Supporting Information

An Amino-Decorated NbO-Type Metal-Organic Framework for High
C$_2$H$_2$ Storage and Selective CO$_2$ Capture

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Materials and methods

All reagents were commercially available and used as received. Powder X-ray diffraction (PXRD) patterns were collected on an X’Pert PRO diffractometer with Cu Kα (λ = 1.542 Å) radiation with the 2θ in the range of 3-60° at room temperature. 1H NMR spectra were measured on a Bruker Advance DMX 500 spectrometer using tetramethylsilane (TMS) as an internal standard. Thermogravimetric analyses (TGA) were carried out on a Netzsch TG209F3 with a heating rate of 5 °C/min under N2 atmosphere. Infrared spectrum (IR) was recorded on Thermo Fisher Nicolet iS10 spectrometer with KBr pallets. Elemental analyses for C, H, and N were performed on an EA1112 microelemental analyzer.

Scheme S1. The synthetic route of the ligand H4L

Synthesis of tetramethyl 2'-amino-[1,1':4',1''-terphenyl]-3,3'',5,5''-tetracarboxylate (compound 1, Me4L): dimethyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)isophthalate (9.61 g, 30 mmol), 2,5-dibromoaniline (2.51 g, 10 mmol) and K2CO3 (13.9 g, 100 mmol) were mixed in dry 1,4-dioxane (100 mL), the mixture was purged with argon and stirred for an hour at room temperature. Then Pd(PPh3)2Cl2 (0.30 g, 0.4 mmol) was added and the mixture heated at 85 °C for 72 hours under argon atmosphere. After cooling, the resultant mixture was extracted with CHCl3 three times, the organic solvent was dried over anhydrous MgSO4 and removed under reduced pressure, and the crude product was purified with toluene recrystallization to obtain pure tetramethyl 2'-amino-[1,1':4',1''-terphenyl]-3,3'',5,5''-tetracarboxylate (compound 1, 3.10g). Yield: 65%. 1H NMR (500 MHz, CDCl3), δ = 8.68 (d, 2 H), 8.48 (s, 2H), 8.39 (s, 2H), 7.24 (s, 1H), 7.15 (d, 1H), 7.08 (s, 1H), 3.98 (d, 12H) ppm. Anal. Calcd for C26H23NO8: C, 65.40; H, 4.86; N, 2.93. Found: C, 65.35; H, 4.98; N, 2.90.

Synthesis of 2'-amino-[1,1':4',1''-terphenyl]-3,3'',5,5''-tetracarboxylic acid (compound 2,
\( \text{H}_4\text{L} \): \textbf{compound 1} (2.39 g, 5 mmol) was then suspended in a mixture of THF (20 mL) and \( \text{H}_2\text{O} \) (50 mL), to which 100 mL of 10 M NaOH aqueous solution was added. The mixture was stirred under reflux overnight and the THF was removed under a vacuum. Dilute HCl was added to the remaining aqueous solution until the solution was at pH = 3. The solid was collected by filtration, washed with water, and dried to give \( \text{H}_4\text{L} \) (2.00 g, 97.6% yield). \(^1\)H NMR (500 MHz, DMSO-\( \text{D}_6 \)): \( \delta = 8.48 \) (d, 2H), 8.43 (s, 1H), 8.19 (s, 2H), 7.84 (s, 1H), 7.75 (d, 1H), 7.59 (d, 1H), 3.08 (d, 2H). Anal. Calcd for \( \text{C}_{22}\text{H}_{15}\text{NO}_8 \): C, 62.71; H, 3.59; N, 3.32. Found: C, 62.33; H, 3.88; N, 3.11. Selected FTIR (neat, cm\(^{-1} \)): 1740, 1680, 1559, 1515, 1438, 1285, 1253, 1210, 1148, 1119, 1079, 993, 863, 760, 675, 629, 462.

\textbf{Single-Crystal X-ray Diffraction Collection and Structure Determination.}

Single-crystal X-ray diffraction data of \textbf{ZJU-8} was taken on an Bruker APEX-II diffractometer with an CCD detector using graphite-monochromatic Mo K\( \alpha \) radiation (\( \lambda = 0.71073 \) Å) at 293 K. The determination of the unit cell and data collection were performed with Bruker SAINT program. The structure of \textbf{ZJU-8} was determined by direct methods and refined by the full-matrix least-squares method with the SHELX-97 programpackage.\(^1\) All non-hydrogen atoms were located successfully from Fourier maps and were refined anisotropically. The disordered lattice DMF, and water molecules could not be located successfully from Fourier maps in the refinement cycles. The scattering from the highly disordered lattice guest molecules were removed using the SQUEEZE procedure implemented in the PLATON package.\(^2\) Crystallographic data are summarized in Table S1 (CCDC 1406816).
Table S1. Crystallographic data collection and refinement results for ZJU-8

<table>
<thead>
<tr>
<th></th>
<th>ZJU-8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Framework formula</td>
<td>C_{22}H_{15}NO_{10}Cu_{2}</td>
</tr>
<tr>
<td>Framework formula weight</td>
<td>580.43</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>293(2)</td>
</tr>
<tr>
<td>Wavelength (Å)</td>
<td>0.71073</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Trigonal</td>
</tr>
<tr>
<td>Space group</td>
<td>R-3m</td>
</tr>
<tr>
<td>a(Å)</td>
<td>18.639(4)</td>
</tr>
<tr>
<td>b(Å)</td>
<td>18.639(4)</td>
</tr>
<tr>
<td>c(Å)</td>
<td>38.614(6)</td>
</tr>
<tr>
<td>α</td>
<td>90 °</td>
</tr>
<tr>
<td>β</td>
<td>90 °</td>
</tr>
<tr>
<td>γ</td>
<td>120 °</td>
</tr>
<tr>
<td>V(Å³)</td>
<td>11618(5)</td>
</tr>
<tr>
<td>Z</td>
<td>9</td>
</tr>
<tr>
<td>Density (calculated g/cm³)</td>
<td>0.738</td>
</tr>
<tr>
<td>Absorbance coefficient (mm⁻¹)</td>
<td>0.849</td>
</tr>
<tr>
<td>F(000)</td>
<td>2565</td>
</tr>
<tr>
<td>Crystal size (mm³)</td>
<td>0.19×0.13×0.12</td>
</tr>
<tr>
<td>R(int)</td>
<td>0.1285</td>
</tr>
<tr>
<td>Goodness of fit on $F_2$</td>
<td>1.025</td>
</tr>
<tr>
<td>$R_1, wR_2[I&gt;2\sigma(I)]$</td>
<td>0.0451, 0.1222</td>
</tr>
<tr>
<td>$R_1, wR_2$ (all data)</td>
<td>0.0760, 0.1374</td>
</tr>
<tr>
<td>Largest difference peak and hole (e/Å³)</td>
<td>0.897, -0.381</td>
</tr>
</tbody>
</table>

$$R_1 = \frac{\sum(|F_o| - |F_c|)}{\sum|F_o|}; wR_2 = \left[\frac{\sum w(|F_o| - |F_c|)^2)}{\sum wF_o^2}\right]^{1/2}$$
Table S2. The Selected bond lengths (Å) and angles (°) of ZJU-8

<table>
<thead>
<tr>
<th>Bond Lengths and Angles</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)-O(2B)#1</td>
<td>1.959(2)</td>
</tr>
<tr>
<td>Cu(1)-O(1)#3</td>
<td>1.960(2)</td>
</tr>
<tr>
<td>Cu(1)-O(1C)</td>
<td>2.169(4)</td>
</tr>
<tr>
<td>Cu(1)-O(2B)#2</td>
<td>1.959(2)</td>
</tr>
<tr>
<td>Cu(1)-O(1)</td>
<td>1.960(2)</td>
</tr>
<tr>
<td>Cu(1)-Cu(1)#2</td>
<td>2.650(10)</td>
</tr>
<tr>
<td>O(2B)#1-Cu(1)-O(2B)#2</td>
<td>89.17(16)</td>
</tr>
<tr>
<td>O(2B)#1-Cu(1)-O(1)#3</td>
<td>167.76(9)</td>
</tr>
<tr>
<td>O(2B)#2-Cu(1)-O(1)#3</td>
<td>89.67(11)</td>
</tr>
<tr>
<td>O(2B)#1-Cu(1)-O(1)</td>
<td>89.67(11)</td>
</tr>
<tr>
<td>O(2B)#2-Cu(1)-O(1)</td>
<td>167.76(9)</td>
</tr>
<tr>
<td>O(1)#3-Cu(1)-O(1)</td>
<td>88.89(15)</td>
</tr>
<tr>
<td>O(2B)#1-Cu(1)-O(1C)</td>
<td>94.82(12)</td>
</tr>
<tr>
<td>O(2B)#2-Cu(1)-O(1C)</td>
<td>94.82(12)</td>
</tr>
<tr>
<td>O(1)#3-Cu(1)-O(1C)</td>
<td>97.42(12)</td>
</tr>
<tr>
<td>O(1)-Cu(1)-O(1C)</td>
<td>97.42(12)</td>
</tr>
<tr>
<td>O(2B)#1-Cu(1)-Cu(1)#2</td>
<td>83.69(7)</td>
</tr>
<tr>
<td>O(2B)#2-Cu(1)-Cu(1)#2</td>
<td>83.69(7)</td>
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<tr>
<td>O(1)#3-Cu(1)-Cu(1)#2</td>
<td>84.08(7)</td>
</tr>
<tr>
<td>O(1)-Cu(1)-Cu(1)#2</td>
<td>84.08(7)</td>
</tr>
<tr>
<td>O(1C)-Cu(1)-Cu(1)#2</td>
<td>177.89(15)</td>
</tr>
<tr>
<td>C(4)-O(1)-Cu(1)</td>
<td>122.9(2)</td>
</tr>
<tr>
<td>C(4)-O(2B)-Cu(1)#2</td>
<td>123.7(2)</td>
</tr>
</tbody>
</table>

#1 y,x,-z; #2 -x+1,-y+1,-z; #3 -y+1,-x+1,z; #4 -x+2/3,-y+1/3,-z+1/3; #5 x,x,y,z; #6 -x+2/3,-x+y+1/3,-z+1/3
Figure S1. TGA curves of fresh ZJU-8 under a N$_2$ atmosphere at a heating rate of 5 K/min.

Figure S2 PXRD patterns of fresh sample of ZJU-8 (red) and evacuated sample of ZJU-8a (blue) along with the simulated pattern from single X-ray structure (black).
Figure S3 IR spectrum of ligand H₄L (black) and ZJU-8 fresh sample (red)

\[ Y = 0.00174X + 2.55813 \times 10^{-7} \]

\[ R^2 = 1 \]

\[ S_{BET} = \frac{1}{\text{Slope} + \text{Intercept}} \times \frac{1}{22414 \times 6.023 \times 10^{23} \times 0.162 \times 10^{-18}} = 2501 \text{ m}^2/\text{g} \]

Figure S4. The BET surface area of ZJU-8a obtained from N₂ adsorption isotherm at 77 K

Table S3. Equation parameters for the DSLF isotherm model.

<table>
<thead>
<tr>
<th>Adsorbates</th>
<th>N₁ max (mmol/g)</th>
<th>b₁ (kPa⁻¹)</th>
<th>n₁</th>
<th>N₂ max (mmol/g)</th>
<th>b₂ (kPa⁻¹)</th>
<th>n₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ (273 K)</td>
<td>18.86038</td>
<td>0.00517</td>
<td>1.099674</td>
<td>17.21748</td>
<td>0.00217</td>
<td>1.051138</td>
</tr>
<tr>
<td>CH₄ (273 K)</td>
<td>2.99252</td>
<td>0.00559</td>
<td>1.21122</td>
<td>2.86788</td>
<td>0.000896765</td>
<td>0.748027</td>
</tr>
<tr>
<td>N₂ (273 K)</td>
<td>2.3</td>
<td>0.00116</td>
<td>1.01742</td>
<td>3.14433</td>
<td>0.000401747</td>
<td>1.00162</td>
</tr>
<tr>
<td>CO₂ (298 K)</td>
<td>7.19116</td>
<td>0.00752</td>
<td>1.118568</td>
<td>7.60212</td>
<td>0.000560593</td>
<td>0.720466</td>
</tr>
<tr>
<td>CH₄ (298 K)</td>
<td>3.09099</td>
<td>0.00248</td>
<td>0.99956</td>
<td>1.59676</td>
<td>0.000731969</td>
<td>0.7638369</td>
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<tr>
<td>N₂ (298 K)</td>
<td>2.5746</td>
<td>0.0016</td>
<td>1.04421</td>
<td>4.42351</td>
<td>0.000409024</td>
<td>1.01473</td>
</tr>
</tbody>
</table>
Table S4. \( \text{C}_2\text{H}_2 \) adsorption on various porous MOFs at RT and atmospheric pressure.

<table>
<thead>
<tr>
<th>Material</th>
<th>( S_{\text{BET}} ) ([\text{m}^2\text{g}^{-1}])</th>
<th>( V_p ) ([\text{cm}^3\text{g}^{-1}])</th>
<th>( D_c ) ([\text{g} \text{cm}^{-3}])</th>
<th>( \text{C}_2\text{H}_2 ) uptaked ([\text{cm}^3\text{g}^{-1}]) ([\text{cm}^3\text{cm}^{-1}])</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZJU-8a</td>
<td>2501</td>
<td>1.0224</td>
<td>0.690</td>
<td>195 (134)</td>
<td>This work</td>
</tr>
<tr>
<td>ZJU-5a</td>
<td>2823</td>
<td>1.074</td>
<td>0.679</td>
<td>193 (131)</td>
<td>S3</td>
</tr>
<tr>
<td>ZJU-7a</td>
<td>2198</td>
<td>0.8945</td>
<td>0.750</td>
<td>180 (135)</td>
<td>S4</td>
</tr>
<tr>
<td>ZJU-26a</td>
<td>989</td>
<td>0.572</td>
<td>0.615</td>
<td>84 (52)</td>
<td>S5</td>
</tr>
<tr>
<td>MOF-505</td>
<td>1139</td>
<td>0.67</td>
<td>0.767</td>
<td>148 (137)</td>
<td>S6</td>
</tr>
<tr>
<td>PCN-16</td>
<td>2273</td>
<td>1.06</td>
<td>0.724</td>
<td>176 (126)</td>
<td>S7</td>
</tr>
<tr>
<td>NOTT-101</td>
<td>2805</td>
<td>1.080</td>
<td>0.6838</td>
<td>184 (126)</td>
<td>S8</td>
</tr>
<tr>
<td>NOTT-102</td>
<td>3342</td>
<td>1.280</td>
<td>0.587</td>
<td>146 (86)</td>
<td>S8</td>
</tr>
</tbody>
</table>

\( ^a \) Pore volume. \( ^b \) Crystal density calculated from the single-crystal structure without guest molecules and coordinated water.

**Figure S5.** (a) Details of virial equation fitting to the experimental \( \text{C}_2\text{H}_2 \) adsorption data for ZJU-8a collected at 273 K (black) and 298 K (red); (b) Isosteric heats of \( \text{C}_2\text{H}_2 \) for ZJU-8a

**Figure. S6.** Calculations using Ideal Adsorbed Solution Theory (IAST) for uptake of \( \text{CO}_2 \) and \( \text{N}_2 \) from 15/85 \( \text{CO}_2/\text{N}_2 \) gas mixtures at 273 K (a) and 298 K (b) in ZJU-8a
**Figure S7.** Calculations using Ideal Adsorbed Solution Theory (IAST) for uptake of CO\(_2\) and CH\(_4\) from 50/50 CO\(_2\)/CH\(_4\) gas mixtures at 273 K (a) and 298 K (b) in ZJU-8a.

**Figure S8.** (a) Details of virial equation fitting to the experimental CO\(_2\) adsorption data for ZJU-8a collected at 273 K (black) and 298 K (red); (b) Isosteric heats of CO\(_2\) for ZJU-8a.

**Figure S9.** (a) Details of virial equation fitting to the experimental CH\(_4\) adsorption data for ZJU-8a collected at 273 K (black) and 298 K (red); (b) Isosteric heats of CH\(_4\) for ZJU-8a.
Figure S10. (a) Details of virial equation fitting to the experimental N\textsubscript{2} adsorption data for ZJU-8a collected at 273 K (black) and 298 K (red); (b) Isosteric heats of N\textsubscript{2} for ZJU-8a.
References


