

# Supplementary Information

## A 3D organic-inorganic network constructed from Anderson-type polyoxometalate anion, copper complex and tetrameric $[\text{Na}_4(\text{H}_2\text{O})_{14}]^{4+}$ cluster

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**Fig. S1** Comparison of the calculated and experimental XRD patterns of **1** in the angular range  $2\theta = 5\text{--}40^\circ$  at 293 K.

**Fig. S2** The coordination environment of Cu atom.

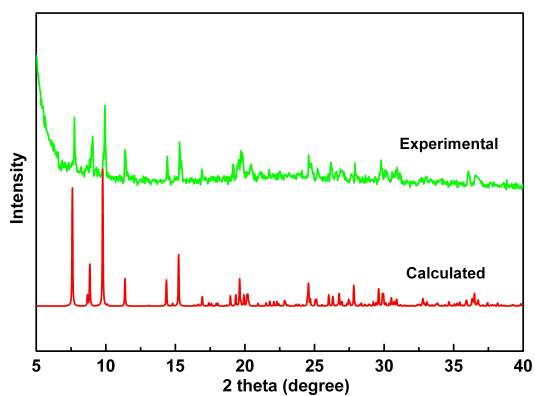
**Fig. S3** (a) XPS spectra of **1** for Mo 3d<sub>5/2</sub> and Mo3d<sub>3/2</sub>. (b) XPS spectra of **1** for Cu 2p<sub>3/2</sub> and Cu2p<sub>1/2</sub>.

**Fig. S4** The IR spectra of **1** and H<sub>2</sub>PDA ligand.

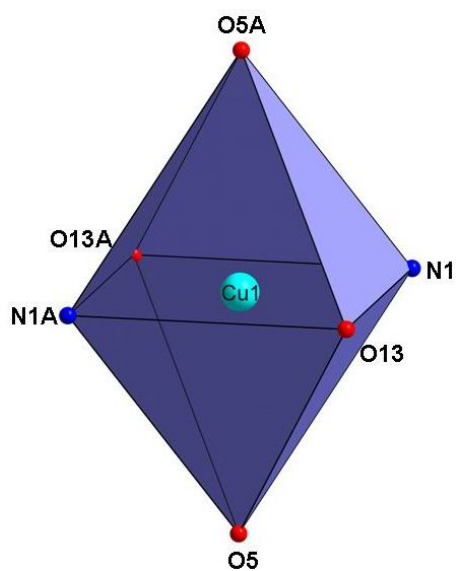
**Fig. S5** The UV spectra of **1**, **2** and H<sub>2</sub>PDA ligand.

**Fig. S6** The TG/DTA curve of **1**.

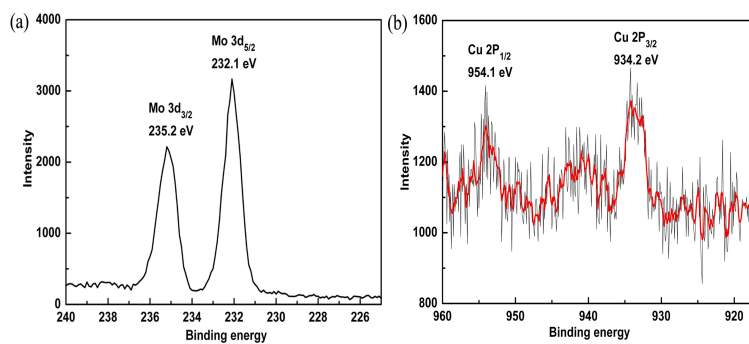
**Fig. S7** The blue crystals of **1**.



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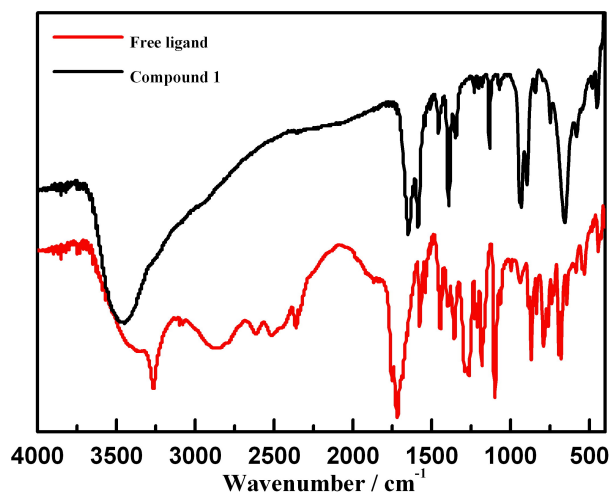


Fig. S4 The IR spectra of **1** and H<sub>2</sub>PDA ligand.

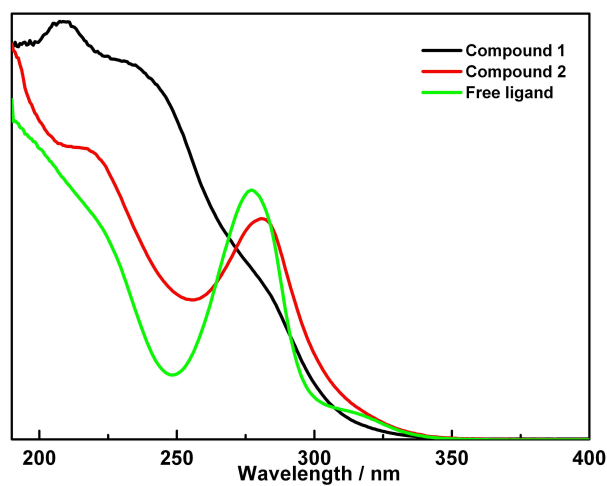


Fig. S5 The UV spectra of **1**, **2** and H<sub>2</sub>PDA ligand.

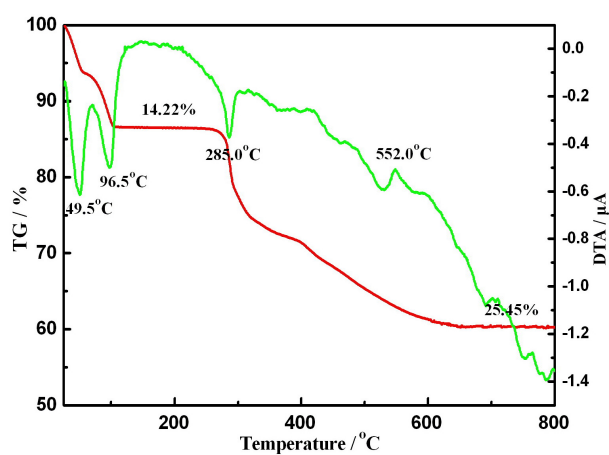


Fig. S6 The TG/DTA curve of **1**.



**Fig. S7** The blue crystals of **1**.