

## Electronic Supplementary Information

### Combination of lacunary polyoxometalates and high-nuclear transition-metal clusters under hydrothermal conditions: first 6<sup>5</sup>·8 CdSO<sub>4</sub>-type 3-D framework built by hexa-Cu<sup>II</sup> sandwiched polyoxotungstates

Jun-Wei Zhao,<sup>a</sup> Shou-Tian Zheng,<sup>a</sup> Zhao-Hui Li,<sup>b</sup> and Guo-Yu Yang<sup>\*,a</sup>

<sup>a</sup> State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter and Graduate School of the Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China. E-mail: ygy@fjirsm.ac.cn; Fax: (+86) 591-83710051

<sup>b</sup> College of Chemistry and Chemical Engineering, Fuzhou University, Fuzhou, Fujian 350002, P. R. China

**Fig. S1** The topologies of (a) the diamond net, (b) the NbO net, (c) PtS (cooperite) net and (d) the CrB<sub>4</sub> net.

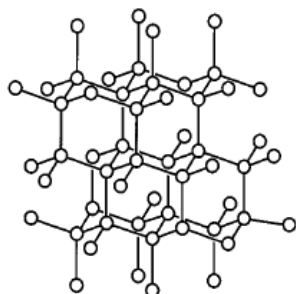
**Fig. S2** The IR spectrum of **1** performed in the range of 4000–400 cm<sup>-1</sup>.

**Fig. S3** The  $\chi_m$  plot at various applied fields for **1** ( $H = 100, 500, 1000$  Oe). The solid line is simply to guide the eye.

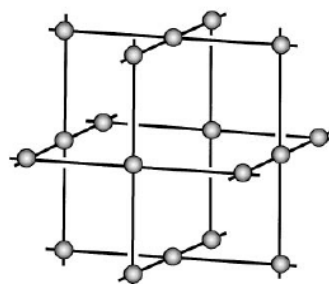
**Fig. S4** The field-cooled (FC) and zero-field-cooled (ZFC) magnetization measured under an applied field of 100 Oe for **1**.

**Fig. S5** In-phase ac susceptibility signals ( $\chi_m'$ ), vs  $T$  (top) and out-of-phase ac susceptibility signals ( $\chi_m''$ ) vs  $T$  (bottom) for **1** at 111, 511, 911, 1511, 2511 and 3511 Hz.

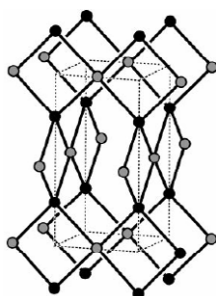
**Fig. S6** The TGA curve of **1** performed under air atmosphere from 30 to 800 °C.



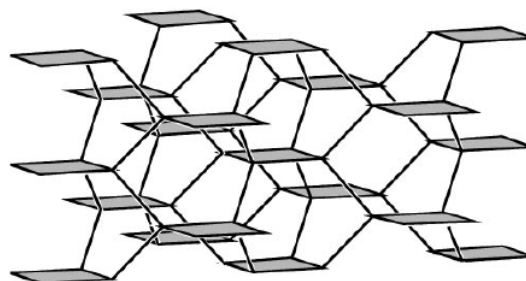
**a)** The diamond net.



**b)** The fragment of the NbO net.

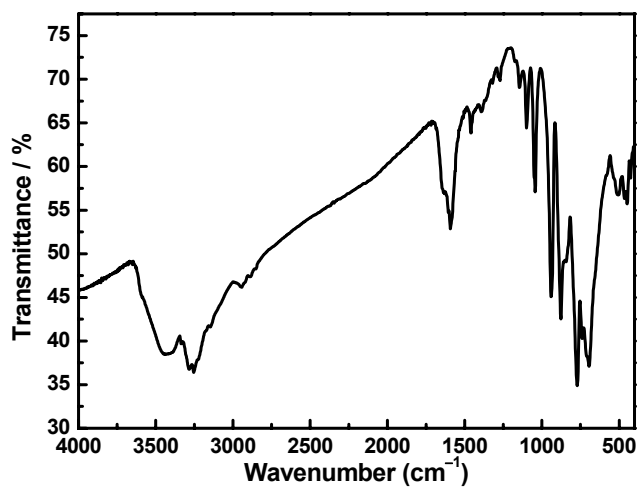


**c)** The PtS (cooperite) net (S, filled circles; Pt, shaded circles)

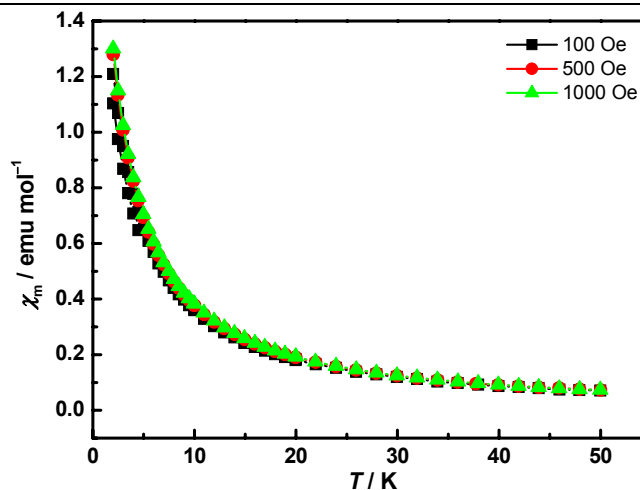


**d)** The CrB<sub>4</sub> net, 4-rings (squares) are shaded.

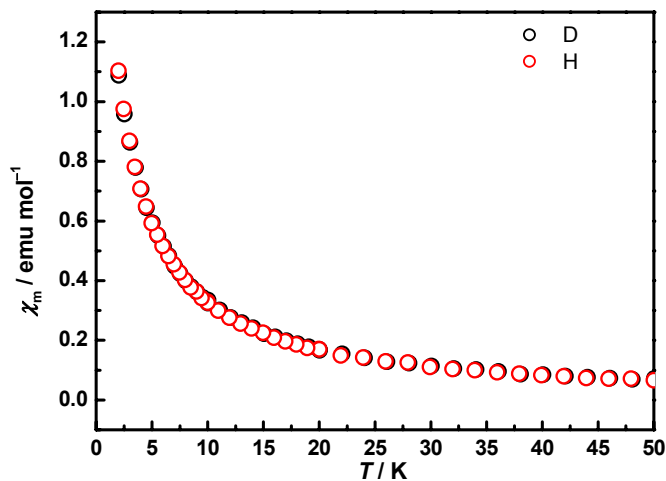
**Manifesto:** Fig. S1a-d are extracted from: M. O’Keeffe, M. Eddaoudi, H. Li, T. Reineke and O. M. Yaghi, *J. Solid State Chem.*, 2000, **152**, 3.



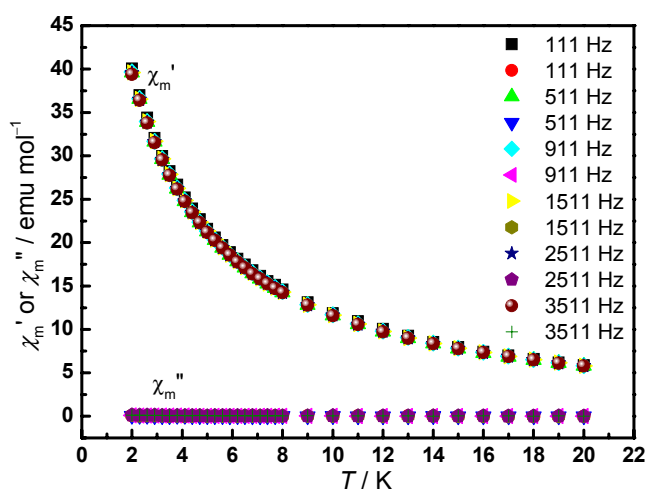
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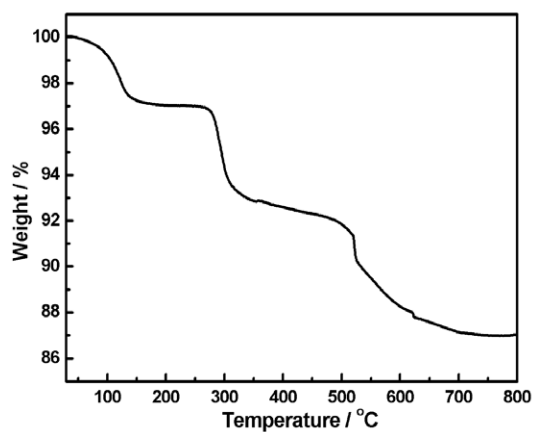


**Fig. S4** The field-cooled (FC) and zero-field-cooled (ZFC) magnetization measured under an applied field of 100 Oe for **1**.



**Fig. S5** In-phase ac susceptibility signals ( $\chi_m'$ ), vs  $T$  (top) and out-of-phase ac susceptibility signals ( $\chi_m''$ ) vs  $T$  (bottom)

for **1** at 111, 511, 911, 1511, 2511 and 3511 Hz.



**Fig. S6** The TGA curve of **1** performed under air atmosphere from 30 to 800 °C.

The thermogravimetric behavior of **1** was investigated in the flowing air atmosphere in the temperature range of 30–800°C (**Fig. S6**). The TG curve of **1** indicates that the weight loss procedure can be divided into three steps. The first weight loss of 3.02 % from 30 to 266 °C is assigned to the release of six lattice water and four coordinated water molecules (calc. 3.04%), followed by the second weight loss of 5.25% between 266 and 494 °C corresponding to the loss of five en ligands (calc. 5.08%). The third weight loss of 4.75% is attributable to the removal of one en and two deta ligands (calc. 4.54%). These observations indicate that the experimental values are in good agreement with the theoretical values.