Electronic Supplementary Information (ESI) for

Ba-MOFs with tetrazole-based acetic acids: unusual configuration, novel topology and high proton conductivity

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Experimental Section

1. General Remarks

The reagents were obtained from commercial sources and used without further purification. The new ligand H 3 L 3 was prepared according to our designed method as shown in Scheme S1. Melting points were determined with an X-4 digital microscope melting-point apparatus (Beijing) and are uncorrected. Elemental analyses (C, H, N) were carried out with a PerkinElmer 240 microanalyzer. 1 H NMR spectra in solution
were recorded on a Bruker AM 500 Hz spectrometer. Chemical shifts are given in ppm. IR spectra were recorded in the range 4000-400 cm\(^{-1}\) using KBr pellets on a Nicolet 380 FT-IR spectrometer. Powder X-ray diffraction patterns (PXRD) were measured using a Bruker D8 Advance diffractometer. The photoluminescence spectra were recorded on a Hitachi F4600 spectrophotometer. Thermogravimetric analyses (TGA) were performed on a NETZSCH STA 449C thermal analyzer under a N\(_2\) atmosphere at a heating rate of 10°C min\(^{-1}\).

2. Synthesis of H\(_3\)L\(_3\) Ligand

\[
\begin{align*}
\text{HN} & \quad \text{CN} \\
\text{HN} & \quad \text{CN} \\
\text{DMF, NH}_4\text{Cl, 120°C} & \quad \overset{\text{NaNO}_3}{\longrightarrow} \quad \text{HN} \quad \text{N} \quad \text{N} \\
\text{HN} & \quad \text{N} \quad \text{NH} \\
\text{1) NaOH, CICH}_2\text{COONa} & \quad \overset{\text{2) HCl}}{\longrightarrow} \quad \text{HN} \quad \text{N} \quad \text{N} \quad \text{NH} \\
\text{HOOCH}_2 & 
\end{align*}
\]

Scheme S1 The synthetic route of 4,5-di(tetrazol-5-yl)imidazolylacetic acid (H\(_3\)L\(_3\))

4,5-dicyanoimidazole (11.8096 g, 0.1 mol) and ammonium chloride (16.0474 g, 0.3 mol) were dissolved in 150 mL DMF. Then, sodium azide (19.5030 g, 0.3 mol) was added. The mixture was refluxed at 120°C with stirring for 24 h. After cooled to room temperature, DMF solvent was removed by rotary evaporation, and the reaction solution was adjusted to pH = 10-11 with NaOH and then filtered. The filtrate was adjusted to pH = 2 with HCl, and the 4,5-di(tetrazol-5-yl)imidazole was obtained as a white solid of 14.9651 g, yield 73.3%. FT-IR (KBr, cm\(^{-1}\)): 3156, 3014, 2765, 2373, 1633, 1568, 1506, 1403, 1160, 1068, 1007, 885.

After 4,5-di(tetrazol-5-yl)imidazole (4.0831 g, 0.02 mol) was dissolved in 30 mL methanol, CICH\(_2\)COONa (11.6479 g, 0.1 mol) was added, and pH of the solution was adjusted with 1 M NaOH solution to 11, the mixture was refluxed at 100°C under stirring for 48 hours. After cooled to room temperature, methanol solvent was removed by rotary evaporation, the residue was acidified with HCl, and the precipitate was separated by filtration, and washed with water, then dried under vacuum to give the target ligand H\(_3\)L\(_3\) in a yield of 84.6%. m.p. 121-123°C. Anal. calcd. for C\(_7\)H\(_6\)N\(_{10}\)O\(_2\) (%): C, 32.07; H, 2.31; N, 53.42. Found (%): C, 32.19; H, 2.13; N, 53.24.
FT-IR (KBr, cm⁻¹): 3500, 3002, 1737, 1631, 1579, 1437, 1401, 1343, 1310, 1207, 1062, 1004, 954, 885, 808. ¹H NMR (500 MHz, DMSO), 13.38 (1H, s, tetrazolyl-H), 12.99 (1H, s, tetrazolyl-H), 10.28 (1H, s, COOH), 8.00 (1H, s, imidazolyl-H), 5.11 (2H, s, CH₂).

3. Molecular Structures of MOFs 1-3

![Molecular Structure Diagram](image)

**Fig. S1** The asymmetric units of 1, hydrogen atoms are omitted for clarity.
Fig. S2 The asymmetric units of 2, hydrogen atoms are omitted for clarity.

Fig. S3 The asymmetric units of 3, hydrogen atoms are omitted for clarity.
Fig. S4 The hydrogen bond interactions in 1

Fig. S5 The hydrogen bonds interactions in 2

Fig. S6 The hydrogen bond interactions in 3
4. Tables of Selected Bond Distance and Angles and Weak Interactions for 1-3

Table S1 Selected bond distance (Å) for MOFs 1-3

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</table>

Symmetry codes: 1: i) 1-x, 1-y, 1-z; ii) 1-x, 1-y, 2-z; iii) 1+x, y, z; 2: (i) 0.5-x, y-0.5, 1.5-z; (ii) 1-x, -y, 2-z; (iii) x-0.5, 0.5-y, z-0.5; (iv) 1-x, y, 1.5-z; (v) x-0.5, y-0.5, z; (vi) 0.5-x, 0.5+y, 1.5-z. 3: i) 1-x, 1-y, 1-z; ii) x, y-1, z; iii) 2-x, 2-y, 1-z; iv) 1+x, y, z; v) 1-x, 2-y, 1-z; vi) 1-x, 1-y, -z; vii) 2-x, 1-y, -z; viii) x, y-1, z-1; ix) 1-x, 1-y, 1-z.

Table S2 Selected bond angles (°) for MOFs 1-3

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**Table 3**

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Table S3 Hydrogen-bond geometry (Å, °) in 1-3

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<td>O6W–H6WA···N8ii</td>
<td>0.85</td>
<td>2.39</td>
<td>3.197(4)</td>
<td>158</td>
</tr>
<tr>
<td>O6W–H6WB···O7WA</td>
<td>0.85</td>
<td>2.21</td>
<td>3.000(4)</td>
<td>155</td>
</tr>
<tr>
<td>O7WA–H7WC···O7WA vii</td>
<td>0.85</td>
<td>1.74</td>
<td>2.340(4)</td>
<td>126</td>
</tr>
<tr>
<td>O7WA–H7WD···N3viii</td>
<td>0.85</td>
<td>2.48</td>
<td>3.137(4)</td>
<td>134</td>
</tr>
<tr>
<td>O7WB–H7WE···O7WA</td>
<td>0.85</td>
<td>1.94</td>
<td>2.558(3)</td>
<td>129</td>
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</tbody>
</table>

Symmetry codes: 1: (i) 1-x, 1-y, 1-z; (ii) 1-x, 1-y, 2-z; (iii) 1+x, y, z; 2: (i) 0.5-x, -0.5-y, 1.5-z; (ii) 1-x, -y, 2-z; (iii) x-0.5, 0.5-y, z-0.5; (iv) 1-x, y, 1.5-z; (v) x-0.5, y-0.5, z; 3: (i) 1-x, -y, 1-z; (ii) x, y-1, z; (iii) 2-x, 2-y, 1-z; (iv) 1+x, y, z; (v) 1-x, 2-y, 1-z; vi) 1-x, 1-y, -z; vii) 2-x, 1-y, -z; viii) x, y-1, z-1.

Table S3 Hydrogen-bond geometry (Å, °) in 1-3
<table>
<thead>
<tr>
<th>Symmetry codes:</th>
<th>Distances</th>
<th>Angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>O7WB–H7WF…N4&lt;sup&gt;iii&lt;/sup&gt;</td>
<td>0.85</td>
<td>2.55</td>
</tr>
<tr>
<td>O7W–H7WA…O6W&lt;sup&gt;i&lt;/sup&gt;</td>
<td>0.85</td>
<td>1.74</td>
</tr>
<tr>
<td>O7W–H7WB…O4WB</td>
<td>0.85</td>
<td>2.44</td>
</tr>
<tr>
<td>N14–H14…N9&lt;sup&gt;iv&lt;/sup&gt;</td>
<td>0.86</td>
<td>2.02</td>
</tr>
<tr>
<td><strong>2</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O1W–H1WA…O2W</td>
<td>0.85</td>
<td>2.04</td>
</tr>
<tr>
<td>O1W–H1WB…O5W&lt;sup&gt;i&lt;/sup&gt;</td>
<td>0.85</td>
<td>2.31</td>
</tr>
<tr>
<td>O2W–H2WA…N5&lt;sup&gt;ii&lt;/sup&gt;</td>
<td>0.85</td>
<td>2.01</td>
</tr>
<tr>
<td>O2W–H2WB…N9&lt;sup&gt;iii&lt;/sup&gt;</td>
<td>0.85</td>
<td>2.21</td>
</tr>
<tr>
<td>O3W–H3WA…O4W&lt;sup&gt;iv&lt;/sup&gt;</td>
<td>0.85</td>
<td>2.05</td>
</tr>
<tr>
<td>O3W–H3WB…O4W</td>
<td>0.85</td>
<td>2.05</td>
</tr>
<tr>
<td>O4W–H4WA…O5V</td>
<td>0.85</td>
<td>2.07</td>
</tr>
<tr>
<td>O4W–H4WB…O4&lt;sup&gt;vi&lt;/sup&gt;</td>
<td>0.85</td>
<td>2.12</td>
</tr>
<tr>
<td>O5W–H5WA…N6&lt;sup&gt;vii&lt;/sup&gt;</td>
<td>0.85</td>
<td>2.31</td>
</tr>
<tr>
<td>O5W–H5WB…O3W</td>
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<td>2.08</td>
</tr>
<tr>
<td>N13–H13A…O2W&lt;sup&gt;viii&lt;/sup&gt;</td>
<td>0.90</td>
<td>2.34</td>
</tr>
<tr>
<td>N13–H13B…O2&lt;sup&gt;viii&lt;/sup&gt;</td>
<td>0.90</td>
<td>1.97</td>
</tr>
<tr>
<td>C16–H16A…N12&lt;sup&gt;ix&lt;/sup&gt;</td>
<td>0.96</td>
<td>2.72</td>
</tr>
<tr>
<td>C16–H16C…N4&lt;sup&gt;x&lt;/sup&gt;</td>
<td>0.96</td>
<td>2.55</td>
</tr>
<tr>
<td>C2–H2A…O4&lt;sup&gt;ii&lt;/sup&gt;</td>
<td>0.97</td>
<td>2.34</td>
</tr>
<tr>
<td>C2–H2B…N11&lt;sup&gt;xii&lt;/sup&gt;</td>
<td>0.97</td>
<td>2.47</td>
</tr>
<tr>
<td>C11–H11A…O2&lt;sup&gt;xiii&lt;/sup&gt;</td>
<td>0.97</td>
<td>2.46</td>
</tr>
<tr>
<td>C11–H11B…O4W&lt;sup&gt;xiv&lt;/sup&gt;</td>
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<td>2.54</td>
</tr>
<tr>
<td>C14–H14B…O1&lt;sup&gt;xv&lt;/sup&gt;</td>
<td>0.97</td>
<td>2.66</td>
</tr>
<tr>
<td><strong>3</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O1W–H1WA…O5W&lt;sup&gt;i&lt;/sup&gt;</td>
<td>0.85</td>
<td>2.03</td>
</tr>
<tr>
<td>O1W–H1WB…N15&lt;sup&gt;ii&lt;/sup&gt;</td>
<td>0.85</td>
<td>2.49</td>
</tr>
<tr>
<td>O2W–H2WA…O6W&lt;sup&gt;ii&lt;/sup&gt;</td>
<td>0.85</td>
<td>1.90</td>
</tr>
<tr>
<td>O2W–H2WB…N18&lt;sup&gt;ii&lt;/sup&gt;</td>
<td>0.85</td>
<td>2.07</td>
</tr>
<tr>
<td>O3W–H3WA…O4W</td>
<td>0.85</td>
<td>2.20</td>
</tr>
<tr>
<td>O3W–H3WB…N15&lt;sup&gt;iii&lt;/sup&gt;</td>
<td>0.85</td>
<td>2.66</td>
</tr>
<tr>
<td>O4W–H4WA…O5W&lt;sup&gt;iv&lt;/sup&gt;</td>
<td>0.85</td>
<td>2.00</td>
</tr>
<tr>
<td>O4W–H4WB…O2W&lt;sup&gt;v&lt;/sup&gt;</td>
<td>0.85</td>
<td>2.20</td>
</tr>
<tr>
<td>O5W–H5WA…N17</td>
<td>0.85</td>
<td>1.93</td>
</tr>
<tr>
<td>O5W–H5WB…N8&lt;sup&gt;ii&lt;/sup&gt;</td>
<td>0.85</td>
<td>2.26</td>
</tr>
<tr>
<td>O6W–H6WA…N10&lt;sup&gt;vi&lt;/sup&gt;</td>
<td>0.85</td>
<td>2.17</td>
</tr>
<tr>
<td>O6W–H6WB…O3&lt;sup&gt;iii&lt;/sup&gt;</td>
<td>0.85</td>
<td>2.28</td>
</tr>
<tr>
<td>C2–H2A…N3</td>
<td>0.97</td>
<td>2.90</td>
</tr>
<tr>
<td>C9–H9A…O2&lt;sup&gt;iii&lt;/sup&gt;</td>
<td>0.97</td>
<td>2.28</td>
</tr>
<tr>
<td>C9–H9B…O6W&lt;sup&gt;iii&lt;/sup&gt;</td>
<td>0.97</td>
<td>2.60</td>
</tr>
</tbody>
</table>

Symmetry codes: 1: i) 1+x, y, z; ii) 1–x, 1–y, 1–z; iii) –x, 1–y, 2–z; iv) 1–x, –y, 2–z; v) –x, 1–y, 1–z; vi) 1–x, 1–y, 1–z; vii) 1–x, 2–y, 1–z; viii) x, 1+y, z; 2: i) 0.5–x, 1.5–y, 1–z; ii) 0.5–x, 0.5–y, 2–z; iii) x–0.5, y–0.5, z; iv) 1–x, y, 0.5–z; v) 1–x, 1–y, 1–z; vi) 1–x, y, 1–z; vii) 1–x, 1.5–y, 1.5–z; viii) 1–x, 1.5–y, 1.5–z; ix) 1–x, 1–y, 1–z; x) x, y, z; xi) 1–x, 1–y, 2–z; xii) x–0.5, 0.5+y, z; xiii) 1–x, –y, 2–z; xiv) 1–x, y–1, 1.5–z; xv) 0.5+x, y–0.5, z; 3: i) x, y–1, z–1; ii) 1–x, 1–y, 1–z; iii) 1–x, 2–y, 1–z; iv) 2–x, 2–y, 1–z; v) x, 1+y, z; vi) –x, 1–y, 1–z.
Table S4 π···π interactions (Å, °) for the MOFs 2 and 3

<table>
<thead>
<tr>
<th>MOFs</th>
<th>π···π interaction</th>
<th>cent···cent (Å)</th>
<th>dihedral angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>π(tez)···π(Ph)\textsuperscript{ix}</td>
<td>3.951</td>
<td>4.7(2)</td>
</tr>
<tr>
<td></td>
<td>π(Ph)···π(tez)\textsuperscript{ix}</td>
<td>3.951</td>
<td>4.7(4)</td>
</tr>
<tr>
<td>3</td>
<td>π(im)···π(tez)\textsuperscript{vii}</td>
<td>3.852</td>
<td>7.2(2)</td>
</tr>
<tr>
<td></td>
<td>π(tez)···π(im)\textsuperscript{vii}</td>
<td>3.852</td>
<td>7.2(3)</td>
</tr>
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</table>


Table S5 Dihedral angles (°) of the ligands in MOFs 1-3

<table>
<thead>
<tr>
<th>MOFs</th>
<th>Tez/Tez\textsuperscript{a}</th>
<th>Ph\textsuperscript{b}/Tez</th>
<th>Im\textsuperscript{c}/Tez</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\textsubscript{2}L\textsuperscript{1}</td>
<td>9.98(2) (C3/C4-Tez)</td>
<td>4.7(1) (C3-Tez)</td>
<td>71.8(6) (C13-Tez)</td>
</tr>
<tr>
<td></td>
<td>6.80(2) (C9/C10-Tez)</td>
<td>3.6(5) (C10-Tez)</td>
<td>18.7(9) (C14-Tez)</td>
</tr>
<tr>
<td>H\textsubscript{2}L\textsuperscript{2}</td>
<td>3.6(5) (C10-Tez)</td>
<td>7.7(4) (C13-Tez)</td>
<td></td>
</tr>
<tr>
<td>H\textsubscript{2}L\textsuperscript{3}</td>
<td></td>
<td>18.7(9) (C14-Tez)</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}Tez: Tetrazole ring; \textsuperscript{b}Ph: Phenyl ring; \textsuperscript{c}Im: Imidazole ring

5. The FT-IR Spectra of MOFs 1-3

![Fig. S7 The IR spectrum of 1.](image-url)
**Fig. S8** The IR spectrum of 2.

**Fig. S9** The IR spectrum of 3.
6. The PXRD Patterns of MOFs 1-3

**Fig. S10** The PXRD patterns of 1.

**Fig. S11** The PXRD patterns of 2 in water (a) and different organic solvents (b) compared to the as-synthesized sample.
7. The Thermogravimetric Analyses of MOFs 1-3

Fig. S12 The PXRD patterns of 3.

Fig. S13 Thermogravimetric analysis curve of 1.
8. Luminescence Spectra
9. Proton Conductivity Measurement

The resistance value was determined from equivalent circuit fits of the first semi-circle using ZView Software.

Proton conductivity was calculated using the following equation:

$$\sigma = \frac{l}{SR} \quad (1)$$

where $l$ and $S$ are the length (cm) and cross-sectional area (cm$^2$) of the samples respectively, and $R$, which was extracted directly from the impedance plots, is the bulk resistance of the sample ($\Omega$). Activation energy ($E_a$) for the materials conductivity was estimated from the following equation:

$$\sigma T = \sigma_0 \exp \left( -\frac{E_a}{k_B T} \right) \quad (2)$$

where $\sigma$ is the proton conductivity, $\sigma_0$ is the preexponential factor, $k_B$ is the Boltzmann constant, and $T$ is the temperature.
Table S6 Proton conductivities at 25°C with different relative humidity and at 98% relative humidity with different temperature

<table>
<thead>
<tr>
<th>RH (%)</th>
<th>σ (S cm⁻¹)</th>
<th>T (°C)</th>
<th>σ (S cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>1.90 × 10⁻⁶</td>
<td>35</td>
<td>2.93 × 10⁻⁴</td>
</tr>
<tr>
<td>60</td>
<td>4.56 × 10⁻⁶</td>
<td>45</td>
<td>6.77 × 10⁻⁴</td>
</tr>
<tr>
<td>70</td>
<td>1.21 × 10⁻⁵</td>
<td>55</td>
<td>9.32 × 10⁻⁴</td>
</tr>
<tr>
<td>80</td>
<td>3.25 × 10⁻⁵</td>
<td>65</td>
<td>1.40 × 10⁻³</td>
</tr>
<tr>
<td>90</td>
<td>1.03 × 10⁻⁴</td>
<td>75</td>
<td>2.49 × 10⁻³</td>
</tr>
<tr>
<td>98</td>
<td>1.72 × 10⁻⁴</td>
<td>85</td>
<td>4.47 × 10⁻³</td>
</tr>
</tbody>
</table>

Table S7 Proton conductivities of representative MOFs materials above 90% RH

<table>
<thead>
<tr>
<th>MOFs</th>
<th>Conductivity (S cm⁻¹)</th>
<th>Condition</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂SO₄@MIL-101-SO₃H</td>
<td>1.82</td>
<td>70°C 90% RH</td>
<td>1</td>
</tr>
<tr>
<td>BUT-8(Cr)A</td>
<td>1.27 × 10⁻¹</td>
<td>80°C 100% RH</td>
<td>2</td>
</tr>
<tr>
<td>UiO-66(SO₃H)₂</td>
<td>8.4 × 10⁻²</td>
<td>80°C 90% RH</td>
<td>3</td>
</tr>
<tr>
<td>{H[(N(CH₃)₆)₂][Gd(NIPA)₆]}·3H₂O</td>
<td>7.17 × 10⁻²</td>
<td>75°C 98% RH</td>
<td>4</td>
</tr>
<tr>
<td>Im@MOF-808</td>
<td>3.45 × 10⁻²</td>
<td>65°C 99% RH</td>
<td>5</td>
</tr>
<tr>
<td>PCMOF-2₁/₂</td>
<td>2.1 × 10⁻²</td>
<td>85°C 90% RH</td>
<td>6</td>
</tr>
<tr>
<td>PCMOF20</td>
<td>1.3 × 10⁻³</td>
<td>85°C 95% RH</td>
<td>7</td>
</tr>
<tr>
<td>PCC-72</td>
<td>1.2 × 10⁻²</td>
<td>95°C 95% RH</td>
<td>8</td>
</tr>
<tr>
<td>MIP-202(Zr)</td>
<td>1.1 × 10⁻³</td>
<td>88°C 95% RH</td>
<td>9</td>
</tr>
<tr>
<td>JLU-Liu44</td>
<td>8.4 × 10⁻³</td>
<td>27°C 98% RH</td>
<td>10</td>
</tr>
<tr>
<td>[Zn(L)Cl]₉</td>
<td>4.73 × 10⁻⁵</td>
<td>100°C 98% RH</td>
<td>11</td>
</tr>
<tr>
<td>Co-MOF-74</td>
<td>4.5 × 10⁻³</td>
<td>90°C 95% RH</td>
<td>12</td>
</tr>
<tr>
<td>(Me₂NH₃)[Ba(L²)(H₂O)]·3H₂O</td>
<td>4.47 × 10⁻³</td>
<td>85°C 98% RH</td>
<td>This work</td>
</tr>
<tr>
<td>(Me₂NH₃)[In(EBTC)]·DMF·5H₂O</td>
<td>3.49 × 10⁻³</td>
<td>25°C 99% RH</td>
<td>13</td>
</tr>
<tr>
<td>(N₂H₃)[CeEu(C₂O₄)₄(N₂H₃)]·4H₂O</td>
<td>3.42 × 10⁻³</td>
<td>25°C 100% RH</td>
<td>14</td>
</tr>
<tr>
<td>MFM-512</td>
<td>2.9 × 10⁻³</td>
<td>25°C 99% RH</td>
<td>15</td>
</tr>
<tr>
<td>[Me₂NH₃][Eu(ox)₂(H₂O)]·3H₂O</td>
<td>2.73 × 10⁻³</td>
<td>55°C 95% RH</td>
<td>16</td>
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<tr>
<td>UiO-66(Zr)-(CO₂H)</td>
<td>2.3 × 10⁻³</td>
<td>90°C 95% RH</td>
<td>17</td>
</tr>
<tr>
<td>JUC-200</td>
<td>1.62 × 10⁻³</td>
<td>80°C 98% RH</td>
<td>18</td>
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</table>

References


