

# Rational synthesis of a microporous metal-organic framework with PtS topology using a semi-rigid tetrahedral linker †

Li-Li Liang, Jun Zhang, Shi-Bin Ren, Gen-Wu Ge, Yi-Zhi Li, Hong-Bin Du\* and Xiao-Zeng You

*State Key Laboratory of Coordination Chemistry, Nanjing National Laboratory of Microstructures, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China. E-mail: [hbd@nju.edu.cn](mailto:hbd@nju.edu.cn)*

## Supporting Information

### Contents:

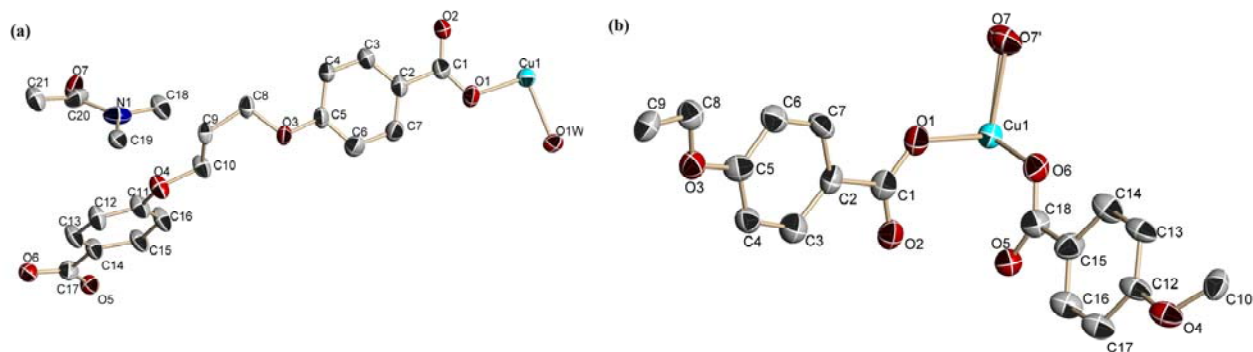
1. Materials and methods.
2. Figure S1. ORTEP drawings of the asymmetric unit of complexes **1** and **1'**.
3. Figure S2. TGA profiles for complex **1**.
4. Figure S3. PXRD patterns of **1**.

## 1. Materials and Methods

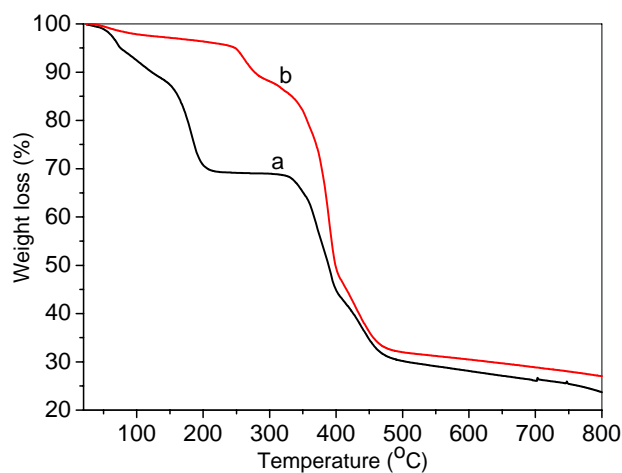
Ligand Tetrakis[4-(carboxyphenyl)oxamethyl]methane acid ( $H_4X$ ) was prepared according to the literature (Macromolecules, 1999, 32, 4819–4825.). All other reagents and solvents were commercially purchased without further purification.

Infrared spectra were obtained on a Bruker Vector 22 spectrophotometer with KBr pellets in the 4000 – 400  $cm^{-1}$  region. Elemental analyses for C, H, and N were performed on a CHN-O-Rapid analyzer and an Elementar Vario MICRO analyzer. Thermogravimetric analysis (TGA) was carried out in a nitrogen stream using Pysis 1 DTA equipment with a heating rate of 20  $^{\circ}C/min$ . Powder X-ray diffraction (PXRD) patterns were collected in the  $2\theta = 5\text{--}30^{\circ}$  range with a scan speed of 0.2  $sec/deg$ . on a Bruker D8 diffractometer with Cu  $K\alpha$  radiation equipped with a LynxEye detector at room temperature. The adsorption isotherms of nitrogen and hydrogen were measured at 77 K by using an ASAP 2020 M+C volumetric adsorption equipment made by Micromeritics Instrument Corporation. The sorption isotherms for  $CO_2$  and  $CH_4$  were measured on a Hidenisochema IGA 100 high-pressure adsorption instrument at 293 K. For the measurements, approximately 100 mg of sample was taken in a stainless-steel sample holder and degassed at 373 K under a 10 mbar vacuum for about 10 h.

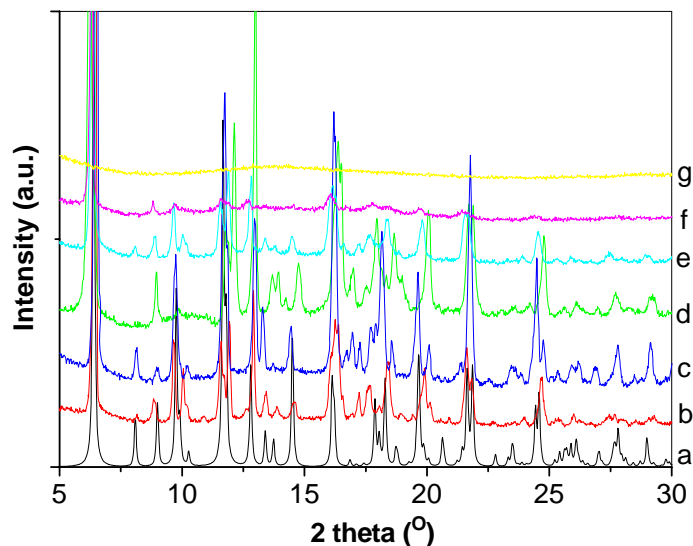
Single-crystal X-ray diffraction analysis. The suitable crystals of **1** and **1'** with the dimensions *ca.*  $0.28 \times 0.22 \times 0.20$   $mm^3$  were selected for single crystal X-ray diffraction and the data were collected at 291 K on a Bruker Smart CCD diffractometer with a graphite-monochromatic  $K\alpha$  radiation ( $\lambda = 0.71073$   $\text{\AA}$ ) from an enhanced optic X-ray tube. Data reductions and absorption corrections were performed using the SAINT and SADABS software packages, respectively. The structure was solved by direct methods and refined by full matrix least-squares methods on F2 using the SHELXS-97 and SHELXL-97 programs, using atomic scattering factors for neutral atoms. Hydrogen atoms were placed in calculated positions and refined as riding atoms with a uniform value of  $U_{iso}$ . In the asymmetric unit, one DMA molecule was located and refined normally and the PLATON/SQUEEZE program was used to deal with the rest disordered guest molecules. The final structural model was refined without the guest molecules. The identity and number of the guest molecules were determined from the IR spectra, elemental analyses, and TGA data.



**Fig. S1.** ORTEP drawings of the asymmetric unit of complexes **1** (a) and **1'** (b) at the 50% probability (H atoms and guest water molecules are omitted for clarity).



**Fig. S2.** TGA curves of complex **1** under nitrogen: (a) as-synthesized, (b) after sorption measurements.



**Fig. S3.** PXRD patterns for **1**: (a) simulated, (b) as-synthesized, (c) after sorption experiments and heated at (d) 100, (e) 150, (f) 200, and (g) 250°C for 2h in air, respectively.