Electric Supplemental Information for:

The Factors Affecting on the Assembly of Keggin-Metal-Bimb

System: Charge/Polarity of Keggin Polyanions and Coordination

modes of Metal Cations

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| Compound coordination mode123456Coordination modeImage: Construction modeImage: Construction mode | | | geometries of i | inetal cations in con | iipounus 1-0 | | |
|---|----------------------|------------------------------|--|--|--|---|---|
| Coordination modeIIIIIIIPOM cluster $\widetilde{\mathcal{M}}_{2}^{(0)}$ | Compound | 1 | 2 | 3 | 4 | 5 | 6 |
| POM clusterImage: c | Coordination mode | | | | | | |
| tritopic PW12hexadentate W12hexadentate W12hexadentate W12hexadentate W12ditopic BW12hexadentate BW12Metal cation v_{12}^{0000} v_{2000}^{00000} v_{12}^{000000} $v_{1000000000000000000000000000000000000$ | POM cluster | | | | A A A A A A A A A A A A A A A A A A A | Contraction of the second | |
| Metal cation 0^{00271} 1^{002} N_{1}^{0} 0^{002} N_{1}^{0} 0^{012} N | | tritopic PW ₁₂ | hexadentate W ₁₂ | hexadentate W ₁₂ | hexadentate W ₁₂ | ditopic BW ₁₂ | hexadentate BW ₁₂ |
| $\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 &$ | Metal cation | 0W2#1 N1 OW2 OW2 | 010 N1 | 010 N2 07#2 N1 | 010 N2 06#3 010 | 011#1 011#2 | 024 020 Ag1 01 N1 |
| $\begin{bmatrix} \mathbf{N}_{14} \\ \mathbf{O}_{24} \\ \mathbf{O}_{3} \\ \mathbf{O}_{043} \\ \mathbf{N}_{6} \\ N$ | | N9 N3 N3 O5 | | | | | |
| crystallographic-ally independent Co2+One crystallographic- ally independentOne crystallographic- ally independentOne crystallographic- | | OW4 Co3 N7 | | | | | |
| independent Co2+One crystallographic- ally independentOne crystallographic- ally independentOne crystallographic- ally independentOne crystallographic- ally independentOne | | crystallographic-ally | | | | | |
| | | independent Co ²⁺ | One crystallographic- ally independent Co ²⁺ | One crystallographic- ally independent Co ²⁺ | One crystallographic- ally independent Co ²⁺ | One crystallographic-ally independent Cu ⁺ | One crystallographic-ally independent Ag ⁺ |

 Table S1. A summarization of the coordination modes of POM clusters and the coordination geometries of metal cations in compounds 1-6



Fig. S1. (a) Ball-and-stick representation of the (4,4) sheet structure in **1**. (b) The ladder-like chain in **1**.



Fig. S2. View of bamboo-shaped cylinder in 2.



Fig. S3. View of per joint in the bamboo-shaped cylinder in 2.



Fig. S4. View of the 1D undulated chain in **2**. (b) the topology of the 3D framework in **2**. Color codes: pink, connected nodes of Co cations, blue, connected nodes of GeW₁₂ anions.



Fig. S5. XPS of compound 1.



Figure S6. The IR spectra of compounds 1-6.



Fig. S7. The simulative (red) and experimental (black) powder X-ray diffraction patterns for 1-6.



Fig. S8. Solid-state emission spectrum of bimb ($\lambda_{ex} = 310$ nm) at room temperature.