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# Supplementary Information: Designing optimal core-shell MOFs for direct air capture

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# **1** Computational Predictions

### **1.1** Preparation of Functionalized MOF files

To create functionalized variations of each base MOF, we used the find and replace operation of MOFUN<sup>1</sup> to find all linkers in each base MOF and replace them with functionalized linkers. For both the UiO-66 and UiO-67 MOFs, we built functionalized forms of the linkers in Avogadro<sup>2</sup> for each of the 30 functional group variations. We assigned Universal Force Field (UFF)<sup>3</sup> atom types and parameters to each of the functionalized linkers using MOFUN's rule-based UFF typer and parameterizer. For the larger functional groups, we kept the functional group atoms as near as possible to the linker to avoid overlapping with other functional groups once the functionalized form was incorporated into the MOF. These functionalized and parameterized linkers were then substituted into UiO-66 or UiO-67. As the functional groups were placed in a relatively compressed configuration to avoid overlap, we ran a short NVT molecular dynamics simulation in LAMMPS<sup>4</sup> to relax the functional group into a reasonable configuration. The atoms of the MOF's metal center and parent ligand were kept fixed; only the functional group atoms were allowed to move based on their assigned UFF parameters. We ran 2,000 timesteps of an NVT molecular dynamics simulation for each of 1e-5, 1e-4, 1e-3, and 1e-2 fs and finished with 12,000 timesteps at 0.1 fs. For some of the denser structures, the UFF parameters occasionally resulted in the two hydrogens from an H-C-H unit in an alkane chain being unreasonably close to each other, and sometimes overlapping on the same point. For structures with this problem, we increased the force constant of the H-C-H angle from ~75 kcal / mol to 200 kcal /mol and reran the NVT simulation. After the functional groups were relaxed, the final coordinates of all the atoms were stored for use in fixed framework diffusion and adsorption simulations.

# **1.2 Diffusion Calculations**

Diffusion calculations were run in LAMMPS<sup>4</sup> with the NVT ensemble at 298K. Because the framework was modeled as fixed for computational efficiency, NVT was required to keep the gas molecules at standard temperature. For each UiO-67-based MOF and gas, 10 molecules of the gas were randomly inserted into the MOF using Packmol<sup>5</sup> for five independent simulations, giving 50 trajectories per gas total. The trajectories for the centers of each gas molecule were averaged together to calculate the mean squared displacement (MSD). The diffusivity was calculated by attempting fits to MSD vs time at various intervals from 0.1 to 0.5 of the total simulation time and selecting the fit with the highest R<sup>2</sup>. Per the procedure described in Maginn, et al,<sup>6</sup> the uncertainty was estimated by generating 500 random subsets (of 50 trajectories each) randomly selected with replacement from the original 50 trajectories and estimating the diffusivities of each subset. Upper and lower bounds on the diffusivities were calculated using a 95% confidence interval.

The same procedure was used for UiO-66-based MOFs and gases, but only 10 molecules total of the gas were simulated or 10 trajectories total. We eliminated UiO-66-based MOFs for consideration based on the results of the diffusivities calculated with the 10 initial trajectories and did not run the additional 40 trajectories. The two CH<sub>3</sub> functional groups were added to our simulation list after we disqualified UiO-66 so we only report CH<sub>3</sub> for UiO-67.

# **1.3 Gas Loading Calculations**

Single component gas adsorption calculations were run in RASPA<sup>31</sup> using GCMC<sup>32</sup> to get absolute gas loadings in V/V (cm<sup>3</sup> gas [STP] / cm<sup>3</sup> framework) at typical atmospheric concentrations: 78% N<sub>2</sub> (79,033 Pa), 400 ppm CO<sub>2</sub>(42.18 Pa), and 50% relative humidity H<sub>2</sub>O. It can be difficult and computationally expensive to calculate H<sub>2</sub>O adsorption this way;<sup>7,8</sup> so instead,

we calculated Henry's constants for  $H_2O$ , and estimated loading at 50% humidity by multiplying the Henry's constant by the partial pressure of 50% of the saturation loading of  $H_2O$  of the TIP4P model, or 2050 Pa.

### 1.4 Custom CO<sub>2</sub>-NH<sub>2</sub> Interaction Force-Field Parameters

Our GCMC simulations of gas loading do not allow bonds to break and reform (i.e., for chemical reactions to take place). For most functional groups we have chosen to study, only physisorption of gases is expected. However,  $CO_2$  is expected to chemically react with the amino groups (for further details on the likely mechanism, see reference 35). Modeling the full reaction pathway is complex and beyond the scope of our investigation, where we are primarily interested in the *amount* of  $CO_2$  that loads into the pores. Thus, to emulate such chemisorption behavior, we simply adjusted the strength of the  $CO_2$ -framework interactions by amplifying the Lennard-Jones parameter for  $CO_2$ -amino interactions from the UFF default values. We ran four sets of adsorption simulations for the MOFs UiO-67-amino<sub>1</sub> and UiO-67-amino<sub>2</sub> with different epsilon strengths: 1x, 2x, 10x and 100x of normal. These simulation results were compared to experimental values (see Figure S1) and the epsilon strength that is closest to the experimental values for amino<sub>1</sub> and amino<sub>2</sub> is 10x. The 100x simulations reported gas loadings above that shown in Figure S1. The 10x epsilon parameters were used for both the diffusion and adsorption calculations for the amino<sub>1</sub> and amino<sub>2</sub> MOFs.



**Figure S1:** Simulated CO<sub>2</sub> loadings at 1x, 2x, and 10x of the normal CO<sub>2</sub>-amino interaction strength epsilon compared to experimental CO<sub>2</sub> loadings for the two MOFs UiO-67-amino<sub>1</sub> and UiO-67-amino<sub>2</sub>.

# 1.5 Simulated Diffusivities



**Figure S2:** Simulated diffusivities of CO<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub>O for all UiO-66 and UiO-67 functional groups. Error bars to 95% confidence shown for all points.



# 1.6 Simulated Gas Loadings

**Figure S3:** Simulated gas loading of  $CO_2$ ,  $N_2$ , and  $H_2O$  for all UiO-66 and UiO-67 functional groups. Atmospheric  $CO_2$ ,  $N_2$ , and  $H_2O$  partial pressures shown by vertical yellow, grey and blue lines. Error bars to 95% confidence shown for all points (though error for most points is too small to be visible).

# 2 Experimental

# 2.1 General methods

All purchased chemicals were used without further purification. Powder X-ray diffraction patterns were collected using a Bruker AXS D8 Discover powder diffractometer at 40 kV, 40 mA for Cu K<sub> $\alpha$ </sub> ( $\lambda$  = 1.5406 Å) with a scan speed of 0.20 sec/step from 5 to 30° at a step size of 0.02°. The data were analyzed using the EVA program from the Bruker Powder Analysis Software package. The simulated powder patterns were calculated using Mercury 3.8 based on MOF crystal structures.

Thermogravimetric analysis (TGA) was conducted on a TGA Q500 thermal analysis system under a constant  $N_2$  UHP flow from room temperature to 800 °C at a rate of 1 °C/min.

Gas adsorption isotherms were collected on a Micromeritics 3-flex gas adsorption analyzer. As-synthesized MOF crystals soaking in DMF were exchanged with 10 mL of dry methanol three times a day at 65 °C for one day. Then, the crystals were dried under a N<sub>2</sub> stream until they became a free-flowing powder. Approximately 40-60 mg of each sample were added into a pre-weighed sample analysis tube that had been evacuated and backfilled with He before massing. The samples were degassed at 298 K under vacuum for ~24 hours until the pressure change rate was no more than 3.5 mTorr/min. A liquid N<sub>2</sub> bath was used for the N<sub>2</sub> adsorption experiments at 77 K. A water/ethylene glycol bath was used for isotherms collected at 298 K. UHP grade N<sub>2</sub> and CO<sub>2</sub> gas adsorbates (99.999 %) were used in this study.

<sup>1</sup>H NMR spectra were obtained using Bruker Avance III 400 MHz spectrometers. Chemical shifts are in parts per million (ppm) using the residual solvent peak (DMSO-d<sub>6</sub> or D<sub>2</sub>O) as references. MOF samples were digested with DMSO-d<sub>6</sub> and a small amount of  $K_3PO_4$  and  $D_2O$ .

### 2.2 Synthesis and characterization of MOF ligands

# **2.2.1 Dimethyl 2-nitro-1, 1'-biphenyl-4,4'-dicarboxylate (1)** Compound 1 was synthesized according to literature conditions.<sup>9</sup>

#### 2.2.2 Dimethyl 2-amino-1, 1'-biphenyl-4,4'-dicarboxylate (2)

To a 100 mL Schlenk flask equipped with a stir bar were added compound **1** (710 mg, 2 mmol), 10 wt. % palladium on carbon (70 mg) and ethyl acetate (30 mL). The Schlenk flask was quickly evacuated on a vacuum line and then backfilled with argon gas. This evacuation and backfill process was repeated 3 times. The Schlenk flask was then evacuated and attached to a H<sub>2</sub> balloon. The reaction mixture was stirred at room temperature under H<sub>2</sub> atmosphere and monitored via thin layer chromatography (TLC). After 6 hours, the reaction was stopped by removing Pd catalyst via vacuum filtration through a celite cake. The filtrate was concentrated in vacuo to yield light yellow solid compound **2** (570 mg, 93%). Compound **2** was used without further purification. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.15 (m, 2H), 7.53 (m, 2H), 7.49 (dd, J = 7.9, 1.4 Hz, 1H), 7.47 (d, J = 1.4 Hz, 1H), 7.22 (d, J = 7.9 Hz, 1H), 3.97 (s, 3H), 3.94 (s, 3H), 3.88 (s, 2H).

#### 2.2.3 2-Amino-1, 1'-biphenyl-4,4'-dicarboxylic acid (3)

Compound **3** was synthesized using compound **2** as starting material based on literature conditions.<sup>9</sup> <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  12.83 (s, 2H), 8.03 (d, J = 8.5 Hz, 2H), 7.63 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 1.5 Hz, 1H), 7.22 (dd, J = 7.5, 1.5 Hz, 1H), 7.16 (d, J = 7.5 Hz, 1H), 5.25 (s, 2H).

#### 2.2.4 Dimethyl-2,2'-dinitro-[1,1'-biphenyl]-4,4'-dicarboxylate (4)<sup>10</sup>

To a solution of commercial dimethyl-biphenyl-4,4'-dicarboxylate (10 g, 37 mmol) in 100 mL of concentrated  $H_2SO_4$  at ~278 K a mixture of nitric acid (56%, 12 mL, 74 mmol) in 15 mL of concentrated sulfuric acid was added dropwise. The reaction mixture was stirred vigorously for 2 h at ~278 K and then was carefully poured onto ice (300 g). The pale yellow precipitated was filtered, washed with abundant cold water until neutral pH and air-dried to obtain 9.8 g of compound 4. <sup>1</sup>H NMR (400 MHz, DMSO-d6)  $\delta$ : 8.77 (s, 2H), 8.23 (dd, J = 7.8, 1.7 Hz, 2H), 7.35 (d, J = 7.8 Hz, 2H), 3.98 (s, 6H).





NH-

#### 2.2.5 Dimethyl 2,2'-diamino-[1,1'-biphenyl]-4,4'-dicarboxylate (5)

A 250-mL three-necked round-bottomed flask was charged with 2.0 g of 10 wt.% Pd/C, 5 g of 4 (13.8 mmol), and 165 mL of THF. The flask was then evacuated and attached to a H<sub>2</sub> balloon. The reaction mixture was stirred at room temperature under H<sub>2</sub> atmosphere and monitored via thin layer chromatography (TLC). After filtration over Celite, the solvent was removed in vacuo affording 3.3 g of light yellow compound **5**. <sup>1</sup>H NMR (400 MHz, DMSO-d6)  $\delta$ : 7.42 (d, J = 1.3 Hz, 2H), 7.26 (dd, J = 7.8, 1.3 Hz, 2H), 7.09 (d, J = 7.8 Hz, 2H), 4.95 (s, 4H), 3.82 (s, 6H).

### 2.2.6 2,2'-diamino-[1,1'-biphenyl]-4,4'-dicarboxylic acid (5)<sup>10</sup>

Compound 4 (3.75 g, 12.5 mmol) was dissolved in a mixture of 50:50 v/v THF/5% KOH (total volume 200 mL). The mixture was stirred overnight at 353 K. The aqueous layer was separated, then concentrated HCl was added until acid pH to give a yellowish solid. The solid was filtered, washed with abundant cold water and air-dried to obtain the desired product (3.01 g). <sup>1</sup>H NMR (400 MHz, DMSO-d6)  $\delta$ : 7.47 (d, J = 1.4 Hz, 2H), 7.28 (dd, J = 7.8, 1.4 Hz, 2H), 7.12 (d, J = 7.9 Hz, 2H).

#### 2.2.7 Dimethyl 2-methyl-1, 1'-biphenyl-4,4'-dicarboxylate (6)<sup>11</sup>

Ethylene glycol dimethyl ether (DME, 200 mL) was bubbled with nitrogen for about one hour before introduced into nitrogen-protected solid mixture of methyl 4iodo-3-methylbenzoate (5.0 g, 18.1 mmol), 4-methoxyl carbonylphenylboronic acid (3.9 g, 21.7 mmol), potassium carbonate (7.5 g, 54.25 mmol) and tetrakis (triphenylphosphine) palladium (0.3 g, 0.26 mmol). The mixture was allowed to reflux for 3 days under nitrogen protection. After cooling to room temperature, the solvent was evaporated to dryness. The residue was washed with a large amount of water followed by acetone. After removing the solvent, the residue was purified with column chromatography (silica gel,  $CH_2Cl_2$ ) to give the ester as a white solid (3.4 g). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  8.05 (s, 2H), 7.94 (s, 1H), 7.86 (s, 1H), 7.56 (s, 1H), 7.41 (s, 1H), 3.89 (s, 6H), 2.30 (s, 3H).

# 2.2.8 2-methyl-1, 1'-biphenyl-4,4'-dicarboxylate (7)<sup>11</sup>

Compound **5** (3.0 g, 10.6 mmol) was suspended in a mixture of THF/MeOH (50 mL, v/v = 1/1,) and 30 mL aqueous solution of 2 M KOH. The resultant mixture was stirred and refluxed overnight. After cooling to room temperature, organic solvents were removed, and the remaining solution was acidified with 1 M HCl to give a precipitate, which was collected and washed with water. Dried in the oven to produce 2.0 g of compound **6**. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz)  $\delta$ : 12.98 (s, 2H), 8.02 (s, 2H), 7.91 (s, 1H), 7.86 (s, 1H), 7.53 (s, 2H), 7.38 (s, 1H), 2.30 (s, 3H).





## 2.2.9 Dimethyl 2,2'-dimethyl-1, 1'-biphenyl-4,4'-dicarboxylate (8)<sup>11</sup>

Methyl 4-iodo-3-methylbenzoate (5.0 g, 18.1 mmol) and copper powder (20.0 g, 314.7 mmol) were thoroughly mixed under argon atmosphere. The resulting mixture was heated up to 250 °C overnight. After cooling, the reaction mixture was extracted with chloroform (30 mL x 3). The combined extracts were evaporated to dryness. Flash chromatography with ethyl acetate/hexanes (5% - 10%) as eluent afforded dimethyl 2,2'-dimethylbiphenyl-4,4'-dicarboxylate (1.4 g). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ : 7.90 (d, 2H), 7.89 (dd, 2H), 7.10 (d, 2H), 3.87 (s, 6H), 2.0 (s, 6H).

# 2.2.10 2,2'-dimethyl-1, 1'-biphenyl-4,4'-dicarboxylate (9)<sup>11</sup>

Compound 7(1.0, 3.3 mmol) was suspended in a mixture of THF/MeOH (50 mL, v/v = 1/1, THF = tetrahydrofuran, MeOH = methanol), to which an aqueous solution of 2 M KOH (20 mL) was added. The resulting mixture was stirred and refluxed overnight. After cooling to room temperature, organic solvents were evaporated, and the remaining aqueous solution was acidified with 1 M HCl to give a precipitate, which was collected by filtration, washed with water, and dried in the oven to produce 0.6 g of compound **8**. 1H NMR (DMSO-d6, 400 MHz)  $\delta$ : 12.97 (s, 2H), 7.92 (d, 2H), 7.86 (dd, 2H), 7.23 (d, 2H), 2.05 (s, 6H).



# 2.3 Synthesis of MOFs

# 2.3.1 Synthesis of UiO-67

To a 20 mL Pyrex vial was added  $ZrCl_4$  (9.8 mg, 0.04 mmol), DMF (10 mL), CH<sub>3</sub>COOH (0.5 mL) and 1, 1'-biphenyl-4,4'-dicarboxylic acid (H<sub>2</sub>-BPDC) (9.3 mg, 0.04 mmol). After sonication for 5 min, the vial was placed in in a 100 °C for 24 hours. The reaction suspension was then centrifuged at 10,000 rpm for 3 min to obtain white precipitate. The precipitate was washed with fresh DMF (16 mL, 4x) and dispersed in DMF (5 mL).

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

To a 20 mL Pyrex vial was added  $ZrCl_4$  (9.8 mg, 0.04 mmol), DMF (10 mL), CH<sub>3</sub>COOH (0.5 mL) and 2-amino-1, 1'-biphenyl-4,4'-dicarboxylic acid (H<sub>2</sub>-NH<sub>2</sub>-BPDC) (9.9 mg, 0.04 mmol). After sonication for 5 min, the vial was placed in in a 100 °C for 24 hours. The reaction suspension was then centrifuged at 10,000 rpm for 3 min to obtain white precipitate. The precipitate was washed with fresh DMF (16 mL, 4x) and dispersed in DMF (5 mL).

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

To a 20 mL Pyrex vial was added  $ZrCl_4$  (9.8 mg, 0.04 mmol), DMF (10 mL), CH<sub>3</sub>COOH (0.5 mL) and 2,2'-diamono-1, 1'-biphenyl-4,4'-dicarboxylic acid (H<sub>2</sub>-2NH<sub>2</sub>-BPDC) (10.5 mg, 0.04 mmol). After sonication for 5 min, the vial was placed in in a 100 °C for 24 hours. The reaction suspension was then centrifuged at 10,000 rpm for 3 min to obtain white precipitate. The precipitate was washed with fresh DMF (16 mL, 4x) and dispersed in DMF (5 mL).

# 2.3.4 Synthesis of CH<sub>3</sub>-UiO-67

To a 20 mL Pyrex vial was added  $ZrCl_4$  (9.8 mg, 0.04 mmol), DMF (10 mL), CH<sub>3</sub>COOH (0.5 mL) and 2-methyl-1, 1'-biphenyl-4,4'-dicarboxylic acid (H<sub>2</sub>-Me-BPDC) (9.8 mg, 0.04 mmol). After sonication for 5 min, the vial was placed in in a 100 °C for 24 hours. The reaction suspension was then centrifuged at 10,000 rpm for 3 min to obtain white precipitate. The precipitate was washed with fresh DMF (16 mL, 4x) and dispersed in DMF (5 mL).

# 2.3.5 Synthesis of (CH<sub>3</sub>)<sub>2</sub>-UiO-67

To a 20 mL Pyrex vial was added  $ZrCl_4$  (9.8 mg, 0.04 mmol), DMF (10 mL), CH<sub>3</sub>COOH (0.5 mL) and 2,2'-dimethyl-1, 1'-biphenyl-4,4'-dicarboxylic acid (H<sub>2</sub>-Me<sub>2</sub>-BPDC) (10.4 mg, 0.04 mmol). After sonication for 5 min, the vial was placed in in a 100 °C for 24 hours. The reaction suspension was then centrifuged at 10,000 rpm for 3 min to obtain white precipitate. The precipitate was washed with fresh DMF (16 mL, 4x) and dispersed in DMF (5 mL).

# 2.4 Characterization of MOFs

2.4.1 Powder X-ray diffraction data



**Figure S4:** Simulated PXRD pattern of UiO-67 (black) and experimental PXRD of as synthesized UiO-67 (dark red), NH<sub>2</sub>-UiO-67 (blue),  $(NH_2)_2$ -UiO-67 (orange), CH<sub>3</sub>-UiO-67 (green) and  $(CH_3)_2$ -UiO-67 (dark blue). These data confirm the crystallinity and phase purity of the synthesized MOFs.

# 2.4.2 Thermogravimetric analysis



Figure S5: TGA curves of UiO-67 (dark red),  $NH_2$ -UiO-67 (blue),  $(NH_2)_2$ -UiO-67 (orange),  $CH_3$ -UiO-67 (green) and  $(CH_3)_2$ -UiO-67 (dark blue).

### 2.4.3 Elemental analysis

Elemental and thermogravimetric analyses were used to determine the MOF molecular formulas. The theoretical molecular formulas  $Zr_6O_4(OH)_4(X-BPDC)_{n1} \cdot n_2DMF$  were determined based on TGA analysis according to literature method.<sup>12</sup> TGA analysis of MOFs revealed an initial loss of ~4% between 90-200 °C corresponding to the DMF molecules within the framework (Figure S5). In TGA analysis, we denoted the mass right before the MOF samples started to decompose (~450 °C) as **a**, which represented  $Zr_6O_4(OH)_4(X-BPDC)_n$ . The final mass in TGA analysis after reaching plateau at ~500-750 °C was the remaining  $ZrO_2$ . This was then used to calculate mass **b** for  $Zr_6O_4(OH)_4$  in the corresponding MOFs. The difference between mass **a** and **b** was attributed to ligands and used to calculate the number of ligand X-BPDC per molecule.

*UiO-67* 

Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(BPDC)<sub>5.7</sub>•DMF, weight loss % in TGA by 200 °C: 3.7% Calcd.: C,46.57; H, 2.67; N, 0.66. Found: C, 46.99; H, 2.58; N, 0.34

*NH*<sub>2</sub>-*UiO*-67

Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(NH<sub>2</sub>-BPDC)<sub>5.4</sub>•0.8DMF, weight loss % in TGA by 200 °C: 2.8% Calcd.: C,45.17; H, 2.80; N, 4.19. Found: C, 45.23; H, 2.89; N, 4.21

(NH<sub>2</sub>)<sub>2</sub>-UiO-67

Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(2NH<sub>2</sub>-BPDC)<sub>5.6</sub>•1.4DMF, weight loss % in TGA by 200 °C: 4.6% Calcd.: C,43.34; H, 3.12; N, 7.89. Found: C, 43.39; H, 3.07; N, 7.83

*CH*<sub>3</sub>-*UiO*-67

Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(CH<sub>3</sub>-BPDC)<sub>5.4</sub>•1.2DMF, weight loss % in TGA by 200 °C: 4.2% Calcd.: C,46.57; H, 3.18; N, 0.80. Found: C, 46.53; H, 3.12; N, 0.74

*(CH<sub>3</sub>)*<sub>2</sub>-*UiO*-67

Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>((CH<sub>3</sub>)<sub>2</sub>-BPDC)<sub>5.8</sub>•1.1DMF, weight loss % in TGA by 200 °C: 3.5% Calcd.: C,51.12; H, 3.60; N, 0.68. Found: C, 50.99; H, 3.58; N, 0.64



**Figure S6:** N<sub>2</sub> sorption isotherms of UiO-67 (dark red), NH<sub>2</sub>-UiO-67 (blue), (NH<sub>2</sub>)<sub>2</sub>-UiO-67 (orange), CH<sub>3</sub>-UiO-67 (green) and (CH<sub>3</sub>)<sub>2</sub>-UiO-67 (dark blue) at 77 K. Filled and hollow circles indicate adsorption and desorption respectively. These data were used to calculate the Branauer-Emmett-Teller (BET) surface areas for the MOFs: UiO-67, 2572 m<sup>2</sup>/g ; NH<sub>2</sub>-UiO-67, 2074 m<sup>2</sup>/g ; (NH<sub>2</sub>)<sub>2</sub>-UiO-67, 1705 m<sup>2</sup>/g; CH<sub>3</sub>-UiO-67, 2042 m<sup>2</sup>/g; and (CH<sub>3</sub>)<sub>2</sub>-UiO-67, 1647 m<sup>2</sup>/g. These values are consistent with literature data for UiO-67<sup>13,14</sup> as well as NH<sub>2</sub>-UiO-67 and CH<sub>3</sub>-UiO-67.<sup>14</sup> The difunctionalized analogues have lower BET surface areas, as expected due to the additional functional groups.



**Figure S7:** CO<sub>2</sub> adsorption isotherms of UiO-67 (dark red square), NH<sub>2</sub>-UiO-67 (blue circle), (NH<sub>2</sub>)<sub>2</sub>-UiO-67 (orange left-triangle), CH<sub>3</sub>-UiO-67 (green down-triangle) and (CH<sub>3</sub>)<sub>2</sub>-UiO-67 (dark blue right-triangle) at 298 K.



**Figure S8:** N<sub>2</sub> adsorption isotherms of UiO-67 (dark red square), NH<sub>2</sub>-UiO-67 (blue circle),  $(NH_2)_2$ -UiO-67 (orange left-triangle), CH<sub>3</sub>-UiO-67 (green down-triangle) and  $(CH_3)_2$ -UiO-67 (dark blue right-triangle) at 298 K.



**Figure S9:** Water adsorption isotherms of UiO-67 (dark red square), NH<sub>2</sub>-UiO-67 (blue circle),  $(NH_2)_2$ -UiO-67 (orange left-triangle), CH<sub>3</sub>-UiO-67 (green down-triangle) and  $(CH_3)_2$ -UiO-67 (dark blue right-triangle) at 298 K.

# 2.4.5 Calculation of CO<sub>2</sub>: N<sub>2</sub> adsorption selectivity

	CO <sub>2</sub> -298 K (cm <sup>3</sup> /g) @ 42 Pa	N <sub>2</sub> -298 K(cm <sup>3</sup> /g) @ 79 kPa	CO <sub>2</sub> /N <sub>2</sub> Adsorption Selectivity
Ui <b>O-67</b>	0.029	6.29	9.33
NH <sub>2</sub> -UiO-67	0.032	3.38	17.8
(NH <sub>2</sub> ) <sub>2</sub> -UiO-67	0.058	2.84	38.4
CH <sub>3</sub> -UiO-67	0.033	3.54	17.5
(CH <sub>3</sub> ) <sub>2</sub> -UiO-67	0.013	2.68	9.42

Table S1. Experimental CO<sub>2</sub>:N<sub>2</sub> adsorption selectivity.

CO<sub>2</sub>:N<sub>2</sub> adsorption selectivity was calculated using following equation:

Adsorption selectivity =  $\frac{a/42}{b/7.9 * 10^4}$ a: CO<sub>2</sub> loading at 42 Pa, 298 K

b: N<sub>2</sub> loading at 79 KPa, 298 K

	CO <sub>2</sub> /N <sub>2</sub> Adsorption Selectivity	Simulation (default epsilon / 10x epsilon)
UiO-67	9.33	7.11
NH <sub>2</sub> -UiO-67	17.8	7.45 / 11.01
(NH <sub>2</sub> ) <sub>2</sub> -UiO-67	38.4	8.33 / 16.45
CH <sub>3</sub> -UiO-67	17.5	13.5
( CH <sub>3</sub> ) <sub>2</sub> -UiO-67	9.42	10.0

Table S2. Comparison of experimental and simulated CO<sub>2</sub>:N<sub>2</sub> adsorption selectivity.



**Figure S10:** Comparison between experimental and simulated  $CO_2:N_2$  adsorption selectivity of UiO-67, NH<sub>2</sub>-UiO-67 and (NH<sub>2</sub>)<sub>2</sub>-UiO-67: (left) simulation data with default force field parameters for NH<sub>2</sub>-CO<sub>2</sub> interaction, (right) simulation data with 10x epsilon force field parameters for NH<sub>2</sub>-CO<sub>2</sub> interaction.



**Figure S11:** Comparison between experimental and simulated CO<sub>2</sub>:N<sub>2</sub> adsorption selectivity of UiO-67, CH<sub>3</sub>-UiO-67 and (CH<sub>3</sub>)<sub>2</sub>-UiO-67.



**Figure S12:** Comparison between experimental and simulated  $CO_2:N_2$  adsorption selectivity of UiO-67, NH<sub>2</sub>-UiO-67 and CH<sub>3</sub>-UiO-67: (left) simulation data with default force field parameters for NH<sub>2</sub>-CO<sub>2</sub> interaction, (right) simulation data with 10x epsilon force field parameters for NH<sub>2</sub>-CO<sub>2</sub> interaction.



**Figure S13:** Comparison between experimental and simulated  $CO_2:N_2$  adsorption selectivity of UiO-67,  $(NH_2)_2$ -UiO-67 and  $(CH_3)_2$ -UiO-67: (left) simulation data with default force field parameters for  $NH_2$ - $CO_2$  interaction, (right) simulation data with 10x epsilon force field parameters for  $NH_2$ - $CO_2$  interaction.

# 3 COMSOL Multiphysics® model

For the COMSOL Multiphysics<sup>®</sup> model case study, the Langmuir equation (Equation X) was fitted to experimental data in order to simulate gas adsorption. The fitted constants from that equation ( $K_L$  and  $C_{Pmax}$ ) are presented for CO<sub>2</sub>, H<sub>2</sub>O and N<sub>2</sub> in Supplemental Table S3 for the two MOFs simulated in this paper: NH<sub>2</sub> and (CH<sub>3</sub>)<sub>2</sub>. The diffusivity values of CO<sub>2</sub>, H<sub>2</sub>O and N<sub>2</sub> for these two MOFs are also reported in this table. Figure S14 shows our modeled Langmuir curve fits to experimental data for CO<sub>2</sub>, H<sub>2</sub>O and N<sub>2</sub> for NH<sub>2</sub> and (CH<sub>3</sub>)<sub>2</sub>.

**Table S3:** Langmuir adsorption constants (KL), adsorption maximums (CPmax), and diffusivity values for the two MOFs modeled in this paper.

	Constant	NH <sub>2</sub>	<b>(CH₃)</b> 2
	K <sub>L</sub> [m³/mol]	0.197871	0.321812
<i>CO</i> <sub>2</sub>	C <sub>Pmax</sub> [mol/kg]	8.375795	1.72746
	D <sub>CO2</sub> [m <sup>2</sup> /s]	5.05E-09	3.45E-09
	K <sub>L</sub> [m³/mol]	2.121584	0.691886
H₂O	C <sub>Pmax</sub> [mol/kg]	11.81449	15.87641
	D <sub>H20</sub> [m <sup>2</sup> /s]	6.15E-11	9.24E-11
	K <sub>L</sub> [m³/mol]	0.006575	0.00263
N <sub>2</sub>	C <sub>Pmax</sub> [mol/kg]	26.45345	50.87282
	D <sub>H20</sub> [m <sup>2</sup> /s]	1.26E-08	6.75E-09



**Figure S14:** Experimental vs. modeled Langmuir adsorption isotherms for  $CO_2$  (left),  $H_2O$  (middle), and  $N_2$  (right). Experimental values are shown with markers; modeled values are

shown with solid lines. Values for our simulated core MOF, NH<sub>2</sub>, are shown in blue; values for our simulated shell MOF, (CH<sub>3</sub>)<sub>2</sub>, are shown in red.

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