled/empty symbols represent adsorption/desorption) of UiO-67, UiO-67-(NH<sub>2</sub>)<sub>2</sub>, and UiO-67-(OH)<sub>2</sub>.



**Figure S8.** Pore size distributions for the activated (a) group 1 and (b) group 2 UiO-type MOFs, determined by NLDFT model based on 77 K N<sub>2</sub> adsorption isotherms.



**Figure S9.** Water adsorption isotherms of UiO-66 at different temperatures under absolute pressure normalized by saturation pressure.



**Figure S10.** Water adsorption isotherms of UiO-66-N at different temperatures under absolute pressure normalized by saturation pressure.



**Figure S11.** Water adsorption isotherms of UiO-66-(OH)<sub>2</sub> at different temperatures under absolute pressure normalized by saturation pressure.



**Figure S12.** Water adsorption isotherms of UiO-66-NH<sub>2</sub> at different temperatures under absolute pressure normalized by saturation pressure.



**Figure S13.** Water adsorption isotherms of UiO-66-OH at different temperatures under absolute pressure normalized by saturation pressure.



**Figure S14.** Water adsorption isotherms of UiO-66-Cl at different temperatures under absolute pressure normalized by saturation pressure.



**Figure S15.** The comparison of experimental isosteric heat of water adsorption ( $-\Delta_{ads}H$ ) of UiO-66 (black), UiO-66-N (red) and UiO-66-(OH)<sub>2</sub> (blue) calculated by the Clausius–Clapeyron equation.



**Figure S16.** The experimental isosteric heat of water adsorption  $(-\Delta_{ads}H)$  of UiO-66-Cl calculated by the Clausius–Clapeyron equation.



Figure S17. Diagram of the measurement device for water adsorption-desorption kinetics.



**Figure S18.** Mono-exponential approximation of the dynamic water vapor adsorption of UiO-66 at 298 K, 20% RH, and 40% RH, respectively. Experimental data is represented by black lines, and the corresponding mono-exponential fitting is represented by red lines.



**Figure S19.** Mono-exponential approximation of the dynamic water vapor adsorption of group 1 UiO-type MOFs at 298 K, 20% RH, and 40% RH: (a) UiO-66-N, (b) UiO-66-(OH)<sub>2</sub>, (c) UiO-66-NH<sub>2</sub>, and (d) UiO-66-OH. Experimental data is represented by black lines, and the corresponding mono-exponential fitting is represented by red lines.



**Figure S20.** Mono-exponential approximation of the dynamic water vapor adsorption of group 2 UiO-type MOFs at 298 K, 20% RH, and 40% RH: (a) UiO-66-Cl, (b) UiO-66-Br, (c) UiO-66-CH<sub>3</sub>, and (d) UiO-66-NO<sub>2</sub>. Experimental data is represented by black lines, and the corresponding mono-exponential fitting is represented by red lines.



**Figure S21.** Mono-exponential approximation of the dynamic water vapor adsorption of group 3 UiO-type MOFs at 298 K, 20% RH, and 40% RH: (a) DUT-52, and (b) UiO-67. Experimental data is represented by black lines, and the corresponding mono-exponential fitting is represented by red lines.



**Figure S22.** Mono-exponential approximation of the dynamic water vapor adsorption of other benchmark MOF materials at 298 K and 20% RH: (a) MIL-160, (b) MOF-303, (c) MIP-200, and (d) KMF-1. For Experimental data is represented by black lines, and the corresponding mono-exponential fitting is represented by red lines.



**Figure S23.** The comparison of the corresponding normalized value  $R_{0,norm}$  (normalized to 1.0 for UiO-66 at 20% RH) of UiO-type MOFs at 40% RH and 298 K.



**Figure S24.** TGA measurements of the dynamic water vapor adsorption profiles of UiO-66, DUT-52, and UiO-67: (a) water adsorption at 298 K and 20% RH, (b) water adsorption at 298 K and 40% RH. Prior to adsorption, the test samples were fully activated.



**Figure S25.** The dynamic water vapor adsorption profiles of MIL-160, MOF-303, KMF-1 and MIP-200 measured at 298 K and 20% RH. Prior to adsorption, the test samples were fully activated.



**Figure S26.** TGA measurements of the dynamic water vapor desorption profiles of UiO-66, UiO-66-OH, UiO-66-NH<sub>2</sub>, UiO-66-(OH)<sub>2</sub>, and UiO-66-N: (a) water desorption at 338 K and 0% RH, (b) water desorption at 358 K and 0% RH. Prior to desorption, the test samples were saturated at 298 K and 40% RH.



**Figure S27.** TGA measurements of the dynamic water vapor desorption profiles of UiO-66, UiO-66-CH<sub>3</sub>, UiO-66-NO<sub>2</sub>, UiO-66-Cl, and UiO-66-Br: (a) water desorption at 338 K and 0% RH, (b) water desorption at 358 K and 0% RH. Prior to desorption, the test samples were fully-saturated at 298 K and 40% RH.



**Figure S28.** TGA measurements of the dynamic water vapor adsorption and desorption profiles of UiO-66, DUT-52, and UiO-67: (a) water desorption at 338 K and 0% RH, (b) water desorption at 358 K and 0% RH. Prior to desorption, the test samples were saturated at 298 K and 40% RH.



**Figure S29.** The three typical water adsorption stages of UiO-66 on the water adsorption isotherms measured at 298 K.



**Figure S30.** (a) The primary adsorption site, and (b) and (c) the arrangement of the adsorbed water molecules within the cage of UiO-66-Cl, determined by GCMC theoretical simulations.



Figure S31. The thermodynamic diagram of adsorption-driven heat chiller cycle.



**Figure S32**. COP<sub>C</sub> versus volumetric working capacity ( $\Delta W$ ) defined as the volume of liquid water per volume of dry adsorbent, examined under standard AC conditions ( $T_{ev} = 5 \text{ °C}$ ,  $T_{ads} = 30 \text{ °C}$ , and  $T_{des} = 65 \text{ °C}$ ) of UiO-66-N, UiO-66, and other benchmark materials.



Figure S33. The characteristic curve of UiO-66-N determined by equation 4.



Figure S34. The characteristic curve of UiO-66 determined by equation 4.



**Figure S35**. (a) The PXRD patterns of as-synthesized UiO-67-2N compared with the simulated XRD patterns derived from the crystal structures. (b) Comparison of water adsorption isotherms for UiO-66-N and UiO-67-2N measured at 298 K.

# Supplementary Tables

Table	<b>S1.</b>	Summary	of	the	pore	structure	characteristics	of	UiO-type	MOFs	and
compa	riso	n with repo	rted	l lite	rature						

Classification	Matarial	BET surface	area (m $^2$ g $^{-1}$ )	Pore volume (cm <sup>3</sup> g <sup><math>-1</math></sup> )		
Classification	Material	Literature	This work	Literature	This work <sup><i>a</i></sup>	
Pristine-MOF	UiO-66	$1405^{21}$	1421	0.56 <sup>21</sup>	0.58	
group 1	UiO-66-N	1376 <sup>22</sup>	1413	$0.54^{22}$	0.57	
	UiO-66-NH <sub>2</sub>	1328 <sup>23</sup>	1280	0.59 <sup>23</sup>	0.55	
	UiO-66-OH	$1000^{8}$	1099	-	0.44	
	UiO-66-(OH) <sub>2</sub>	930 <sup>24</sup>	1065	-	0.41	
group 2	UiO-66-CH <sub>3</sub>	1166 <sup>21</sup>	1155	0.39 <sup>21</sup>	0.50	
	UiO-66-Br	856 <sup>6</sup>	830	$0.30^{25}$	0.34	
	UiO-66-NO <sub>2</sub>	741 <sup>21</sup>	798	$0.24^{21}$	0.35	
	UiO-66-Cl	814 <sup>6</sup>	744	0.23 <sup>25</sup>	0.29	
group 3	DUT-52	1399 <sup>26</sup>	1639	$0.60^{26}$	0.66	
	UiO-67-(OH) <sub>2</sub>	2220 <sup>5</sup>	1443	0.855	0.58	
	UiO-67-(NH <sub>2</sub> ) <sub>2</sub>	1360 <sup>9</sup>	1880	0.64 <sup>9</sup>	0.74	
	UiO-67	2064 <sup>23</sup>	2025	0.97 <sup>23</sup>	0.90	

<sup>*a*</sup> Pore volume is calculated from N<sub>2</sub> adsorption isotherm (at 77 K).

Classification	Madania1	Inflection point	Water uptake, g g <sup>-1</sup>		
Classification	Material	$(\alpha)^a$	$P/P_0 = 0.2$	P/P <sub>0</sub> =0.9	
Pristine-MOF	UiO-66	0.28	0.10	0.51	
group 1	UiO-66-OH	0.24	0.14	0.39	
	UiO-66-NH <sub>2</sub>	0.21	0.17	0.39	
	UiO-66-(OH) <sub>2</sub>	0.08	0.26	0.35	
	UiO-66-N	0.14	0.37	0.48	
group 2	UiO-66-CH <sub>3</sub>	0.29	0.11	0.44	
	UiO-66-NO <sub>2</sub>	0.29	0.09	0.32	
	UiO-66-Cl	0.28	0.08	0.23	
	UiO-66-Br	0.28	0.05	0.28	
group 3	DUT-52	0.40	0.04	0.33	
	UiO-67-(OH) <sub>2</sub>	0.31	0.09	0.28	
	UiO-67-(NH) <sub>2</sub>	0.22	0.11	0.24	
	UiO-67	0.52	0.05	0.19	

 Table S2. Summary of the water adsorption performances of UiO-type MOFs.

<sup>*a*</sup> The relative pressure at which half of the total capacity is reached.

Classification	Material	RHSaturation working up(298 K)(g g^{-1})		$R_{0,\mathrm{norm}}{}^a$
Pristine-MOF	UiO-66		0.10	1.00
group 1	UiO-66-N		0.36	2.03
	UiO-66-(OH) <sub>2</sub>		0.27	1.94
	UiO-66-NH <sub>2</sub>		0.15	1.61
	UiO-66-OH		0.13	1.20
group 2	UiO-66-Br	20%	0.05	0.58
	UiO-66-NO <sub>2</sub>		0.05	0.84
	UiO-66-Cl		0.08	0.88
	UiO-66-CH <sub>3</sub>		0.08	0.90
group 3	DUT-52		0.04	0.51
	UiO-67		0.05	0.85
Pristine-MOF	UiO-66		0.44	1.71
group 1	UiO-66-N		0.38	3.35
	UiO-66-(OH) <sub>2</sub>		0.28	3.21
	UiO-66-NH <sub>2</sub>		0.34	2.05
	UiO-66-OH		0.34	3.07
group 2	UiO-66-Cl	40%	0.19	1.04
	UiO-66-Br		0.24	1.56
	UiO-66-NO <sub>2</sub>		0.25	1.56
	UiO-66- CH <sub>3</sub>		0.37	1.59
group 3	DUT-52		0.10	1.61
	UiO-67		0.07	0.46

Table S3. Summary of kinetic adsorption behaviors of the studied UiO-66-type MOFs atdifferent humidity.

<sup>*a*</sup>  $R_{0,\text{norm}}$  is calculated according to previous literature.<sup>13</sup>

Table S4. Comparison the kinetic adsorption behaviors of UiO-66-N to other benchmarkMOFs measured at 20% RH and 298 K.

Material	RH (298 K)	Saturation working uptake (g g <sup>-1</sup> )	$R_{0,\mathrm{norm}}^{a}$
UiO-66-N		0.36	2.03
MIL-160		0.36	1.56
MOF-303	20%	0.37	1.58
KMF-1		0.40	1.52
MIP-200		0.36	1.92

<sup>*a*</sup>  $R_{0,\text{norm}}$  is calculated according to previous literature.<sup>13</sup>

Table S5.	. Summary	of kinetic of	lesorption	behaviors	of the studied	UiO-66-type	MOFs at
different	desorption	temperatu	res.				

Classification	Material	Desorption temperature (K)	Desorption time (min) <sup><i>a</i></sup>	
Pristine-MOF	UiO-66		10	
group 1	UiO-66-N		25	
	UiO-66-(OH) <sub>2</sub>		29	
	UiO-66-NH <sub>2</sub>		14	
	UiO-66-OH		13	
group 2	UiO-66-Cl	338	6	
	UiO-66-Br		7	
	UiO-66-CH <sub>3</sub>		8	
	UiO-66-NO <sub>2</sub>		9	
group 3	DUT-52		8	
	UiO-67		9	
Pristine-MOF	UiO-66		7	
group 1	UiO-66-N		9	
	UiO-66-(OH) <sub>2</sub>		16	
	UiO-66-NH <sub>2</sub>		10	
	UiO-66-OH		11	
group 2	UiO-66-Cl	358	5	
	UiO-66-Br		5	
	UiO-66-CH <sub>3</sub>		6	
	UiO-66-NO <sub>2</sub>		5	
group 3	DUT-52		5	
	UiO-67		6	

<sup>*a*</sup> The desorption time is the time corresponding to the desorption amount over 95%.

## **Supplementary References**

- J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga and K. P. Lillerud, J. Am. Chem. Soc., 2008, 130, 13850–13851.
- [2] L. Chen, J. Ou, H. Wang, Z. Liu, M. Ye and H. Zou, ACS Appl. Mater. Interfaces, 2016, 8, 20292–20300.
- [3] Z. Wang, Y. Huang, J. Yang, Y. Li, Q. Zhuang and J. Gu, *Dalton Trans.*, 2017, 46, 7412– 7420.
- [4] J. Noh, Y. Kim, H. Park, J. Lee, M. Yoon, M. H. Park, Y. Kim and M. Kim, J. Ind. Eng. Chem., 2018, 64, 478–483.
- [5] H. Furukawa, F. Gándara, Y. Zhang, J. Jiang, W. L. Queen, M. R. Hudson and O. M. Yaghi, J. Am. Chem. Soc., 2014, 136, 4369–4381.
- [6] M. Kalaj, M. R. Momeni, K. C. Bentz, K. S. Barcus, J. M. Palomba, F. Paesani and S. M. Cohen, *Chem. Commun.*, 2019, 55, 3481–3484.
- [7] J. F. Kurisingal, Y. Rachuri, A. S. Palakkal, R. S. Pillai, Y. Gu, Y. Choe and D. Park, ACS Appl. Mater. Interfaces, 2019, 11, 41458–41471.
- [8] M. J. Katz, Z. J. Brown, Y. J. Colon, P. W. Siu, K. A. Scheidt, R. Q. Snurr, J. T. Hupp and O. K. Farha, *Chem. Commun.*, 2013, **49**, 9449–9451.
- [9] N. Ko, J. Hong, S. Sung, K. E. Cordova, H. J. Park, J. K. Yang and J. Kim, *Dalton Trans.*, 2015, 44, 2047–2051.
- [10]X.-W. Gu, J.-X Wang, E. Wu, H. Wu, W. Zhou, G. Qian, B. Chen and B. Li, J. Am. Chem. Soc., 2022, 144, 2614–2623.
- [11]S. Wang, J. S. Lee, M. Wahiduzzaman, J. Park, M. Muschi, C. Martineau-Corcos, A. Tissot, K. H. Cho, J. Marrot, W. Shepard, G. Maurin, J.-S. Chang and C. Serre, *Nat. Energy*, 2018, 3, 985–993.
- [12] A. Cadiau, J. S. Lee, D. D. Borges, P. Fabry, T. Devic, M. T. Wharmby, C. Martineau, D. Foucher, F. Taulelle, C.-H. Jun, Y. K. Hwang, N. Stock, M. F. De Lange, F. Kapteijn, J. Gascon, G. Maurin, J.-S. Chang and C. Serre, *Adv. Mater.*, 2015, 27, 4775–4780.
- [13] N. Hanikel, M. S. Prevot, F. Fathieh, E. A. Kapustin, H. Lyu, H. Wang, N. J. Diercks, T. G. Glover and O. M. Yaghi, ACS Cent. Sci., 2019, 5, 1699–1706.
- [14]K. H. Cho, D. D. Borges, U.-H. Lee, J. S. Lee, J. W. Yoon, S. J. Cho, J. Park, W. Lombardo, D. Moon, A. Sapienza, G. Maurin and J.-S. Chang, *Nat. Commun.*, 2020, **11**, 5112.
- [15] D. Frohlich, S. K. Henninger and C. Janiak, *Dalton Trans.*, 2014, 43, 15300–15304.
- [16] A. K. Rappe, C. J. Casewit, K. S. Colwell, W. A. Goddard III and W. M. Skiff, J. Am. Chem. Soc., 1992, 114, 10024–10035.
- [17] S. L. Mayo, B. D. Olafson and W. A. Goddard III, J. Phys. Chem., 1990, 94, 8897-8909.
- [18] J. L. F. Abascal and C. Vega, J. Chem. Phys., 2005, 123, 234505.
- [19] M. F. de Lange, K. J. F. M. Verouden, T. J. H. Vlugt, J. Gascon and F. Kapteijn, *Chem. Rev.*, 2015, **115**, 12205–12250.
- [20]K. I. Hadjiivanov, D. A. Panayotov, M. Y. Mihaylov, E. Z. Ivanava, K. K. Chakarova, S. M. Andonova and N. L. Drenchev, *Chem. Rev.*, 2021, **121**, 1286–1424.
- [21] M. Lelorie, C. Walshe, P. Devaux, R. Giovine, S. Duval, T. Bousquet, S. Chibani, J.-F. Paul, A. Moissette, H. Vezin, P. Nerisson, L. Cantrel, C. Volkringer and T. Loiseau, *Chem. -Eur.* J., 2022, 28, e202104437.

- [22]S. Waitschat, D. Fröhlich, H. Reinsch, H. Terraschke, K. A. Lomachenko, C. Lamberti, H. Kummer, T. Helling, M. Baumgartner, S. Henninger and N. Stock, *Dalton Trans.*, 2018, 47, 1062–1070.
- [23] F. Jeremias, V. Lozan, S. K. Henninger and C. Janiak, *Dalton Trans.*, 2013, 42, 15967– 15973.
- [24] Y. Wang, Z. Hu, T. Kundu, Y. Cheng, J. Dong, Y. Qian, L. Zhai and D. Zhao, ACS Sustainable Chem. Eng., 2018, 6, 11904–11912.
- [25]D. Cunha, C. Gaudin, I. Colinet, P. Horcajada, G. Maurin and C. Serre, *J. Mater. Chem. B*, 2013, **1**, 1101–1108.
- [26] V. Bon, I. Senkovska, M. S. Weiss and S. Kaskel, CrystEngComm, 2013, 15, 9572-9577.