Electronic Supplementary Information for

An rht-type metal-organic framework constructed from an unsymmetrical ligand exhibiting high hydrogen uptake capability

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Scheme S1. Synthetic route for ligand H6-1. EDC = 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide; THF = tetrahydrofuran; TMSA = trimethylsilylacetylene; TEA = triethylamine; TFA = trifluoracetic acid.

Fig. S1 The photograph of crystals of as-synthesized Cu-ABTA, showing they have good and regular morphologies and shapes.
Fig. S2 The zoomed-in comparison of PXRD patterns (2Theta = 2-21°) of as-synthesized MOF Cu-ABAT (upper) and simulation from MOF NTU-105 (bottom) single crystal data. Although some of peaks in NTU-105 (3’ and 3”; 4’ and 4”; 12’ and 12”; 13’ and 13”; 21’ and 21”) are merged into corresponding one peak in Cu-ABTA, mainly due to the different organic ligand in the two MOFs. However, most of the position of main peaks matches very well. This indicates that the overall framework structure of Cu-ABTA is the same as that of MOF NTU-105.

Fig. S3 Experimental (black), calculated (red), and difference (green below observed and calculated patterns) X-ray powder diffraction profiles for Cu-ABTA. All diffraction patterns were indexed using DICVOL9113 to obtain lattice parameters that were subsequently refined in a Pawley fit. A modified Thompson-Cox-Hastings pseudo-Voigt profile function with a simple axial correction was used in TOPAS (Topas V3.0: General Profile and Structure Analysis Software for Powder Diffraction Data Bruker AXS Ltd, 2004). The cell parameters are $a = 30.03$ Å, $b = 30.03$ Å, $c = 43.11$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$ with a tetragonal space group I4/m, which are close to these of NTU-105. The results of PXRD measurements and simulation indicate that Cu-ABTA still possesses the same (3,24)-connected rht-framework as our reported MOF NTU-105.
**Fig. S4** TGA plot of as-synthesized (upper) and desolvated (bottom) MOF Cu-ABTA. The initial weight loss (red line) of activated sample can be attributed to the reabsorbed water during sample weighing. This suggests the framework was stable up to ~250 °C, which is similar to NTU-105.

**Fig. S5** XRD pattern of desolvated Cu-ABTA (indicating the framework was retained well after activation).
Fig. S6 Pore-size distribution plot for Cu-ABTA as calculated from experimental N\textsubscript{2} adsorption isotherm using the nonlocal density functional theory (NLDFT).

Fig. S7 N\textsubscript{2} sorption isotherm (left) at 77 K and pore-size distribution plot (right) for NTU-105 as calculated from experimental N\textsubscript{2} adsorption isotherm using the NLDFT.

Fig. S8 H\textsubscript{2} adsorption isotherms (left) and isosteric heat of H\textsubscript{2} adsorption (right) for NTU-105 calculated from the adsorption isotherms at 77 K and 78 K.
Fig. S9 Another three hydrogen sorption measurements for MOF Cu-ABTA (and corresponding $Q_{st}$ calculated from the adsorption isotherms at 77 K and 78 K) by using different samples every time to avoid the accidental error. These indicated the good reproducibility.

Fig. S10 Another three hydrogen sorption measurements for MOF NTU-105 (and corresponding $Q_{st}$ calculated from the adsorption isotherms at 77 K and 78 K) by using different samples every time to avoid the accidental error. These indicated the good reproducibility.
Fig. S11 Two hydrogen sorption measurements for MOF Cu-TPBTM (the ligand is connected by three amide groups, *J. Am. Chem. Soc.*, 2011, **133**, 748.) (and corresponding $Q_{st}$ calculated from the adsorption isotherms at 77 K and 78 K) by using two different samples.

![Graph 1](image1)

![Graph 2](image2)

Fig. S12 The comparison of $Q_{st}$ for hydrogen adsorption of MOFs Cu-ABTA, NTU-105 and Cu-TPBTM. As shown in Fig. S9-12, although there are no huge differences in the amount of hydrogen gas uptake among these three MOFs, however, some differences of the isosteric heat of adsorption ($Q_{st}$) are presented. The results show that the $Q_{st}$ of our reported MOF Cu-ABTA is higher than both of NTU-105 and Cu-TPBTM instead of in between of them (Cu-ABTA > NTU-105 > Cu-TPBTM).
Fig. S13 CO₂ adsorption isotherms (left) and isosteric heat of CO₂ absorption (right) for NTU-105 calculated from the adsorption isotherms at 273 K and 298 K.

Fig. S14 Comparison of isosteric heat for CO₂ adsorption of MOF Cu-ABTA and NTU-105 under the same uptake amount.
Scheme S2. The chemical structure of reported $C_3$-symmetric ligands used in constructing $rht$-type MOFs.
### Table S1. Summary of the porosities, and gas uptake capacities of various rth-type MOFs.

<table>
<thead>
<tr>
<th>MOF [ligand]</th>
<th>( S_{\text{BET}} ) [m² g⁻¹]</th>
<th>( V_{\text{pore}} ) [cm³ g⁻¹]</th>
<th>( \text{H}_2 ) uptake [wt%]</th>
<th>( \text{CO}_2 ) uptake [wt%]</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-ABTA [H6-1]</td>
<td>2840</td>
<td>1.19</td>
<td>2.75</td>
<td>30.1</td>
<td>This work</td>
</tr>
<tr>
<td>NTU-105[^c] [L1]</td>
<td>3543</td>
<td>1.33</td>
<td>2.75</td>
<td>36.7</td>
<td>S1</td>
</tr>
<tr>
<td>Cu-TDPAT[^e] [L2]</td>
<td>1938</td>
<td>0.93</td>
<td>2.65</td>
<td>44.5</td>
<td>S2</td>
</tr>
<tr>
<td>Cu-TPBTM [L3]</td>
<td>3160</td>
<td>1.27</td>
<td>—</td>
<td>42.6</td>
<td>S3</td>
</tr>
<tr>
<td>NU-100[^i] [L4]</td>
<td>6143</td>
<td>2.82</td>
<td>1.82</td>
<td>12.3[^g]</td>
<td>S4</td>
</tr>
<tr>
<td>NOTT-112 [L5]</td>
<td>3800</td>
<td>1.62</td>
<td>2.3</td>
<td>—</td>
<td>S5</td>
</tr>
<tr>
<td>PCN-68[^j] [L6]</td>
<td>5109</td>
<td>2.13</td>
<td>1.87</td>
<td>—</td>
<td>S6</td>
</tr>
<tr>
<td>PCN-66 [L7]</td>
<td>4000</td>
<td>1.63</td>
<td>1.79</td>
<td>—</td>
<td>S6, S7</td>
</tr>
<tr>
<td>PCN-61 [L8]</td>
<td>3000</td>
<td>1.36</td>
<td>2.25</td>
<td>—</td>
<td>S6, S7</td>
</tr>
<tr>
<td>PCN-69[^j] [L9]</td>
<td>3989</td>
<td>2.17</td>
<td>1.72</td>
<td>—</td>
<td>S8</td>
</tr>
<tr>
<td>Cu-TATB [L10]</td>
<td>3360</td>
<td>1.91</td>
<td>—</td>
<td>17.3</td>
<td>S9</td>
</tr>
<tr>
<td>Cu-BTB [L11]</td>
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<td>1.77</td>
<td>—</td>
<td>17.2</td>
<td>S9</td>
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<tr>
<td>NU-111 [L12]</td>
<td>5000</td>
<td>2.38</td>
<td>2.1</td>
<td>—</td>
<td>S10</td>
</tr>
<tr>
<td>rht-MOF-9 [L13]</td>
<td>2420[^j]</td>
<td>1.01[^i]</td>
<td>2.72</td>
<td>25.3</td>
<td>S11</td>
</tr>
</tbody>
</table>

[^a]: calculated from N₂ isotherms at 77 K;[^b]: at 77 K, 1 atm;[^c]: also known as NOTT-122[^s12] or NU-125[^s13];[^d]: also known as rht-MOF-7[^s14];[^e]: also known as PCN-610[^s6];[^f]: data at 298 K, 1 atm, due to the absence of the data at 273 K, 1 atm;[^g]: also known as NOTT-116[^s15];[^h]: also known as NOTT-119[^s16];[^i]: calculated from Ar isotherms at 87 K

References:


