Electronic Supplementary Information (ESI)

Two solvent-dependent porous coordination polymers with -OH decorated ligand: unusual non-crystallographic net and fsh topology

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General Information: All the reagents and solvents were commercially available and used as received. The IRspectrawere recorded in the range of 4000-400 cm^{-1} on a Nicolet ID5 ATR spectrometer. Thermal analyses were performed on a Rigaku TG8120 instrument from room temperature to 600 °C at a heating rate of 5 °C/min under flowing nitrogen. Powder X-ray diffraction was obtained using a Rigaku RINT powder diffractometer with Cu Kα anode. Magnetic susceptibility measurements were performed using a Quantum Design SQUID VSM magnetometer.

Synthesis of H_6L ligand: 5-Acetyl-2-hydroxy-benzoic acid methyl ester (1 g, 5.15 mmol) was dissolved in 40ml ethanol, cooled to 0 °C. 6 ml of $SiCl_4$ was added slowly accompanied by the rapid stirring, and the temperature was kept under 0°C. After the addition was completed, it is kept on stirring under room temperature for overnight. The powder was filtered and washed three times by ethanol (20ml×3). 2 with very high yield was obtained. ^{1}H NMR ($CHCl_3$) δ : 8. 138 (s, 3H), 7.791 (s, 3H), 7.625 (s, 3H), 7.123 (s, 3H), 4.864 (s, 3H), 3.995 (s, 6H).

To a stirring solution of 2 (0.9 g, 1.7 mmol) in THF/MeOH (45/25 mL), NaOH (1.2 g) in 60 mL water was added. The resulting mixture was refluxed overnight. After removal of the solvents, the residue was dissolved in water and filtered. The aqueous solution was acidified to pH = 2 using HCl (15% aqueous solution). The resulting precipitate was collected via filtration, washed with H_2O (100 mL), and dried under high vacuum to afford H_6L ligand as a white solid. ^{1}H NMR (DMSO-d^6) δ : 8.168 (s, 3H), 8.02 (s, 3H), 7.74 (d, 3H), 7.10 (d, 3H); ^{13}C NMR (DMSO-d^6): δ 113.351, 117.778, 123.135, 128.414, 131.205, 134.523, 140.624, 160.804, 171.813. MS (calc.) m/z = 487 ($[M-H]^+$) (Fig. S2-4).

Synthesis of $[Cu_6(L)_4\cdot(H_2O)_6]\cdot10DMA\cdot4EtOH$, (**1**) : $Cu(NO_3)_2\cdot6H_2O$ (16 mg) and H_6L (8 mg) were mixed with 2 ml of DMA/EtOH (4:2) in a glass container and tightly capped with a Teflon vial and heated at 65 °C for two days. After cooling to room temperature, green crystals were obtained. Yield: 63% (based on ligand).The EA for **1'**: Anal. Calcd. $C_{108}H_{60}Cu_6O_{36}$: C, 56.04; H, 2.61% Found: C, 55.81; H, 2.72%.

Synthesis of $[Cu_5(L)_2(OH)_2\cdot(H_2O)_2\cdot DMA_2]\cdot2DMA\cdot EtOH\cdot2H_2O$ (**2**) : $Cu(NO_3)_2\cdot6H_2O$ (16 mg) and H_6L (8 mg) were mixed with 2 ml of DMA/EtOH/H_2O (4:2:0.5) in a glass container and tightly capped with a Teflon vial and heated at 65 °C for two days. After cooling to room temperature, green crystals were obtained. Yield: 46% (based on ligand). EA for **2'**:Anal. Calcd. $C_{54}H_{34}Cu_5O_{22}$: C, 47.95; H, 2.53% Found: C, 47.58; H, 2.65%.

Single crystal X-ray study: The single crystal X-ray diffraction measurement was performed at 223 K with a Rigaku AFC10 diffractometer with Rigaku Saturn Kappa CCD system equipped with a MicroMax-007 HF/VariMax rotating-anode X-ray generator with confocal monochromated MoKα radiation. Data were processed using Crystal Clear TM-SM (Version 1.4.0). The structure was solved by direct methods and refined using the full-matrix least squares technique using the SHELXTL package.[33] Nonhydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Organic hydrogen atoms were placed in calculated positions with isotropic displacement parameters set to 1.2Ueq of the attached atom. The unit cell includes a large region of disordered solvent molecules, which could not be modeled as discrete atomic sites. We employed PLATON/SQUEEZE to calculate the diffraction contribution of the solvent molecules and, thereby, to produce a set of solvent-free diffraction intensities; the structure was then refined again using the data generated. In these two heavy-atom structures as it was not possible to see clear electron-density peaks in difference maps which would correspond with acceptable locations for the various H atoms bonded to water oxygen atoms, the refinements were completed with no allowance for these water H atoms in the models. CCDC number: 1023464-1023465.

Table S1. Crystal data and structure refinement of **1** and **2**

	1	**2**
Empirical formula	$C_{154}H_{182}Cu_6O_{18}N_{10}$	$C_{71}H_{78}Cu_5O_{30}N_4$
Formula weight	3448.78	1768.81
Crystal system	Triclinic	Triclinic
Space group	*P-1*	*P-1*
Unit cell dimensions	a = 22.777(5) Å b = 25.033(5) Å c = 25.074(5) Å α = 119.76(3) ° β = 93.50(3) ° γ= 92.99(3) °	a = 12.079(2) Å b = 12.382(3) Å c = 12.568(3) Å α = 99.99(3) ° β = 96.00(3) ° γ= 91.29(3) °
Volume	12331(4) Å^3	1839.5(7)Å^3
Z	2	1
Density (calculated)	0.913 g/cm^3	1.596 g/cm^3
Mu(MoKa)	0.547 mm^{-1}	1.493 mm^{-1}
F(000)	3660	916
Index ranges	-26<=h<=26 -29<=k<=28 -24<=l<=29	-14<=h<=14 -14<=k<=11 -14<=l<=14
Tot., Uniq. Data, R(int)	63655, 36795, 0.057	12526, 6363, 0.065
Observed data [I > 2σ (I)]	20944	4193
Nref, Npar	36795, 1417	6363, 418
R_1, wR_2, S	0.0975, 0.2959, 1.04	0.0976, 0.3022, 1.05
Max Shift	0	0

$R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma[w(|F_o|^4)]\}^{1/2}$ and $w = 1/[\sigma^2(F_o^2) + (0.1452P)^2]$ where $P = (F_o^2+2F_c^2)/3$

Adsorption Experiments: Before the measurement, the solvent-exchanged sample (about 100 mg) was prepared by immersing the as-synthesized samples in methanol for 3 days to remove the nonvolatile solvents, and the extract was decanted every 8 h and fresh methanol was replaced. The completely activated sample was obtained by heating the solvent-exchanged sample at 120 °C under a dynamic high vacuum for 30 h. In the gas sorption measurement, ultra-high-purity grade were used throughout the adsorption experiments. Gas adsorption isotherms were obtained using a Belsorp-mini volumetric adsorption instrument from BEL Japan Inc. using the volumetric technique.

Selectivity Prediction for Binary Mixture Adsorption: Ideal adsorbed solution theory (IAST) of Myers and Prausnitz was used to predict binary mixture adsorption from the experimental pure-gas isotherms. To perform the integrations required by IAST, the single-component isotherms should be fitted by a proper model.There is no restriction on the choice of the model to fit the adsorption isotherms, however, data over the pressure range under study should be fitted very precisely. Several isotherm models were tested to fit the experimental pure isotherms for CH_4 and CO_2 of **2'**, and the dual-site Langmuir-Freundlich equation were found to the best fit to the experimental data:

$$q = q_{m1} \cdot \frac{b_1 \cdot P^{1/n_1}}{1 + b_1 \cdot P^{1/n_1}} + q_{m2} \cdot \frac{b_2 \cdot P^{1/n_2}}{1 + b_2 \cdot P^{1/n_2}}$$

Here, P is the pressure of the bulk gas at equilibrium with the adsorbed phase (kPa), q is the adsorbed amount per mass of adsorbent (mol/kg), q_{m1} and q_{m2} are the saturation capacities of sites 1 and 2 (mol/kg), b_1 and b_2 are the affinity coefficients of the sites (1/kPa), and n_1 and n_2 are measures of the deviations from an ideal homogeneous surface. Fig.4 shows that the dual-site Langmuir-Freundlich equation fits the single-component isotherms extremely well. The R_2 values for all of the fitted isotherms were over 0.9998. Hence, the fitted isotherm parameters were applied to perform the integrations in IAST.

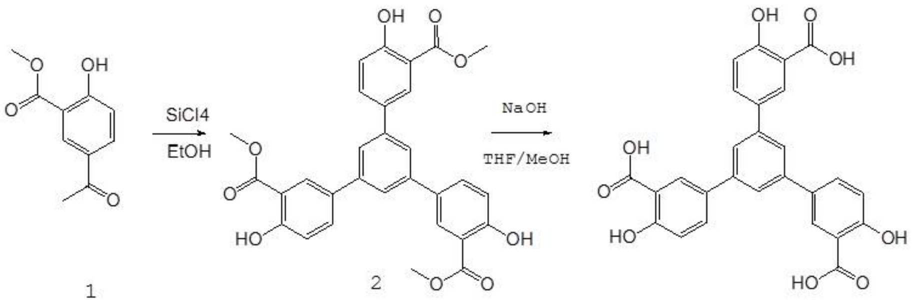


Fig. S1 Route for synthesis of the ligand

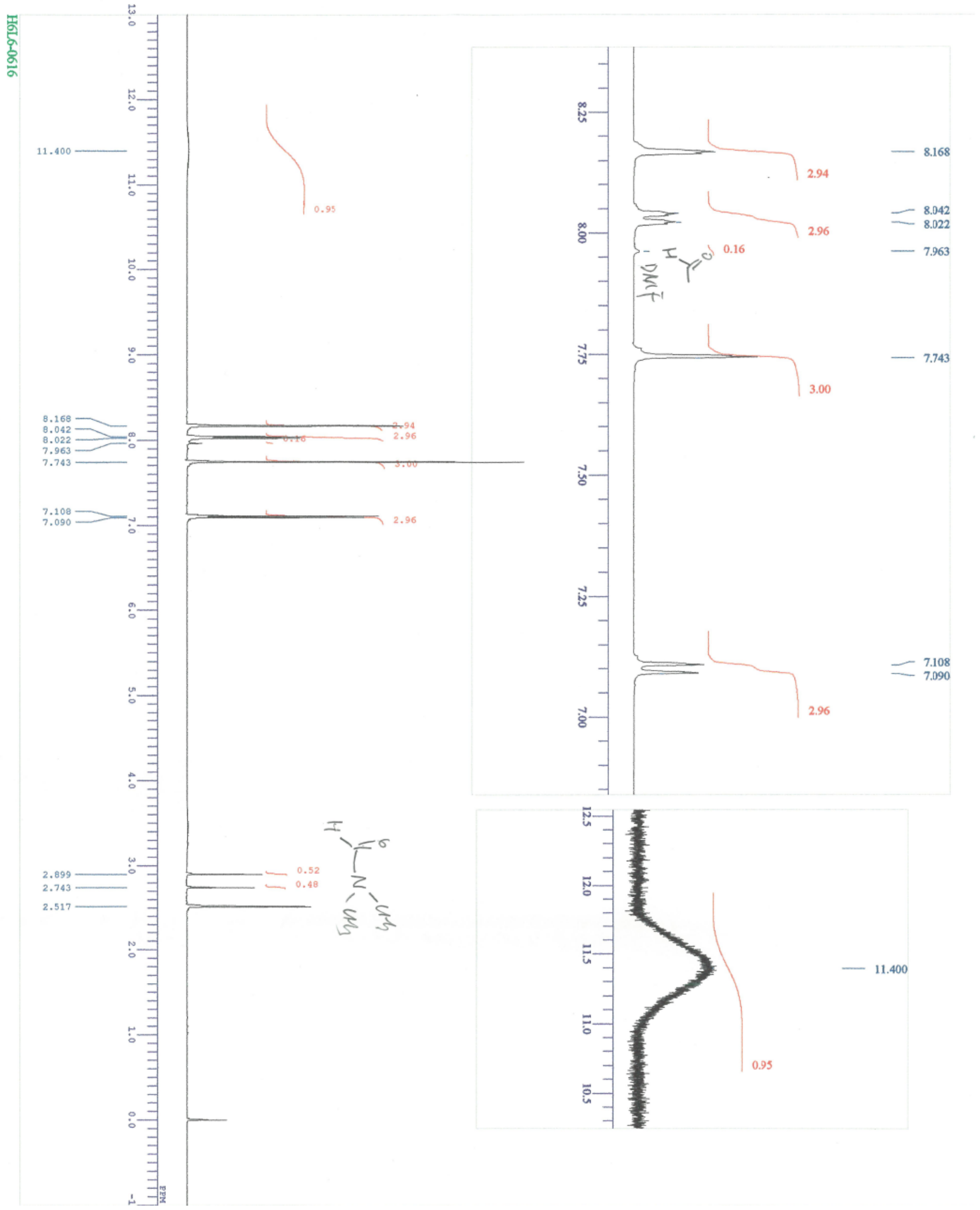


Fig. S2 The H^1 NMR of H_6L ligand

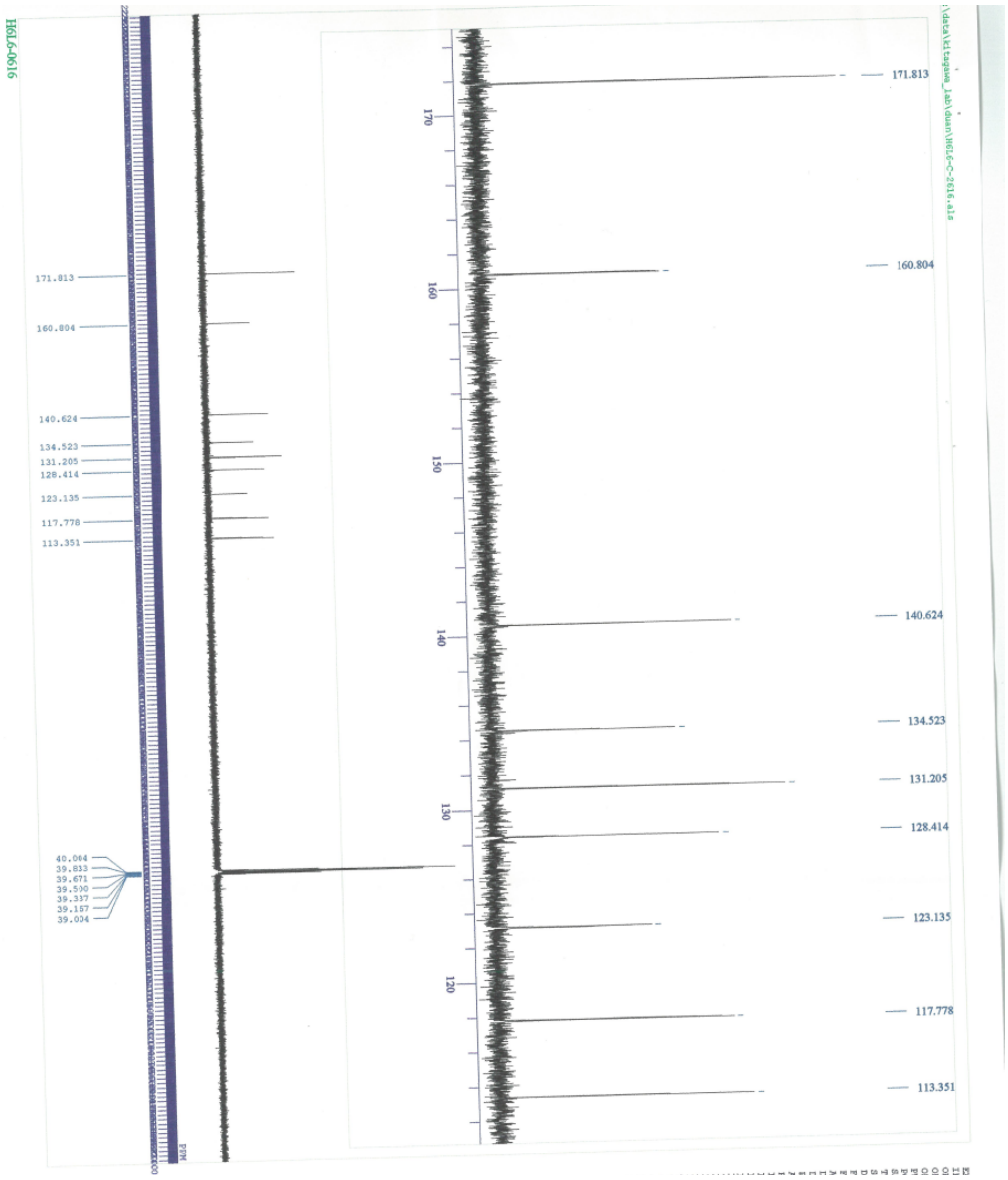


Fig. S3 The C^{13} NMR of H_6L ligand

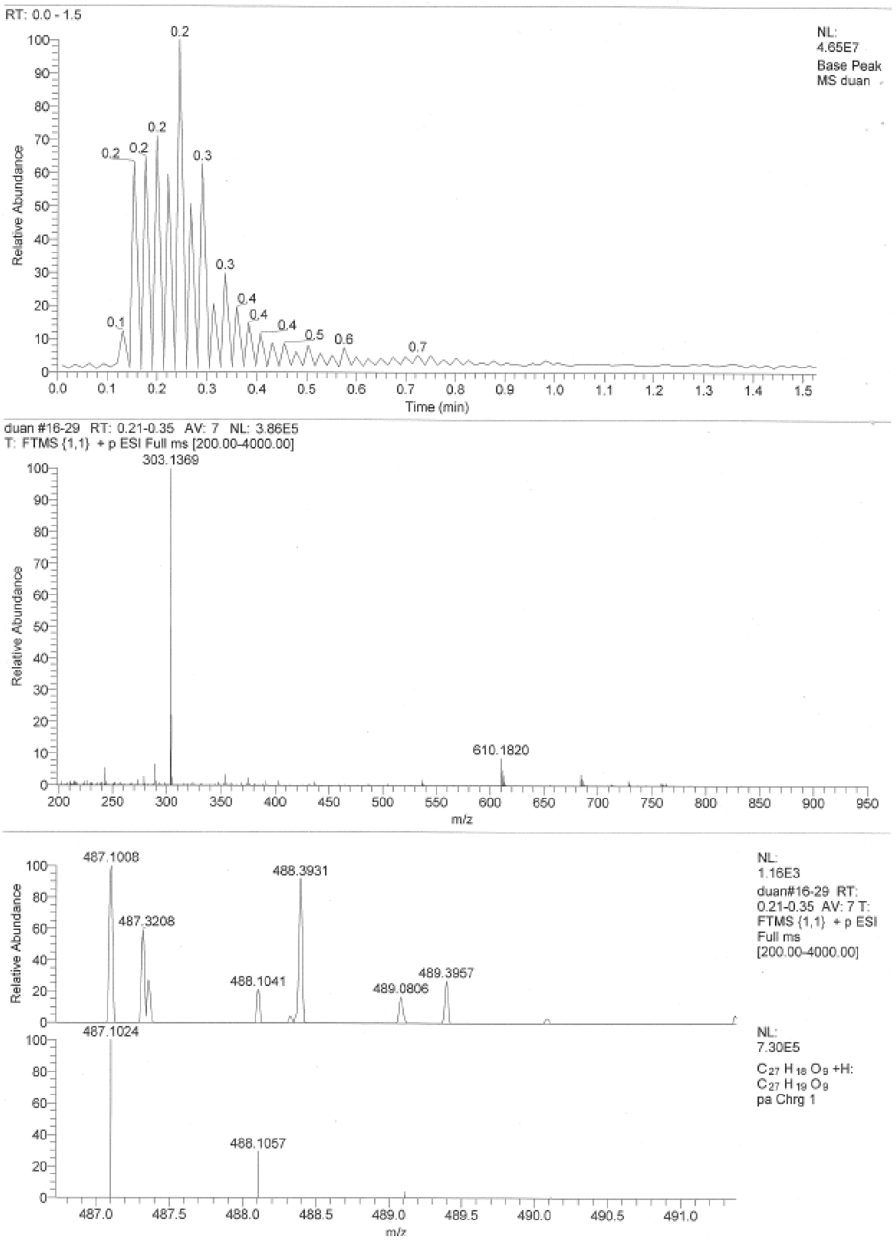


Fig. S4 The mass spetra of H_6L ligand

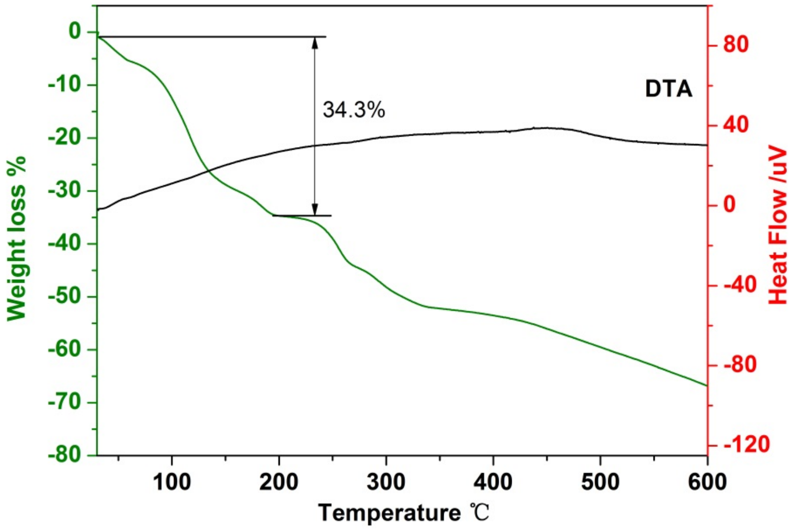


Fig. S5 TG and DTA of compound **1**: Before 190℃, the TG curve shows that the weight loss is 34.3% that coincides with the value of 33.5%, calculated for the loss of ten DMA moleculesand four EtOH molecules. Then, the continued weight loss corresponds to the decomposition of the ligands, and the final solid product at maybe CuO.

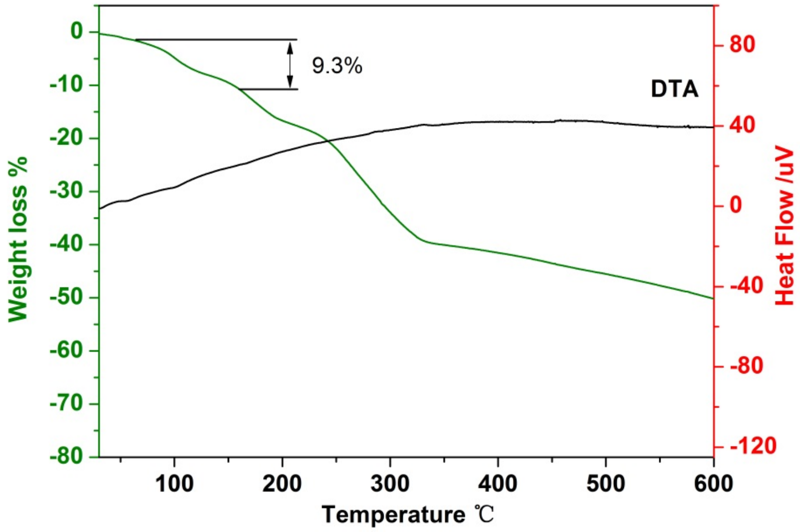


Fig. S6 TG and DTA of compound **2**: Before 200℃, the TG curve shows that the weight loss is 9.3% that coincides with the value of 8.9%, calculated for the loss of two DMA molecules, two H_2O molecules and one EtOH molecule. Then, the continued weight loss corresponds to the decomposition of the ligands, and the final solid product at maybe CuO.

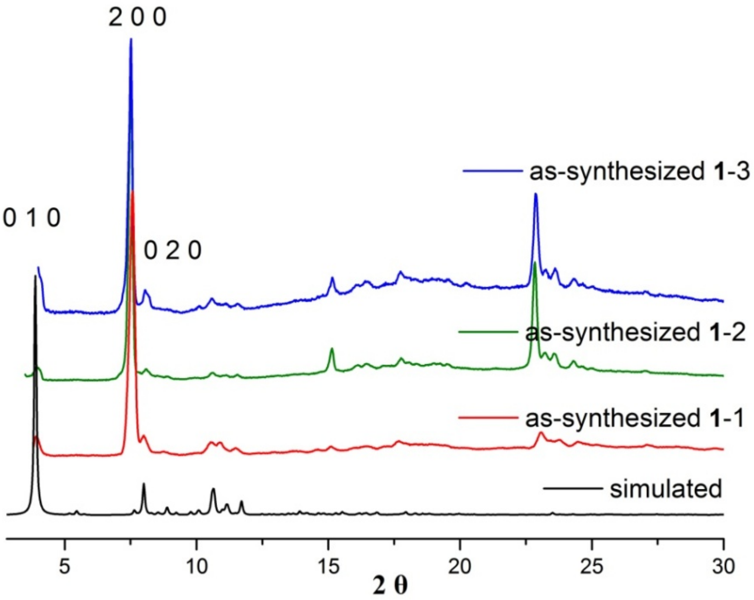


Fig. S7 PXRD patterns of **1.** We re-checked the PXRD for as-synthesized **1** for three times by different machines.

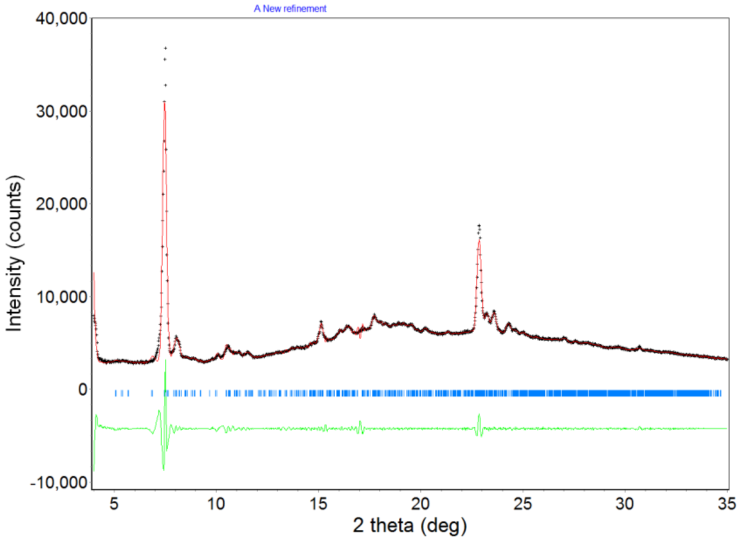


Fig. S8 The results of Le Bail analysis for the PXRD of **1**. Refined parameters and reliability factors are as follows: a = 22.9441 Å, b = 25.0816Å, c = 25.0861Å; α = 119.9474°, β = 93.8603°, γ = 93.0705°; R_p = 0.0252 and R_{wp} = 0.0553.

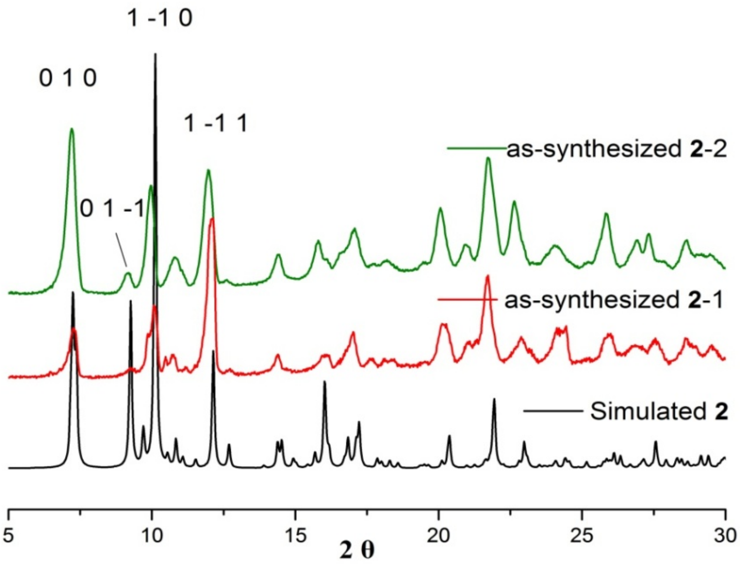


Fig. S9 PXRD patterns of **2.** We re-checked the PXRD for as-synthesized **2** for two times by different machines. The experimental results matched very well with the simulated pattern.

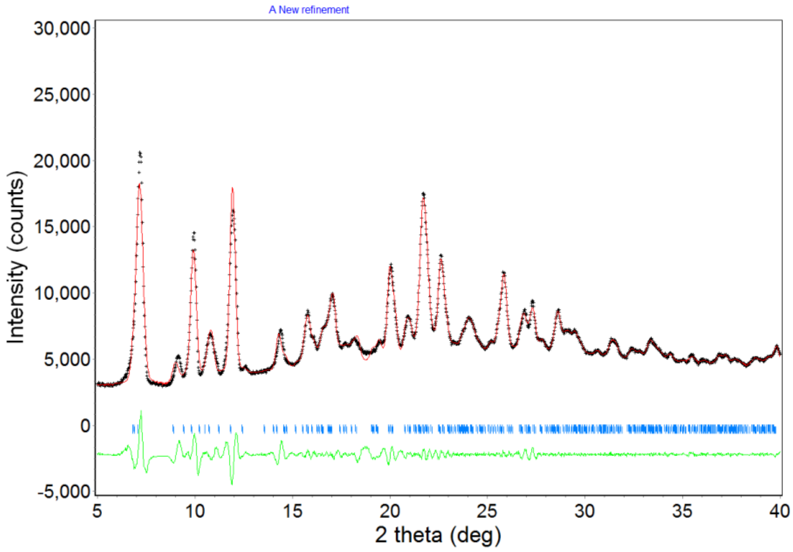


Fig. S10 The results of Le Bail analysis for the PXRD of **2**. Refined parameters and reliability factors are as follows:a = 11.9635 Å, b = 12.3952Å,c = 12.5843Å; α = 100.0544°, β = 95.6577°, γ = 91.1685°; R_p = 0.0293 and R_{wp} = 0.0495.

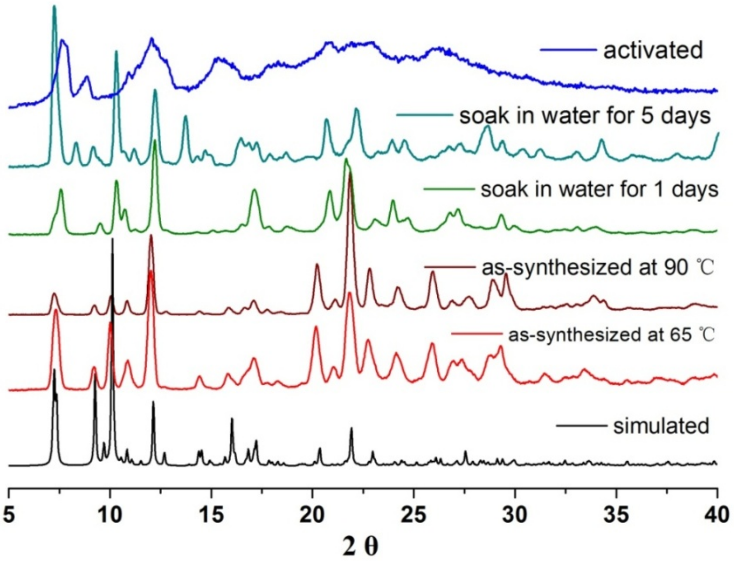


Fig. S11 PXRD patterns of **2**

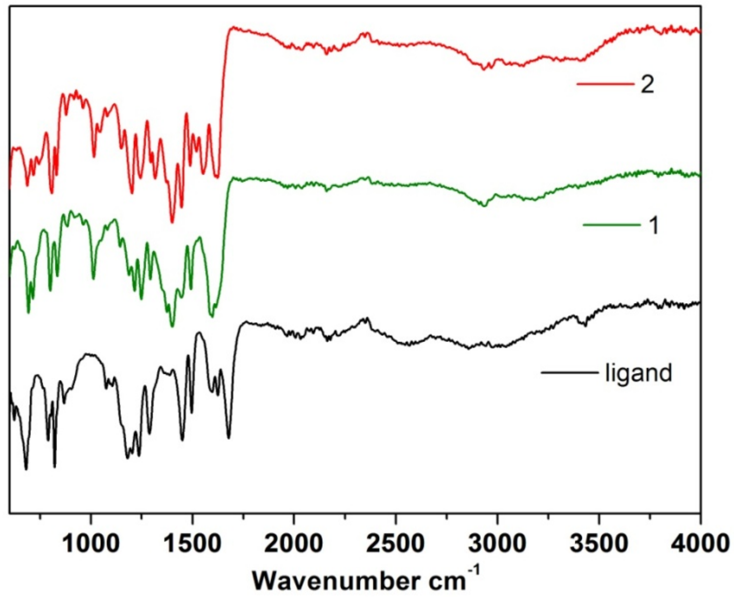
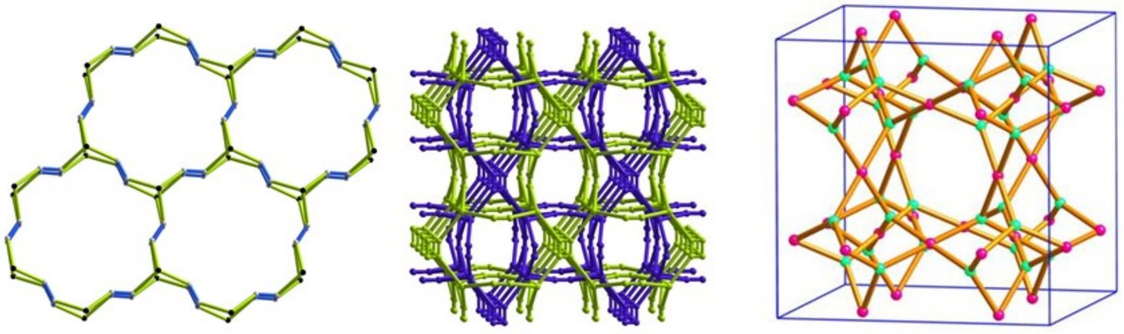


Fig. S12 Infrared spectra of the ligand, as-synthesized **1** and **2**



topology of 1 | **pto** topology of MOF-14 | **tbo** topology of HKUST-1

Fig. S13 The comparsion of 3, 4- connected framework of **1**, MOF-14 and HKUST-1.

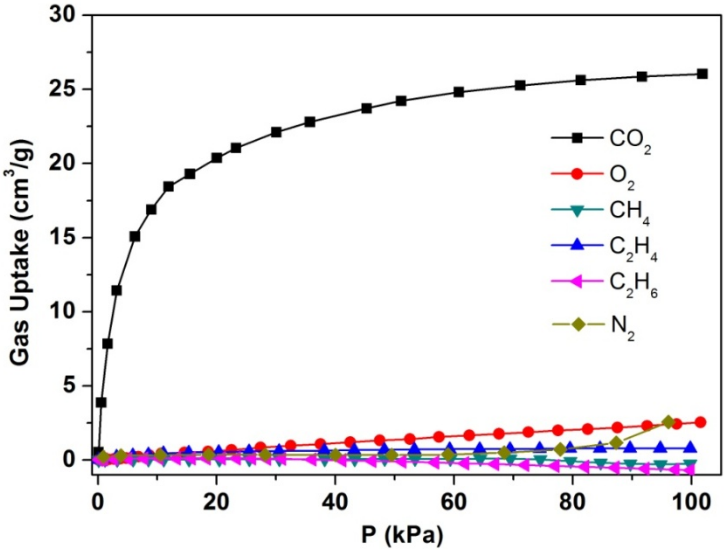


Fig. S14 Series adsorption isotherms of **2’** at low temperature (N_2: 77 K, others at 195 K).

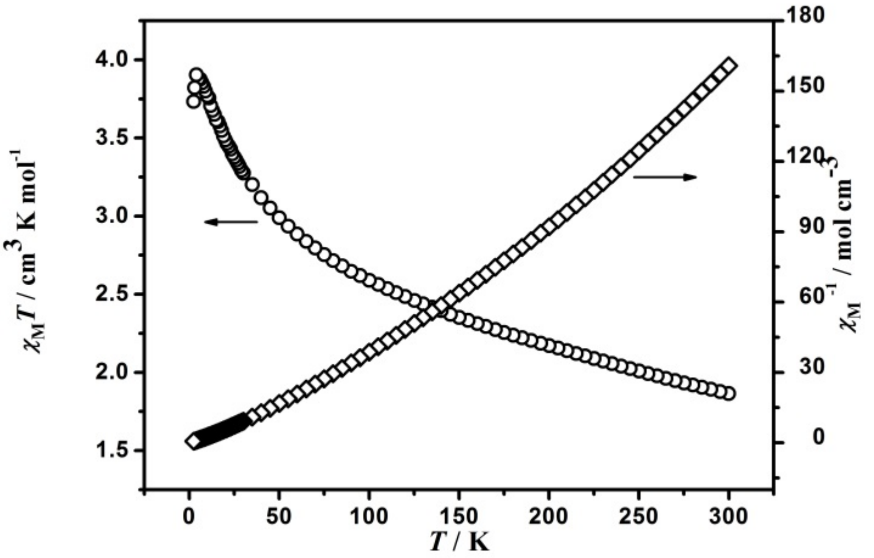


Fig. S15 Temperature dependence of $\chi_M T$ and $\chi_M^{-1}$for **2**: Variable temperature magnetic susceptibility measurements for complex**2** were measured on polycrystalline samples with the temperature range of 1.8-300K and an applied magnetic field of 1kOe.The $\chi_M T$ and χ_M^{-1} vs. T plot is shown in FigureS15. The value of $\chi_M T$ of complex **2**at 300 K is 1.88 cm^3*K*mol^{-1}, which is almost same as the expected value of 1.875 cm^{3}Kmol^{-1}for four spin-only Cu(II) ions (S = 1/2, g = 2.0). Upon cooling, $\chi_M T$ increases steadily and reaches 3.90 cm^{3}Kmol^{-1} at 5.7 K, indicating that possible ferromagnetic coupling interactions may be dominant between the Cu(II) ions. Below this temperature, the value of $\chi_M T$ falls rapidly to 3.73 cm^{3}Kmol^{-1} at 2.4 K, which may be attributed to the weak inter-molecular antiferromagnetic interactions and/or zero-field splitting.