

Electronic Supporting Information

An unprecedentedly water stable acylamide-functionalized metal-organic framework for highly efficient CH₄/CO₂ gas storage/separation and acid-base cooperative catalytic activity

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Materials and Methods

All chemical reagents were obtained from commercial sources and used without further

purification unless otherwise noted. ^1H NMR spectra were recorded on a Bruker AVANCE III 500 MHz spectrometer with tetramethylsilane as an internal reference. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240 analyzer. The IR spectra were recorded in the 400-4000 cm^{-1} on a VECTOR TM 22 spectrometer using KBr pellets. Thermal gravimetric analysis (TGA) were performed under N_2 atmosphere ($100 \text{ mL}\cdot\text{min}^{-1}$) with a heating rate of $5 \text{ K}\cdot\text{min}^{-1}$ using a 2960 SDT thermogravimetric analyzer. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 ADVANCE X-ray diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at room temperature. Simulation of the PXRD spectrum was carried out by the single-crystal data and diffraction-crystal module of the Mercury program available free of charge *via* Internet at <http://www.ccdc.cam.ac.uk/products/mercury/>.

Activation of HNUST-8

The solvent-exchanged HNUST-8 was prepared by immersing the as-synthesized sample firstly in dry methanol for 48 hours and then in dry CH_2Cl_2 for another 48 hours to remove the non-volatile solvates (DMF and water), the extract was decanted every 8 hours and fresh methanol or CH_2Cl_2 was replaced. The completely activated HNUST-8 sample was obtained by heating the solvent-exchanged sample at $100 \text{ }^\circ\text{C}$ under a dynamic high vacuum for 24 hours. During this time, the pale blue sample changed to a deep purple-blue colour (Fig. S2), indicative of the presence of open copper(II) sites. The completely-activated samples were moisture sensitive and a few minutes of exposure to air could change the sample's color back to pale blue. Anal. Calcd (Found) for $[\text{Cu}_2(\text{C}_{35}\text{H}_{19}\text{N}_3\text{O}_{10})]$: C, 54.69 (54.65), H 2.49 (2.60), N 5.47 (5.39). The fully-activated samples were moisture sensitive and a few minutes of exposure to air could change the sample's color back to pale-blue. Selected IR (KBr, cm^{-1} , Fig. S11): 1664, 1604, 1517, 1366, 1107, 833, 772, 726.

Temperature-Programmed Desorption of NH_3 (NH_3 -TPD)

Activated sample (about 30 mg) was loaded in the center of the U-type cell. The system was then degassed at $100 \text{ }^\circ\text{C}$ for 5 h. After the temperature cooled down, NH_3 gas ($30 \text{ mL}\cdot\text{min}^{-1}$) was introduced to pass through the cell for 30 minutes. In order to wash the free NH_3 , the He gas ($30 \text{ mL}\cdot\text{min}^{-1}$) was used to blow the cell for another 60 minutes. The NH_3 -TPD data were collected using a heating rate of $5 \text{ K}\cdot\text{min}^{-1}$ under He gas ($30 \text{ mL}\cdot\text{min}^{-1}$).

Framework stability test

As-synthesized HNUST-8 (about 800 mg) was collected from the mother liquor, washed with DMF, and then distributed equally in 4 vials containing 30 mL aqueous solution with different pH value of 3, 7 and 10, respectively (adjusted by HCl or NaOH). After immersion for 2 days at room temperature, the samples were collected by filtration and analyzed by PXRD. Similarly, after Deacetalization-Knoevenagel condensation reaction as a catalyst, HNUST-8 was collected by centrifugal separation, washed with methanol, and analyzed by PXRD. Moreover, to further check the chemical and water stability of HNUST-8, the HNUST-8 samples after treatment by aqueous solution with pH value of 3 and 10 were selected to collect the N_2 sorption isotherms at 77 K.

Table S1. Crystal data and structure refinement for HNUST-8.

Identification code	HNUST-8
CCDC number	1581346
Empirical formula	C₃₅ H₁₇ Cu₂ N₃ O₁₁
Formula weight	782.60
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Cubic
Space group	Im-3m
<i>a</i>	36.244(8) Å
<i>b</i>	36.244(8) Å
<i>c</i>	36.244(8) Å
<i>α</i>	90°
<i>β</i>	90°
<i>γ</i>	90°
Volume	47611(18) Å³
Z	24
Density (calculated)	0.655 g cm⁻³
Absorption coefficient	0.564 mm⁻¹
F(000)	9456
Crystal size	0.24 x 0.20 x 0.16 mm
Theta range for data collection	2.25 to 25.00 deg
Limiting indices	-43 ≤ <i>h</i> ≤ 42, -37 ≤ <i>k</i> ≤ 43, -43 ≤ <i>l</i> ≤ 43
Reflections collected unique	129764 / 3919 [R(int) = 0.0666]
Completeness	99.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9152 and 0.8765
Refinement method	Full-matrix least-squares on F²
Data / restraints / parameters	3919 / 42 / 171
Goodness-of-fit on F²	1.106
Final R indices [I > 2σ(I)]	R1 = 0.0466, wR2^a = 0.1309
R indices (all data)	R1 = 0.0560, wR2^a = 0.1375
Largest diff. peak and hole	0.510 and -0.353 e. Å⁻³

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

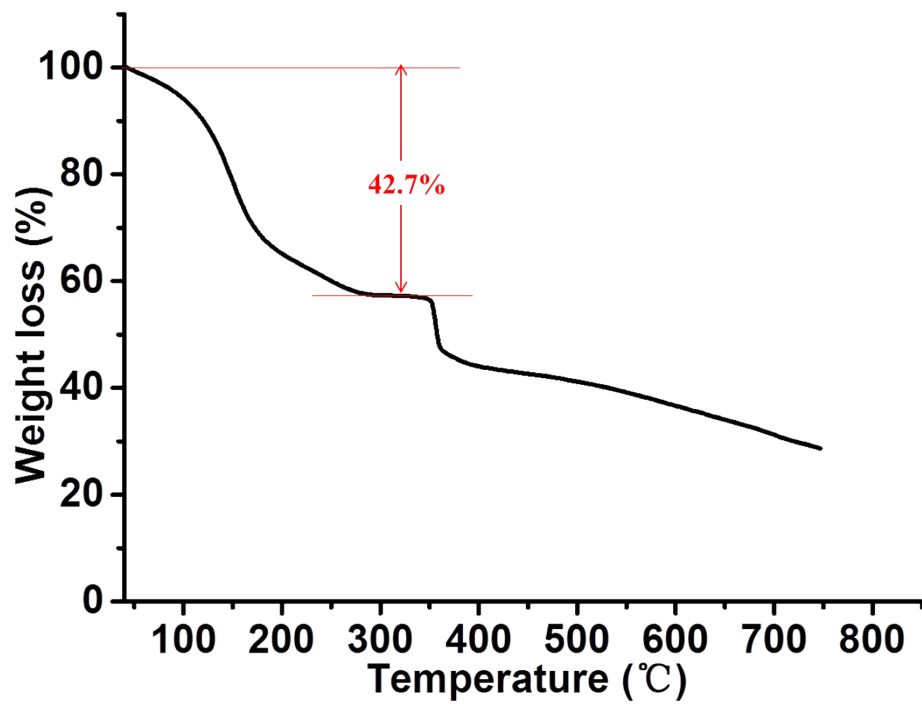


Fig. S1 TGA data of as-synthesized HNUST-8.

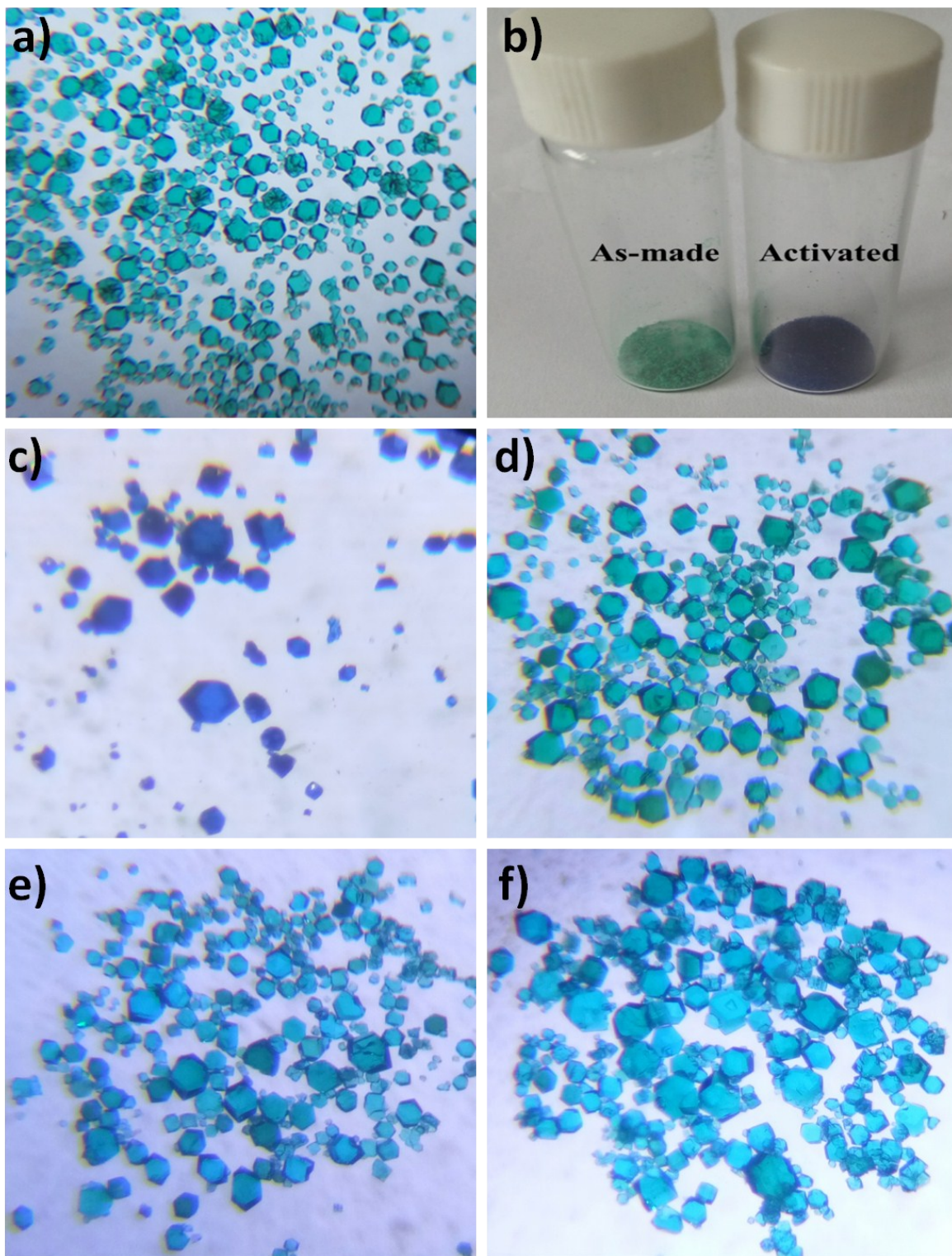


Fig. S2 Photographic image of **HNUST-8**: a) as-synthesized in DMF, b) visual color change between as-synthesized and activated, c) activated in N_2 atmosphere, d) firstly activated and then immersed in water for 2 days, e) firstly activated and then immersed in HCl solution ($pH = 3$) for 2 days, f) firstly activated and then immersed in NaOH solution ($pH = 10$) for 2 days. NOTE: the crystal size of **HNUST-8** has been magnified about 80-100 times.

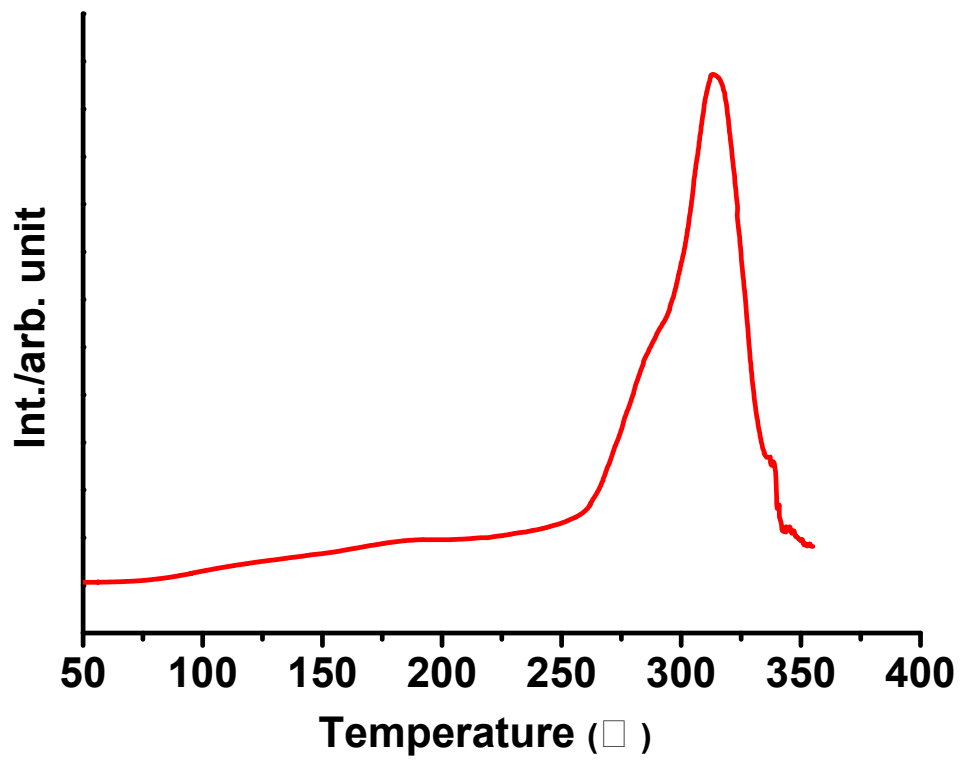


Fig. S3 NH_3 -TPD profile of HNUST-8.

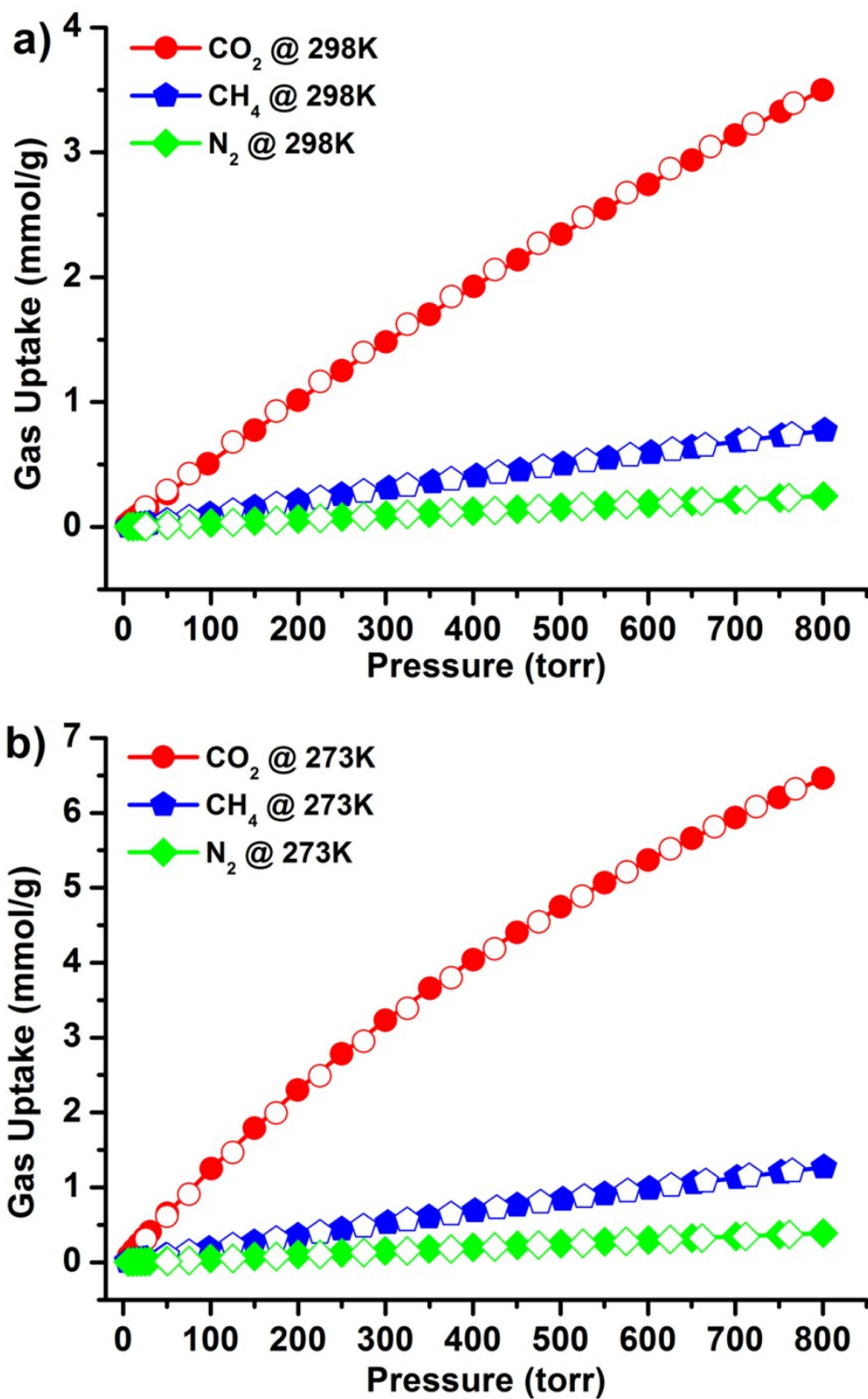


Fig. S4 Low-pressure gas (CO_2 , CH_4 and N_2) sorption isotherms of HNUST-8 at 298 K and 273 K (filled symbols, adsorption; open symbols, desorption).

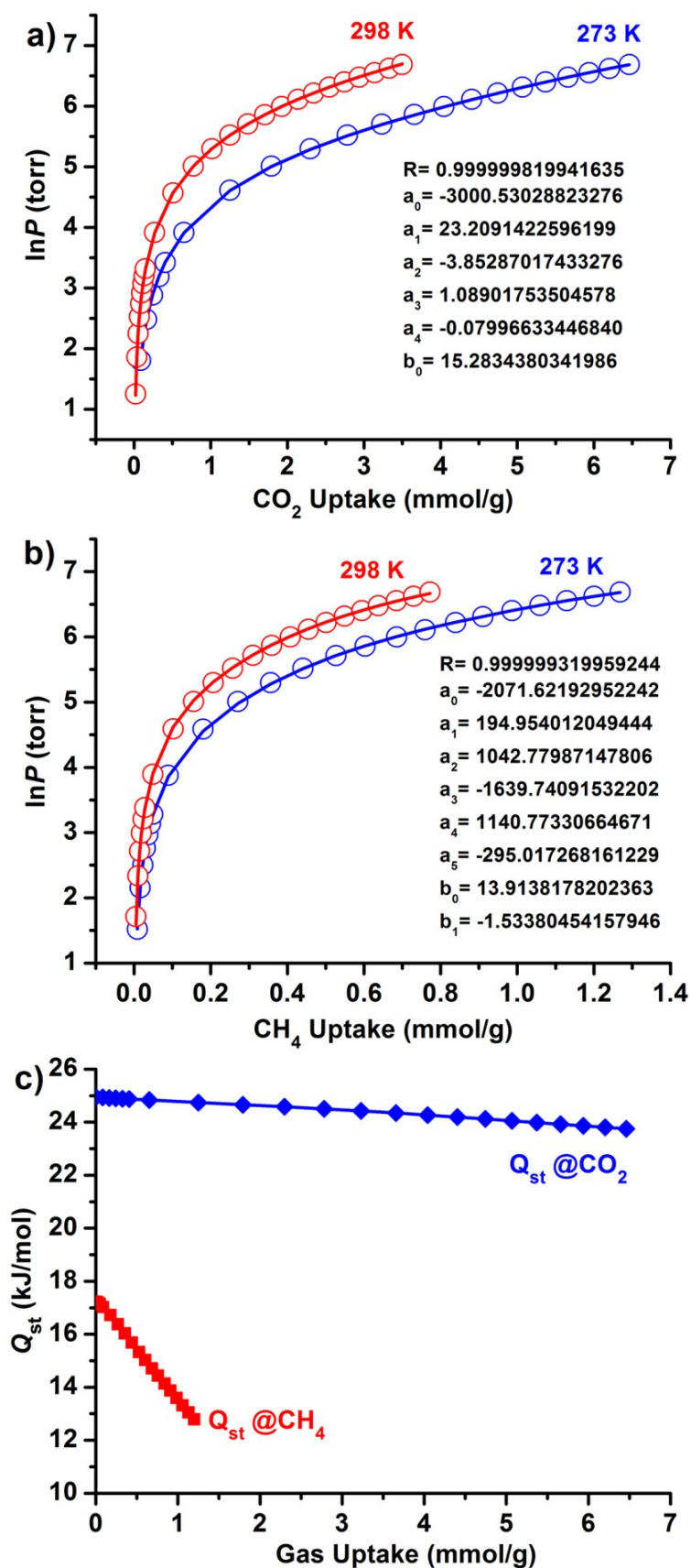


Fig. S5 a-b) Details of virial equation (symbols) fitting to the experimental CO_2 and CH_4 adsorption data (solid lines) for **HNUST-8** collected at 273 K and 298 K; c) The CO_2 and CH_4 isosteric adsorption enthalpies of **HNUST-8**.

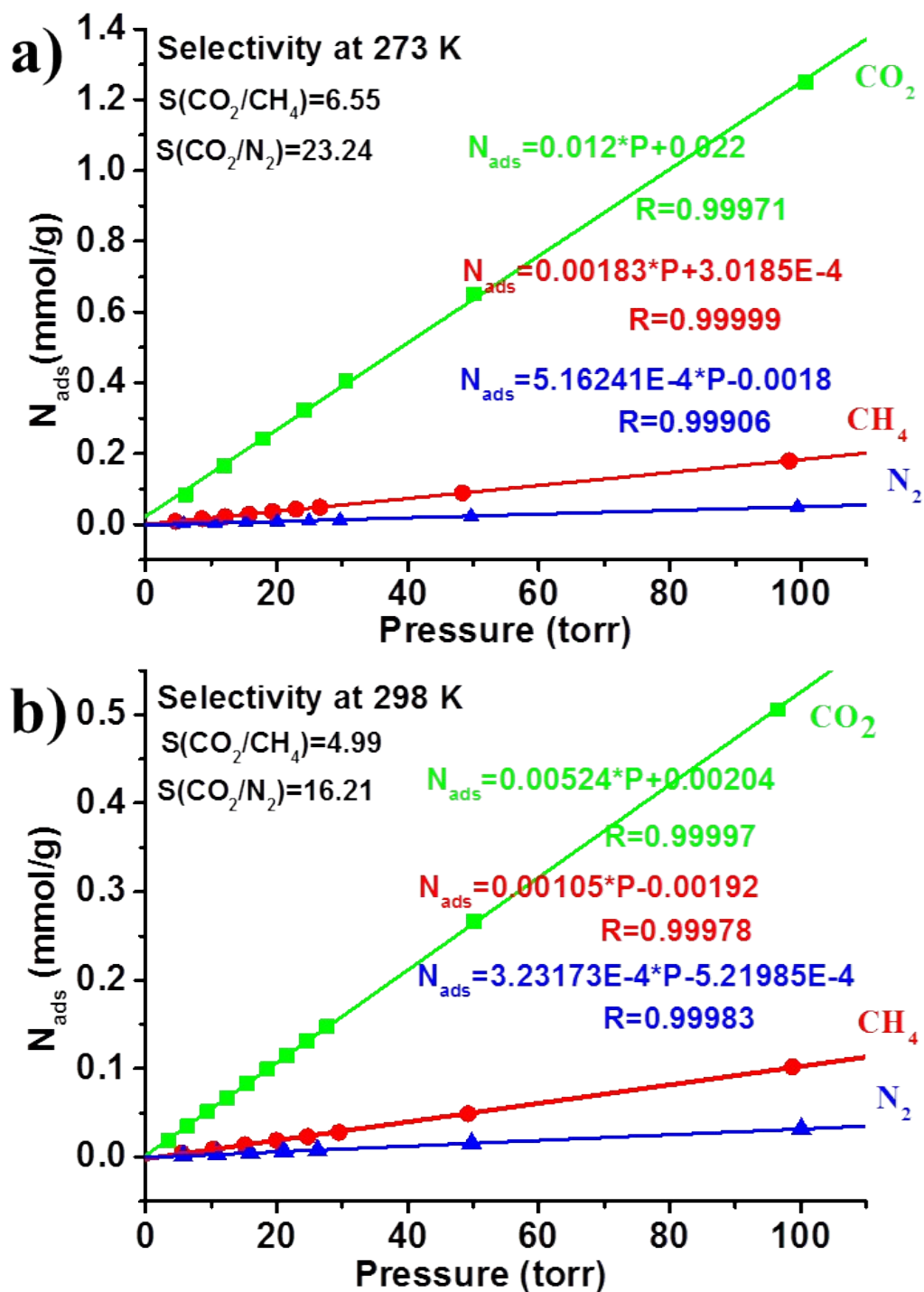


Fig. S6 The fitting initial slope for CO₂, CH₄ and N₂ isotherms for **HNUST-8** collected at 273 K and 298 K (N_{ads} = gas uptake; R = related coefficient). The calculated selectivity of CO₂/CH₄ and CO₂/N₂ is 6.55 and 23.24 at 273 K, 4.99 and 16.21 at 298 K, respectively.

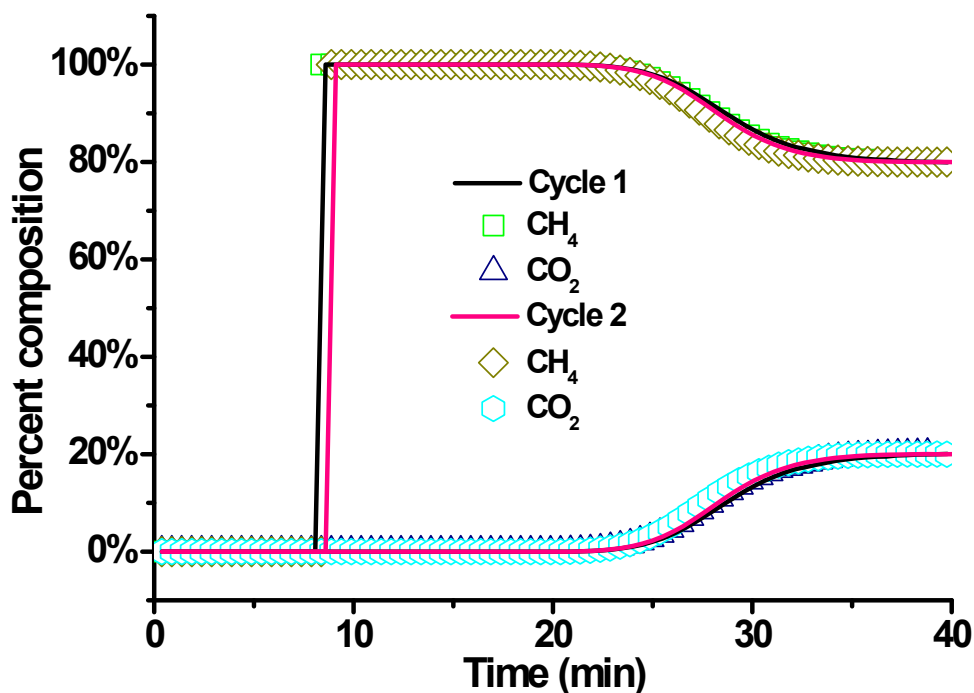


Fig. S7 Repeated CO₂/CH₄ breakthrough experiments of HNUST-8 after 20 min helium gas blowing at 298 K.

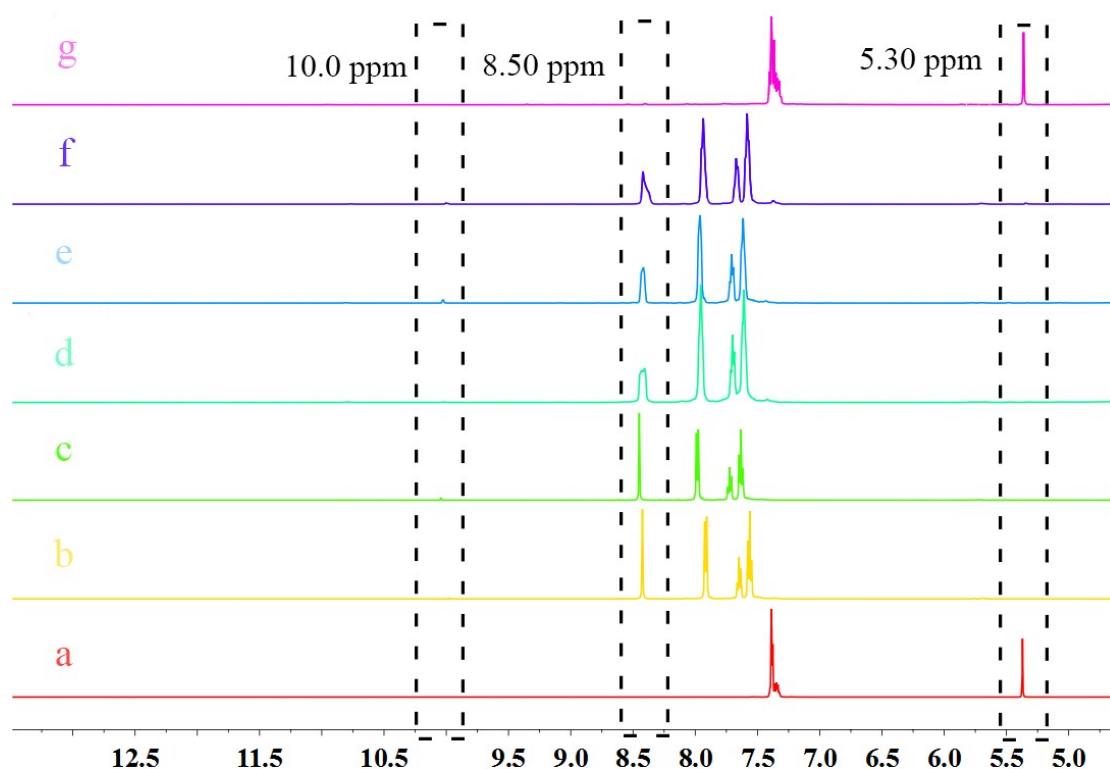


Fig. S8 The ¹H NMR spectrum of a solution after the Deacetalization-Knoevenagel condensation: a) without catalyst, b) first cycle, c) second cycle, d) third cycle, e) fourth cycle, f) fifth cycle and g) control experiment in the presence of ethylenediamine. The yields of the reaction have been calculated by integration of benzylic protons at the end of the reaction, due to the distinct chemical shifts for the corresponding benzylic proton (the starting material **dimethoxymethylbenzene**: ~ 5.3 ppm, the intermediate **benzaldehyde**: ~ 10.0 ppm, and the final product **Benzylidene malononitrile**: ~ 8.5 ppm).

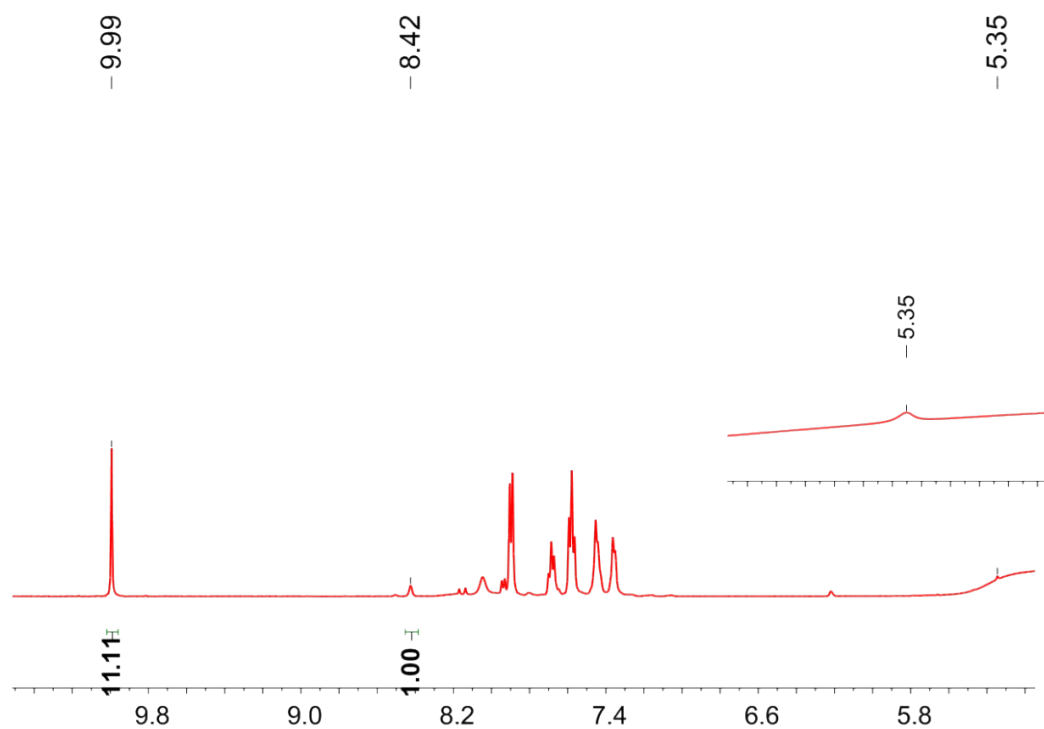


Fig. S9 ¹H NMR spectrum of a solution after the Deacetalization-Knoevenagel condensation in acidic control reaction.

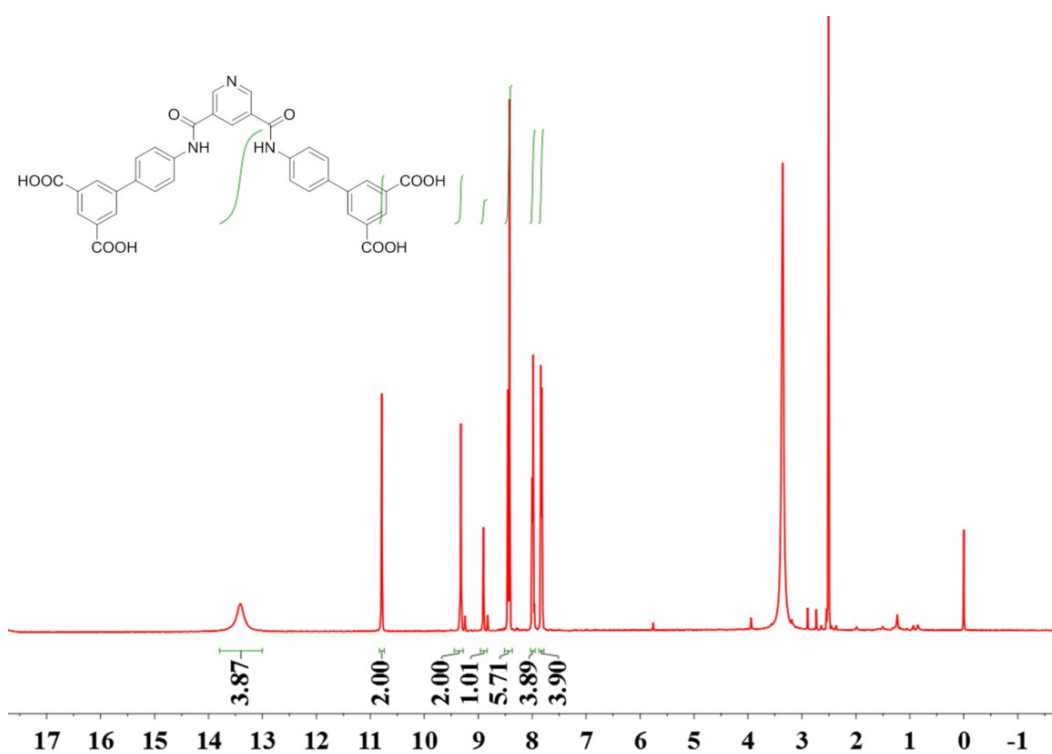


Fig. S10 ¹H NMR spectrum of the ligand (PDBAD), 4,4'''-((pyridine-3,5-dicarbonyl)bis(azanediyl))bis((1,1'-biphenyl)-3,5-dicarboxylic acid) in DMSO-*d*₆.

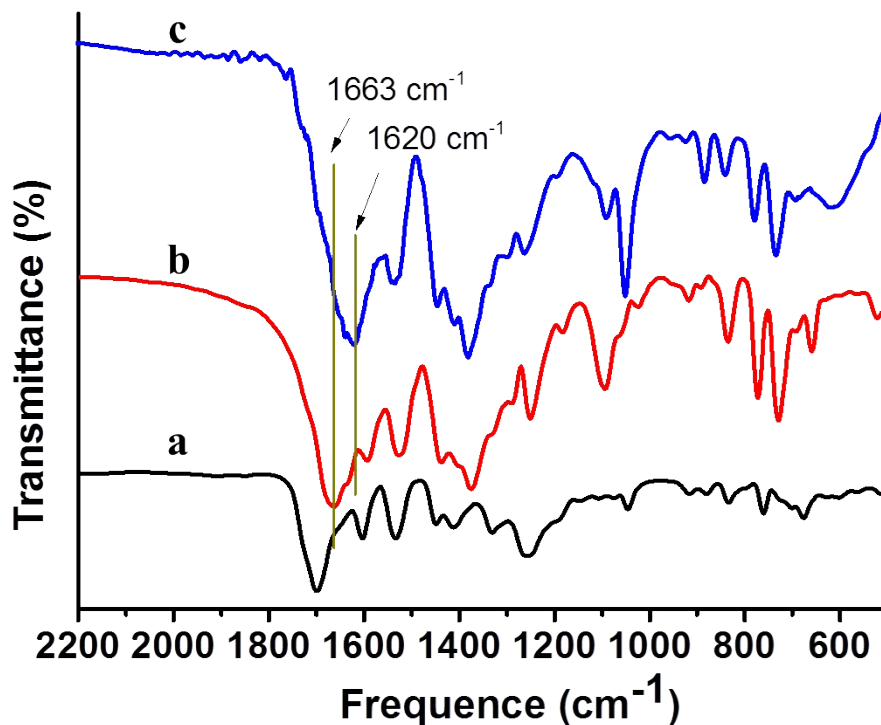


Fig. S11 The IR spectra for **HNUST-8**. a) ligand, b) as-synthesized, and c) activated **HNUST-8**. Note the absence of the vibration frequencies of the solvent DMF and methanol molecules in the both activated samples. The frequencies at 1663 cm^{-1} attributes to the $\nu(\text{CO})$ vibration of the DMF, and the presence of the $\nu(\text{OH})$ stretching frequencies at 1620 cm^{-1} in activated samples may result from the rapid re-adsorption of trace moisture during the IR measurements.

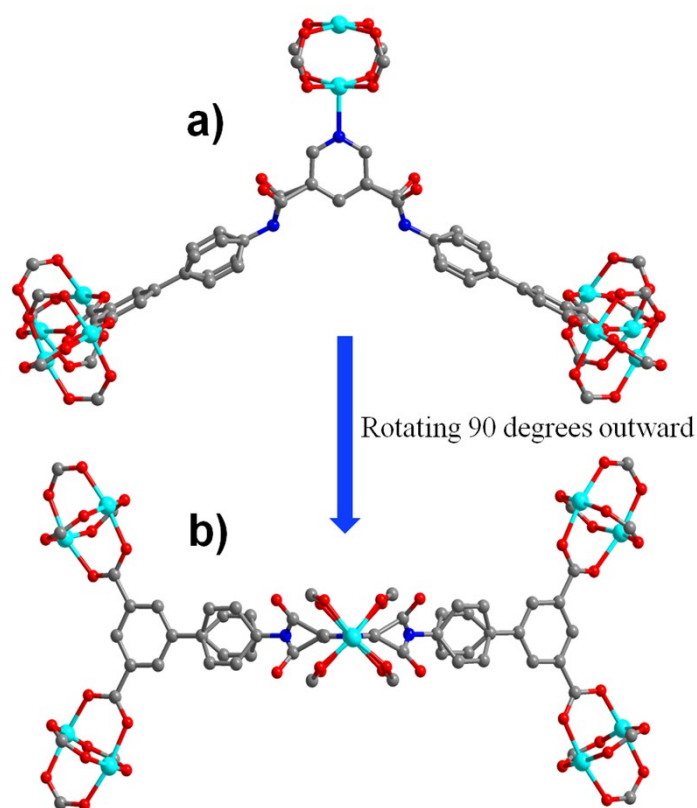


Fig. S12 The acylamide and benzene moieties of the **PDBAD** ligand in the crystal structure of **HNUST-8** are disordered over two positions with equal probability.

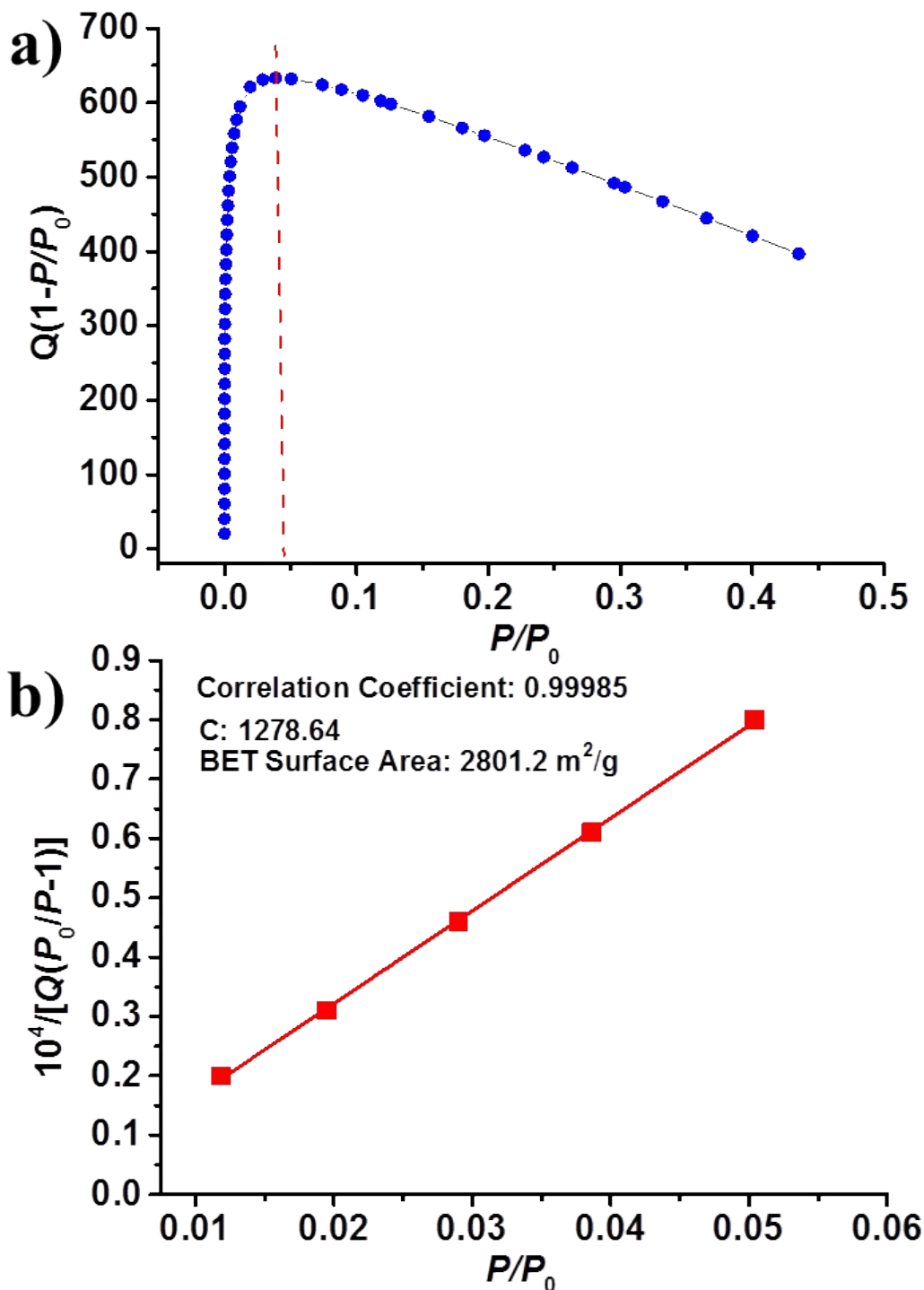


Fig. S13 The BET plots for **HNUST-8** in the chosen range ($P/P_0 = 0.01-0.05$). This range was chosen according to two major criteria established in literatures [(a) J. Rouquerol, P. Llewellyn and F. Rouquerol, *Stud. Surf. Sci. Catal.*, **2007**, 160, 49-56; (b) K. S. Walton and R. Q. Snurr, *J. Am. Chem. Soc.*, **2007**, 129, 8552 -8556.]: (1) The pressure range selected should have values of $Q(P_0-P)$ increasing with P/P_0 . (2) The y intercept of the linear region must be positive to yield a meaningful value of the C parameter, which should be greater than zero.