

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 MORFs.

Compounds	Types of the MROFs	References
$[\text{Ag}(\text{btX})]_4[\text{SiMo}_{12}\text{O}_{40}]$	I	19a
$(\text{bix})[\text{Cu}(\text{bix})][\text{Cu}_2(\text{bix})_2(\text{P}_2\text{W}_{18}\text{O}_{62})]$	II	19b
$[\text{Na}_2(\text{H}_2\text{O})_8\text{Ag}_2(\text{HINA})_3(\text{INA})][\text{Na}(\text{H}_2\text{O})_2\text{Ag}_2(\text{HINA})_4(\text{H}_2\text{W}_{12}\text{O}_{40})]$	III	19c
$[\text{Cd}(\text{BPE})(\text{Mo}_8\text{O}_{26})][\text{Cd}(\text{BPE})(\text{DMF})_4]$	III	19d
$[\text{Ag}_2(3\text{atrz})_2][\text{Ag}_2(3\text{atrz})_2(\text{Mo}_8\text{O}_{26})]$	III	19e
$[\text{Cu}(\text{bbi})]_2[\text{Cu}_2(\text{bbi})_2(\text{Mo}_8\text{O}_{26})_{0.5}][\text{Mo}_8\text{O}_{26}]_{0.5}$	III	19f
$[\text{Cu}(\text{bbi})][\text{Cu}(\text{bbi})(\text{Mo}_8\text{O}_{26})_{0.5}]$	III	19f
$[\text{Cu}^{\text{II}}(\text{L})_2(\text{H}_2\text{O})_2][\text{Cu}^{\text{I}}_2(\text{L})_2]\text{PMo}_{12}\text{O}_{40}$	IV	19g

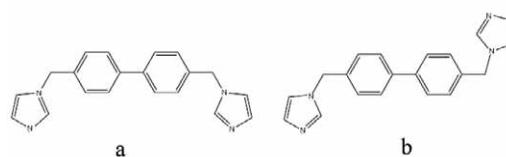


Chart S1 The "U"-type *syn*-conformation (a) and the "Z"-type *trans*-conformation (b) of bimb.

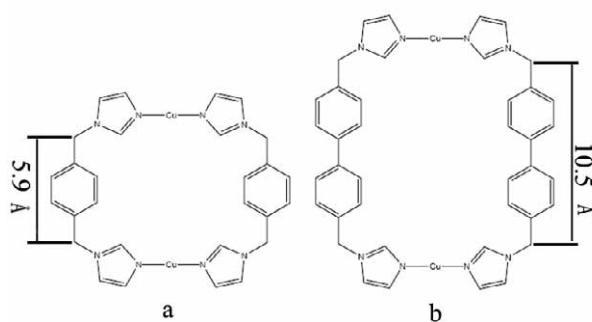


Chart S2 The 26-membered $\text{Cu}_2(\text{bix})_2$ macrocycles (a) and the 36-membered $\text{Cu}_2(\text{bimb})_2$ macrocycles (b).

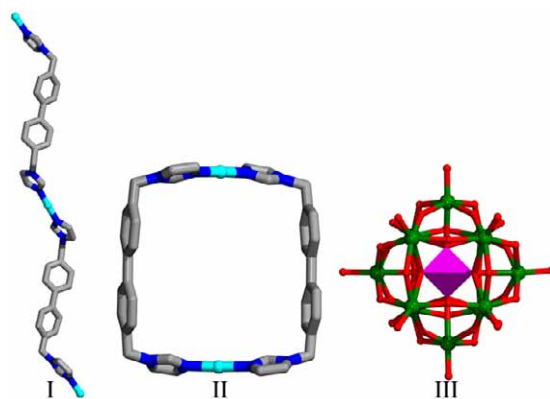


Fig. S1 The three crystallographically distinct motifs in **1**: **I**, $[\text{Cu}(\text{bimb})]^+$ chain; **II**, $[\text{Cu}_2(\text{bimb})_2]^{2+}$ macrocycle; **III**, $[\text{PW}_{12}\text{O}_{40}]^{3-}$ Keggin cluster.

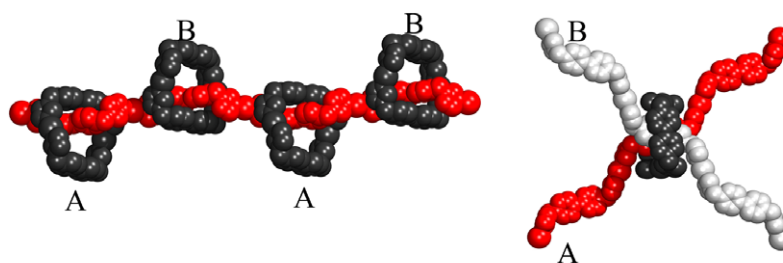


Fig. S2 A space-filling model showing the arrangement of molecular “loops” intercalated by one molecular “string” (left), and the unusual intercalated fashion of two “strings” in one “loop” (right).

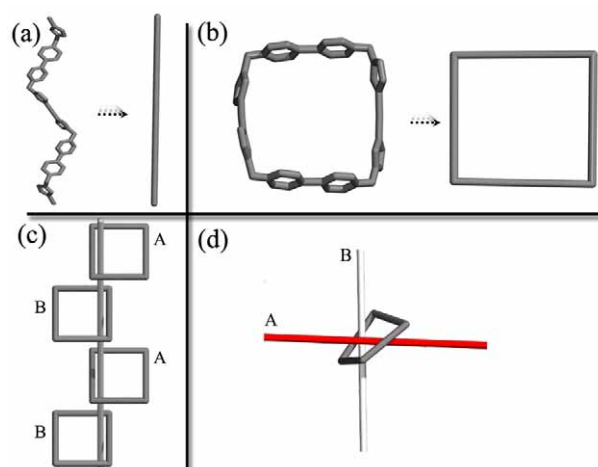


Fig. S3 A schematic presentation of the molecular “string” (a), molecular “string” (b), the arrangement of molecular “loops” intercalated by one molecular “string” (c), and the unusual intercalated fashion of two “strings” in one “loop” (d).

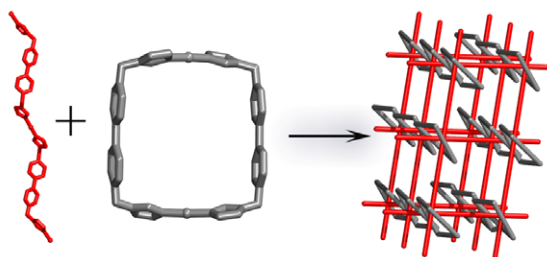


Fig. S4 Illustration of the 3D pseudo-*rotaxane* structure formed from the 1D $[\text{Cu}(\text{bimb})]^+_n$ chain and the 0D 34-membered $[\text{Cu}_2(\text{bimb})_2]^{2+}$ macrocycle.

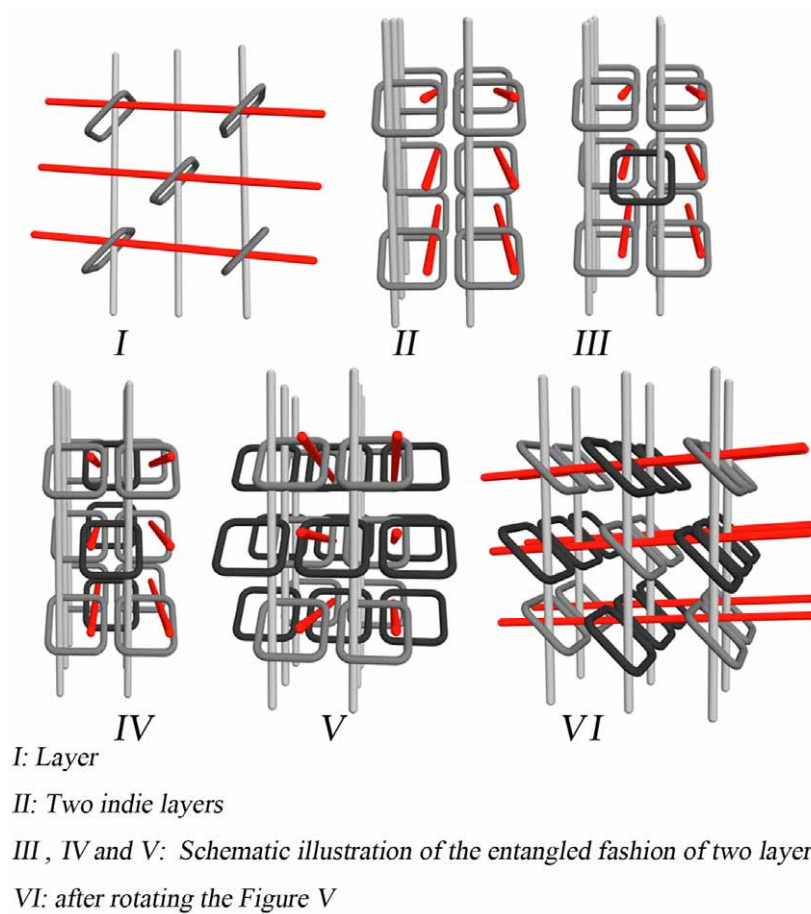


Fig. S5 A schematic illustration of detailed entangled fashion in the MORF.

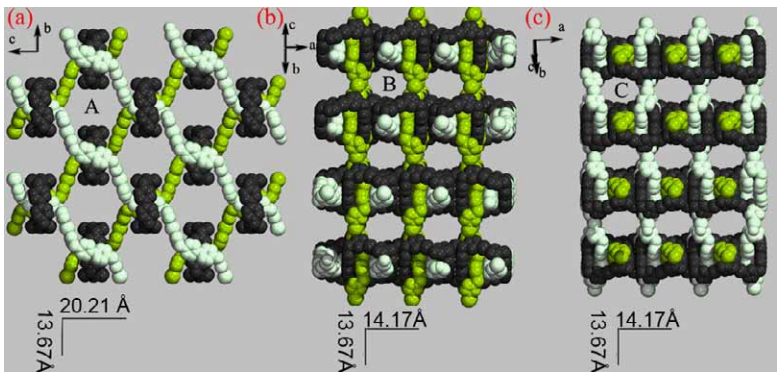


Fig. S6 The space-filling models showing the unusual MORF with three-directional tunnels.

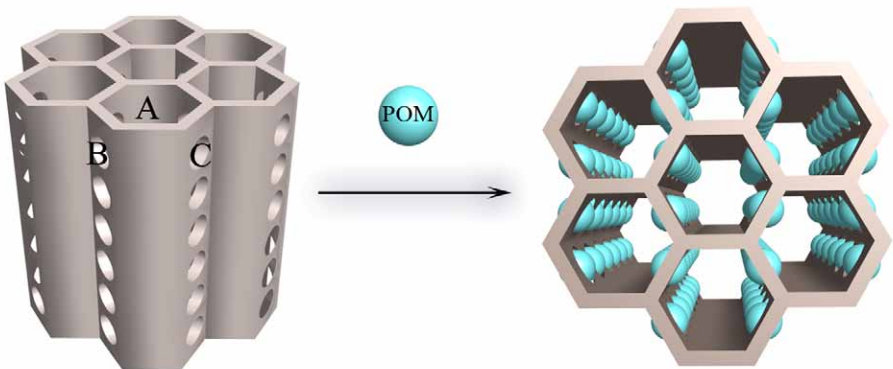


Fig. S7 The arrangement of POMs in the tunnels composed of **B** and **C** pores.

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.

POMs	Distance 1	Distance 2	Distance 3	Distance 4	Distance 5	Distance 6	Average Distance
PW ₁₂	10.433 Å	10.467 Å	10.475 Å	10.459 Å	10.482 Å	10.470 Å	10.464 Å
SiW ₁₂	10.439 Å	10.425 Å	10.394 Å	10.370 Å	10.397 Å	10.390 Å	10.402 Å
CoW ₁₂	10.385 Å	10.352 Å	10.325 Å	10.358 Å	10.370 Å	10.320 Å	10.351 Å

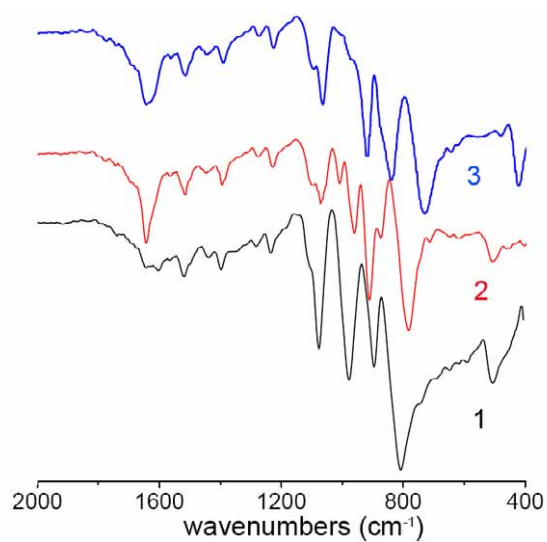


Fig. S8 IR spectra of 1-3.

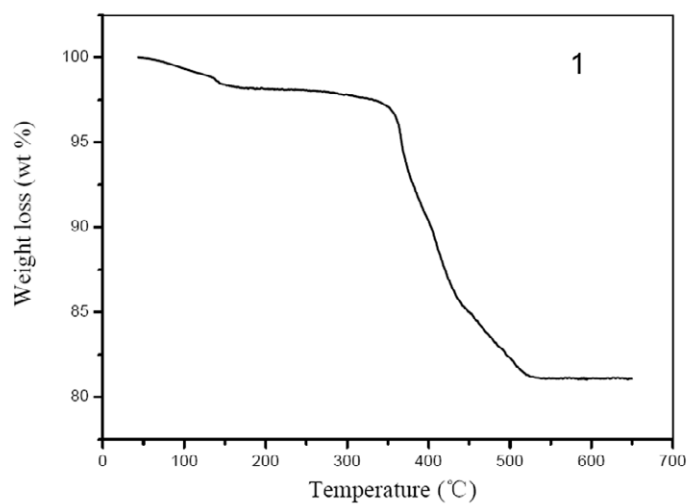


Fig. S9 TG curve of 1.

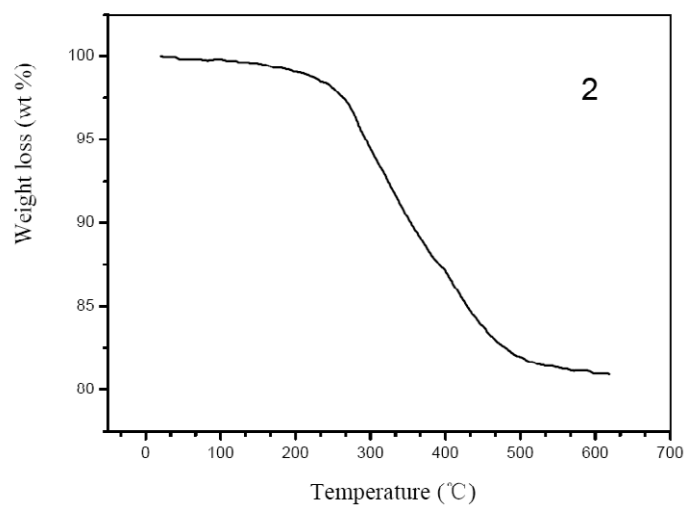


Fig. S10 TG curve of 2.

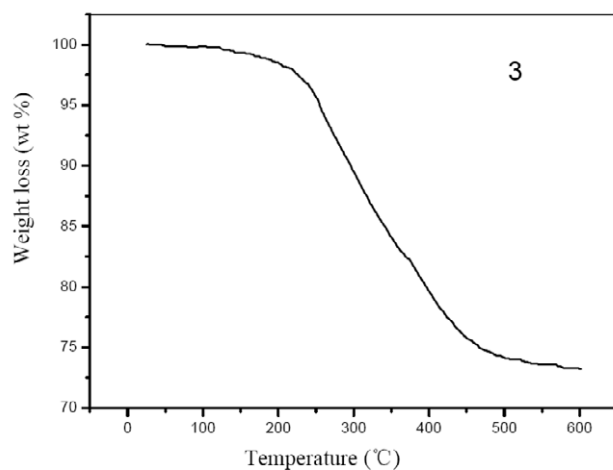


Fig. S11 TG curve of **3**.

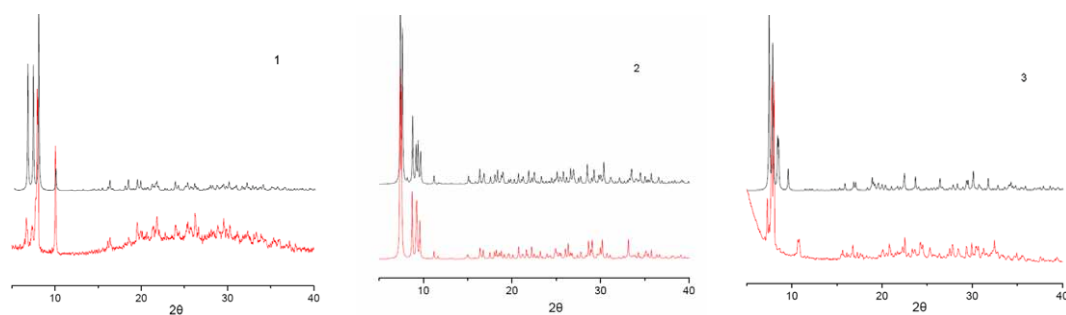


Fig. S12 The simulative (bottom) and experimental (top) powder X-ray diffraction patterns for **1** (left), **2** (middle) and **3** (right).

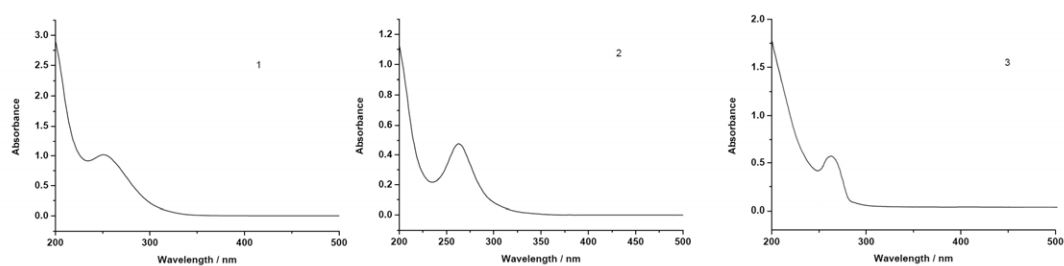


Fig. S13 The UV-visible absorption spectra of **1-3**.