Electronic supplementary information

Cooperative Effect of Temperature and Linker Functionality on CO₂ Capture from Industrial Gas Mixtures in Metal-Organic Frameworks: A Combined Experimental and Molecular Simulation Study

1 Experimental details

1.1 Preparation of the MOFs

A standard synthesis of UiO-66 was performed by dissolving ZrCl₄ (0.932 g) and 1,4-benzenedicarboxylic acid (H₂BDC) (1.449 g) in DMF (24 mL) at room temperature, then, added 0.67 ml hydrochloric acid to get more crystal nucleus. The slurry was then introduced in a 100 mL Teflon liner and further introduced in a metallic PAAR bomb. The system was placed in an oven with 1 °C/min heating up to 220 °C, then held at 220°C for 16 h. Then, the solution was cooled to room temperature at the speed of 1 °C/min. The resulting white product was filtered off, washed with DMF and ethanol to remove the excess of unreacted terephthalic acid, then washed again with acetone and dried under vacuum at 150 °C. UiO-66-NH₂, UiO-66-NO₂ and UiO-66-Br were synthesized analogously by replacing H₂BDC with the equivalent molar amounts of H₂N-H₂BDC, O₂N-H₂BDC and Br-H₂BDC, respectively.¹⁻⁸

1.2 PXRD analysis

Approximately 5 mg of samples were soaked in ethanol dispersed and dried as a thin layer on a glass plate before the PXRD measurements. PXRD data were collected at ambient atmosphere and
temperature on a SHIMADZU XRD-6000 instrument. Diffractometer at 40 kV, 40 mA for monochromatic Cu Kα (λ = 1.5418 Å) with a scan speed of 5°/min, a step size of 0.02° in 2θ, and a 2θ range of 5-45°.

Fig. S1 Powder XRD pattern of UiO-66 compared with reference.¹

Fig. S2 Powder XRD pattern of four UiO-66 analogues.
1.3 N\textsubscript{2} adsorption isotherms at 77 K

![Graph showing N\textsubscript{2} adsorption isotherms for UiO-66 analogues.](image)

**Fig. S3** N\textsubscript{2} adsorption isotherms at 77 K for the four UiO-66 analogues.

2 Structural properties and model parameters for the UiO-66 analogues

2.1 Structural properties of the four UiO-66 analogues

<table>
<thead>
<tr>
<th>materials</th>
<th>(\rho_{\text{cryt}}^a) (g/cm(^3))</th>
<th>(S_{\text{acc}}^a) (m(^2)/g)</th>
<th>(V_{\text{free}}^a) (cm(^3)/g)</th>
<th>BET(^b) surface area (m(^2)/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UiO-66</td>
<td>1.19</td>
<td>939.37</td>
<td>0.49</td>
<td>1262</td>
</tr>
<tr>
<td>UiO-66-Br</td>
<td>1.53</td>
<td>594.47</td>
<td>0.36</td>
<td>966</td>
</tr>
<tr>
<td>UiO-66-NH(_2)</td>
<td>1.26</td>
<td>745.01</td>
<td>0.44</td>
<td>1080</td>
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<tr>
<td>UiO-66-NO(_2)</td>
<td>1.39</td>
<td>593.59</td>
<td>0.39</td>
<td>922</td>
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</tbody>
</table>

\(^a\) Calculated with the Materials Studio package.\(^9\)

\(^b\) Calculated by N\textsubscript{2} adsorption isotherms at 77 K in this work.

2.2 LJ force field parameters for the UiO-66 analogues

<table>
<thead>
<tr>
<th>atom</th>
<th>(\epsilon/k_B) (K)</th>
<th>(\sigma) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOF(_Zr)</td>
<td>33.68</td>
<td>2.70</td>
</tr>
<tr>
<td>MOF(_N)</td>
<td>37.78</td>
<td>3.16</td>
</tr>
<tr>
<td>MOF(_C)</td>
<td>46.42</td>
<td>3.37</td>
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<tr>
<td>MOF(_H)</td>
<td>7.42</td>
<td>2.76</td>
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<tr>
<td>MOF(_O)</td>
<td>46.72</td>
<td>2.94</td>
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<tr>
<td>MOF(_Br)</td>
<td>180.61</td>
<td>3.41</td>
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</tbody>
</table>
2.3 The partial charges of the four UiO-66 analogues

![Atomic partial charges of four UiO-66 analogues](image)

(a) UiO-66  
(b) UiO-66-Br  
(c) UiO-66-NH₂  
(d) UiO-66-NO₂

**Fig. S4** Atomic partial charges of four UiO-66 analogues. (Zr, aquamarine blue; O, red; C, gray; H, white; N, blue; Br, brown).

3 Comparison between the simulated isotherms using the force field with and without parameter rescaling and the experimental values.

![Comparison of the experimental and simulated isotherms of CO₂ and CH₄ in the four UiO-66 analogues at 298 K](image)

**Fig. S5** Comparison of the experimental and simulated isotherms of CO₂ and CH₄ in the four UiO-66 analogues at 298 K.
4 Selectivities of CO$_2$ in the equimolar CO$_2$/CO and CO$_2$/N$_2$ mixtures.

Fig. S6 Selectivities of CO$_2$ in the equimolar CO$_2$/CO and CO$_2$/N$_2$ mixtures in UiO-66, UiO-66-Br and UiO-66-NH$_2$ as a function of temperature at 0.1 and 3.0 MPa.

5 TSA working capacity of CO$_2$ in the equimolar CO$_2$/CH$_4$, CO$_2$/CO and CO$_2$/N$_2$ mixtures.

Fig. S7 Simulated working capacity of CO$_2$ at different intake temperatures as a function of pressure at $T_{\text{purge}} = 473$ K in UiO-66, UiO-66-Br, UiO-66-NH$_2$ and UiO-66-NO$_2$. 
Fig. S8 Simulated working capacity of CO$_2$ at $T_{\text{purge}} = 473$ K as a function of intake temperature at different pressures in UiO-66, UiO-66-Br, UiO-66-NH$_2$ and UiO-66-NO$_2$.

References:


