Electronic Supplementary Information for:

Study of a Hydrothermal Reaction System of Copper, Imidazole and Polyoxometalates: Selective assembly of a 3D Porous Metal-organic Pseudo-rotaxane Framework and Encapsulation of Polyoxometalate Clusters

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**Table S1** Summarization of known POM-based MOFs.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Types of the MOFs</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ag(btx)]₄[SiMo₁₂O₄₀]</td>
<td>I</td>
<td>19a</td>
</tr>
<tr>
<td>(bix)[Cu(bix)][Cu₂(bix)(P₂W₁₈O₆₂)]</td>
<td>II</td>
<td>19b</td>
</tr>
<tr>
<td>[Na₂(H₂O)₆Ag₂(HINA)₃(INA)][Na(H₂O)₂Ag₂(HINA)₂(H₂W₁₆O₄₀)]</td>
<td>III</td>
<td>19c</td>
</tr>
<tr>
<td>[Cd(BPE)(Mo₈O₅₀)][Cd(BPE)(DMF)₄]</td>
<td>III</td>
<td>19d</td>
</tr>
<tr>
<td>[Ag₃(3atrz)₃][Ag₃(3atrz)₃(Mo₅O₂₆)]</td>
<td>III</td>
<td>19e</td>
</tr>
<tr>
<td>[Cu(bbi)]₂[Mo₈O₅₀]₀.₅</td>
<td>III</td>
<td>19f</td>
</tr>
<tr>
<td>[Cu(bbi)]₂[Mo₈O₅₀]₀.₅</td>
<td>III</td>
<td>19f</td>
</tr>
<tr>
<td>[CuⅡ(L)₂(H₂O)₂][CuⅠ₂(L)₂]PMo₁₂O₄₀</td>
<td>IV</td>
<td>19g</td>
</tr>
</tbody>
</table>

![Chart S1](image1.png)  
**Chart S1** The “U”-type syn-conformation (a) and the “Z”-type trans-conformation (b) of bimb.

![Chart S2](image2.png)  
**Chart S2** The 26-membered Cu₅(bix)₂ macrocycles (a) and the 36-membered Cu₅(bimb)₂ macrocycles (b).
Fig. S1 The three crystallographically distinct motifs in 1: I, [Cu(bimb)]⁺ chain; II, [Cu₂(bimb)₂]²⁺ macrocycle; III, [PW₁₂O₄₀]³⁻ Keggin cluster.

Fig. S2 A space-filling model showing the arrangement of molecular “loops” intercalated by one molecular “string” (left), and the unusual intercalated fashion of two “strings” in one “loops” (right).

Fig. S3 A schematic presentation of the molecular “string” (a), molecular “string” (b), the arrangement of molecular “loops” intercalated by one molecular “string” (c), and the unusual intercalated fashion of two “strings” in one “loop” (d).
**Fig. S4** Illustration of the 3D pseudo-rotaxane structure formed from the 1D \([\text{Cu(bimb)}]_n^+\) chain and the 0D 34-membered \([\text{Cu}_2(\text{bimb})_2]^{2+}\) macrocycle.

**Fig. S5** A schematic illustration of detailed entangled fashion in the MORF.

*Fig. S5* A schematic illustration of detailed entangled fashion in the MORF.
Fig. S6 The space-filling models showing the unusual MORF with three-directional tunnels.

Fig. S7 The arrangement of POMs in the tunnels composed of B and C pores.

Table S2 The spherical diameter of three clusters: the distance 1-6 are obtained by the measurement of six pair opposite terminal oxygen atoms in the Keggin cluster.

<table>
<thead>
<tr>
<th>POMs</th>
<th>Distance 1</th>
<th>Distance 2</th>
<th>Distance 3</th>
<th>Distance 4</th>
<th>Distance 5</th>
<th>Distance 6</th>
<th>Average Distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoW$_{12}$</td>
<td>10.385 Å</td>
<td>10.352 Å</td>
<td>10.325 Å</td>
<td>10.358 Å</td>
<td>10.370 Å</td>
<td>10.320 Å</td>
<td>10.351 Å</td>
</tr>
</tbody>
</table>
Fig. S8 IR spectra of 1-3.

Fig. S9 TG curve of 1.

Fig. S10 TG curve of 2.
**Fig. S11** TG curve of 3.

**Fig. S12** The simulative (bottom) and experimental (top) powder X-ray diffraction patterns for 1 (left), 2 (middle) and 3 (right).

**Fig. S13** The UV-visible absorption spectra of 1-3.