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A novel methoxy-decorated Metal-Organic Framework exhibiting high acetylene and carbon dioxide storage capacities

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Materials and Methods

All solvents and reagents were obtained from commercial sources, and were used without further purification. ^{1}H NMR spectra were collected on a Bruker Advance DMX 500 MHz spectrometer in $CDCl_3$ and DMSO solution using tetramethylsilane (TMS, 0 ppm) as an internal standard at room temperature. The X-ray powder diffraction (PXRD) expariment was carried out on a PANalytical X'Pert Pro X-ray diffractometer with Cu-K_α (λ = 1.542 Å) at room temperature and the data were collected in the 2θ = 3°~40° range. Thermogravimetric analyses (TGA) were recorded on a Netszch TGA 209 F3 thermogravimeter under N_2 atmosphere heated from room temperature to 900 ^{o}C at the heating rate of 5 K min^{-1}. Elemental analyses (C, H, and N) were performed on an EA1112 microelemental analyzer.

X-ray Collection and Structure Determination

Crystal structure analyses: The determination of the unit cell and data collection for the crystals of **ZJU-12** was performed with *CrysAlisPro* program. Diffraction data were collected on an Oxford Xcalibur Gemini Ultra diffractometer with an Atlas detector using graphite-monochromatic Mo K_α radiation (λ = 0.71073 Å) at 296 K. The data were calculated by the SCALE3 ABSPACK scaling algorithm and the proper correction was porfermed by empirical adsorption correction using spherical harmonics.[1] The structure was carried out by direct method, and refined with the full-matrix least-squares on F^2 with the SHELX-97 program package.[2] Because the solvent molecules are highly disordered, PLATON SQUEEZE subroutine was used to remove the solvent molecules. The newly generated files were used for further structural optimization, and H atoms and C atoms were added according to the geometric configurations. Crystallographic data, data collection parameters, and refinement are summarized in Table S1 in Supporting Information. CCDC-1510153.

Derivation of the Isosteric Heat of Adsorption

A virial-type expression comprising the temperature-independent parameters a_i and b_i was employed to calculate the enthalpies of adsorption for C_2H_2 and CO_2 (at 273 and 298 K) on **ZJU-12a**. In each case, the data were fitted using the equation:

$$lnP = lnN + 1/T\sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i \qquad (1)$$

Here, P is the pressure expressed in mmHg, N is the amount adsorbed in mmol/g, T is the temperature in K, a_i and b_i are virial coefficients, and m, n represents the number of coefficients required to adequately describe the isotherms. The values of the virial coefficients a_0 through a_m were then used to calculate the isosteric heat of adsorption using the following expression.

$$Q_{st} = -R\sum_{i=0}^{m} a_i N^i \qquad (2)$$

Here, Q_{st} is the coverage-dependent isosteric heat of adsorption and R is the universal gas constant of 8.3147 $JK^{-1}mol^{-1}$.

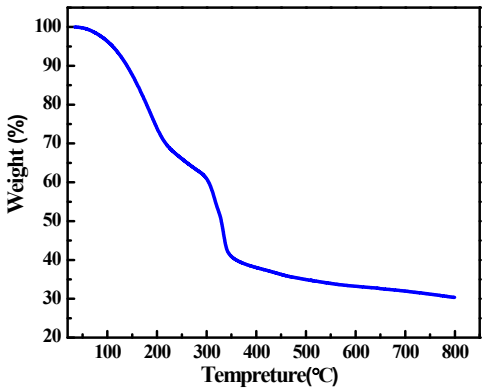


Fig. S1.TGA curves of as-synthesized **ZJU-12**.

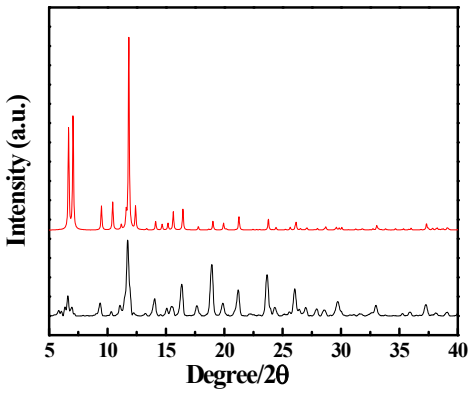
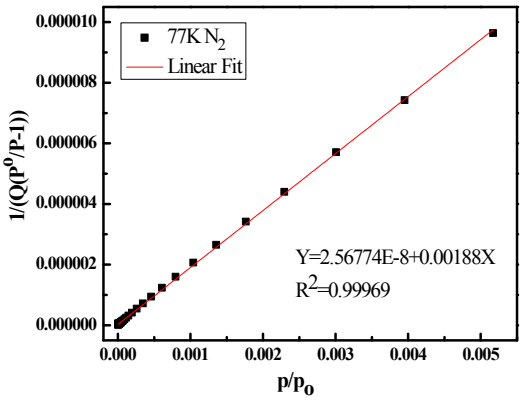


Fig. S2. PXRD patterns of simulated sample (red) and as-synthesized **ZJU-12** (black).



S_{BET}=1/(Slope+Intercept)/22414×6.023×10^{23}×0.162×10^{-18} = 2316 m^2/g

Fig. S3. BET plot of **ZJU-12a**. Only the range below *P*/*P*0 = 0.05 satisfies the first consistency criterion for applying the BET theory.

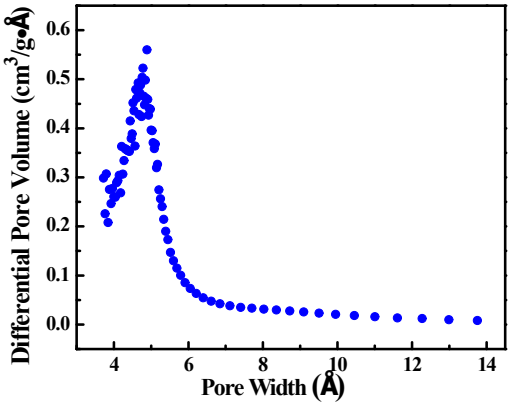


Fig. S4. The pore size distribution of **ZJU-12**.

Table1 S1. Crystallographic Data Collection and Refinement Results for **ZJU-12.**

	ZJU-12
Chemical formla	$C_{28}H_{18}Cu_2O_{12}$
Formula weight	673.5
Temperature(K)	296(2)
Wavelength(Å)	0.71073
Crystal system	Trigonal
Space group	R -3m
a(Å)	18.6401(5)
b(Å)	18.6401(5)
c(Å)	39.7480(9)
V(Å^3)	11960.3(5)
Z	9
Density(calculated g/cm^3)	0.842
Absorbance coefficient(mm^{-1})	0.834
F(000)	3060
Crystal size(mm^3)	0.43X0.32X0.21

Goodness of fit on F^2	1.171
R_1,wR_2[I>2σ(I)]	0.0405,0.1199
R_1,wR_2(all data)	0.0500,0.1239
Largest difference peak and hole(e/Å^3)	0.605,-0.448
CCDC	1510153

1. *CrysAlisPro*, version 1.171.33.56; Oxford Diffraction Ltd.: Oxfordshire, U.K., 2010

2. Sheldrick, G. M. Program for Structure Refinement; Germany, 1997.