Supporting Information

An Amino-Decorated NbO-Type Metal-Organic Framework for High C_2H_2 Storage and Selective CO_2 Capture

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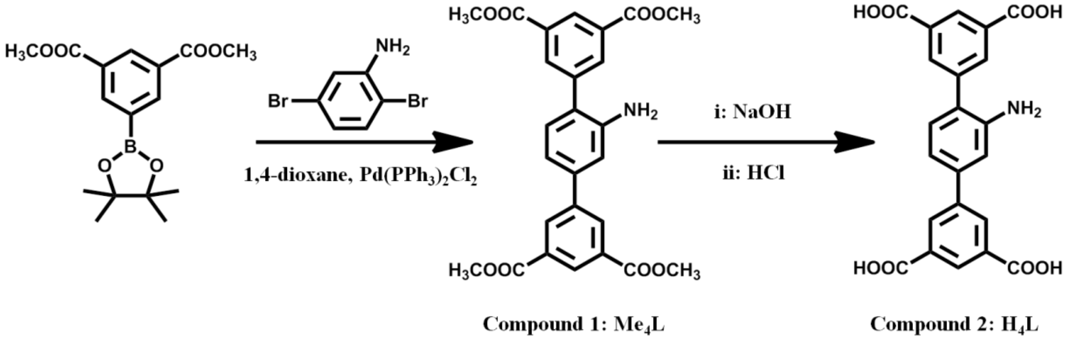
Materials and methods

All reagents were commercially available and used as received. Powder X-ray diffraction (PXRD) patterns were collected on an X'Pert PRO diffractometer with Cu Kα ($\lambda = 1.542$ Å) radiation with the 2θ in the range of 3-60 ° at room temperature. ^{1}H NMR spectra were measured on a Bruker Advance DMX 500 spectrometer using tetramethylsilane (TMS) as an internal standard. Thermogravimetric analyses (TGA) were carried out on a Netzsch TG209F3 with a heating rate of 5 ℃/min under N_2 atmosphere. Infrared spectrum (IR) was recorded on Thermo Fisher Nicolet iS10 spectrometer with KBr pallets. Elemental analyses for C, H, and N were performed on an EA1112 microelemental analyzer.



Scheme S1. The synthetic route of the ligand H_4L

Synthesis of tetramethyl 2'-amino-[1,1':4',1''-terphenyl]-3,3'',5,5''-tetracarboxylate (compound 1, Me$_4$L): dimethyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)isophthalate (9.61 g, 30 mmol), 2,5-dibromoaniline (2.51 g, 10 mmol) and K_2CO_3 (13.9 g, 100 mmol) were mixed in dry 1,4-dioxane (100 mL), the mixture was purged with argon and stirred for an hour at room temperature. Then $Pd(PPh_3)_2Cl_2$ (0.30 g, 0.4 mmol) was added and the mixture heated at 85 ℃ for 72 hours under argon atmosphere. After cooling, the resultant mixture was extracted with $CHCl_3$ three times, the organic solvent was dried over anhydrous $MgSO_4$ and removed under reduced pressure, and the crude product was purified with toluene recrystallization to obtain pure tetramethyl 2'-amino-[1,1':4',1"-terphenyl]-3,3",5,5"-tetracarboxylate (**compound 1**, 3.10g). Yield: 65%. ^{1}H NMR (500 MHz, $CDCl_3$), δ = 8.68 (d, 2 H), 8.48 (s, 2H), 8.39 (s, 2H), 7.24 (s, 1H), 7.15 (d, 1H), 7.08 (s, 1H), 3.98 (d, 12H) ppm. Anal. Calcd for $C_{26}H_{23}NO_8$: C, 65.40; H, 4.86; N, 2.93. Found: C, 65.35; H, 4.98; N, 2.90.

Synthesis of 2'-amino-[1,1':4',1''-terphenyl]-3,3'',5,5''-tetracarboxylic acid (compound 2,

H_4L): compound 1 (2.39 g, 5 mmol) was then suspended in a mixture of THF (20 mL) and H_2O (50 mL), to which 100 mL of 10 M NaOH aqueous solution was added. The mixture was stirred under reflux overnight and the THF was removed under a vacuum. Dilute HCl was added to the remaining aqueous solution until the solution was at pH = 3. The solid was collected by filtration, washed with water, and dried to give H_4L (2.00 g, 97.6% yield). ^{1}H NMR (500 MHz, DMSO-D_6): δ= 8.48 (d, 2H), 8.43 (s, 1H), 8.19 (s, 2H), 7.84 (s, 1H), 7.75 (d, 1H), 7.59 (d, 1H), 3.08 (d, 2H). Anal. Calcd for $C_{22}H_{15}NO_8$: C, 62.71; H, 3.59; N, 3.32. Found: C, 62.33; H, 3.88; N, 3.11. Selected FTIR (neat, cm-1): 1740, 1680, 1559, 1515, 1438, 1285, 1253, 1210, 1148, 1119, 1079, 993, 863, 760, 675, 629, 462.

Single-Crystal X-ray Diffraction Collection and Structure Determination.

Single-crystal X-ray diffraction data of **ZJU-8** was taken on an Bruker APEX-II diffractometer with an CCD detector using graphite-monochromatic Mo Kα radiation (λ = 0.71073 Å) at 293 K. The determination of the unit cell and data collection were performed with Bruker SAINT program. The structure of **ZJU-8** was determined by direct methods and refined by the full-matrix least-squares method with the SHELX-97 programpackage.[1] All non-hydrogen atoms were located successfully from Fourier maps and were refined anisotropically. The disordered lattice DMF, and water molecules could not be located successfully from Fourier maps in the refinement cycles. The scattering from the highly disordered lattice guest molecules were removed using the SQUEEZE procedure implemented in the PLATON package.[2] Crystallographic data are summarized in Table S1 (CCDC 1406816).

Table S1. Crystallographic data collection and refinement results for **ZJU-8**

	ZJU-8
Framework formula	$C_{22}H_{15}NO_{10}Cu_2$
Framework formula weight	580.43
Temperature(K)	293(2)
Wavelength(Å)	0.71073
Crystal system	Trigonal
Space group	R-3m
a(Å)	18.639(4)
b(Å)	18.639(4)
c(Å)	38.614(6)
α	90 °
β	90 °
γ	120 °
V(Å^3)	11618(5)
Z	9
Density(calculated g/cm^3)	0.738
Absorbance coefficient(mm^{-1})	0.849
F(000)	2565
Crystal size(mm^3)	0.19×0.13×0.12
R(int)	0.1285
Goodness of fit on F_2	1.025
R1,wR2[I>2σ(I)][a]	0.0451, 0.1222
R1,wR2(all data)[a]	0.0760, 0.1374
Largest difference peak and hole(e/Å^3)	0.897,-0.381

[a] $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|\,;\, wR2 = \left[\frac{\sum w(|F_o|-|F_C|^2)}{\sum wF_o^2}\right]^{1/2}$

Table S2. The Selected bond lengths (Å) and angles (°) of **ZJU-8**

Cu(1)-O(2B)#1	1.959(2)
Cu(1)-O(1)#3	1.960(2)
Cu(1)-O(1C)	2.169(4)
Cu(1)-O(2B)#2	1.959(2)
Cu(1)-O(1)	1.960(2)
Cu(1)-Cu(1)#2	2.6508(10)
O(2B)#1-Cu(1)-O(2B)#2	89.17(16)
O(2B)#1-Cu(1)-O(1)#3	167.76(9)
O(2B)#2-Cu(1)-O(1)#3	89.67(11)
O(2B)#1-Cu(1)-O(1)	89.67(11)
O(2B)#2-Cu(1)-O(1)	167.76(9)
O(1)#3-Cu(1)-O(1)	88.89(15)
O(2B)#1-Cu(1)-O(1C)	94.82(12)
O(2B)#2-Cu(1)-O(1C)	94.82(12)
O(1)#3-Cu(1)-O(1C)	97.42(12)
O(1)-Cu(1)-O(1C)	97.42(12)
O(2B)#1-Cu(1)-Cu(1)#2	83.69(7)
O(2B)#2-Cu(1)-Cu(1)#2	83.69(7)
O(1)#3-Cu(1)-Cu(1)#2	84.08(7)
O(1)-Cu(1)-Cu(1)#2	84.08(7)
O(1C)-Cu(1)-Cu(1)#2	177.89(15)
C(4)-O(1)-Cu(1)	122.9(2)
C(4)-O(2B)-Cu(1)#2	123.7(2)
#1 y,x,-z; #2 -x+1,-y+1,-z; #3 -y+1,-x+1,z; #4 -x+2/3,-y+1/3,-z+1/3; #5 x,x-y,z; #6 -x+2/3,-x+y+1/3,-z+1/3	

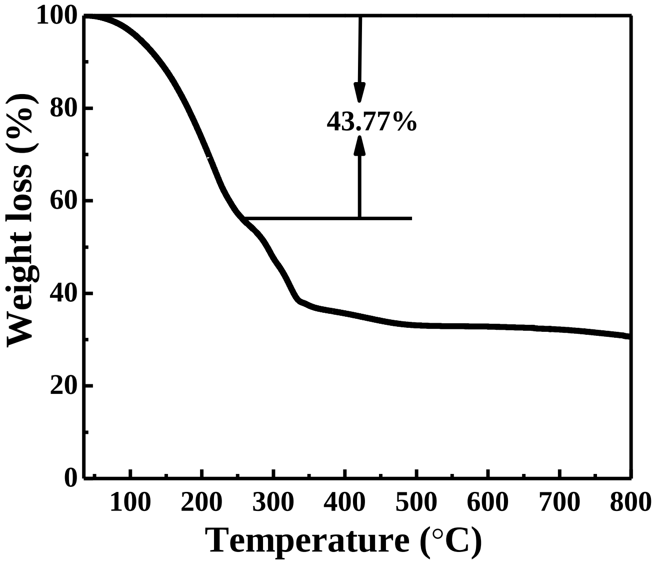


Figure S1. TGA curves of fresh **ZJU-8** under a N_2 atmosphere at a heating rate of 5 K/min.

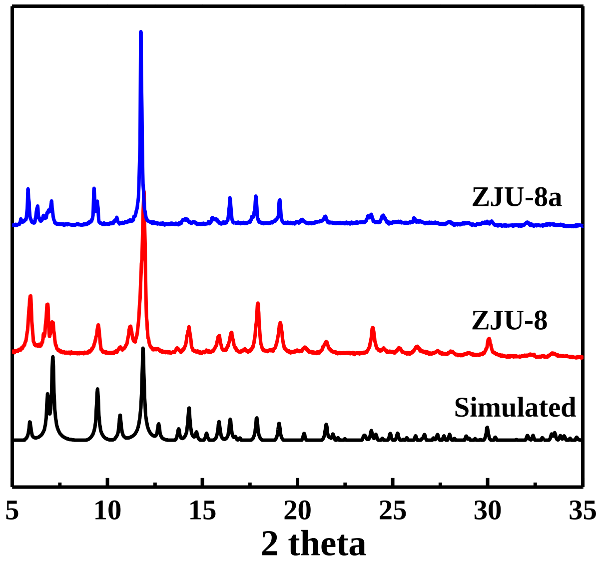


Figure S2 PXRD patterns of fresh sample of **ZJU-8** (red) and evacuated sample of **ZJU-8a** (blue) along with the simulated pattern from single X-ray structure (black).

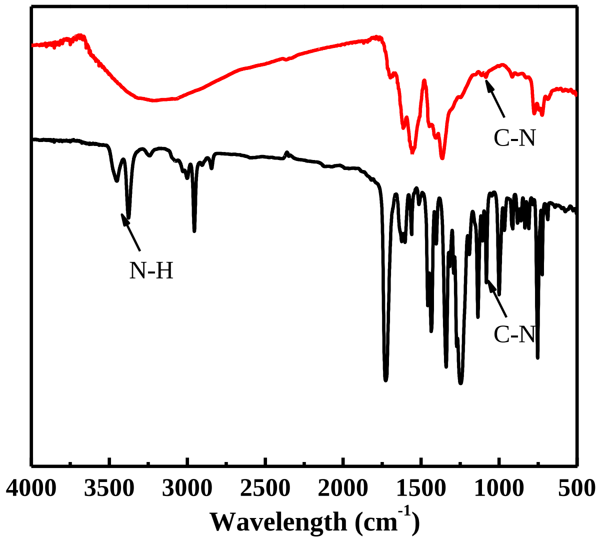
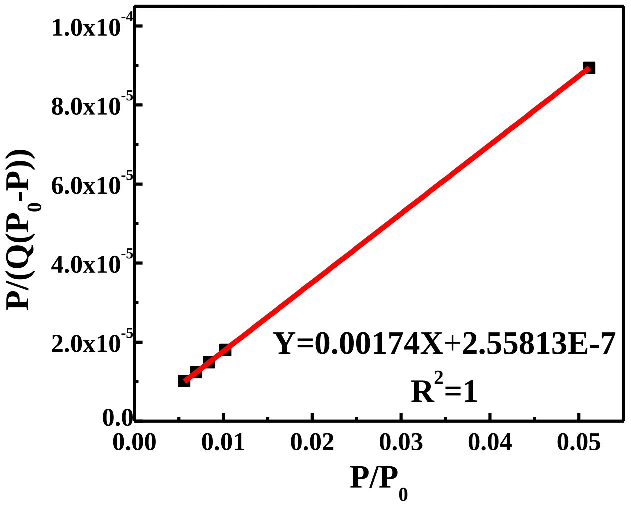


Figure S3 IR spectrum of ligand H_4L(black) and **ZJU-8** fresh sample (red)



$$S_{BET}=1/(\text{Slope}+\text{Intercept})/22414\times6.023\times10^{23}\times0.162\times10^{-18}=2501\ m^2/g$$

Figure S4. The BET surface area of **ZJU-8a** obtained from N_2 adsorption isotherm at 77 K

Table S3. Equation parameters for the DSLF isotherm model.

Adsorbates	N_1^{max} (mmol/g)	b_1 (kPa^{-1})	n_1	N_2^{max} (mmol/g)	b_2 (kPa^{-1})	n_2
CO_2 (273 K)	18.86038	0.00517	1.099674	17.21748	0.00217	1.051138
CH_4 (273 K)	2.99252	0.00559	1.21122	2.86788	0.000896765	0.748027
N_2 (273 K)	2.3	0.00116	1.01742	3.14433	0.000401747	1.00162
CO_2 (298 K)	7.19116	0.00752	1.118568	7.60212	0.000560593	0.720466
CH_4 (298 K)	3.09099	0.00248	0.99956	1.59676	0.000731969	0.7638369
N_2 (298 K)	2.5746	0.0016	1.04421	4.42351	0.000409024	1.01473

Table S4. C_2H_2 adsorption on various porous MOFs at RT and atmospheric pressure.

Material	S_{BET} [m^2g^{-1}]	$V_p{}^a$ [cm^3g^{-1}]	$D_c{}^b$ [$g\ cm^{-3}$]	C_2H_2 uptaked [cm^3g^{-1}]([cm^3cm^{-1}])	Ref.
ZJU-8a	2501	1.0224	0.690	195 (134)	This work
ZJU-5a	2823	1.074	0.679	193 (131)	S3
ZJU-7a	2198	0.8945	0.750	180 (135)	S4
ZJU-26a	989	0.572	0.615	84 (52)	S5
MOF-505	1139	0.67	0.767	148 (137)	S6
PCN-16	2273	1.06	0.724	176 (126)	S7
NOTT-101	2805	1.080	0.6838	184 (126)	S8
NOTT-102	3342	1.280	0.587	146 (86)	S8

[a] Pore volume. [b] Crystal density calculated from the single-crystal structure without guest molecules and coordinated water.

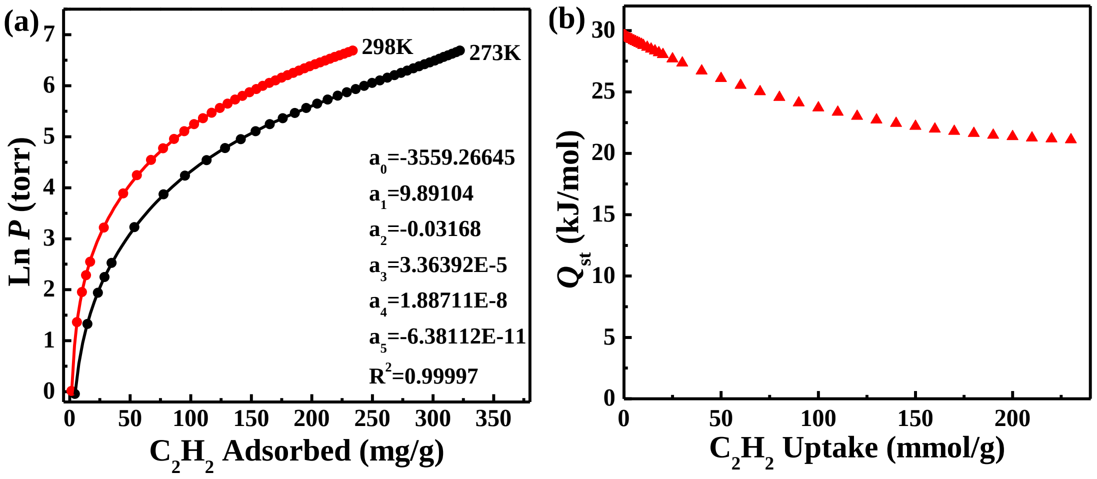


Figure S5. (a) Details of virial equation fitting to the experimental C_2H_2 adsorption data for **ZJU-8a** collected at 273 K (black) and 298 K (red); (b) Isosteric heats of C_2H_2 for **ZJU-8a**

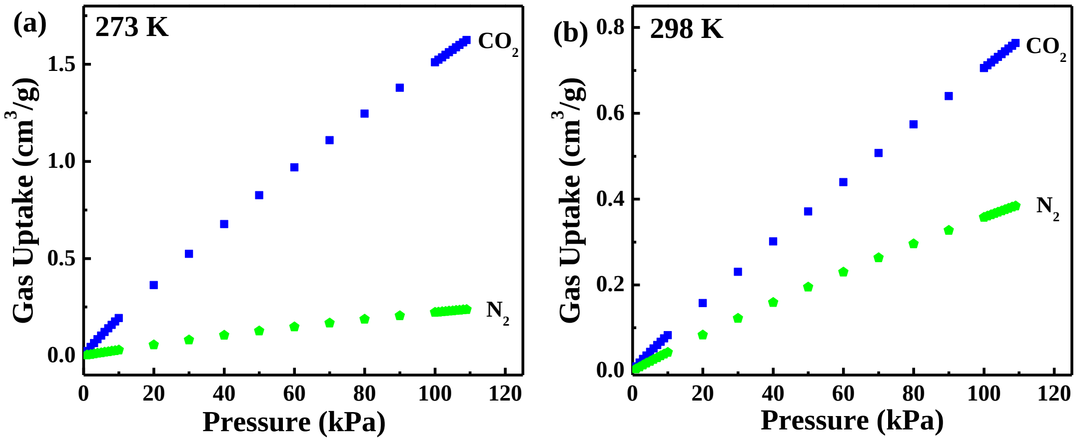


Figure. S6. Calculations using Ideal Adsorbed Solution Theory (IAST) for uptake of CO_2 and N_2 from 15/85 CO_2/N_2 gas mixtures at 273 K (a) and 298 K (b) in **ZJU-8a**

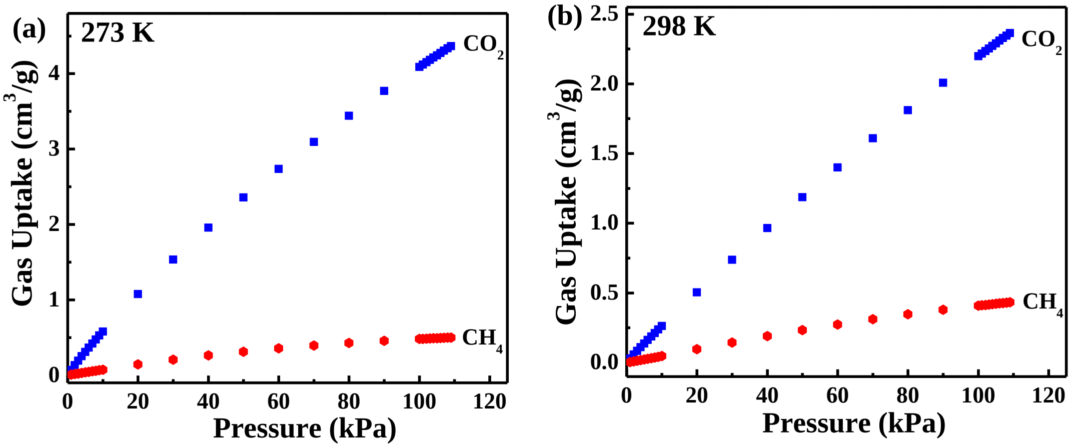


Figure. S7. Calculations using Ideal Adsorbed Solution Theory (IAST) for uptake of CO_2 and CH_4 from 50/50 CO_2/CH_4 gas mixtures at 273 K (a) and 298 K (b) in **ZJU-8a**

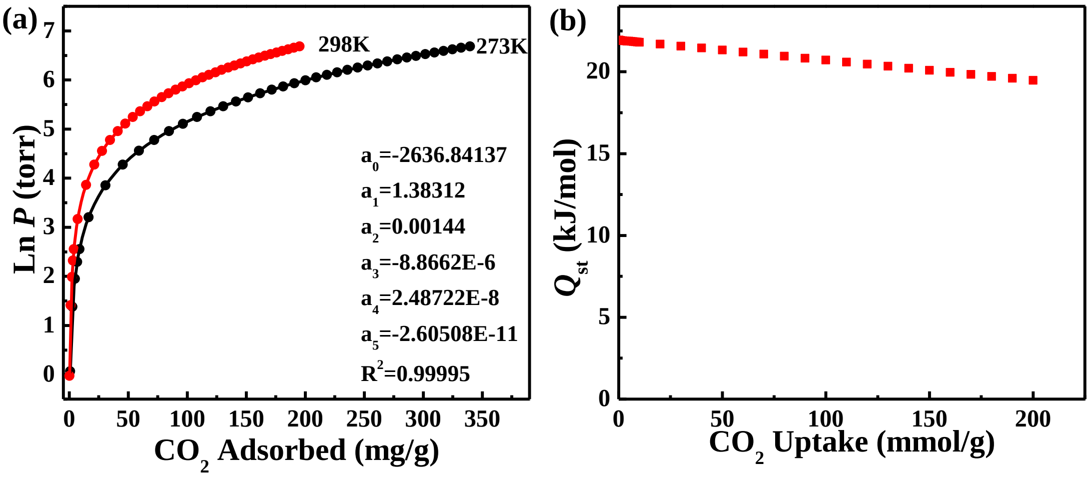


Figure S8. (a) Details of virial equation fitting to the experimental CO_2 adsorption data for **ZJU-8a** collected at 273 K (black) and 298 K (red); (b) Isosteric heats of CO_2 for **ZJU-8a**

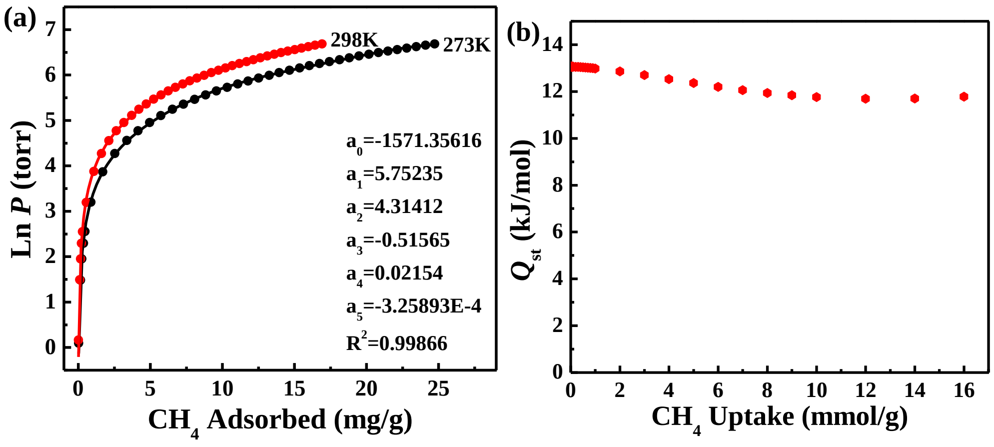


Figure S9. (a) Details of virial equation fitting to the experimental CH_4 adsorption data for **ZJU-8a** collected at 273 K (black) and 298 K (red); (b) Isosteric heats of CH_4 for **ZJU-8a**

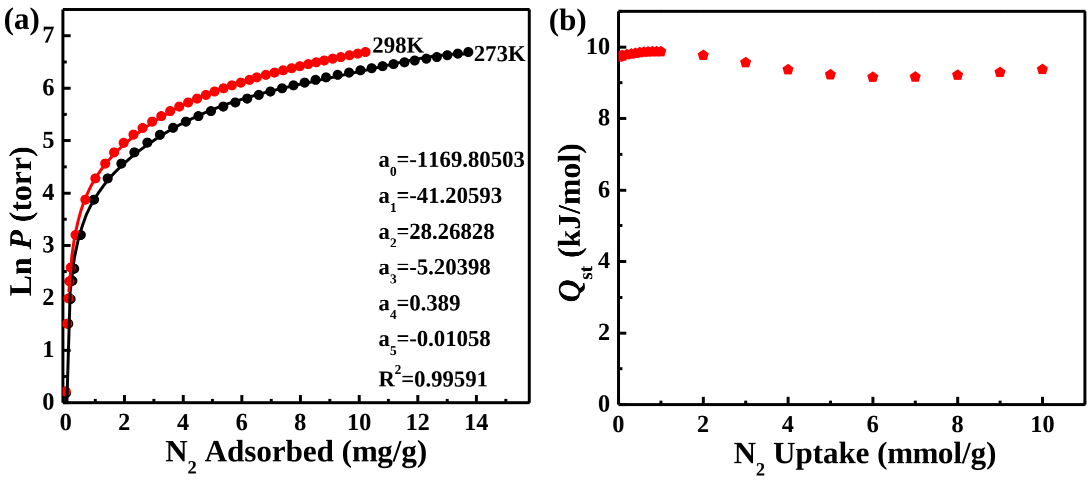


Figure S10. (a) Details of virial equation fitting to the experimental N_2 adsorption data for **ZJU-8a** collected at 273 K (black) and 298 K (red); (b) Isosteric heats of N_2 for **ZJU-8a**

References

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