Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

A New NbO Type Metal-Organic Framework for High Acetylene and Methane Storage

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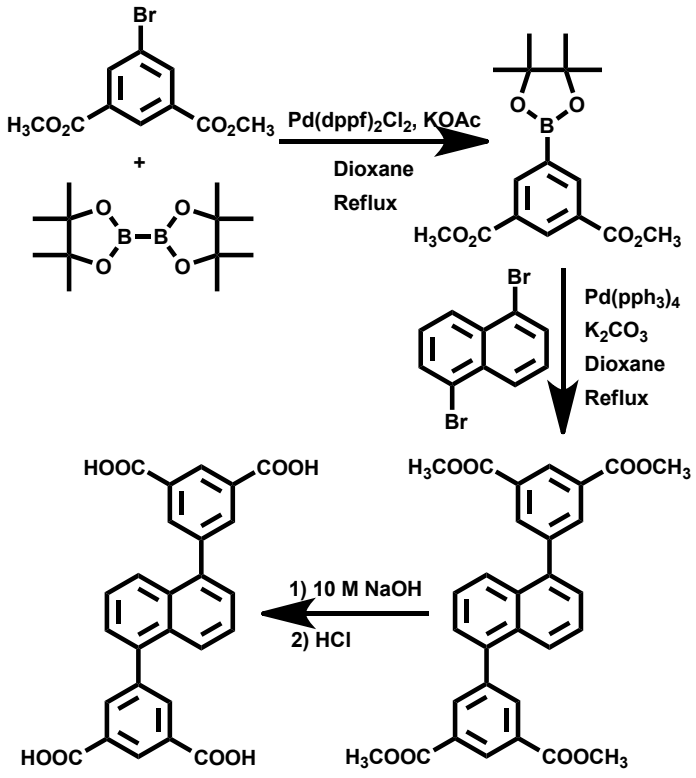
X-ray Collection and Structure Determination: Crystallographic measurements for **ZJU-9** were taken on an Oxford Xcalibur Gemini Ultra diffractometer with an Atlas detector using graphite-monochromatic Mo K_α radiation (λ = 0.71073Å) at 296 K. The determinations of the unit cells and data collections for the crystals of **ZJU-9** were performed with CrysAlisPro. The data sets were corrected by empirical absorption correction using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm.[1] All structures were determined by direct methods and refined by the full-matrix least-squares method with the SHELX-97 programpackage.[2] All non-hydrogen atoms, including solvent molecules, were located successfully from Fourier maps and were refined anisotropically. H atoms on C atoms were generated geometrically. The solvent molecules in **ZJU-9** are highly disordered. The SQUEEZE subroutine of the PLATON software suit was used to remove the scattering from the highly disordered guest molecules.[3] Crystallographic data are summarized in *Table 1*.



Scheme S1. Synthetic route to the organic linker used to construct **ZJU-9**.

Synthesis of the organic linekr H4NPA: H_4NPA was synthesized via Suzuki coupling followed by hydrolysis and acidification as shown in *Scheme S1*.

Dimethyl-(5-pinacolboryl)isopthalate was synthesized by stirring the mixture of dimethyl 5-bromo-benzene-1,3-dicarboxylate (5.4 g, 19.8 mmol), bis(pinacolato)diborane (6.0 g, 23.6 mmol), potassium acetate (5.6 g, 57.2 mmol), $Pd(dppf)_2Cl_2$ (0.2 g, 0.28 mmol), and dried 1,4-dioxane (50 mL) at 80^{o}C for 24 h and afterward extracted with ethyl acetate (20 mL). The organic layer was dried with anhydrous $MgSO_4$ and the solvent was removed in a vacuum. The crude product was purified by column chromatography (silica gel, ethylacetate/petroleum ether, 1:8 *v*/*v*). Yield: 66%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.37 (m, 12 H), 3.95 (s, 6 H), 8.64 (d, 2 H), 8.76 (s, 1H) ppm.

1, 5-dibromo-naphthaline (2.86 g, 10.0 mmol), dimethyl-(5-pinacolboryl)isopthalate (9.26 g, 30.0 mmol), and K_2CO_3 (13.82 g, 100.0 mmol) were added to 1,4- dioxane (250 mL), and the mixture deaerated under Ar for 15 min. $Pd(PPh_3)_4$ (0.47 g,0.43 mmol) was added to the reaction mixture with stirring, and the mixture heated to 80°C for 3 days under Ar. The resultant mixture was evaporated to dryness and taken up in $CHCl_3$ which had been dried over $MgSO_4$. The $CHCl_3$ solution was evaporated to dryness and purified by column chromatography (silica gel, ethyl acetate/petroleum ether, 1:10 *v*/*v*). Yield: 75%. ^{1}H NMR (500 MHz, $CDCl_3$), δ = 3.98 (s, 12 H), 7.47 (d, 2H), 7.52 (d, 2 H), 7.80 (d, 2H), 8.39 (s, 4H), 8.79 (s, 2H) ppm.

1, 5-naphthaline-dimethyl-isophthalate (H_4NPA-Me) (3.07 g, 6.00mmol) was then suspended in a mixture of 1,4-dioxane (20 mL), to which 50 mL of 10 M NaOH aqueous solution was added. The mixture was stirred under reflux overnight and the THF were removed under a vacuum. Dilute HCl was added to the remaining aqueous solution until the solution was at *p*H = 2. The solid was collected by filtration, washed with water, and dried to give 1, 5-naphthaline-*m*-phthalic acid (H_4NPA) (2.63 g, 97% yield). ^{1}H NMR (500 MHz, DMSO), δ = 7.60 (d, 2H), 7.64 (d, 2H), 7.81 (d, 2H), 8.59 (s, 2H) 8.25 (s, 4H) 13.48 (s, 4H) ppm.

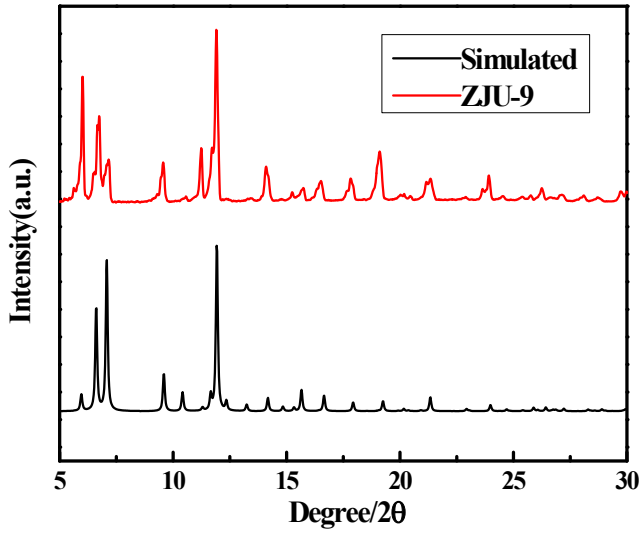


Fig. S1. PXRD patterns of as-synthesized MOF **ZJU-9** (red) and the simulated from single crystal structure (black).

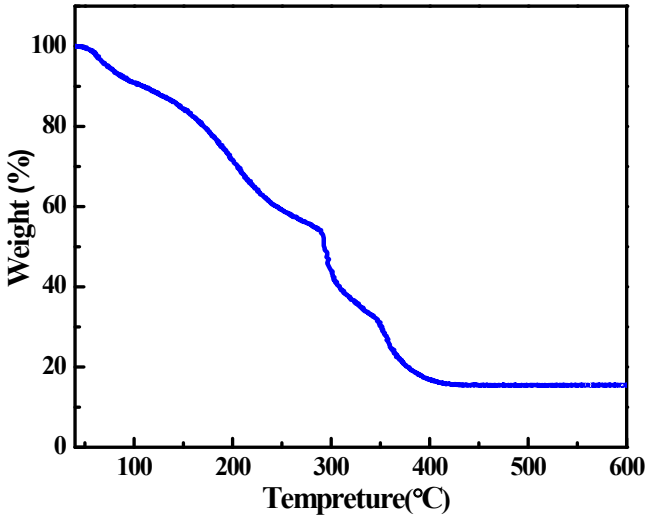
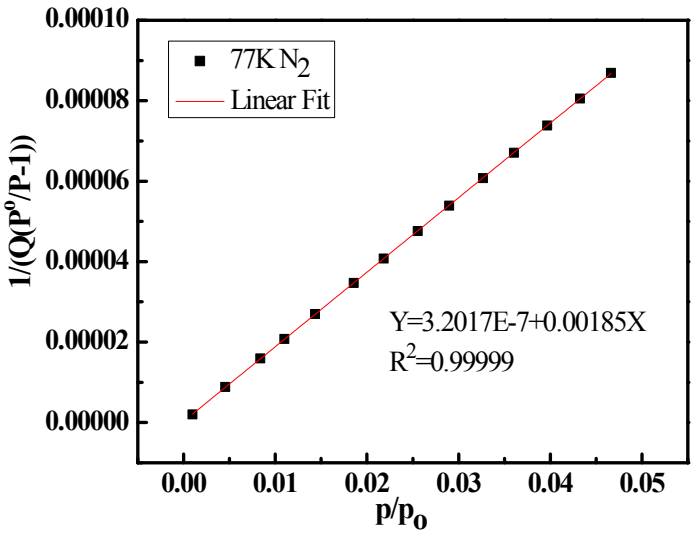


Fig. S2. TGA curve of as-synthesized **ZJU-9** in flowing N_2 atmosphere.



S_{BET}=(1/(3.2017×10^{-7}+0.00185))/22414×6.023×10^{23}×0.162×10^{-18}=2352.67 m^2/g

Fig. S3. BET plot of **ZJU-9a** under the activation of 100 ºC . Only the range below *P*/*P*0 = 0.05 satisfies the first consistency criterion for applying the BET theory.

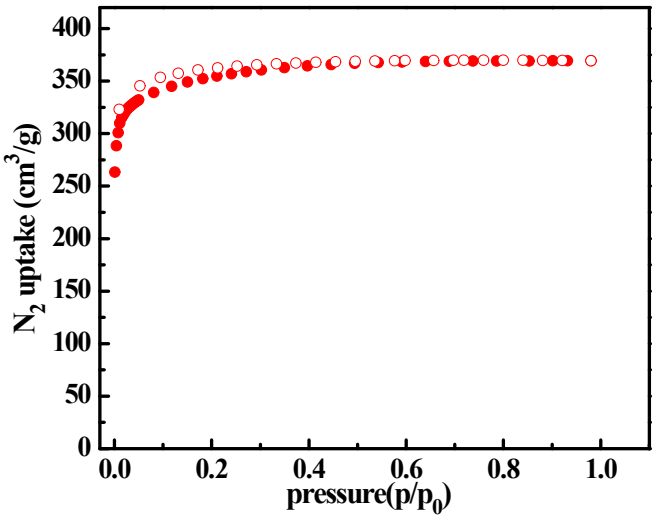
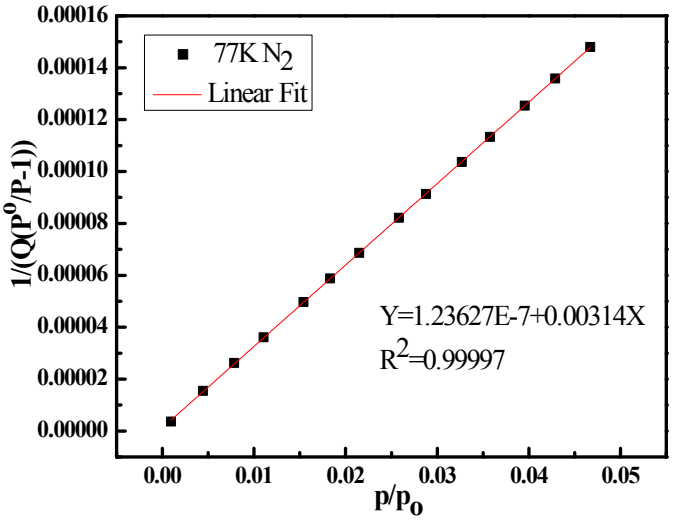


Fig. S4. N_2 sorption isotherm of **ZJU-9a** at 77 K under the activation of 25 ºC. Solid symbols: adsorption, open symbols: desorption.



S_{BET}=(1/(1.23627×10^{-7}+0.00314))/22414×6.023×10^{23}×0.162×10^{-18}=1386.31 m^2/g

Fig. S5. BET plot of **ZJU-9a** under the activation of 25 °C .

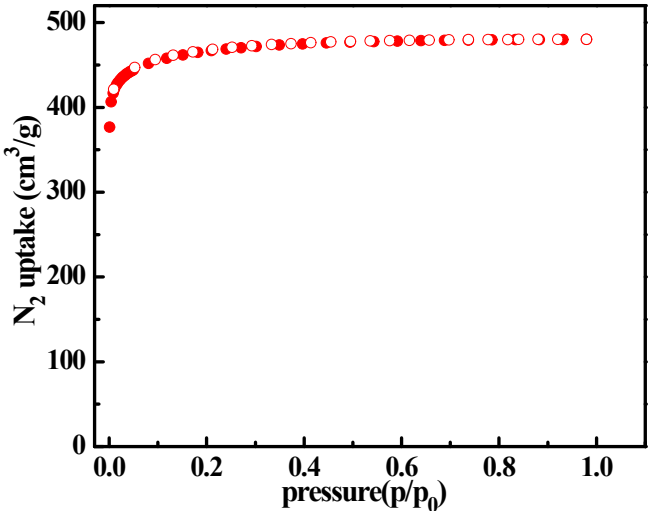
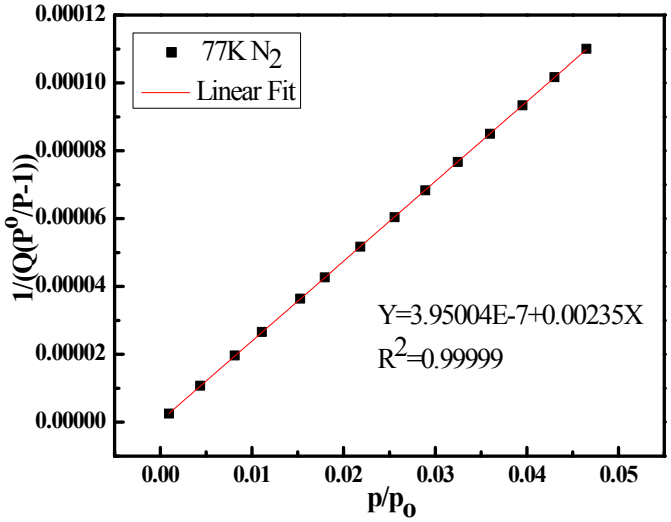


Fig. S6. N_2 sorption isotherm of **ZJU-9a** at 77 K under the activation of 60 °C. Solid symbols: adsorption, open symbols: desorption.



S_{BET}=(1/(3.95004×10^{-7}+0.00235))/22414×6.023×10^{23}×0.162×10^{-18}=1852.11 m^2/g

Fig. S7. BET plot of **ZJU-9a** under the activation of 60 ºC .

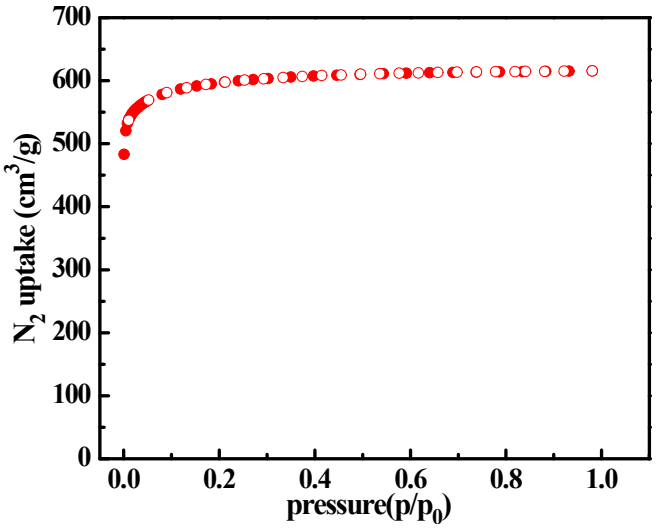
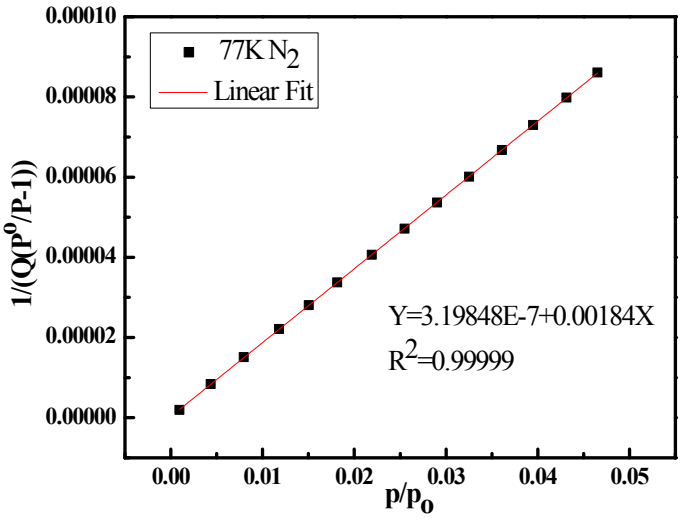


Fig. S8. N_2 sorption isotherm of **ZJU-9a** at 77 K under the activation of 100 ºC. Solid symbols: adsorption, open symbols: desorption.



S_{BET}=(1/(3.19848×10^{-7}+0.00184))/22414×6.023×10^{23}×0.162×10^{-18}=2365.45 m^2/g

Fig. S9. BET plot of **ZJU-9a** under the activation of 100 ºC .

Table S1. Crystallographic Data Collection and Refinement Results for **ZJU-9.**

	ZJU-9
Chemical formla	$C_{13}H_6CuO_5$
Formula weight	305.72
Temperature(K)	296(2)
Wavelength(Å)	0.71073
Crystal system	Trigonal
Space group	C -3m

a(Å)	18.4284 (17)
b(Å)	18.4284 (17)
c(Å)	40.081(3)
V(Å^3)	11788(2)
Z	18
Density(calculated g/cm^3)	0.775
Absorbance coefficient(mm^{-1})	0.839
F(000)	2754
Crystal size(mm^3)	0.26×0.25×0.21
Goodness of fit on F^2	1.053
R_1,wR_2[I>2σ(I)]	0.0800, 0.2093
R_1,wR_2(all data)	0.1494, 0.2598
Largest difference peak and hole(e/Å^3)	1.179, -0.448
CCDC	1406720

1. *CrysAlisPro*, version 1.171.33.56; Oxford Diffraction Ltd.: Oxfordshire, U.K., 2010
2. Sheldrick, G. M. Program for Structure Refinement; Germany, 1997.
3. Spek, L. PLATON: The University of Utrecht: Utrecht, The Netherlands, 1999.