Electronic Supplementary Information for:

**Optimizing volumetric surface area of UiO-66 and its functionalized analogs through compression**

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General Considerations
All solvents and reagents were purchased through commercial vendors and no additional purification or drying was performed prior to use.

Gas Adsorption Measurements
Gas adsorptions measurement were performed at 77 K using N$_2$ with a Tristar II Plus manufactured by Micromeritics. The materials were activated under vacuum on a Schlenk line at 120 °C for 18 hours the materials were then transferred to tared gas adsorption tubes and placed under ultra-high vacuum for 48 hours at 150 °C for 48 hours.

Compaction Equipment
An OEM Tools 25087 hydraulic press was used during compaction experiments, using a stainless-steel die which produced 5 mm cylindrical pellets. All experiments were performed in a glove box under an N$_2$ atmosphere.

Pelletization Procedure
Using mineral oil, the shaft and pin of the pellet die was lightly oiled. ~100 mg of MOF was placed into the die and compressed to the required pressure (0.15, 0.40, 0.65, 1.01 GPa). After 5 minutes, a reduction in pressure is observed due to a pressure equalization and the initial pressure was applied a second time. The pellet was then removed from the die and activated using flowing N$_2$ while heated to 120 °C.

Tap Density Experiment
To determine the tap density of all powders, an in-house constructed automatic tapper was employed. ~50 mg of activated MOF was placed into 2 mL vial under an N$_2$ atmosphere and covered with Parafilm. The tube was secured in the automatic tapper sample holder and variable-speed induction motor was set to a speed of 2.1 which corresponds to 94 taps/minutes and allowed to run for 18 hours.

Ligand Syntheses

Synthesis of 2-(acetylamido) terephthalic acid
2-Aminoterephthalic acid (4.891 g, 27 mmol) and acetyl chloride (2.543 g, 32.4 mmol) were added to a 250 ml RBF with 100 ml of THF and stirred under reflux at 80 °C for 12 hours. Solvent was removed under vacuum at 50 °C, leaving a tan solid behind. 30 ml of CHCl$_3$ was added to the crude product, stirred until powder was fully dispersed and under reduced pressure, solvent was removed via Büchner funnel. Two more washings with CHCl$_3$ were performed to obtain 5.484 g
Synthesis of 2-(lauroylamido) terephthalic acid
2-Aminoterephthalic acid (4.891 g, 27 mmol) and lauroyl chloride (7.437 g, 32.4 mmol) were added to a 250 ml RBF along with 100 ml of THF and stirred under reflux at 80 °C for 12 hours. Solvent was removed under vacuum at 50 °C, leaving a tan solid behind. 30 ml of CHCl₃ was added to the crude product, stirred until powder was fully dispersed and under reduced pressure, solvent was removed via Büchner funnel. Two more washings with CHCl₃ were performed to obtain 6.415 g of pure product (68 % yield). ¹H-NMR (400MHz, DMSO): δ = 11.07 (s, 1H, NH), 9.04 (s, 1H, CH), 8.04 (d, J = 7.7 Hz, 1H, CH), 7.65 (dd, J = 8.1 Hz, 1H, CH), 2.39 (t, J = 3.5, 2H, CH₂), 1.62 (m, J = 3.5, 2H, CH₂), 1.23 (m, 16H, CH₂), 0.83 (t, J = 0.93, 3H, CH₃).

Synthesis of 2-(3,3,5-trimethylhexanoylamido) terephthalic acid
2-Aminoterephthalic acid (4.891 g, 27 mmol) and 3,3,5-trimethylhexanoyl chloride (2.998 g, 32.4 mmol) were added to a 250 ml RBF along with 100 ml of THF and stirred under reflux at 80 °C for 12 hours. Solvent was removed under vacuum at 50 °C, leaving a tan solid behind. 30 ml of CHCl₃ was added to the crude product, stirred until powder was fully dispersed and under reduced pressure, solvent was removed via Büchner funnel. Two more washings with CHCl₃ were performed to obtain 8.156 g of pure product (94 % yield). ¹H-NMR (400MHz, DMSO): δ = 11.06 (s, 1H, NH), 9.04 (s, 1H, CH), 8.04 (d, J = 7.7 Hz, 1H, CH), 7.65 (dd, J = 7.9 1H, CH), 2.48 (t, J = 3.5, 1H CH), 2.25 (m, 2H, CH), 1.2 (m, 14H, CH).

Metal-Organic Framework Experimental Procedures

Synthesis of UIO-66
Terephthalic acid (5.3 g, 32 mmol), ZrCl₄ (7.7 g, 33 mmol) and 300 mL dimethyl formamide (DMF) were combined in a 500 mL round bottom flask. The solution was sonicated for an hour and 122 mL of formic acid was slowly added. A standard rubber balloon was affixed to the opening of the round bottom flask and placed in an oil bath. The solution was stirred and heated to 120 °C for five hours and allowed to cool until reaching ambient temperature. A washing procedure was performed, by decanting the DMF, filling six 50 mL Falcon conical centrifuge tubes with unwashed MOF, equally, and adding fresh DMF. After 24 hours, the Falcon tubes were centrifuged for 10 minutes, the old solvent was decanted, and fresh solvent was added. This process was repeated
for six days, where three DMF washes took place, along with three acetone washes. The washed MOF was dried in a filter flask under air, resulting in a flowing powder.

**Synthesis of UIO-66-NH$_2$**

ZrCl$_4$ (1.0 g, 4.3 mmol) was combined with 40 mL dimethyl formamide (DMF) and 18 mL HCl in a 250 mL VWR jar and was sonicated for 20 minutes. 2-aminoterephthalic acid (3.2 g, 14.3 mmol) was dissolved in 80 mL DMF and combined with the zirconium solution and the contents were sonicated for an addition 20 minutes. The VWR jar was capped and heated at 80 ºC for 18 hours. A washing procedure was performed, by decanting the DMF, filling six 50 mL Falcon conical centrifuge tubes with unwashed MOF, equally, and adding fresh DMF. After 24 hours, the Falcon tubes were centrifuged for 10 minutes, the old solvent was decanted, and fresh solvent was added. This process was repeated for six days, where three DMF washes took place, along with three acetone washes. The washed MOF was dried in a filter flask under air, resulting in a flowing powder.

**Synthesis of UIO-66-Acetal**

2-(acetylamido) terephthalic acid (3.2 g, 14.3 mmol), ZrCl$_4$ (2.0 g, 8.6 mmol) and 240 mL dimethyl formamide (DMF) were combined in a 1000 mL VWR jar. The solution was sonicated until no solids remained and 12 mL of formic acid was slowly added. The VWR jar was capped and placed in an oven at 80 ºC for 18 hours. A washing procedure was performed, by decanting the DMF, filling six 50 mL Falcon conical centrifuge tubes with unwashed MOF, equally, and adding fresh DMF. After 24 hours, the Falcon tubes were centrifuged for 10 minutes, the old solvent was decanted, and fresh solvent was added. This process was repeated for six days, where three DMF washes took place, along with three acetone washes. The washed MOF was dried in a filter flask under air, resulting in a flowing powder.

**Synthesis of UIO-66-Hexanoyl**

2-(3,3,5-trimethylhexanoylamido) terephthalic acid (3.7 g, 11.5 mmol), ZrCl$_4$ (2.0 g, 8.6 mmol) and 480 mL dimethyl formamide (DMF) were combined in a 1000 mL VWR jar. The solution was sonicated until no solids remained and 15 mL of formic acid was slowly added. The VWR jar was capped and placed in an oven at 110 ºC for 42 hours. A washing procedure was performed, by decanting the DMF, filling six 50 mL Falcon conical centrifuge tubes with unwashed MOF, equally, and adding fresh DMF. After 24 hours, the Falcon tubes were centrifuged for 10 minutes, the old solvent was decanted, and fresh solvent was added. This process was repeated for six days, where three DMF washes took place, along with three acetone washes. The washed MOF was dried in a filter flask under air, resulting in a flowing powder.
Synthesis of UIO-66-Lauroyl

2-(lauroylamido) terephthalic acid (2.0 g, 5.4 mmol), ZrCl₄ (2.0 g, 8.6 mmol) and 120 mL dimethyl formamide (DMF) were combined in a 500 mL VWR jar. The solution was sonicated until no solids remained and 12 mL of formic acid was slowly added. The VWR jar was capped and placed in an oven at 110 ºC for 42 hours. A washing procedure was performed, by decanting the DMF, filling six 50 mL Falcon conical centrifuge tubes with unwashed MOF, equally, and adding fresh DMF. After 24 hours, the Falcon tubes were centrifuged for 10 minutes, the old solvent was decanted, and fresh solvent was added. This process was repeated for six days, where three DMF washes took place, along with three acetone washes. The washed MOF was dried in a filter flask under air, resulting in a flowing powder.
Figure S1. NMR spectrum of 2-acetylamido terephthalic acid.

Figure S2. NMR spectrum of 3,5,5'-trimethylhexanoylamido terephthalic acid.

Figure S3. NMR spectrum of 2-lauroylamido terephthalic acid.
Figure S4. PXRD diffraction pattern of UiO-66 prior to (top) and after (bottom) compression.
Figure S5. PXRD pattern of UiO-66-acetylamido prior to (top) and after (bottom) compression.
Figure S6. PXRD pattern of UiO-66-hexanoylamido prior to (top) and after (bottom) compression.
Figure S7. PXRD pattern of UiO-66-lauroylamido prior to (top) and after (bottom) compression.
Figure S8. Using thermogravimetric analysis with cycling CO₂ and N₂, the cyclability of UIO-66 powder (upper plot) was compared to the pelletized version (lower plot).
Table S1. Predominant pore sizes before and after compression to 1.3 Mg.

<table>
<thead>
<tr>
<th>MOF</th>
<th>Initial (Å)</th>
<th>After compression</th>
</tr>
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<tbody>
<tr>
<td>UiO-66</td>
<td>14, 13, 15</td>
<td>12, 13, 10</td>
</tr>
<tr>
<td>UiO-66-NH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>14, 13, 15</td>
<td>12, 13</td>
</tr>
<tr>
<td>UiO-66-acetylamido</td>
<td>11, 10</td>
<td>9, 8</td>
</tr>
<tr>
<td>UiO-66-3,5,5-</td>
<td>6, 7, 5</td>
<td>6, 5</td>
</tr>
<tr>
<td>trimethylhexanoylamido</td>
<td></td>
<td></td>
</tr>
<tr>
<td>UiO-66-lauroylamido</td>
<td>4, 3, 5</td>
<td>4, 5</td>
</tr>
</tbody>
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