

Electronic Supplementary Information

Enhanced water stability of a microporous acylamide-functionalized Metal-Organic Framework via interpenetration and methyl decoration

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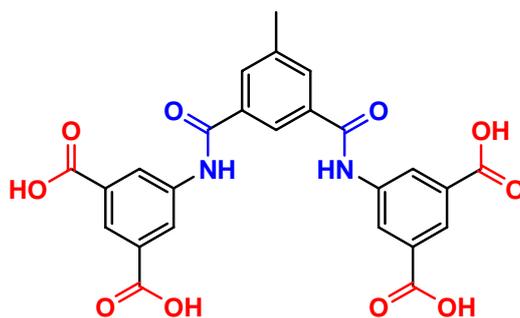
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1. Materials and General methods

All chemical reagents were obtained from commercial sources and, unless otherwise noted, were used as received without further purification. The IR spectra were recorded in the 400-4000 cm^{-1} on a Bruker VERTEX 80V spectrometer using KBr pellets. ^1H NMR spectra were recorded on a Bruker AVANCE III 600 MHz spectrometer with tetramethylsilane as an internal reference. Thermal gravimetric analyses (TGA) were performed under N_2 atmosphere (100 ml/min) with a heating rate of 5 $^\circ\text{C}/\text{min}$ using a 2960 SDT thermogravimetric analyzer. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 ADVANCE X-ray diffractometer with $\text{Cu K}\alpha$ radiation.

2. Synthesis of 5,5'-[(5-methyl-1,3-phenylene)bis(carbonylimino)]diisophthalic acid, MPBD

Into a dried 200 mL flask, 5-methylisophthalic acid (2.0 g, 11.1 mmol) was placed and 30 mL SOCl_2 was added. *N,N*-dimethylformamide (0.45 mL) was carefully added dropwise with a syringe pump. The mixture was refluxed for 12 h and then the excess SOCl_2 was removed under vacuum in a well-ventilated hood to obtain the solid of 5-methylisophthaloyl chloride. 5-methylisophthaloyl chloride was dissolved in anhydrous acetonitrile (30 mL) and added dropwise to a mixture of 5-aminoisophthalic acid (4.3 g, 22.2 mmol) in acetonitrile (30 mL). The mixture was refluxed 2 h after stirring for 24 h at room temperature. The precipitated solids were filtered off and washed with fresh acetonitrile followed by water, washed repeatedly with hot methanol and then dried in a vacuum oven at 100 $^\circ\text{C}$ to obtain about 1.2 g (yield: ~21 %) of pure **MPBD** as a white powder. Selected IR (KBr, cm^{-1}): 3133, 1701, 1560, 1401, 1276, 1236, 950, 760, 671, 595, 523. ^1H NMR (600MHz, $\text{DMSO-}d_6$, δ ppm): 13.28 (s, 4H, COOH), 10.71 (s, 2H, CONH), 8.60 (s, 4H, ArH), 8.43 (s, 1H, ArH), 8.22(t, 2H, ArH), 8.04 (s, 2H, ArH), 2.50 (t, 3H, CH_3).



3. Synthesis of $[\text{Cu}_2(\text{MPBD}^{4-})(\text{H}_2\text{O})_2] \cdot x\text{G}$ (G=guest molecule), HNUST-4

A mixture of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (20 mg, 0.08 mmol), **MPBD** (10.2 mg, 0.02 mmol), HBF_4 (0.475 mL, 40 % aqueous solution) and DMF/ethanol/ H_2O (5: 3: 2 in volume, 4 mL) was stirred for 10 min in air and sealed in a 20 mL Teflon-lined autoclave, which was heated at 75 $^\circ\text{C}$ for 48 h. After cooling to the

room temperature, the pale blue block-shaped crystals of HNUST-4 were filtered and washed with fresh solution of DMF/ethanol/H₂O (5:3:2 in volume). Yield: ~ 58 % based on the ligand. Selected IR (KBr, cm⁻¹): 3133, 1655, 1401, 1276, 1237, 1084, 774, 731, 587.

4. Activation of HNUST-4

The solvent-exchanged HNUST-4 was prepared by immersing the as-synthesized samples in anhydrous acetone for 3 days to remove the nonvolatile solvates, and the extract was decanted every 8 hours and fresh acetone was replaced. The completely activated HNUST-4 was obtained by heating the solvent-exchanged sample at 100 °C under a dynamic high vacuum for 24 hours. During this time, the pale blue sample changed to a deep purple-blue color indicative of the presence of unsaturated metal Cu^{II} sites. Selected IR (KBr, cm⁻¹): 1633, 1656, 1401, 1276, 1237, 1085, 778, 734, 587.

5. X-ray Crystallography

Single-crystal X-ray diffraction data were measured on a Bruker Smart Apex CCD diffractometer at room temperature using graphite monochromated Mo/K α radiation ($\lambda = 0.71073 \text{ \AA}$). 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^[1]. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Organic hydrogen atoms were placed in calculated positions with isotropic displacement parameters set to $1.2 \times U_{eq}$ of the attached atom. The hydrogen atoms of the ligated water molecules could not be located, but are included in the formula. The unit cell includes a large region of disordered solvent molecules, which could not be modelled as discrete atomic sites. We employed PLATON/SQUEEZE^[2] to calculate the diffraction contribution of the solvent molecules and, thereby, to produce a set of solvent-free diffraction intensities; structures were then refined again using the data generated.

In the structure, ligand MPBD⁴⁻ exhibits two crystallographically independent conformations (*syn*- and *anti*-) and the carbonyl moiety of acylamide group is disordered over two positions with equal probability (Fig. S1). CCDC 1006012 contains the supplementary crystallographic data for HNUST-4. The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK.

6. Low-pressure gas sorption measurements

Low-pressure gas (N₂, H₂, CH₄ and CO₂) sorption isotherms (up to 1 bar) were performed on Micromeritics ASAP 2020 M+C surface area and pore size analyzer at different temperatures. Before gas sorption measurements, about 150 mg acetone-exchanged samples were activated by using the “outgas” function of the surface area analyzer. For all isotherms, warm and cold free space correction

measurements were performed using ultra-high purity He gas (UHP grade 5.0, 99.999% purity). A part of the N₂ sorption isotherm at 77 K in the P/P₀ range 0.001–0.03 was fitted to the BET equation to estimate the BET surface area and the Langmuir surface area calculation was performed using all data points. The pore size distribution (PSD) was obtained from the DFT model in the Micromeritics ASAP2020 software package (assuming cylinder pore geometry) based on the N₂ sorption isotherm.

7. Estimation of the isosteric heats of gas adsorption

A virial-type^[3] expression comprising the temperature-independent parameters a_i and b_j was employed to calculate the enthalpies of adsorption for H₂ (at 77 K and 87 K), CO₂ and CH₄ (at 273 and 298 K) on HNUST-4. In each case, the data were fitted using the equation:

$$\ln P = \ln N + 1/T \sum_{i=0}^m a_i N^i + \sum_{j=0}^n b_j N^j \quad (1)$$

Here, P is the pressure expressed in Torr, N is the amount adsorbed in mmol/g, T is the temperature in K, a_i and b_j are virial coefficients, and m , n represent the number of coefficients required to adequately describe the isotherms (m and n were gradually increased until the contribution of extra added a and b coefficients was deemed to be statistically insignificant towards the overall fit, and the average value of the squared deviations from the experimental values was minimized). 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} is the coverage-dependent isosteric heat of adsorption and R is the universal gas constant).

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

8. Water-stability test

About 200 mg of as-synthesized HNUST-4 was soaked in water for a day at 298 K and 373 K, respectively. After that, the samples are taken pictures (Fig. S2) and then filtrated. Both the crystalline and phase purity of the samples treated by water (room temperature) and boiling water were confirmed by PXRD patterns (Fig. 2 in manuscript). To confirm the water stability of HNUST-4, the samples treated by water were first acetone-exchanged and then degassed on the ASAP2020 M+C instrument at 100 °C for 12 hours under a dynamic high vacuum prior to N₂ sorption measurement (Fig. S3).

Table S1. Crystal data and structure refinement for HNUST-4.

Identification code	HNUST-4
CCDC number	1006012
Empirical formula	C75 H38 Cu6 N6 O36
Formula weight	1980.41
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Tetragonal
Space group	I4/mmm
<i>a</i>	29.627(3) Å
<i>b</i>	29.627(3) Å
<i>c</i>	29.627 Å
<i>α</i>	90°
<i>β</i>	90°
<i>γ</i>	90°
Volume	26005(4) Å ³
Z	8
Density (calculated)	1.012 g cm ⁻³
Absorption coefficient	1.023 mm ⁻¹
F(000)	7934
Crystal size	0.24 x 0.22 x 0.20 mm
Theta range for data collection	1.68 to 25.35 deg
Limiting indices	-34 ≤ h ≤ 35, -35 ≤ k ≤ 35, -33 ≤ l ≤ 35
Reflections collected unique	96935/ 6535 [R(int) = 0.1435]
Completeness	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8216 and 0.7913
Refinement method	Full-matrix least-squares on F ²
Data /restraints / parameters	6535 / 69 / 324
Goodness-of-fit on F²	1.199
Final R indices [I>2σ(I)]	R1 = 0.0958, wR2 ^a = 0.3059
R indices (all data)	R1 = 0.1257, wR2 ^a = 0.3233
Largest diff. peak and hole	1.444 and -3.997 e. Å ⁻³

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

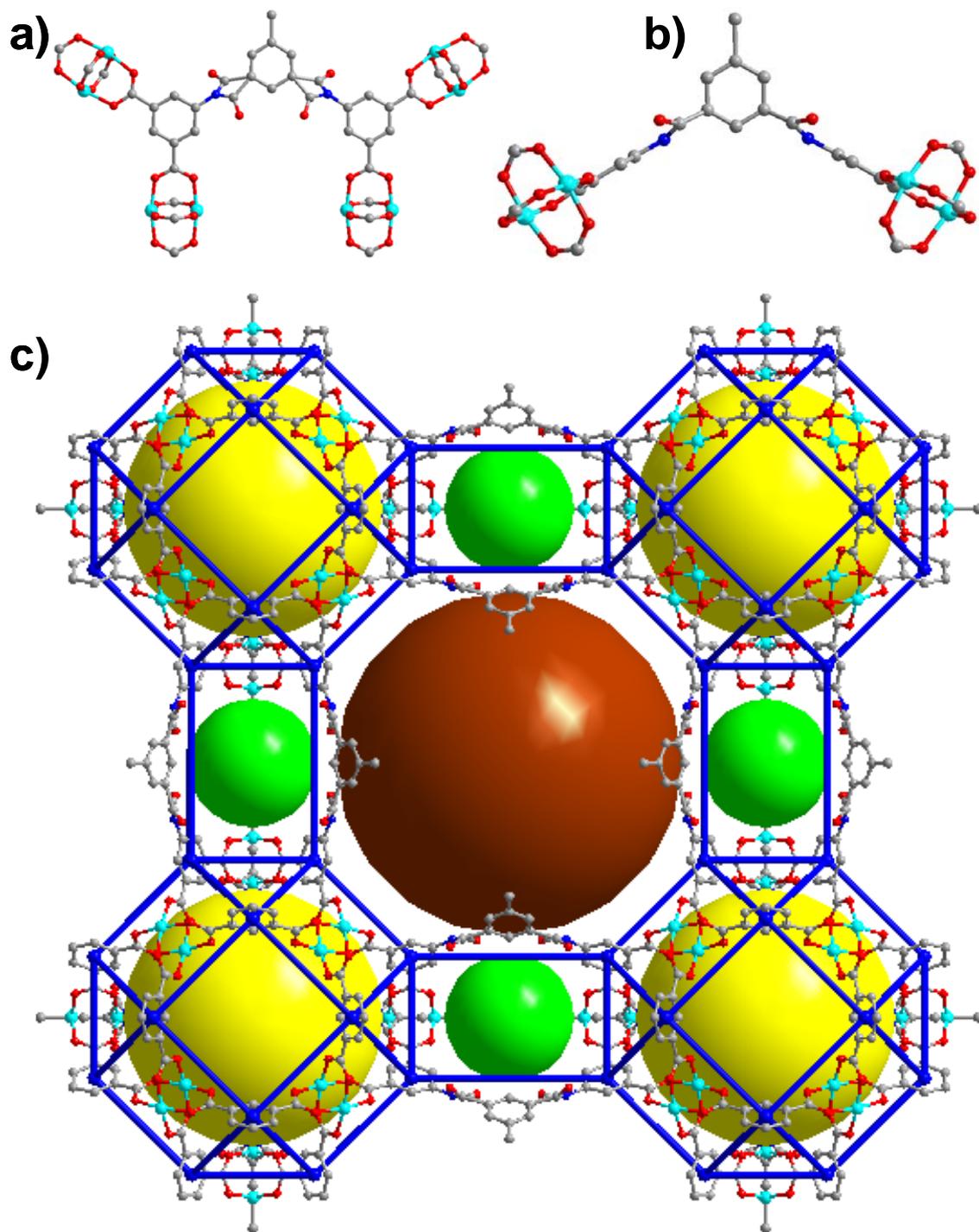


Fig. S1 Two crystallographically independent flexible ligands found in **HNUST-4** (*a-b*: *syn* and *anti* conformation) and (*c*) single network of **HNUST-4** viewed from *c* axis.

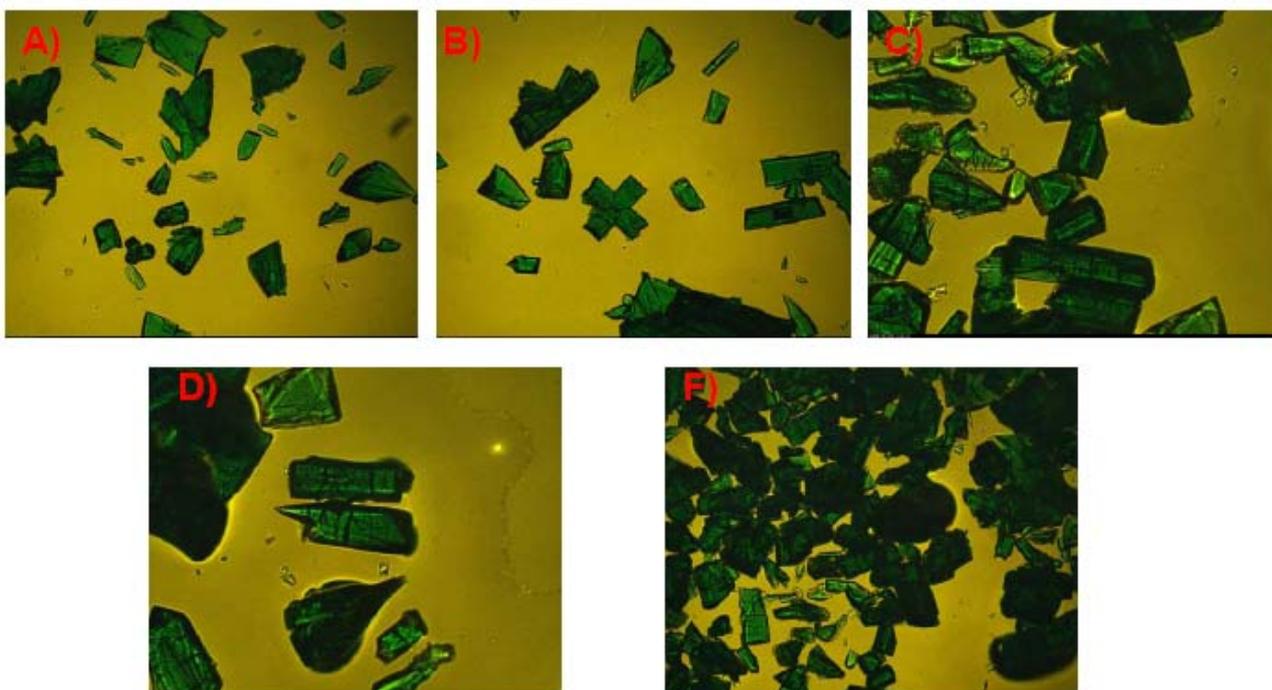
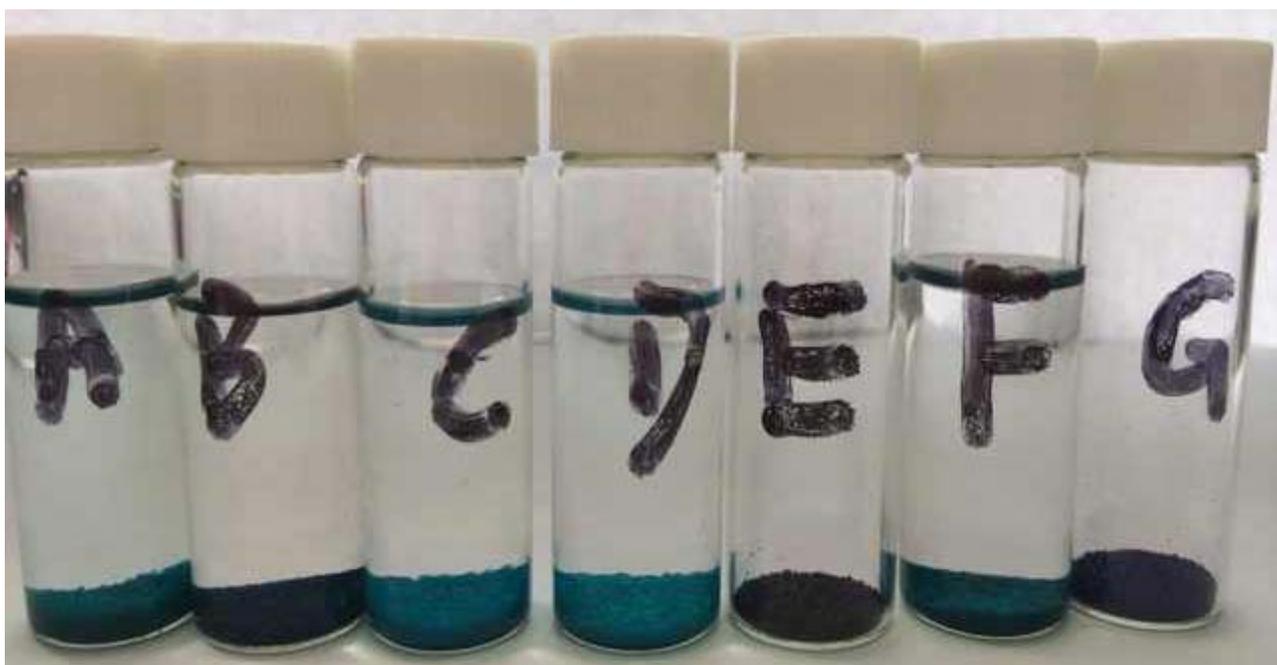


Fig. S2 Photographic images of **HNUST-4** at different conditions. (A) as-synthesized in DMF; (B) acetone-exchanged in acetone; (C) immersed in water at room temperature for a day; (D) immersed in boiling water for a day; (E) activated; (F) the activated sample was immersed in water at room temperature for a day; (G) activated after a week in boiling water.

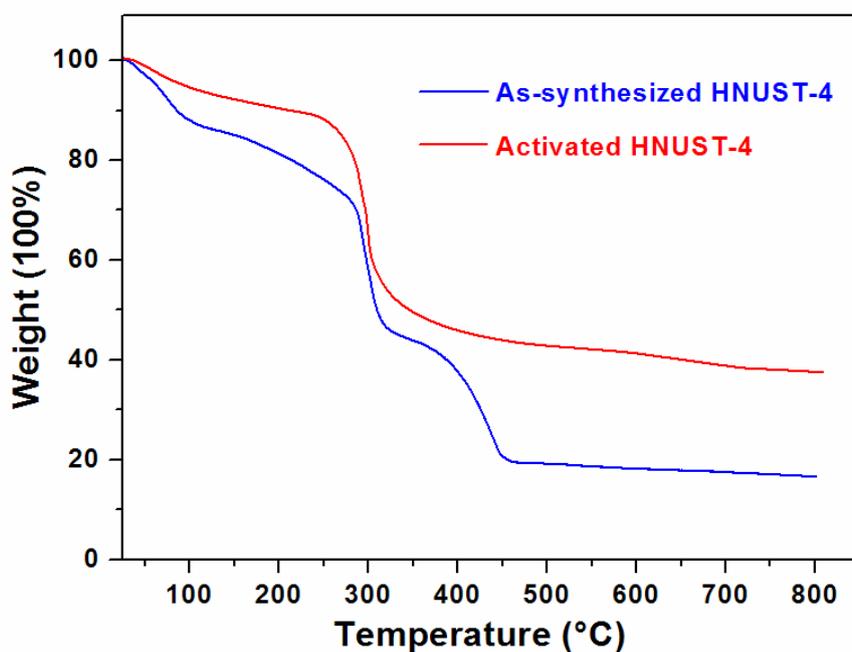


Fig. S3 TGA trace of as-synthesized and activated HNUST-4.

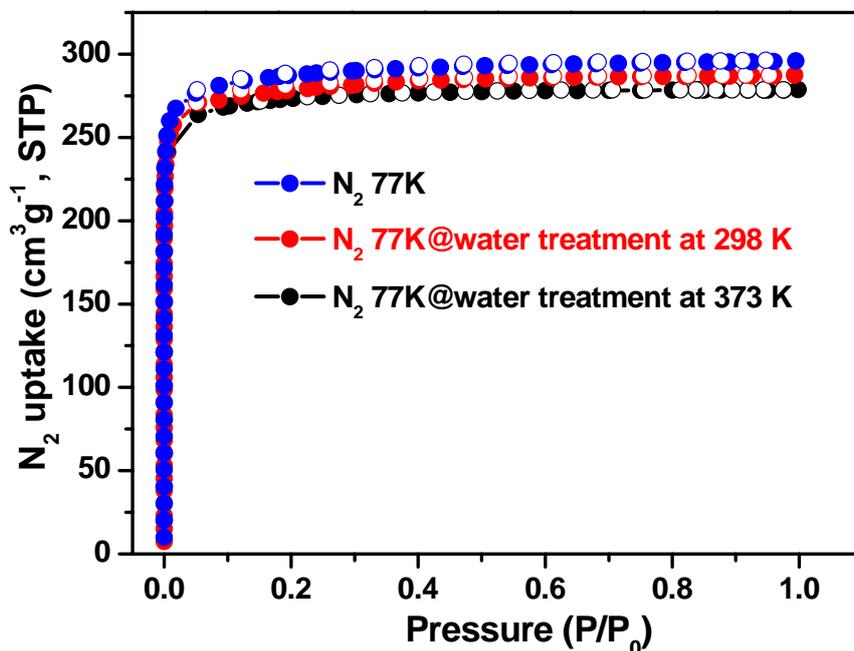


Fig. S4 N₂ adsorption isotherms for HNUST-4 at 77 K, showing the water-stable framework of HNUST-4. Blue: the as-synthesized HNUST-4 was solvent-exchanged by acetone and then degassed at 373 K; Red: the as-synthesized HNUST-4 was immersed in water at room temperature for a day and then solvent-exchanged by acetone, and degassed at 373 K; Black: the as-synthesized HNUST-4 was immersed in boiling water for a day, solvent-exchanged by acetone, and degassed at 373 K.

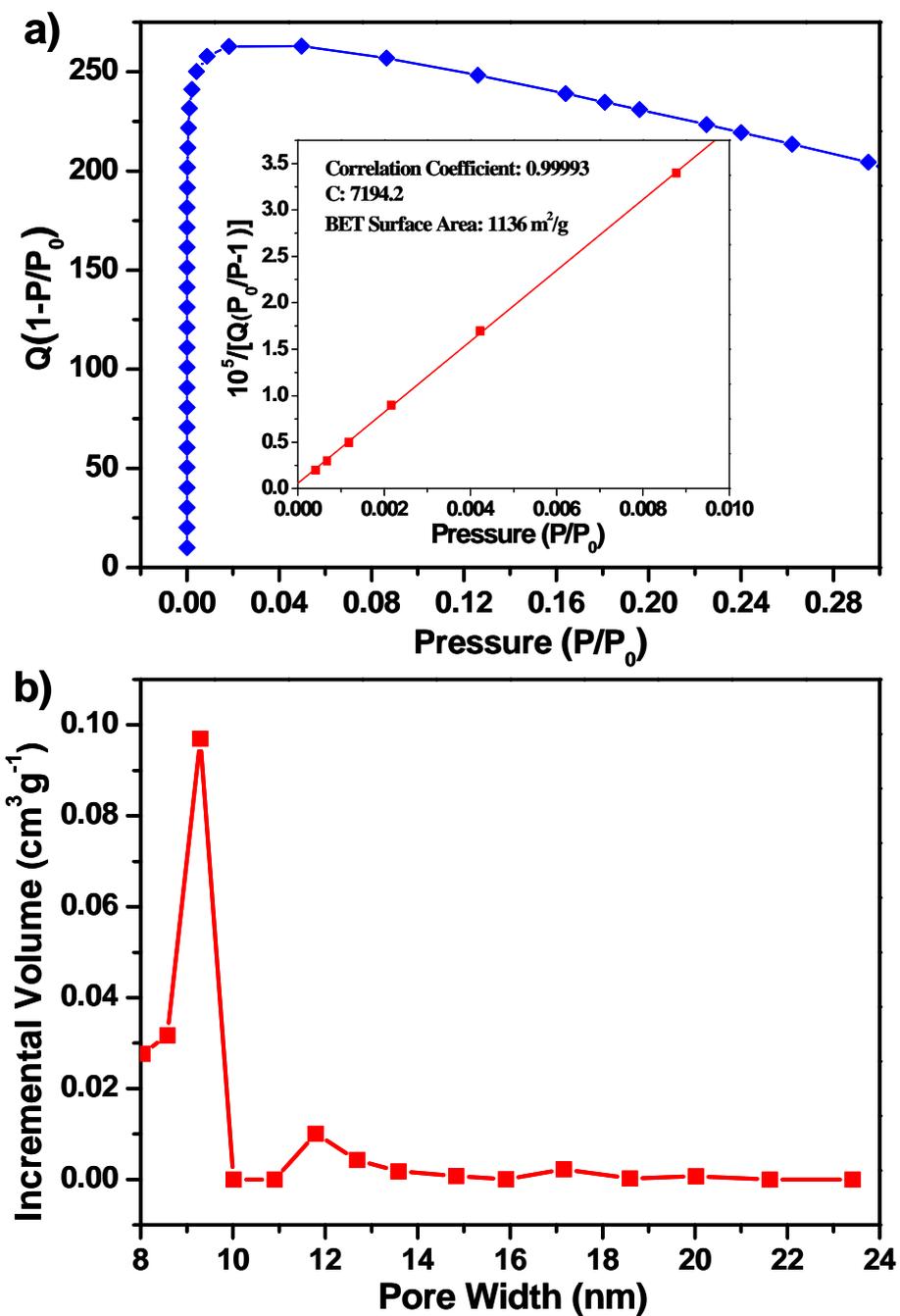


Fig. S5 a) The BET plots for **HNUST-4** in the chosen range ($P/P_0 = 0.0005-0.09$) and b) pore size distributions calculated from the N₂ sorption isotherm.

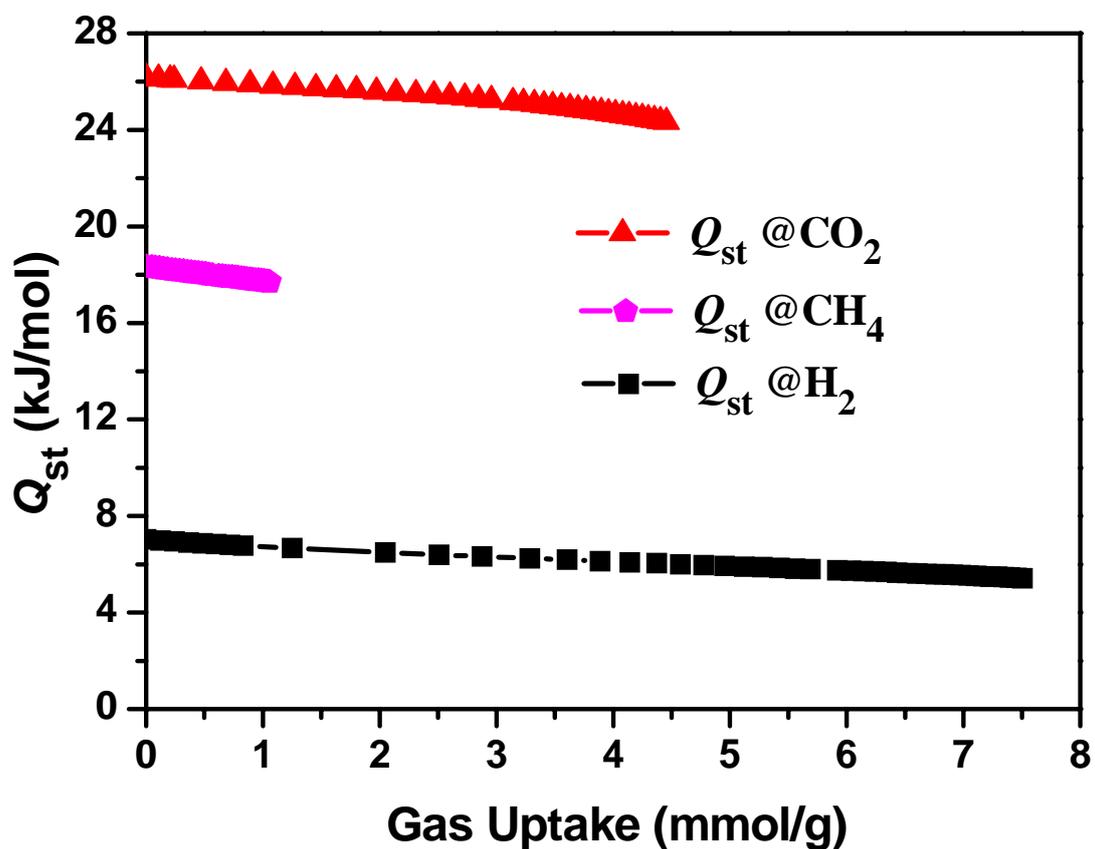


Fig. S6 Isosteric heats of H₂, CO₂ and CH₄ adsorption of HNUST-4 calculated from the adsorptions at two different temperatures (H₂ at 77 K and 87 K, CO₂ and CH₄ at 298 K and 273 K, respectively) through Virial method.

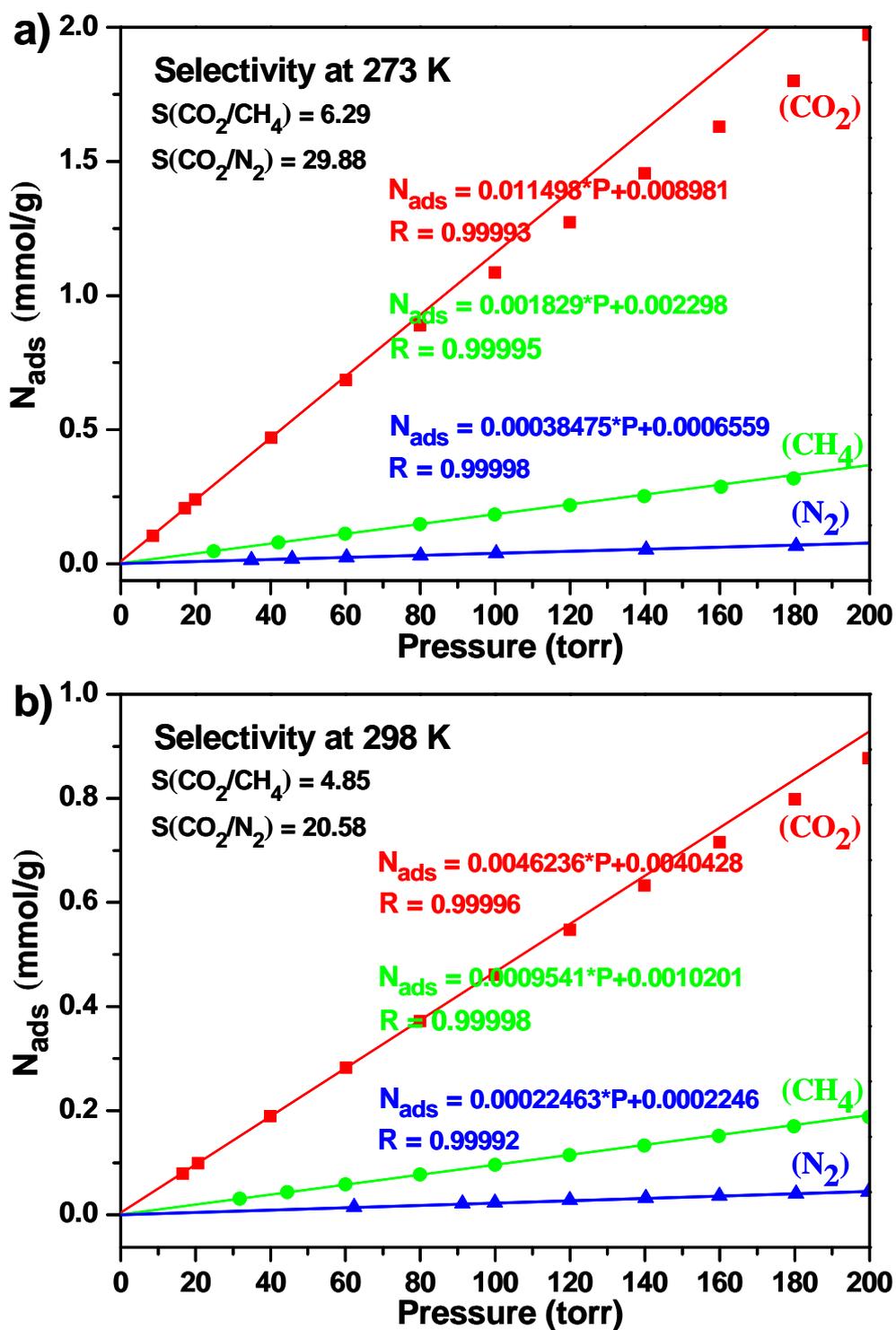


Fig. S7 The fitting initial slope for CO_2 , CH_4 and N_2 isotherms for **HNUST-4** collected at 273 K and 298 K (N_{ads} = gas uptake; R = related coefficient). The calculated selectivity of CO_2/CH_4 and CO_2/N_2 is 6.29 and 29.88 at 273 K, 4.85 and 20.58 at 298 K, respectively.

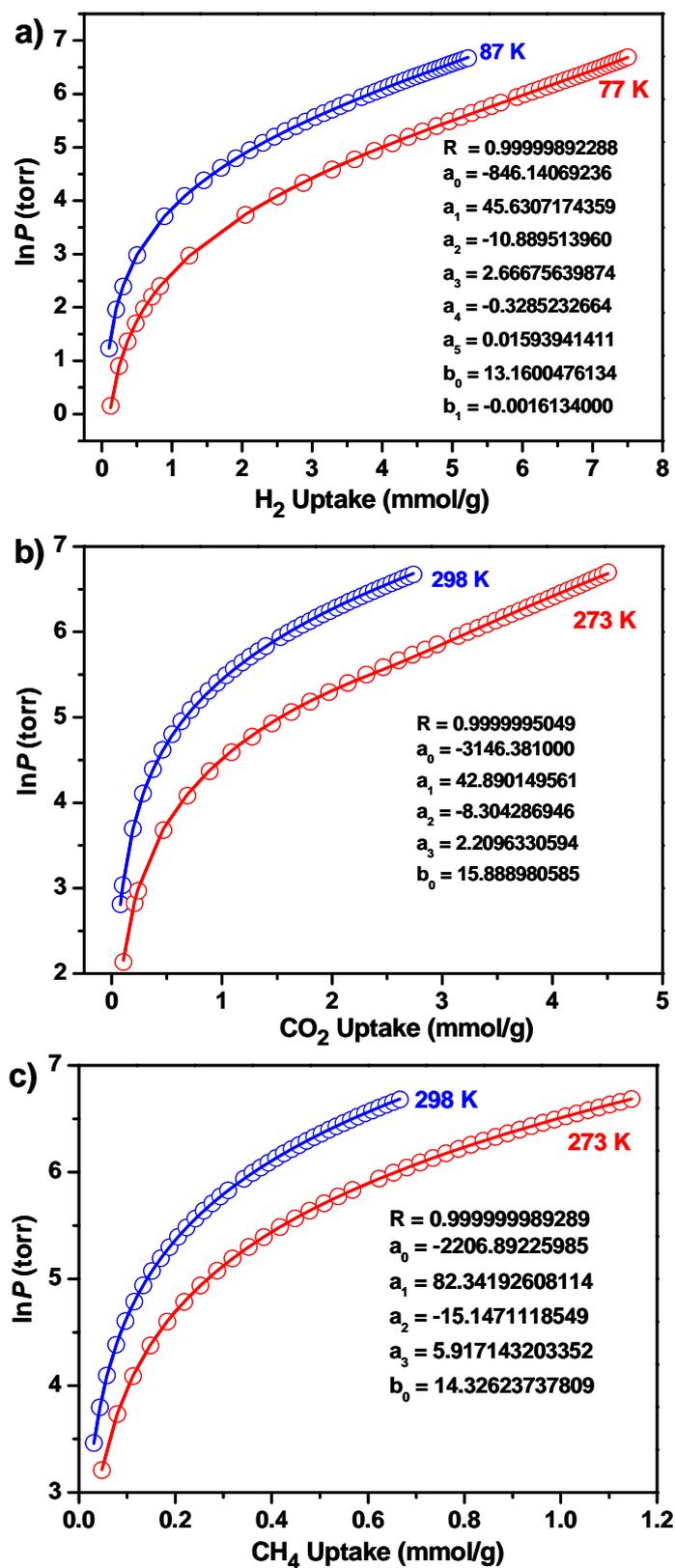


Fig. S8 Details of virial equation (solid lines) fitting to the experimental adsorption data (symbols) for HNUST-4 collected at two different temperatures: a) H_2 , b) CO_2 and c) CH_4 .

References

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- [3]. J. L. C. Rowsell and O. M. Yaghi, *J. Am. Chem. Soc.*, 2006, **128**, 1304.