Electronic Supporting Information (ESI)

A Highly Porous *agw*-type Metal-Organic Framework and Its CO_2 and H_2 Adsorption Capacity

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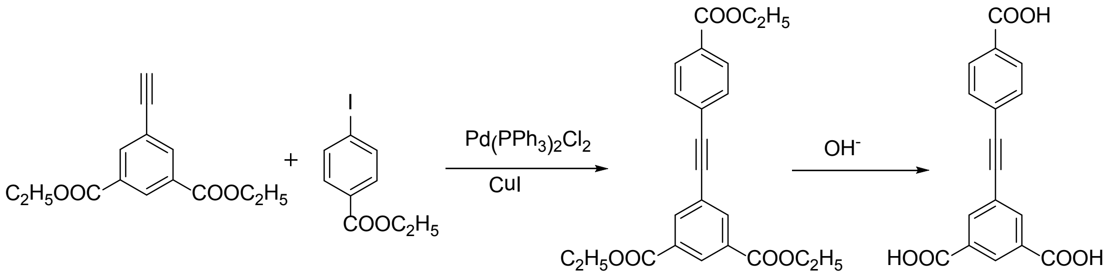
1. Materials and General methods.

All chemical reagents were obtained from commercial sources and, unless otherwise noted, were used as received without further purification. Elemental analyses (C, H) were performed on a Perkin-Elmer 240 analyzer. ^{1}H NMR spectra were recorded on a Bruker DRX-500 spectrometer with tetramethylsilane as an internal reference. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 ADVANCE X-ray diffractometer with Cu Kα radiation.



2. Synthesis of H_3CPEIP (5-((4-carboxyphenyl) ethynyl) isophthalic acid)

Into a flask flushed with N_2, ethyl-4-iodobenzoate (2.47 g, 8.95 mmol), $Pd(PPh_3)_2Cl_2$ (168.5 mg, 0.24 mmol) and CuI (77.4 mg, 0.41 mmol) were added to a solution of tetrahydrofuran (40 mL) and Et_3N (40 mL). After stirring for half an hour, diethyl-5-ethynylbenzoate (2 g, 8.13 mmol) was added. Then the solution was stirring at room temperature overnight. The resultant mixture was evaporated to dryness and taken up in CH_2Cl_2 which had been dried over $MgSO_4$. The volatiles were removed by evaporation under reduced pressure, and then the solid residue was recrystallized in ethyl acetate and finally dried in a vacuum oven at 40 °C. Yield = 2.01 g (62.8%).

The product was then dissolved in THF/H_2O (v/v= 1:1, 80 mL), and KOH (4.14 g, 73.8 mmol) was added with stirring under reflux overnight. The volatiles were removed by evaporation under reduced pressure. The residue dissolved in 100 mL of water was acidified to pH~2-3 using 1.0M HCl and stirred for 3 hours. The white precipitate was separated by filtration, washed with water, and freeze-dried. Yield=1.45g (91.8%). ^{1}H NMR (500 MHz, DMSO-*d*$_6$, δ ppm): 13.52 (s, 3H, COO$\underline{H}$), 8.48 (s, 1H, Ar$\underline{H}$), 8.29 (s, 2H, Ar$\underline{H}$), 8.00 (d, *J*=8 Hz, 2H, Ar$\underline{H}$), 7.76 (d, *J*=8.5 Hz, 2H, Ar$\underline{H}$). MP: > 300 °C. ^{13}C NMR (125 MHz, DMSO-*d*$_6$, δ ppm): 167.1, 166.3, 136.1, 132.6, 132.2, 131.5, 130.6, 126.4, 123.3, 90.5, 90.4. IR (KBr, pellet, cm^{-1}): 3069, 1744, 1686, 1607, 1558, 1444, 1421, 1319, 1280, 1259, 1198, 1154, 1111, 1018, 918, 859, 769, 755, 716, 692, 665.

3. Synthesis of NJU-Bai13

A mixture of $CuCl_2 \cdot 2H_2O$ (30 mg, 0.18 mmol), H_3CPEIP (20 mg, 0.06 mmol), HNO_3 (10 µl, 16 mol/L) and N,N-dimethylacetamide (DMA)/ methanol/ H_2O = 3:3:0.5 (2 mL) was stirred for 10 min in air and sealed in a 20 mL Teflon-lined autoclave, which was heated at 80°C for 72h. After cooling to the room temperature, the blue block crystals were obtained. Yield: 53%. Anal. Calcd (Found) for [C34H14Cu3O15]: C, 47.83; H, 1.64; Found: C, 47.64; H, 1.58. IR (KBr, pellet, cm^{-1}): 3435, 2939, 1609, 1408, 1375, 1259, 1176, 1101, 1016, 860, 777, 727.

4. X-ray Structure Determination

Single crystal suitable for X-ray structure determination were selected and sealed in a capillary under a microscope. The X-ray diffraction intensity data were measured on a Bruker Smart Apex CCD diffractometer at room temperature using graphite monochromated Mo/Kα radiation (λ = 0.71073 Å). Data reduction was made with the Bruker Saint program. The structures were solved by direct methods and refined with full-matrix least squares technique using the SHELXTL package. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms were placed in calculated positions with isotropic displacement parameters set to 1.2 × U_{eq} of the attached atom. The unit cell includes a large region of disordered solvent molecules, which could not be modeled as discrete atomic sites. Crystal data and refinement conditions are shown in Table S1. The crystal data for NJU-Bai13 have been deposited in CSD database, and labeled as 943625. Copies of the data can be obtained, free of charge, on application to the CCDC (e-mail: deposit@ccdc.cam.ac.uk).

Table S1. Crystal data and structure refinement for NJU-Bai13.

Identification code	NJU-Bai13
CCDC number	943625
Empirical formula	C34H14Cu3O15
Formula weight	853.10
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system	Hexagonal
Space group	P63/mmc
a	18.961(4) Å
b	18.961(4) Å
c	50.901(10) Å
α	90°
β	90°
γ	120°
Volume	15848(9) Å^3
Z	6
Density (calculated)	0.536 g cm^{-3}
Absorption coefficient	0.622 mm^{-1}
F(000)	2550
Crystal size	0.3 ×0.28 × 0.09 mm
Theta range for data collection	1.60 to 25.02 °.
Limiting indices	-22<=h<=22, -16<=k<=22, -60<=l<=54
Reflections collected unique	78863 / 5209 [R(int) = 0.1858]
Completeness	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.946 and 0.830
Refinement method	Full-matrix least-squares on F^2
Data /restraints / parameters	5205 / 15 / 135
Goodness-of-fit on F^2	1.037
Final R indices [I>2sigma(I)]	R1 = 0.1028, wR2^a = 0.3510
R indices (all data)	R1 = 0.1701, wR2^a = 0.3943
Largest diff. peak and hole	1.934 and -0.587 e. Å^{-3}

^{a} R1 = $\Sigma||F_o| - |F_c||/|F_o|$; wR2 = $[\Sigma w(\Sigma F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

5. Low-Pressure Gas Sorption Measurements.

The N_2 (99.999 %) adsorption/desorption isotherms were measured volumetrically using a Micromeritics ASAP 2020 surface area and pore size analyzer up to saturated pressure at 77 K. About 200 mg acetone-exchanged samples were charged into a sample tube and activated at 80 °C for 12 hours by using the “outgas” function of the surface area analyzer. The resulting mass of dried material was ~ 140 mg. Helium (99.999 %) was used for the estimation of the free space (dead volume), assuming that it is not adsorbed at any of the studied temperatures. To provide the relative pressure P/P_0 accurately at each data point, the saturation pressure P_0 was monitored and measured throughout the gases analyses by a dedicated saturation pressure transducer. The specific surface areas were determined using the Brunauer-Emmett-Teller (BET) and the Langmuir equation from the N_2 sorption data. When applying the BET theory, we made sure that our analysis satisfies the two consistency criteria as detailed by Walton and co-workers. For the Langmuir surface areas, data from the whole adsorption data were used.

6. High-Pressure Gas Sorption Measurements.

Gravimetric CO_2 (99.995 %), CH_4 (99.999 %) and N_2 (99.999 %) adsorption measurements were performed on an IGA-003 gravimetric adsorption instrument (Hiden-Isochema, UK) over the 0-20 bar range at 273 K and 298 K. Gravimetric H_2 (99.999%) adsorption measurement was performed at 77 K. Prior to sorption measurements, same activation procedures as low-pressure gas sorption measurements were performed with the sample quantities of about 100 mg, and about 70 mg fully desolvated samples were obtained. At each pressure, the sample mass was monitored until equilibrium was reached (within 25 minutes).

7. **Calculating principle of gas loading**

The total adsorption can be calculated from the equation:

$$N_{tot}=N_{exc}+1000\times d_g\times V_{pore} \tag{1}$$

where N_{tot} = total adsorption (mg g^{-1})

N_{exc} = excess adsorption (mg g^{-1})

d_g = density of the compressed gas as a function of temperature and pressure (g cm^{-3})

V_{pore} = pore volume (cm^3 g^{-1})

The density of the compressed gas, d_g, was obtained from the NIST website. The pore volume was measured experimentally from N_2 adsorption isotherm at $P/P_0 = 0.99$ and T = 77 K.

In the manuscript, the wt% gas uptake is defined as:

$$wt\%=\frac{100\times N}{1000+N} \tag{2}$$

where N = excess (or total) adsorption (N_{exc} or N_{tot}, mg g^{-1}) .

The volumetric capacity of the sample was calculated using:

$$C_{vol}=N_{ads}\times d_{dc} \tag{3}$$

where C_{vol} = volumetric adsorption (g L^{-1} or cm^3 cm^{-3})

N_{ads} = quantity of gas adsorbed (mg g^{-1} or cm^3 g^{-1}, if excess adsorption is used then excess volumetric capacity is obtained. If total adsorption is used, then total volumetric capacity is obtained)

d_{dc} = density of the dehydrated crystal (g cm^{-3})

Figure S1.PXRD patterns of as-synthesized complex NJU-Bai13 (red), the simulated (black), and activated (blue).

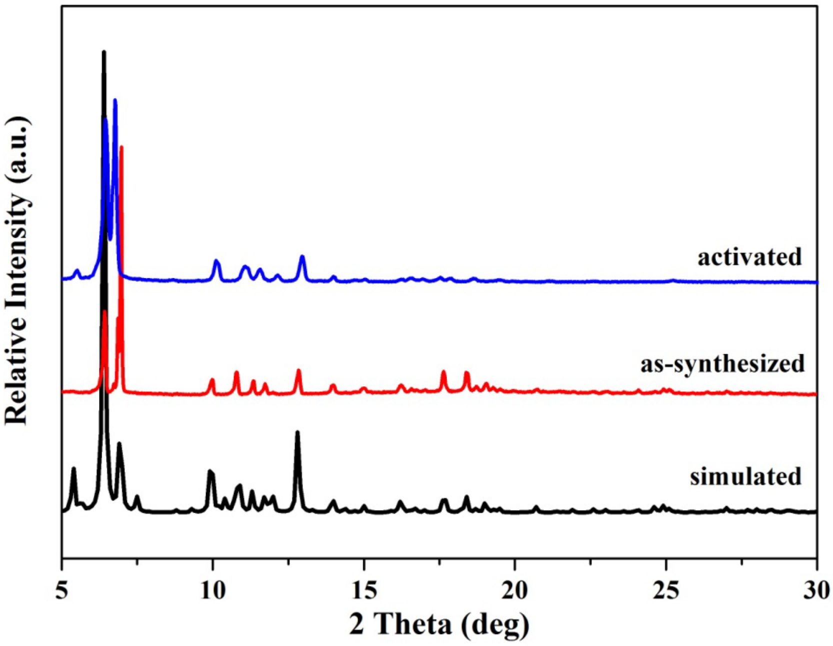


Figure S2. TGA data of as-synthesized sample of NJU-Bai13.

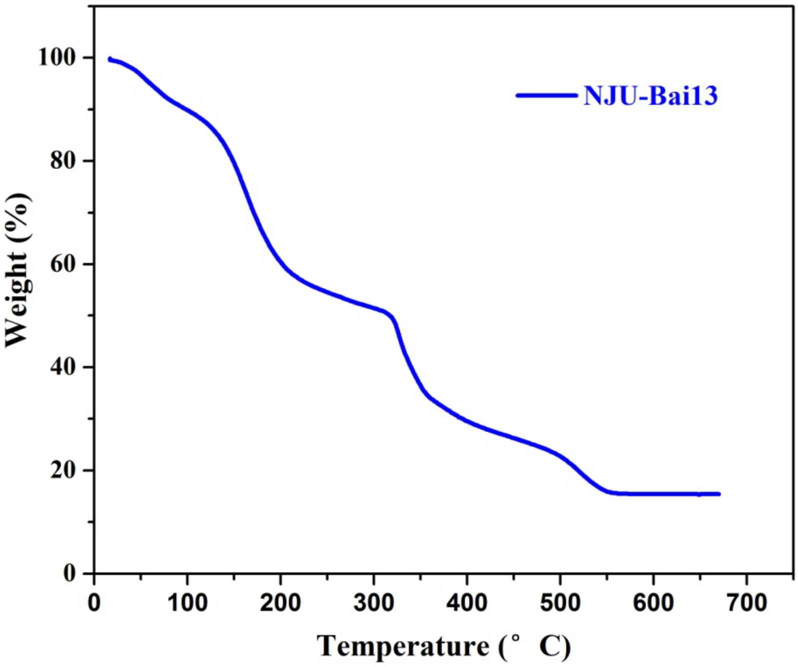


Figure S3. Nitrogen sorption isotherm at 77 K. The N_2-adsorption/desorption isotherms show a typical type I curve demonstrating the existence of microporous structure and physical adsorption mechanism. Adsorption curve (filled circles), desorption curve (open circles).

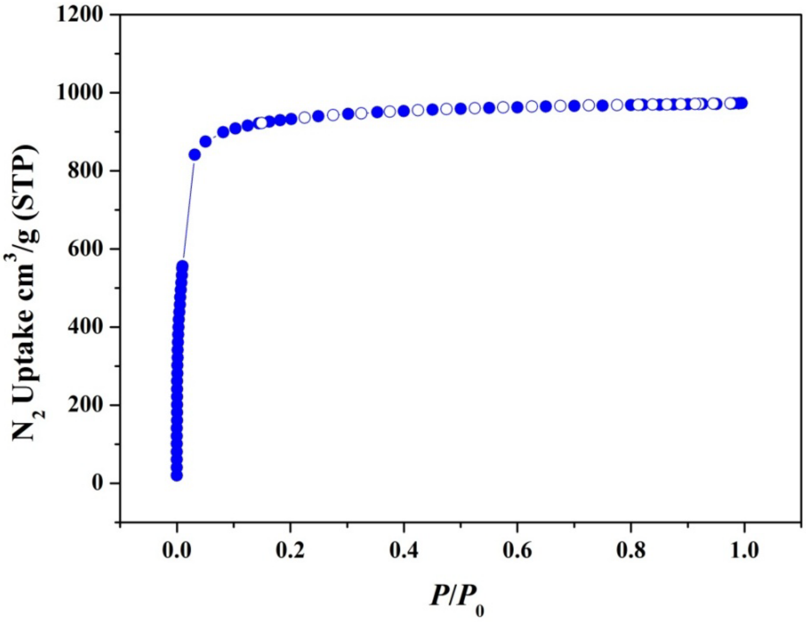


Figure S4. Plot of the linear region for the BET equation, which satisfies the second consistency criteria for application of the BET theory: (1) The pressure range selected should have values of $Q(P_0\text{-}P)$ increasing with P/P_0. (2) The y intercept of the linear region must be positive to yield a meaningful value of the c parameter, which should be greater than zero.

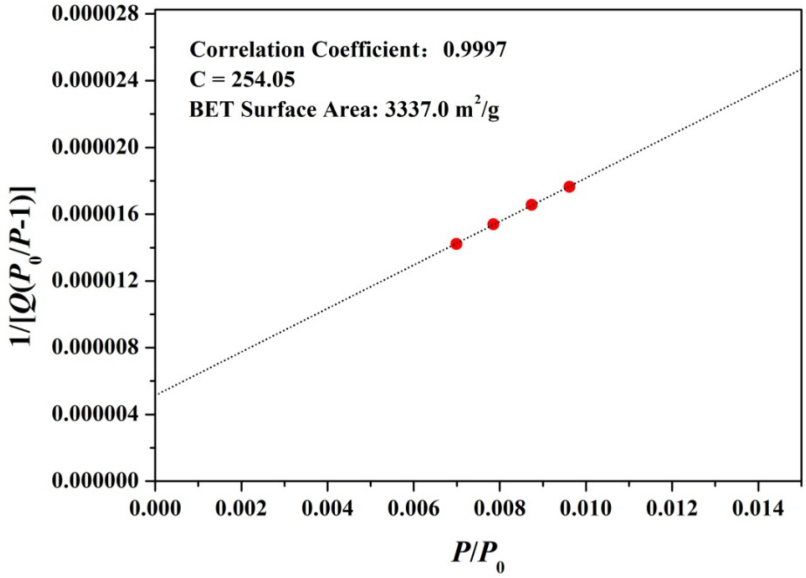


Figure S5. The CO_2 and N_2 isosteric adsorption enthalpies for NJU-Bai13 caculated from the adsorption isotherms at 298 K and 273 K through Virial method.

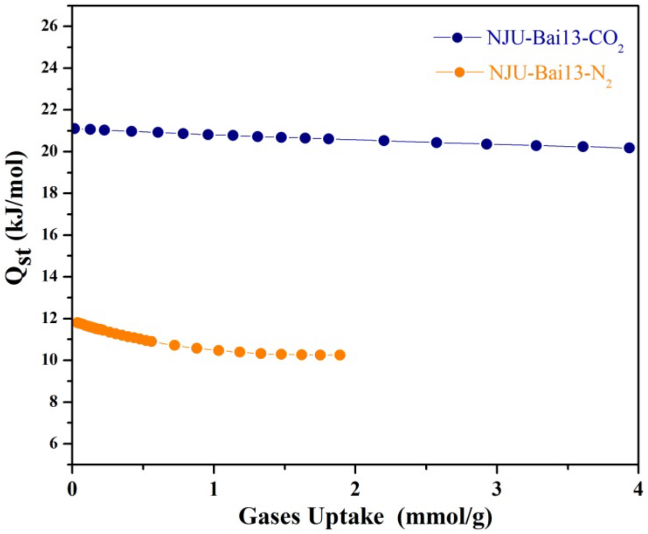


Figure S6. H_2 adsorption isotherms for NJU-Bai13 at 77 K and 87 K at low pressure range (0~1 bar).

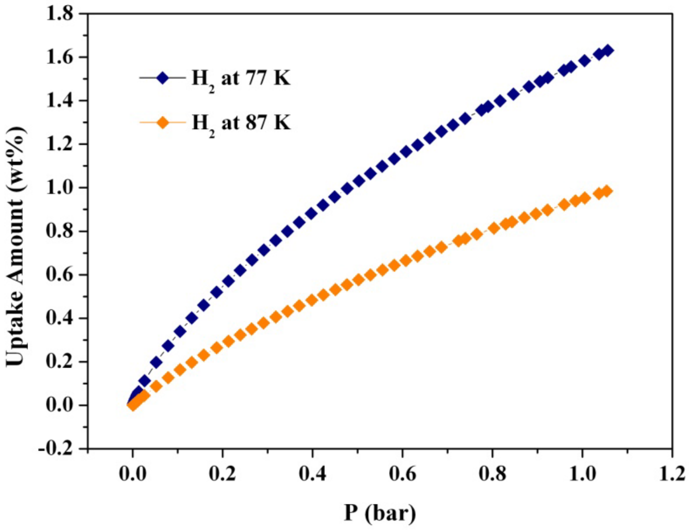


Figure S7. The H_2 isosteric adsorption enthalpy for NJU-Bai13 caculated from the adsorption isotherms at 87 K and 77 K through Virial method.

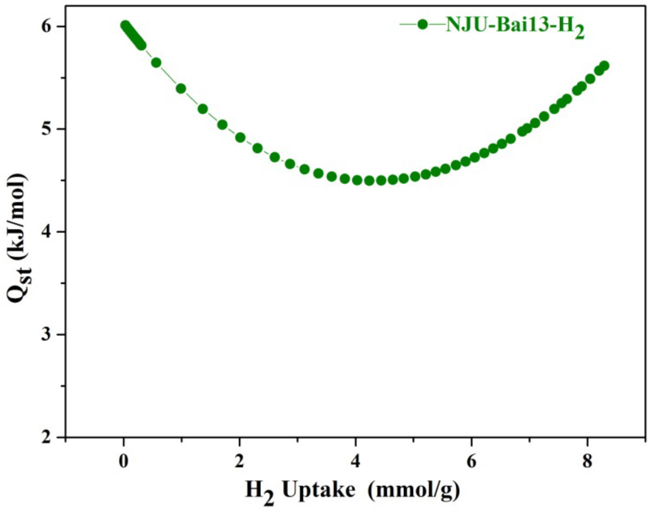


Figure S8. The gases isotherms (red and blue symbols, respectively) and the corresponding virial equation fits (red and blue lines, respectively) for NJU-Bai13. (a-b): CO_2 and N_2 at 273 K and 298 K; (c): H_2 at 77 K and 87 K.