Supporting Information

A new microporous metal-organic framework with open metal sites and exposed carboxylic acid groups for selective separation of CO$_2$/CH$_4$ and C$_2$H$_2$/CH$_4$

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Table S1. Equation parameters for the DSLF isotherm model.

<table>
<thead>
<tr>
<th>Adsorbates</th>
<th>(N_1^{\text{max}}) (mmol/g)</th>
<th>(b_1) (kPa(^{-1}))</th>
<th>(n_1)</th>
<th>(N_2^{\text{max}}) (mmol/g)</th>
<th>(b_2) (kPa(^{-1}))</th>
<th>(n_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_2)H(_2) (273 K)</td>
<td>1.3482</td>
<td>0.00288</td>
<td>1.05418</td>
<td>11.52941</td>
<td>0.06215</td>
<td>1.33581</td>
</tr>
<tr>
<td>CH(_4) (273 K)</td>
<td>4.2875</td>
<td>0.00293</td>
<td>0.00293</td>
<td>1.26519</td>
<td>0.00125</td>
<td>1.03086</td>
</tr>
<tr>
<td>CO(_2) (273 K)</td>
<td>12.84527</td>
<td>0.00284</td>
<td>1.05839</td>
<td>10.42661</td>
<td>0.00935</td>
<td>1.14162</td>
</tr>
<tr>
<td>C(_2)H(_2) (298 K)</td>
<td>4.95847</td>
<td>0.00289</td>
<td>0.99848</td>
<td>8.1522</td>
<td>0.05423</td>
<td>1.11579</td>
</tr>
<tr>
<td>CH(_4) (298 K)</td>
<td>2.90927</td>
<td>0.00281</td>
<td>0.93687</td>
<td>3.74395</td>
<td>0.00067397</td>
<td>0.98588</td>
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<tr>
<td>CO(_2) (298 K)</td>
<td>10.11099</td>
<td>0.00331</td>
<td>1.03233</td>
<td>7.37523</td>
<td>0.00627</td>
<td>1.32127</td>
</tr>
</tbody>
</table>

Table S2. Crystallographic Data Collection and Refinement Results for ZJU-72.

<table>
<thead>
<tr>
<th>ZJU-72</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
</tr>
<tr>
<td>Formula weight</td>
</tr>
<tr>
<td>Temperature(K)</td>
</tr>
<tr>
<td>Wavelength(Å)</td>
</tr>
<tr>
<td>Crystal system</td>
</tr>
<tr>
<td>Space group</td>
</tr>
<tr>
<td>a(Å)</td>
</tr>
<tr>
<td>b(Å)</td>
</tr>
<tr>
<td>c(Å)</td>
</tr>
<tr>
<td>V(Å(^3))</td>
</tr>
<tr>
<td>Z</td>
</tr>
<tr>
<td>Density(calculated g/cm(^3))</td>
</tr>
<tr>
<td>Absorbance coefficient(mm(^{-1}))</td>
</tr>
<tr>
<td>F(000)</td>
</tr>
<tr>
<td>Crystal size(mm(^3))</td>
</tr>
<tr>
<td>Goodness of fit on F(^2)</td>
</tr>
<tr>
<td>R(_1),wR(_2)[I&gt;2σ(I)]</td>
</tr>
<tr>
<td>R(_1),wR(_2)(all data)</td>
</tr>
<tr>
<td>Largest difference peak and hole(e/Å(^3))</td>
</tr>
</tbody>
</table>

Table S3. IAST selectivities of C\(_2\)H\(_2\)/CH\(_4\) (C\(_2\)H\(_2\)/CH\(_4\) = 50:50) and CO\(_2\)/CH\(_4\) (CO\(_2\)/CH\(_4\) = 50:50)

<table>
<thead>
<tr>
<th>mixture</th>
<th>Temperature (K)</th>
<th>component proportion</th>
<th>IAST selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_2)H(_2)/CH(_4)</td>
<td>273</td>
<td>50:50</td>
<td>36.3</td>
</tr>
<tr>
<td>CO(_2)/CH(_4)</td>
<td>273</td>
<td>50:50</td>
<td>8.2</td>
</tr>
<tr>
<td>C(_2)H(_2)/CH(_4)</td>
<td>298</td>
<td>50:50</td>
<td>39.7</td>
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<tr>
<td>CO(_2)/CH(_4)</td>
<td>298</td>
<td>50:50</td>
<td>6.8</td>
</tr>
</tbody>
</table>
Fig. S1. PXRD patterns of as-synthesized MOF ZJU-72 (red) and the simulated from single crystal structure (black).

Fig. S2. TGA curves of as-synthesized ZJU-72.
Fig. S3. Mixture adsorption isotherms predicted by IAST of ZJU-72a for C$_2$H$_2$/CH$_4$=50/50 and CO$_2$/CH$_4$=50/50 at 273 and 298 K, respectively.