Electronic Supplementary Information

Microporous Metal-Organic Framework Built from Pentanuclear Tetrahedral Units: Gas Sorption and Magnetism

Yan-Xi Tan[a,b], Ying Zhang*[a], Yan-Ping He*[b], and Yan-Jun Zheng*[a]

[a] *State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing, No.18 FuXue Road, ChangPing District, Beijing 102249, P.R. China. E-mail: tanyanxi2006@163.com; yingzh1977@163.com.*

[b] 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.

Experimental Section

General Procedures.

All reagents were purchased commercially and used without further purification. All syntheses were carried out in 20 ml vial under autogenous pressure. All powder X-ray diffraction (PXRD) analyses were recorded on a Rigaku Dmax2500 diffractometer with Cu Kα radiation (λ = 1.54056 Å) with a step size of 0.05 °. Thermal stability studies were carried out on a NETSCHZ STA-449C thermoanalyzer with a heating rate of 10 ℃/min under an N_2 atmosphere. Gas adsorption measurement was performed in the ASAP (Accelerated Surface Area and Porosimetry) 2020 System. Magnetic data were collected using crystals of the samples on a Quantum Design MPMS XL7 SQUID magnetometer.

X-ray Crystallography: The diffraction data of **1** was collected on a SuperNova CCD diffractometer with graphite monochromated Cu Kα radiation (λ = 1.5418 Å) at 120 K. Absorption corrections was applied by SADABS. The structure was solved by direct methods and refined with full-matrix least-squares technique using SHELXTL. All non-hydrogen atoms were refined with anisotropic displacement parameters. The structures were solved by direct methods and refined on F^2 full-matrix least-squares using the SHELXTL-97 program package. The SQUEEZE routine of the PLATON software suite was used to remove the highly disordered solvent molecules of compound **1**.

CheckCif alerts are listed according to Alert Level A and B for compound **1**. Responses are in bold.

ALERT LEVEL A

PLAT027 ALERT 3 A diffrn reflns theta full (too) Low ..... 64.99 Degree.

Our response: A full set of data was collected, however the very high angle data was dominated by noise [I/sigma(I) < 1.0] and was omitted. This arbitrary theta limit is inappropriate for highly disordered structures. A limit on data parameter ratio's that properly takes into account the number of restraints constraints and the redundancy of the measurements would be more appropriate. Unfortunately the cifcheck routine does not do this.

ALERT LEVEL B

PLAT201_ALERT_2_B Isotropic non-H Atoms in Main Residue(s) ..... 6 Report

PLAT223_ALERT_4_B Large Solvent/Anion H Ueq(max)/Ueq(min) ... 4.4 Ratio

PLAT413_ALERT_2_B Short Inter XH3 .. XHn H29 .. H67C .. 1.95 Ang.

PLAT420_ALERT_2_B D-H Without Acceptor O8 - H8A ... Please Check

PLAT420_ALERT_2_B D-H Without Acceptor O13 - H68A ... Please Check

Our response: These alerts are generated because there is a large amount of disorder in the structure (see similar responses above).

Crystal data for **1**: monoclinic, a = 19.8290(2) Å, b = 14.3210(2) Å, c = 28.6903(3) Å, β = 91.0550(10) ^{o}, V = 8145.84(16) Å^3, T = 120.01(10) K, space group $P2_1/c$, Z = 4, 31793 reflections measured, 14315 independent reflections (R_{int} = 0.0197). The final R_1 value was 0.716 ($I > 2\sigma(I)$). The final $wR(F^2)$ value was 0.2109 ($I > 2\sigma(I)$).

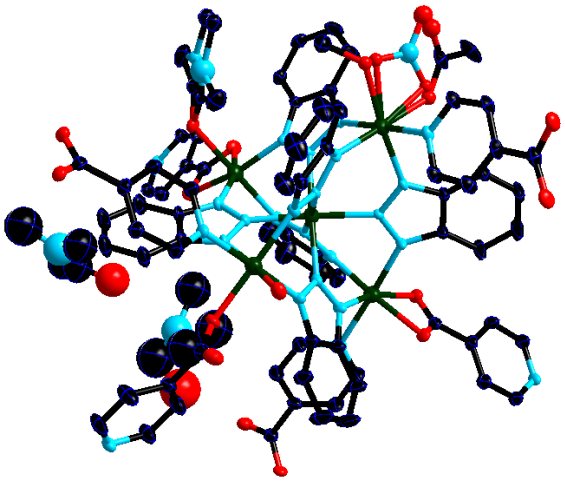

Figure S1 ORTEP figure for metal and ligand coordination of **1**.

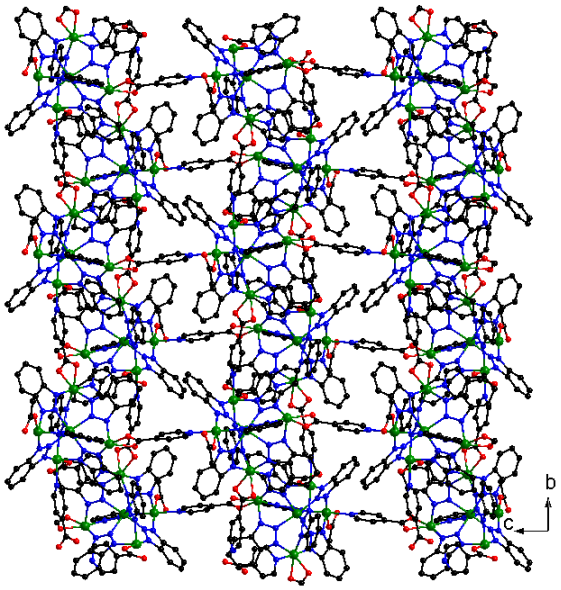

Figure S2 A porous layer motif of **1**.

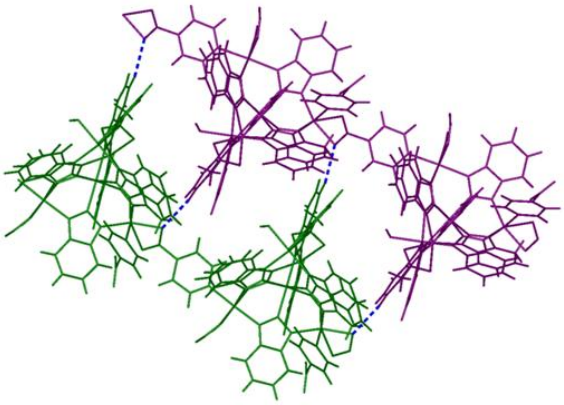

Figure S3 The hydrogen bond between the layers.

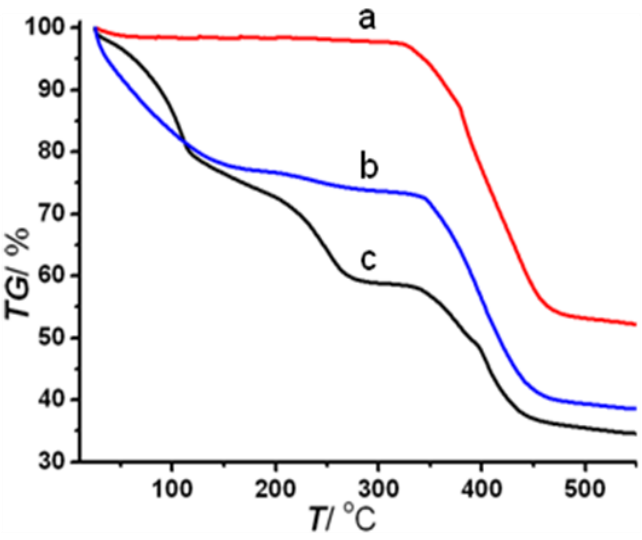

Figure S4 TGA curves of a) **1**, b) solvent-exchanged **1** and c) **1-ht**.

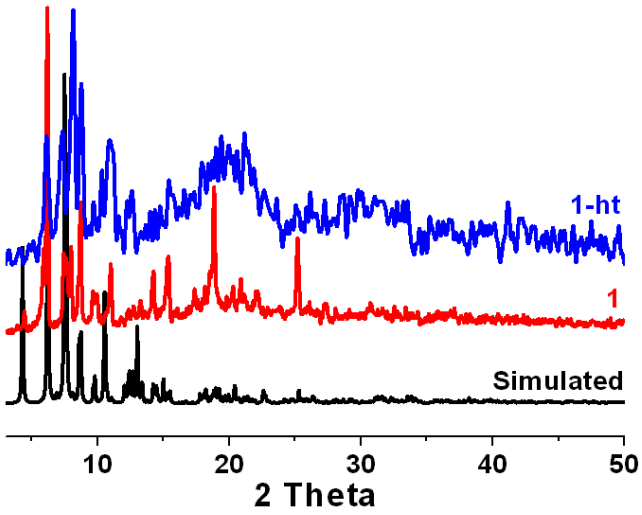

Figure S5 PXRD patterns of simulated from the single-crystal data of **1** (black); as-synthesized **1** (red); desolvated solid **1-ht** (blue).

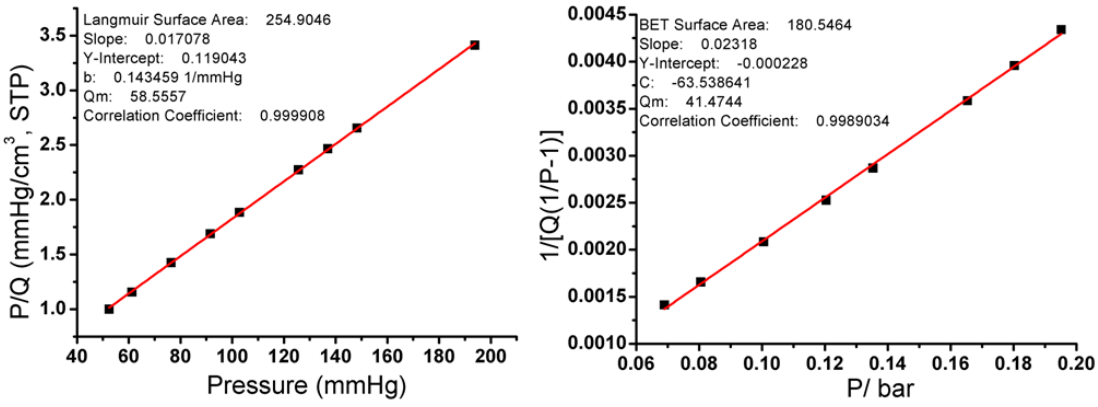

Figure S6 Langmuir (left) and BET (right) plots of **1-ht** calculated from N_2 adsorption isotherm at 77 K.

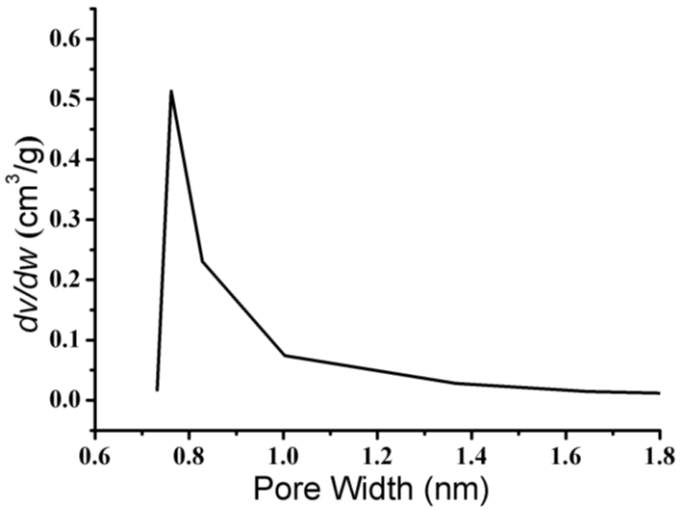

Figure S7 The pore distribution plot of **1-ht**.

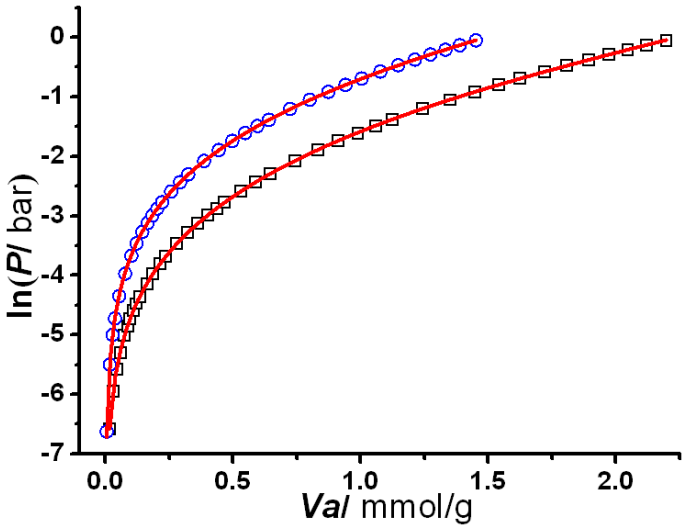

Figure S8 CO_2 adsorption isotherms for **1-ht** fitting by virial method.

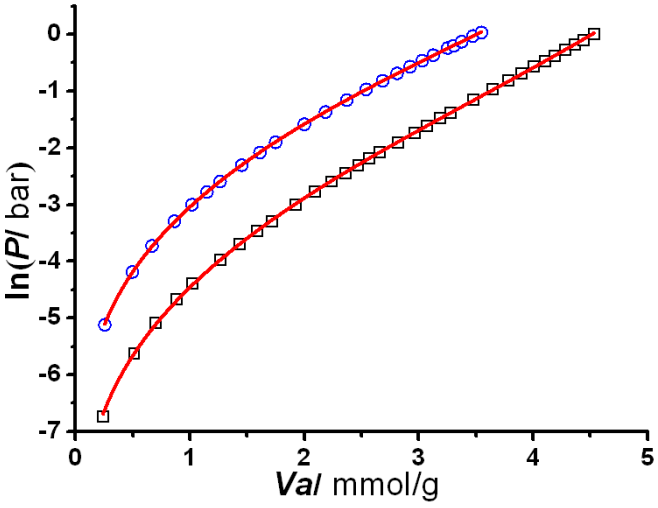

Figure S9 H_2 adsorption isotherms for **1-ht** fitting by virial method.

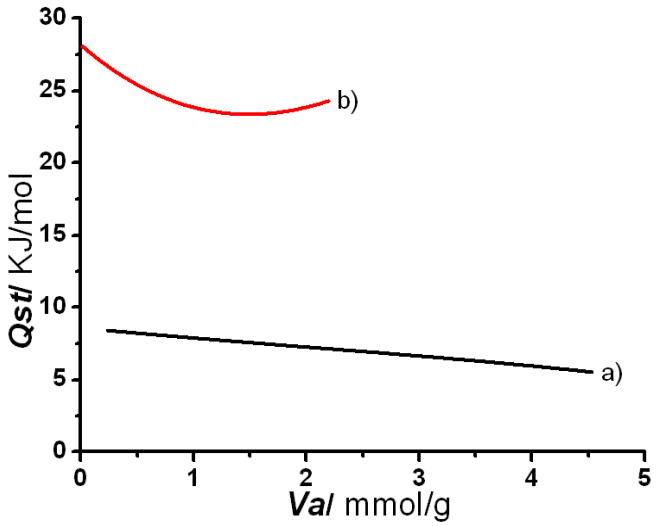

Figure S10 The isosteric heat of H2 (a) and CO_2 (b) adsorption for **1-ht** estimated by the virial equation.

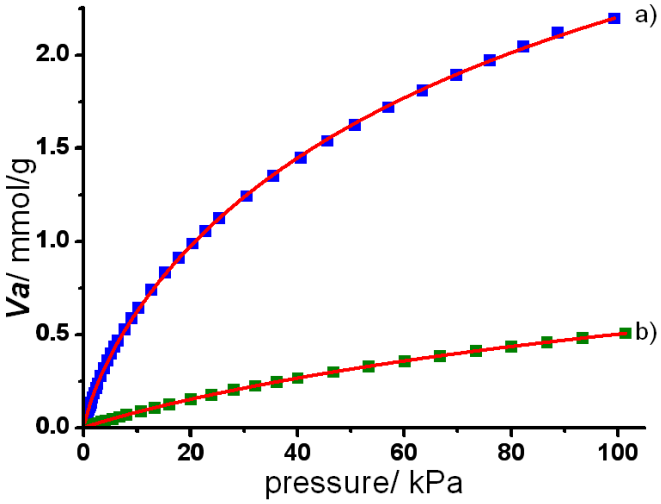

Figure 11 Adsorption isotherms for CO_2 (a) and CH_4 (b) in **1-ht** at 273 K. Solid lines through the experimental data are fits to the dual-site Langmuir-Freundlich model.