

Merging Open Metal Sites and Lewis Basic Sites in a NbO-type Metal-Organic Framework for Improved C₂H₂/CH₄ and CO₂/CH₄ Separation

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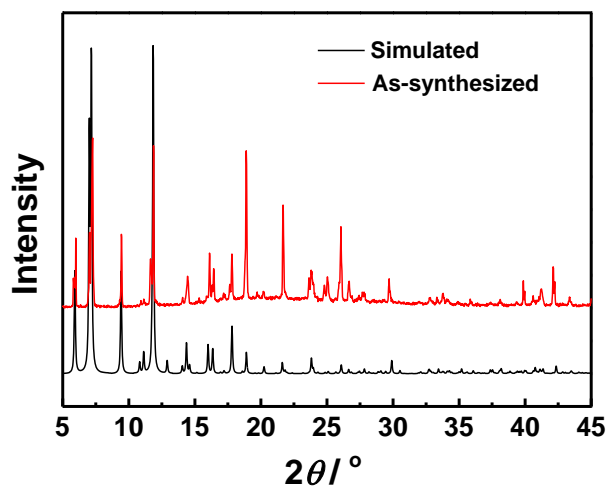


Fig. S1 PXRD pattern of the as-synthesized **ZJNU-47** together with the one simulated from its cif file.

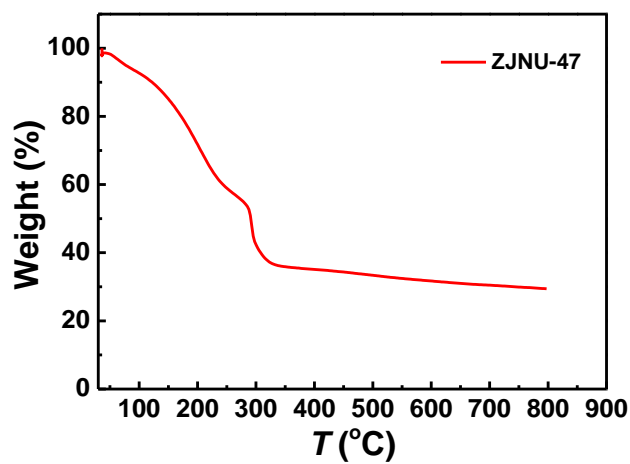


Fig. S2 TGA curve of the as-synthesized **ZJNU-47** under a flowing nitrogen atmosphere.

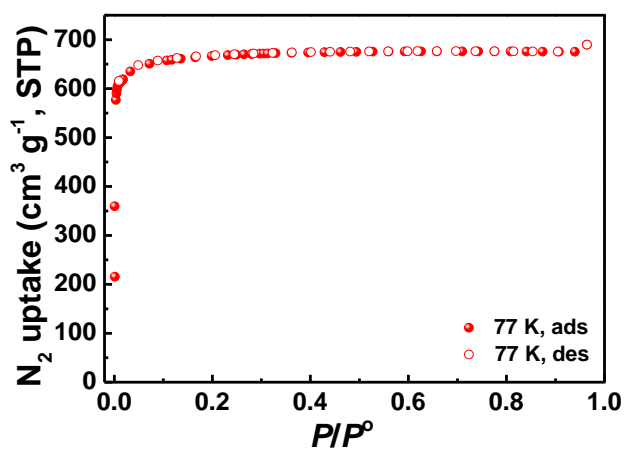


Fig. S3 N_2 adsorption-desorption isotherm of **ZJNU-47a** at 77 K. Solid and open symbols represent adsorption and desorption, respectively.

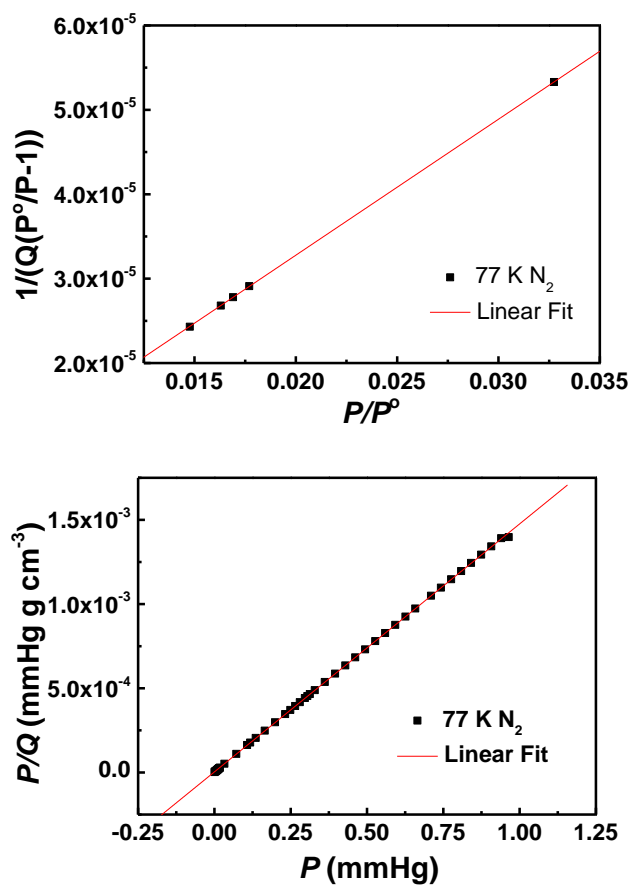


Fig. S4 BET and Langmuir plots.

$$S_{\text{BET}} = 1/(5.58259 \times 10^{-7} + 0.00161)/22414 \times 6.023 \times 10^{23} \times 0.162 \times 10^{-18} = 2703 \text{ m}^2 \text{ g}^{-1}$$

$$S_{\text{Langmuir}} = (1/0.00147)/22414 \times 6.023 \times 10^{23} \times 0.162 \times 10^{-18} = 2961 \text{ m}^2 \text{ g}^{-1}$$

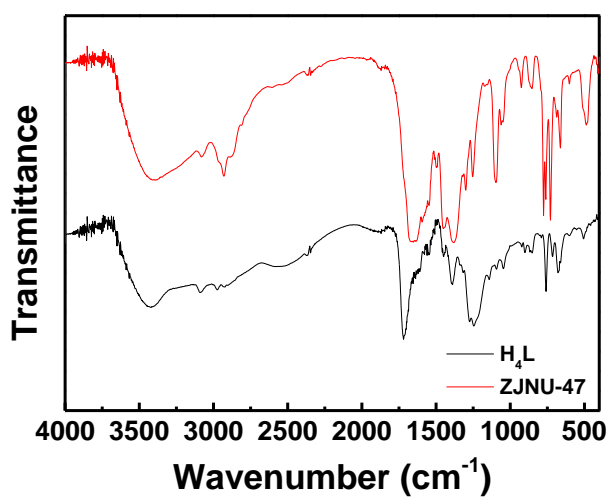


Fig. S5 FTIR spectra of the organic linker H_4L (black) and as-synthesized **ZJNU-47** (red).

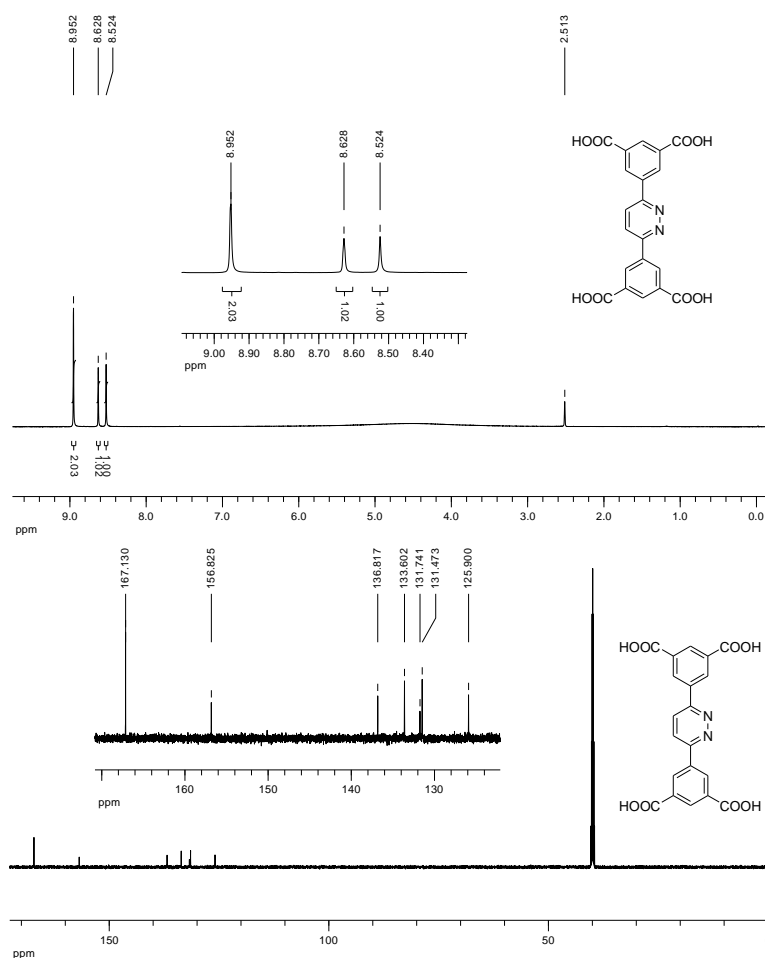


Fig. S6 ^1H NMR (DMSO- d_6 , 600.1 MHz) and ^{13}C NMR (DMSO- d_6 , 150.9 MHz) spectra of the organic linker H_4L .

Computational details

To make sure the gamma point is sufficient for the calculation of binding energies of different gases confined in the cage, we compared the binding energy of the structure C-C₂H₂ using gamma point with those from Monkhorst-Pack grids of 3×3×3 and 5×5×5. The results show that binding energies are all the same, *i.e.*, -35.8 kJ mol⁻¹, indicating gamma point is sufficient for sampling the large primitive cell in our calculations. The parameters for the primitive cell of **ZJNU-47** are as follows: $a = b = c = 16.61 \text{ \AA}$, $\alpha = \beta = \gamma = 68.76^\circ$. Full relaxation of the cell and all the atoms on the framework using vdW-DF2 functional only slightly increases a to 16.69 Å, *i.e.*, by less than 0.5%, indicating there is a good agreement between theory and experiment. Therefore, it is reasonable to use the experimentally measured cell parameters to describe the framework and compute the

binding energies of gases confined in the framework.

The reported unit cell parameters ($a = b = 18.8163 \text{ \AA}$, $c = 38.079 \text{ \AA}$) of **ZJU-5** are almost the same to those ($a = b = 18.7626 \text{ \AA}$, $c = 37.7902 \text{ \AA}$) of **ZJNU-47** due to their very similar structures. To calculate the binding energy of C_2H_2 with similar orientation to structure “C-C₂H₂” (Fig. 3) in **ZJU-5**, we performed calculations using the same vdW-DF2 method as mentioned, where the experimentally measured parameters are held fixed for the framework. The results show that the binding energy is $-29.9 \text{ kJ mol}^{-1}$ at the N group sites, weaker than that ($-35.8 \text{ kJ mol}^{-1}$) by 5.9 kJ mol^{-1} , indicating the double N-N group in **ZJNU-47** is energetically more favorable than the single N group in **ZJU-5**. This difference might explain why **ZJNU-47** has a larger storage capacity than **ZJU-5**.

All of the calculations were performed using Vienna *ab initio* simulation package with version of 5.3.3. Several key parameters employed in our calculations are provided:

ENCUT = 500

EDIFF = 1.0E-05

EDIFFG = -0.01

ADDGRID = .TRUE.

IBRION = 2

ISIF = 2

POTIM = 0.2

SIGMA = 0.2

ISMear = 0

IALGO = 48

LREAL = AUTO

An example of input files for the VASP calculations is provided.

Table S1 Crystal data and structure refinement for **ZJNU-47**.

Empirical formula	C ₁₀ H ₄ CuNO ₅
Formula weight	281.69
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Trigonal
Space group	<i>R</i> -3m
Unit cell dimensions	$a = 18.7626(3) \text{ Å}$ $b = 18.7626(3) \text{ Å}$ $c = 37.7902(14) \text{ Å}$ $\alpha = 90^\circ$ $\beta = 90^\circ$ $\gamma = 120^\circ$
Volume (Å ³)	11521.1(5)
<i>Z</i>	18
Calculated density (g cm ⁻³)	0.731
Absorption coefficient (mm ⁻¹)	0.856
<i>F</i> (000)	2682
Crystal size (mm)	0.35 x 0.26 x 0.20
θ range for data collection (°)	1.36 to 27.49
Limiting indices	$-24 \leq h \leq 18$, $-24 \leq k \leq 24$, $-42 \leq l \leq 49$
Reflections collected / unique	26432 / 3224
<i>R</i> _{int}	0.1003
Completeness to $\theta = 25.02$	99.9 %
Max. and min. transmission	0.8492 and 0.7563
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3224 / 27 / 124
Goodness-of-fit on F^2	1.186
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0708$, $wR_2 = 0.2411$
<i>R</i> indices (all data)	$R_1 = 0.0771$, $wR_2 = 0.2471$
Largest diff. peak and hole (e.Å ⁻³)	1.613 and -0.753
CCDC	1056733