

Polyoxometalates anion- π interactions directed assembly of a three-dimensional hydrogen-bonded supramolecular framework with nanoscale porosity

Jian-Zhen Liao,^{a,b} Xue-Jing Dui,^{a,b} Hai-Long Zhang,^{a,b} Xiao-Yuan Wu^a and Can-Zhong Lu^{*a,c}

^a State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, 350002, P. R. China. E-mail: czlu@fjirsm.ac.cn.

^b Graduate University of Chinese Academy of Sciences, Beijing 100049, China.

^c Key Laboratory of Design and Assembly of Functional Nanostructures, Chinese Academy of Sciences, Beijing 100049, China.

Table of Contents:

- 1. Experimental Section**
- 2. Single Crystal X-ray Diffraction Analyses**
- 3. Crystal data for compound 1**
- 4. Figure of compound 1**
- 5. X-ray Powder Diffraction**
- 6. Thermogravimetric analyses**
- 7. References**

1. Experimental Section

Synthesis of N, N'-di(4-pyridyl)-1,4,5,8-naphthalenediimide (DPNDI) ligand. A mixture of 1,4,5,8-naphthalene-tetracarboxylic dianhydride (NDA) (0.8g, 3mmol) and 4-aminopyridine (6mmol) in DMF (20mL) was heated under reflux for 8 h. When the reaction mixture reached room temperature, a crystalline solid precipitated out, which was collected by filtration. The crude product was purified by recrystallization from DMF to obtain DPNDI as off-white crystalline solids.^{S1} NMR spectra were recorded with a Bruker Avance III 500MHz NMR spectrometer. Chemical shifts are given in parts per million (ppm) and referred to TMS as internal standard. ¹H coupling constants *J* are given in Hertz (Hz). ESI mass spectra were recorded on a LCQ Fleet from Thermo Fisher Scientific. IR spectra were recorded in the range 4000-400 cm⁻¹ on a Perkin-Elmer FT-IR spectrum 2000 spectrometer with pressed KBr pellets. ¹H NMR (500 MHz, CF₃COOD, 298K): δ = 9.12 (d, *J*=7.0 Hz, 4H), 9.05 (s, 4H), 8.38 (d, *J*=7.0 Hz, 4H) (Fig. S1). MS (ESI-MS) *m/z*: Calculated for C₂₄H₁₂N₄O₄ 420.09, Found: 420.09 (Fig. S2). IR(cm⁻¹): 3422(w), 2935(w), 1709(m), 1660(s), 1574(m), 1491(m), 1282(s), 1010(w), 821(s), 750(m), 592(w).

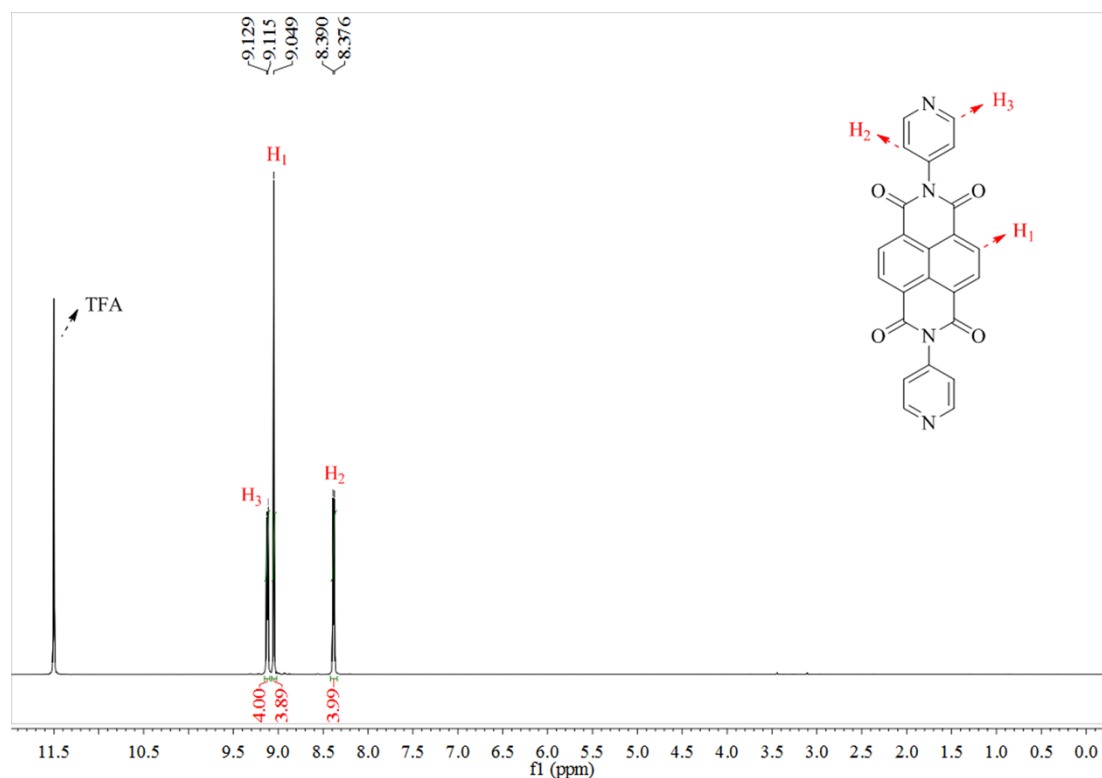


Fig. S1. ¹H NMR of the ligand in CF₃COOD.

NDI #87 RT: 0.37 AV: 1 NL: 9.01E2
T: ITMS - c ESI Full ms [50.00-1000.00]

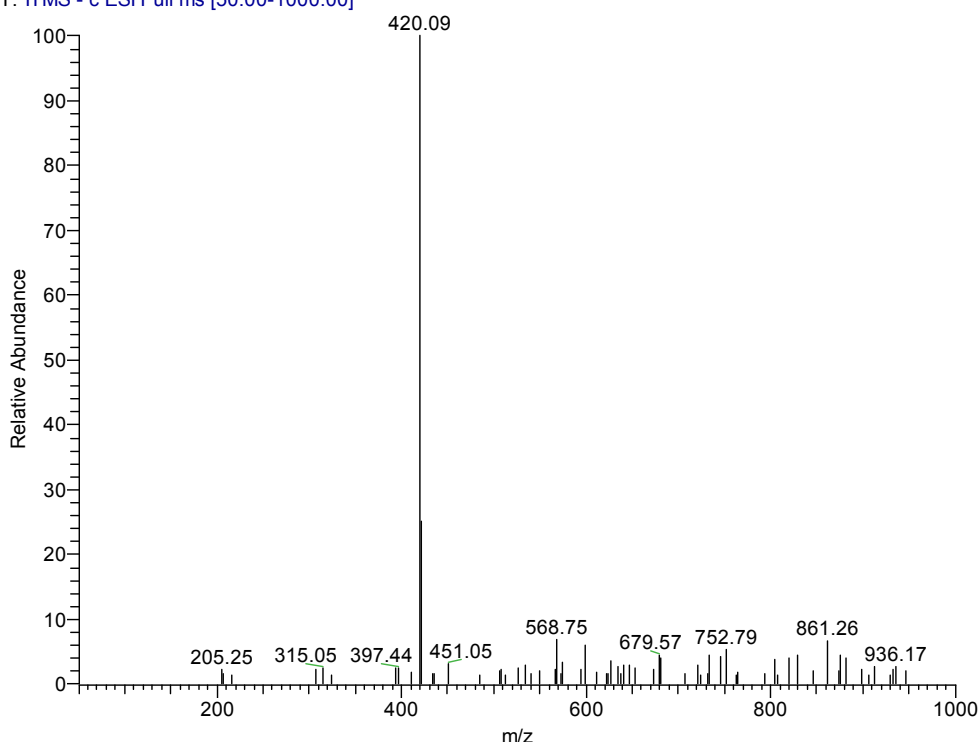


Fig. S2. ESI-MS of the ligand.

Synthesis of compound 1. A solution (1mL) of DMAc/MeCN (1:1, v/v) was carefully layered over a DMAc (10mL) solution of DPNDIs (0.087mmol, 0.039g), and then the solution of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.043mmol, 0.018g) and H3PW12O40 (0.065mmol, 0.187g) in MeCN/MeOH (2:1, v/v) (3mL) mixture was carefully added as a second layer. Green crystals that appeared after several days were collected and washed with MeCN in ca. 45% yield (based on polyoxometalates). Elemental analyses of C, H and N were carried out with a Vario EL III elemental analyzer. Anal. Calcd for $\text{C}_{72}\text{H}_{51}\text{CrN}_{12}\text{O}_{105}\text{P}_2\text{W}_{24}$: C 11.86, H 0.71, N 2.31%. Found: C 14.82, H 1.70, N 3.32%. The difference was probably because of the volatile solvent molecules in the frameworks. Combined with Molecular Weight Calculator, the result we calculated is that there are approximately eight DMAc, thirteen MeCN and ten water molecules. Calcd: C 15.06, H 1.89, N 3.03%. IR(cm^{-1}): 3422(w), 2935(w), 1718(m), 1614(s), 1351(m), 1266(m), 1079(s), 984(s), 816(s), 763(m), 515(w).

2. Crystallographic data collection and refinement

Suitable single crystal of compound **1** was mounted on glass fiber for the X-ray measurement. Diffraction data was collected on SuperNova (Dual source) diffractometer equipped with the CrysAlis^{pro} X-ray crystallography data systems. The measurement was made by using graphic monochromatic Mo $K\alpha$ radiation ($\lambda = 0.71073\text{\AA}$) at 173 K under a cold nitrogen stream. All calculations were performed with the SHELXTL-97 program package^{S2}, and structures were

solved by direct methods and refined by full-matrix least-squares against F^2 . All non-hydrogen atoms except for the disordered moieties were refined anisotropically, and hydrogen atoms of the organic ligands were generated theoretically onto the specific atoms. The hydrogen-bonded non-interpenetrated polyoxometalate-based supramolecular framework crystal has very large pores containing badly disordered solvent molecules, which contributed to an A-level alert. SQUEEZE routine implemented on PLATON was used to remove electron densities corresponding to disordered solvent molecules. Crystallographic data has been deposited at the Cambridge Crystallographic Data Center with reference number CCDC 999638. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

3. Crystal data for compound 1

$\text{CrC}_{72}\text{H}_{51}\text{O}_{105}\text{N}_{12}\text{P}_2\text{W}_{24}$, $M_r=7290.59$, green crystal. Trigonal, space group $R\bar{3}m$, $a=19.4966(8)$ Å, $c=58.604(3)$ Å, $V=19292.1(14)$ Å³, $Z=3$, $\rho_{\text{calcd}} = 1.883$ g·cm⁻³, $\mu=10.80$ mm⁻¹, λ (MoK α)=0.71073 Å, $F(000)= 9711$, $T=173(2)$ K, $GooF = 1.01$, Final R indices: $R1 = 0.084$, $wR2=0.2451$ for 6075 reflections [$I > 2\sigma(I)$]; $R1 = 0.1220$, $wR2 = 0.2871$ for 10356 independent reflections (all data) and 327 parameters.

4. Figures of compound 1

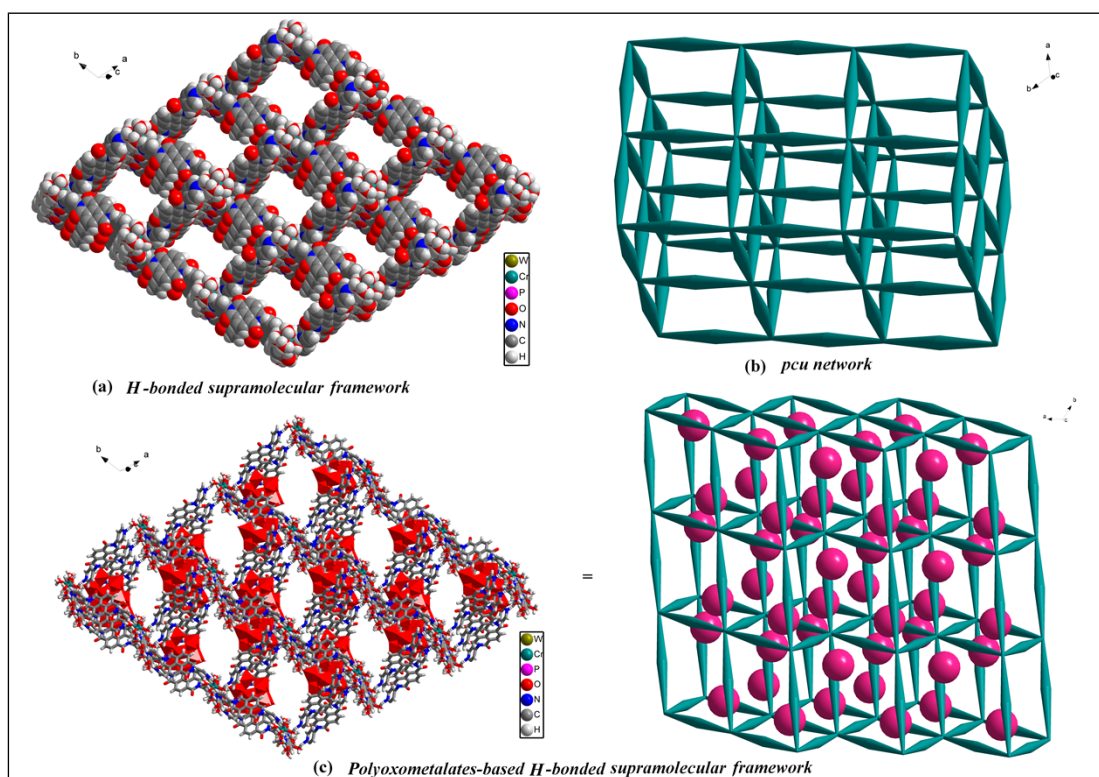


Fig. S3. Representation of the structure of crystals of hydrogen-bonded supramolecular framework (a), showing part of the *pcu* network (b) viewed along the *a*-axis (space-filling image in c), and the polyoxometalates filled in the *pcu* network viewed along the *c*-axis (Purple balls: polyoxometalates anions).

5. X-ray Powder Diffraction

PXRD of the hydrogen-bonded non-interpenetrated polyoxometalate-based supramolecular framework was measured on Rigaku Miniflex II powder diffractometer.

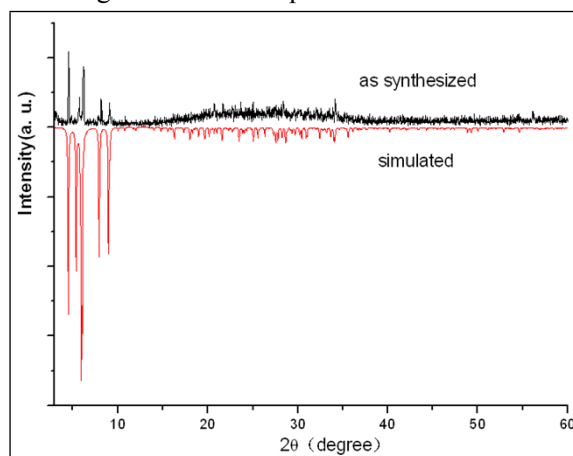


Fig. S4. PXRD pattern of the as-synthesized supramolecular framework and the simulated pattern based on the single crystal 1.

6. Thermogravimetric analyses

TGA of an air-dried ground sample of hydrogen-bonded non-interpenetrated polyoxometalate-based supramolecular framework was conducted on a TGA/DSC 1 STAR^e system with a heating rate of 10 °C/min under an N₂-atmosphere. The initial 10% weight loss at 35–130 °C maybe corresponds to loss of volatile solvents (MeCN, MeOH, or H₂O), the next loss maybe corresponds to the loss of H₂O (from [Cr(H₃O)₃(H₂O)₃]⁶⁺) and DMAc molecules. The hydrogen-bonded supramolecular framework shows relatively poor thermal stability, the following loss corresponds to the collapse of the network and the decomposition of the ligands.

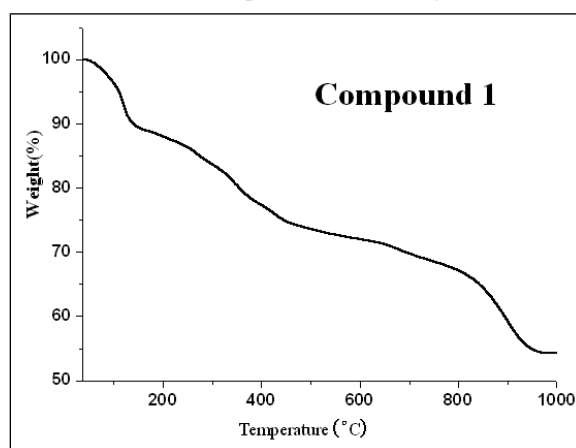


Fig. S5. TGA data of the non-interpenetrated hydrogen-bonded supramolecular framework.

7. References

- S1. S. Guha, F. S. Goodson, L. J. Corson and S. Saha. *J. Am. Chem. Soc.*, 2012, **134**, 13679.
- S2. G. Sheldrick. *Acta Cryst.* **2008**, *A64*, 112-122.