Electronic Supplementary Material (ESI) for CrystEngComm

Supporting Information of:

Direct observation of the formation of micro-cubic porous coordination polymer particles and their size-dependent hydrogen adsorption

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Materials and methods

All the reagents and solvents were commercially available and used as received. The elemental analysis was carried out with a Perkin-Elmer 240C elemental analyzer. The FTIR spectra were recorded from KBr pellets in the range of 4000-400 cm^{-1} on a VECTOR 22 spectrometer. Thermal analyses were performed on a Universal V3.9A TA Instruments from room temperature to 800°C with a heating rate of 10°C/min under flowing nitrogen. ^{1}H NMR spectra were recorded on a Bruker DRX-500 spectrometer at ambient temperature with tetramethylsilane as an internal reference. The powder X-ray diffraction patterns (PXRD) measurements were carried on a Bruker axs D8 Advance 40kV, 40mA for CuK_{α} (θ= 1.5418 Å) with a scan rate of 0.2 s/deg at room temperature. SEM images were obtained on a Hitachi S-4800 field emission scanning electronic microscope, TEM images were obtained on a JEM-2100 transmission electron microscope.

Gas Sorption Measurements

In the gas sorption measurement, Ultra-high-purity grade, N_2 and H_2 were used throughout the adsorption experiments. All of the measured sorption isotherms have been repeated several times to confirm the reproducibility within experimental error.

Low pressure gas sorption measurements: Low-pressure N_2 and H_2 adsorption measurements (up to 1 bar) were performed on Micromeritics ASAP 2020 M+C surface area analyzer. About 90 mg of samples were activated at 140 °C for 30 hours by using the "outgas" function of the surface area analyzer. Helium was used for the estimation of the dead volume, assuming that it is not adsorbed at any of the studied temperatures. To provide high accuracy and precision in determining P/P_0, the saturation pressure P_0 was measured throughout the N_2 analyses by means of a dedicated saturation pressure transducer, which allowed us to monitor the vapor pressure for each data point. A part of the N_2 sorption isotherm in the P/P_0 range 0. 05–0.25 was fitted to the BET equation to estimate the BET surface area and the Langmuir surface area calculation was performed using all data points. The pore size distribution was obtained from the H-K method in the Micromeritics ASAP2020 software package based on the N_2 sorption at 77K.

High pressure gravimetric gas sorption measurements: High pressure adsorptions of H_2 were measured using an IGA-003 gravimetric adsorption instrument (Hiden-Isochema, UK) over a pressure range of 0-20 bar at 77 K (liquid nitrogen bath).

Synthesis and general characterizations

The ligand (H_2L) and NJU-Bai1 were synthesized according to our previous paper [1].

For H_2L: Anal. Calcd. $C_{15}H_{11}NO_5$: C, 63.16; H, 3.89; N, 4.91%. Found: C, 63.12; H, 3.90; N, 4.89%. m.p.: >330℃. IR(KBr, pellet, cm^{-1}): 3317(s), 1686 (s), 1646 (s), 1606 (s), 1572 (s), 1522(s) 1426(s), 1293(w), 1175(s), 935(s), 876(s), 783(s), 695(s), 555(s), 528(s). ^1H NMR (400 MHz, MeOD): d = 7.952 (m, 4H), 8.075 (m, 4H), 10.690(s, 1H).

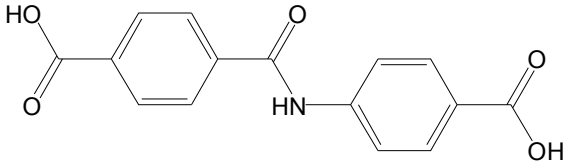

Fig. S1 The structure of H_2L

For NJU-Bai1: a mixture of H_2L(20mg, 0.07mmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (62mg, 0.21mmol) was suspended in 2ml DMF and heated in a sealed vial (20ml) at 80°C for 48h, then cooled to room temperature. Colorless cubic crystals were collected. Yield: 42.1%. The evacuated NJU-Bai1 was formulated as $C_{45}H_{27}N_3O_{16}Zn_4$: C, 47.95; H, 2.41; N, 3.73%. Found: C, 47.32; H, 2.11; N, 3.91%. IR (cm^{-1}): 3377 (s), 1662 (s), 1602(m), 1521 (s), 1397 (m), 1321 (s), 1179 (w), 1106(w), 782(s), 625(s).

For m-NJU-Bai1: a mixture of H_2L(1.67mg, 0.0058mmol) $Zn(NO_3)_2 \cdot 6H_2O$(5.33mg, 0.0197mmol) was suspended in 75ml DMF and heated in a sealed vial (100ml) at 110°C for 7h, then cooled to room temperature. Collected the white sample and washed with DMF three times. Yield: 0.77mg, 29.5%. The result of evacuated m-NJU-Bai1 also was formulated as $C_{45}H_{27}N_3O_{16}Zn_4$: C, 47.95; H, 2.41; N, 3.73%. Found: C, 47.52; H, 2.77; N, 3.51%. IR (cm^{-1}): 3377 (s), 1662 (s), 1602(s), 1521 (m), 1397 (m), 1321 (s), 1179 (w), 1106(w), 782(s), 625(s).

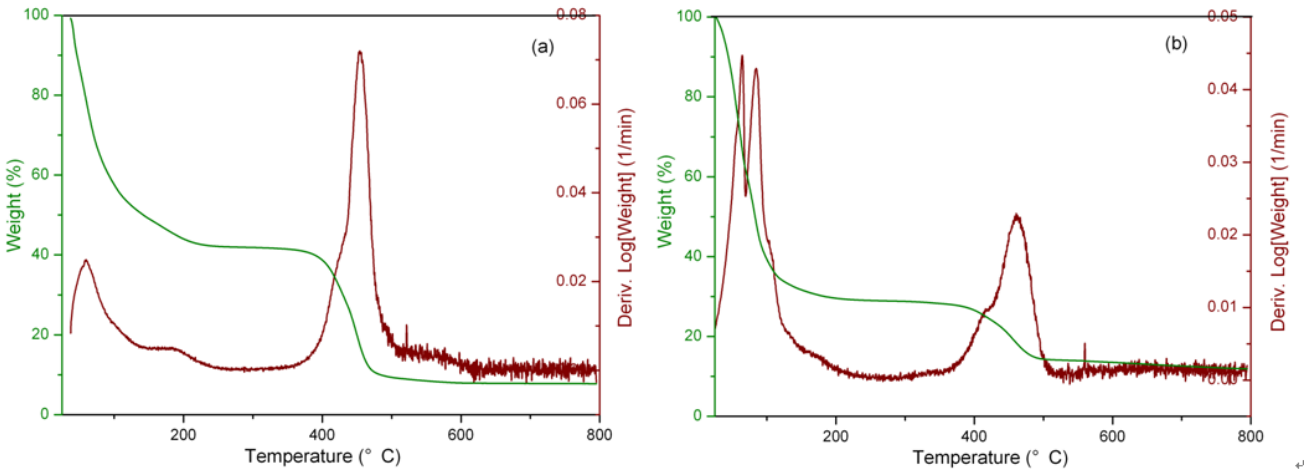

Fig. S2 TG and DSC curves of NJU-Bai1 (a) and m-NJU-Bai1 (b).

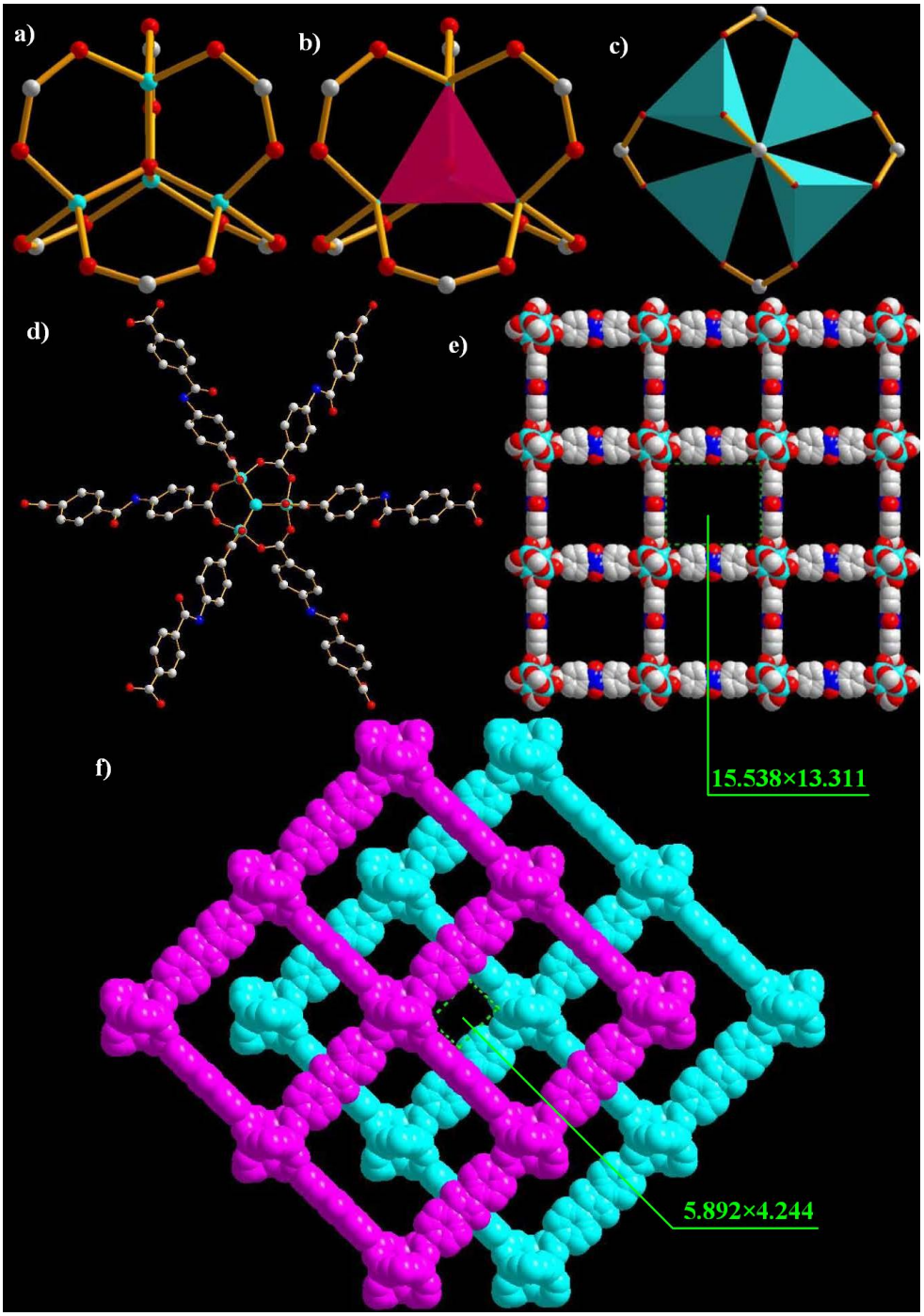

Fig. S3 The structure information of NJU-Bai1: a), b) and c) show the Zn_4O cluster; d) each cluster connects six ligands; e) the framework with large open pore; f) the interpenetrated framework.

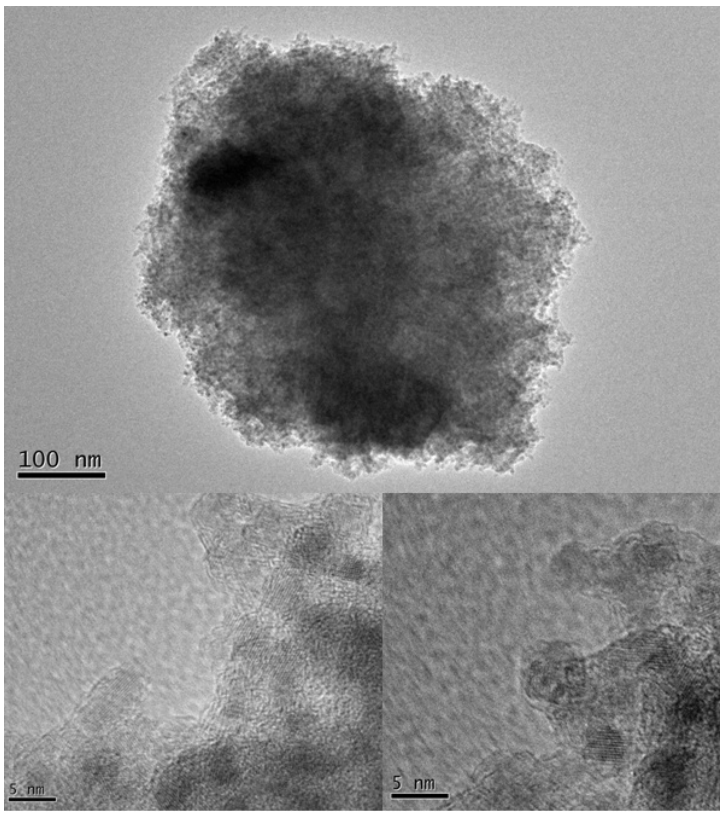

Fig. S4 The TEM images of m-NJU-Bai1 show rich meso-pores in the inner of the cubic particles.

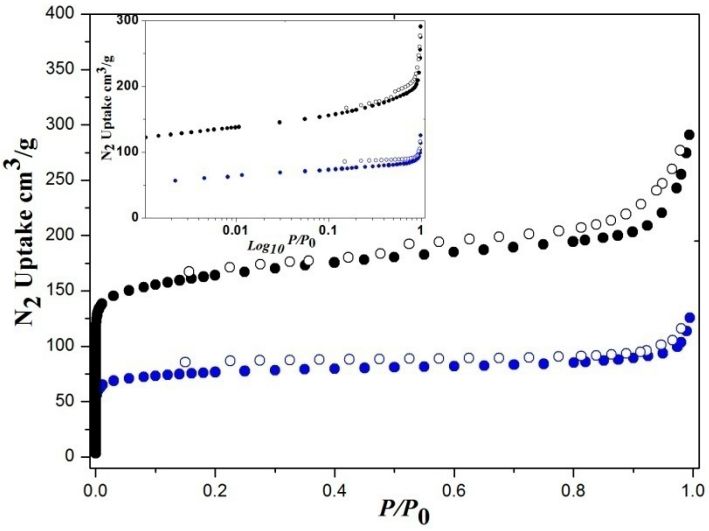

Fig. S5 N_2 adsorption isotherm of NJU-Bai1 (black) and m-NJU-Bai1 (blue), the insert picture shows the adsorption isotherms with logarithmic scale of relative pressure (filled markers represent adsorption points; open markers represent desorption).

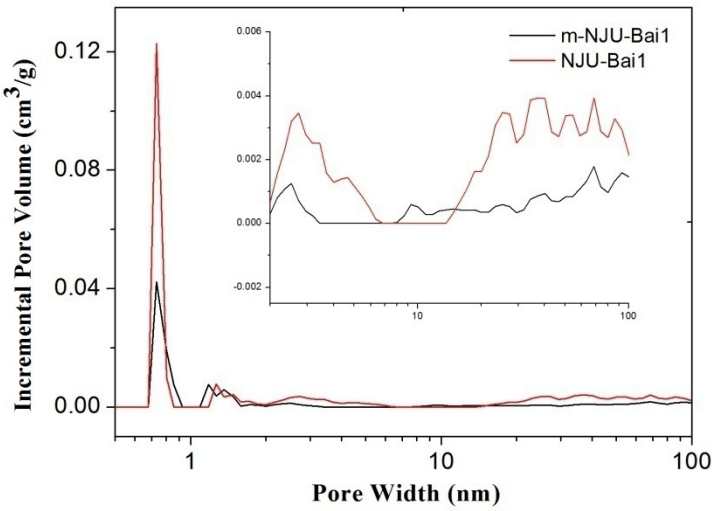

Fig. S6 The calculated pore size distributions of m-NJU-Bai1 and NJU-Bai1.

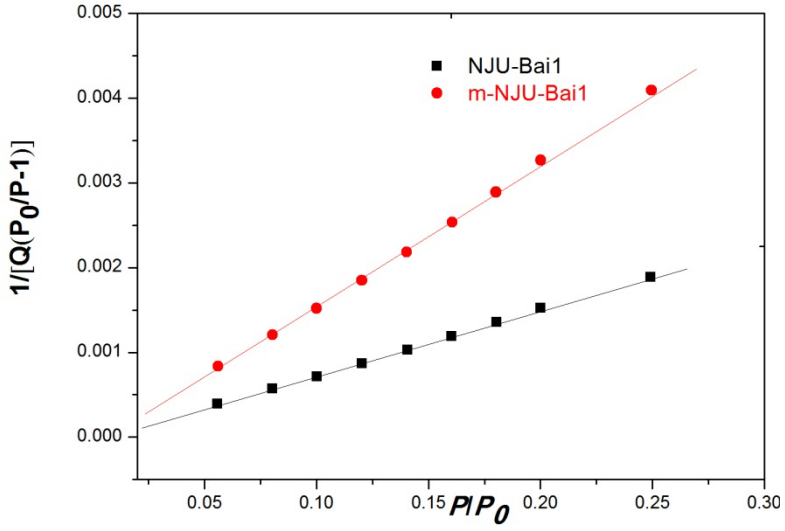

Fig S7. The BET plot calculated from N_2 isotherms of NJU-Bai1 and m-NJU-Bai1.

Reference

1. **J. G. Duan, J. F. Bai, B. S. Zheng, Y. Z. Li and W. C. Ren, *Chem. Commun.*, 2011, 47, 2556.**