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SUPPORTING INFORMATION

A highly porous *rht*-type acylamide-functionalized metal-organic framework exhibiting large CO_2 uptake capability

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Methods and instrumentation

All starting materials for synthesis were purchased commercially, and unless otherwise noted, were used without further purification. The IR spectra were recorded in the 400 - 4000 cm^{-1} on a VECTOR TM 22 spectrometer using KBr pellets. ^1H NMR spectra were recorded on a Bruker ADVANCE-AV 500 MHz spectrometer with tetramethylsilane as an internal reference. Thermal gravimetric analyses (TGA) were performed under N_2 atmosphere (flow rate: 100 mL/min) with a heating rate of 5 °C/min using a 2960 SDT thermogravimetric analyzer. Powder X-ray diffraction (PXRD) date was collected over the 2ϑ range 5 - 50^o on a Bruker D8 ADVANCE X-ray diffractometer using Cu $K\alpha$ radiation (wavelength: 1.5418 Å) at room temperature with a scan speed of 5 º/min and a step size of 0.02 in 2ϑ at 40 kV and 40 mA. Scanning electron microscopy (SEM) images were collected using a JEOL JSM-6380LV instrument.

Synthesis of the ligand, 5,5',5"-((triphenylene-2,6,10-tricarbonyl)tris(azanediyl)triisophthalic acid (TTTT)

Into a flask flushed with N_2, triphenylene-2, 6, 10-tricarboxylic acid (Ref 1) (0.36 g, 1.0 mmol) with 2 drops of DMF was placed, and $SOCl_2$ (20 mL, 275 mmol) was slowly added dropwise. The mixture was refluxed over night and then the excess $SOCl_2$ was removed under vacuum. To the resulting solid, 10 mL of anhydrous 1-Methyl-2-Pyrrlione (NMP) was added and the solution was cooled with an ice bath. While under nitrogen flow, 4-(dimethylamino)pyridine (0.15 g, 1.2 mmol) was added followed by addition of 5-aminoisophthalic acid (0.6 g, 3.3 mmol). After stirring for 30 min at 0 °C and 48 hours at room temperature, the reaction solution was poured into a large excess of water. The precipitated solids were filtered off and washed repeatedly with hot methanol. The wet solid was finally dried in a vacuum oven at 90 °C to yield pure product as a pale yellow powder (0.71 g, ~ 83 % yield). ^1H NMR (500 MHz, DMSO-d_6, δ ppm, see Fig. S1): 13.42 (broad peak, 6H, COO$\underline{H}$), 11.04 (s, 3H, CON$\underline{H}$), 9.60 (s, 3H, Ar$\underline{H}$), 9.27 (d, 3H, Ar$\underline{H}$), 8.86 (s, 6H, Ar$\underline{H}$), 8.52 (d, 3H, Ar$\underline{H}$), 8.35 (s, 3H, Ar$\underline{H}$). Selected IR (KBr, cm^{-1}): 1710, 1660, 1609, 1551, 1500, 1451, 1332, 1278, 1226, 1126, 908, 843, 809, 760, 665. MP: > 300 °C.

Synthesis of HNUST-5

Linker TTTT (17.0 mg, 0.02 mmol) and $Cu(OAc)_2 \bullet H_2O$ (20.0 mg, 0.1 mmol) in 2.6 mL DMF/DMSO/H_2O (1:1.5:0.1 in volume) with 0.25 mL HBF_4 (40 % in water) were sonicated for a few minutes in air and the clear solution was transferred into a 20-mL scintillation vial. The vial was sealed and placed in an isothermal oven at 75 °C for 2 days and then cooled to room temperature. Pale blue octahedron-shaped microcrystalline products of **HNUST-5** (HNUST denotes Hunan University of Science and Technology) were filtered and washed with DMF. Yield 15 mg (~ 55 % based on the ligand). The crystals of **HNUST-5** are stable for common organic solvents except for water; it becomes opaque after exposure several hours in air. Despite extensive efforts, the elemental analyses are not well-reproduced, such case probably results from the fact that the extent of the solvent molecules in the cavities may vary depending on the exposure time of the sample to air. Selected IR (KBr, cm^{-1}): 1636, 1590, 1551, 1410, 1376, 1323, 1275, 1230, 1083, 1022, 946, 821, 770, 726, 484.

Sample activation procedure

As-synthesized **HNUST-5** crystals were immersed in anhydrous acetone for 3 days to remove the nonvolatile solvates (DMF, DMSO and water), the extract was decanted every 8 h, and fresh anhydrous acetone was replaced. After removal of acetone by decanting, the sample was further activated by drying under a dynamic high vacuum at 105 °C overnight to obtain the desolvated sample. During this process, a color change from pale-blue (in DMF) to blue (in acetone) to deep blue-violet (desolvated) was observed (as shown in Fig. S2), typical for Cu(II)-paddlewheel frameworks in which open copper(II) sites were generated (Ref 2). The desolvated sample was moisture-sensitive, and a few minutes of exposure to air could change the sample's color back to pale blue. Desolvated **HNUST-5** ($C_{15}H_7NO_5Cu$, Mw = 344.77 g mol^{-1}): Anal. Calcd: C 52.26, H 2.05, N 4.06; Found: C 52.21, H 2.17, N 3.97. Selected IR (KBr, cm^{-1}): 1618, 1551, 1407, 1368, 1275, 896, 846, 823, 770, 726.

Structure determination

Laboratory powder X-ray diffraction (PXRD) data were collected over the 2ϑ range 5 - 50° on a Bruker D8 ADVANCE X-ray diffractometer using Cu Kα radiation (wavelength: 1.5418 Å) at 303 K with a scan speed of 5 º/min and a step size of 0.02 in 2ϑ at 40 kV and 40 mA. Crystal structure of **HNUST-5** was refined by Rietveld method using RIETAN-FP program (Ref 3). The initial structure was developed manually based on previously reported analogues Cu-TPBTM and Cu-FTDTT (Ref 4). Some disorders (mainly in the triphenylene unit of the ligand), which actually included in the structure, are not considered in the refinement because this will make the structure too complex, and can't be refined based on the current PXRD data. The CCDC number and some important crystallographic data for **HNUST-5** are listed in Table S1.

Low-pressure gas-sorption measurements

Low-pressure gas (N_2, CO_2, and CH_4) 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. A part of the N_2 sorption isotherm at 77 K in the P/P_0 range 0. 002 - 0.1 was fitted to the BET equation to estimate the BET surface area (Ref 5) and the Langmuir surface area calculation was performed using all data points (Ref 6). The pore size distribution (PSD) was obtained from the DFT model in the Micromeritics ASAP2020 software package (assuming split pore geometry) based on the N_2 sorption isotherm. Ultra-high purity grade N_2 (99.999 %), He (99.999 %), CO_2 (99.9995 %) and CH_4 (99.9995 %) were used for all adsorption measurements.

High pressure gravimetric gas sorption measurements

High pressure excess adsorption isotherms of CO_2, CH_4, and N_2 were measured using a Belsorp-HP volumetric adsorption instrument from BEL Japan over a pressure range of 0-36 bar at 273 K and 298 K after an activation procedure same to that in low-pressure volumetric gas adsorption measurement. Before measurements, about 150 mg acetone-exchanged samples were degassed at 105 °C for 24 h under a dynamic high vacuum to obtain fully desolvated samples. Ultra-high purity grade N_2 (99.999 %), CO_2 (99.9995 %) and CH_4 (99.9995 %) were used for all adsorption measurements.

Estimation of the isosteric heats of gas adsorption

A Virial-type (Ref 7) expression comprising the temperature-independent parameters a_i and b_j was employed to calculate the enthalpies of adsorption for CO_2 and CH_4 (at 273 K and 298 K) on **HNUST-5**. In each case, the data were fitted using the equation:

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

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:

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

Q_{st} is the coverage-dependent isosteric heat of adsorption. The heat of CO_2 and CH_4 sorption for **HNUST-5** in the manuscript is determined by using the low-pressure sorption data measured in the pressure range from 0 - 1 bar (273 K and 298 K), which is fitted by the Virial-equation very well ($R^2>0.9999$, see Fig. S12).

Temperature-programmed desorption of NH_3 (NH_3-TPD)

Desolvated **HNUST-5** (30 mg) was loaded in the center of the U-type cell. The system was then degassed at 105 °C for 5 h. After the temperature cool down, NH_3 gas (30 mL/min) was introduced to pass through the cell for 30 minutes. In order to wash the free NH_3, the He gas (30 mL/min) was used to blow the cell for another 60 minutes. The NH_3-TPD data were collected using a heating rate of 5 K/min under He (30 mL/min) and the results were shown in Fig. S7.

Table S1. Crystallographic data for **HNUST-5**.

Compound	**HNUST-5**
CCDC number	1499031
Space Group	*Fm-3m*
Crystal System	Cubic
a / Å	46.542 (2)
b / Å	46.542 (2)
c / Å	46.542 (2)
α / °	90
β / °	90
γ / °	90
V / Å^3	100815 (9)
Wavelength / Å	Cu K$_\alpha$ (1.5418 Å)
R$_p$ / %	7.766
R$_{wp}$ / %	11.048
GoF	12.161
R$_{Bragg}$ / %	11.19

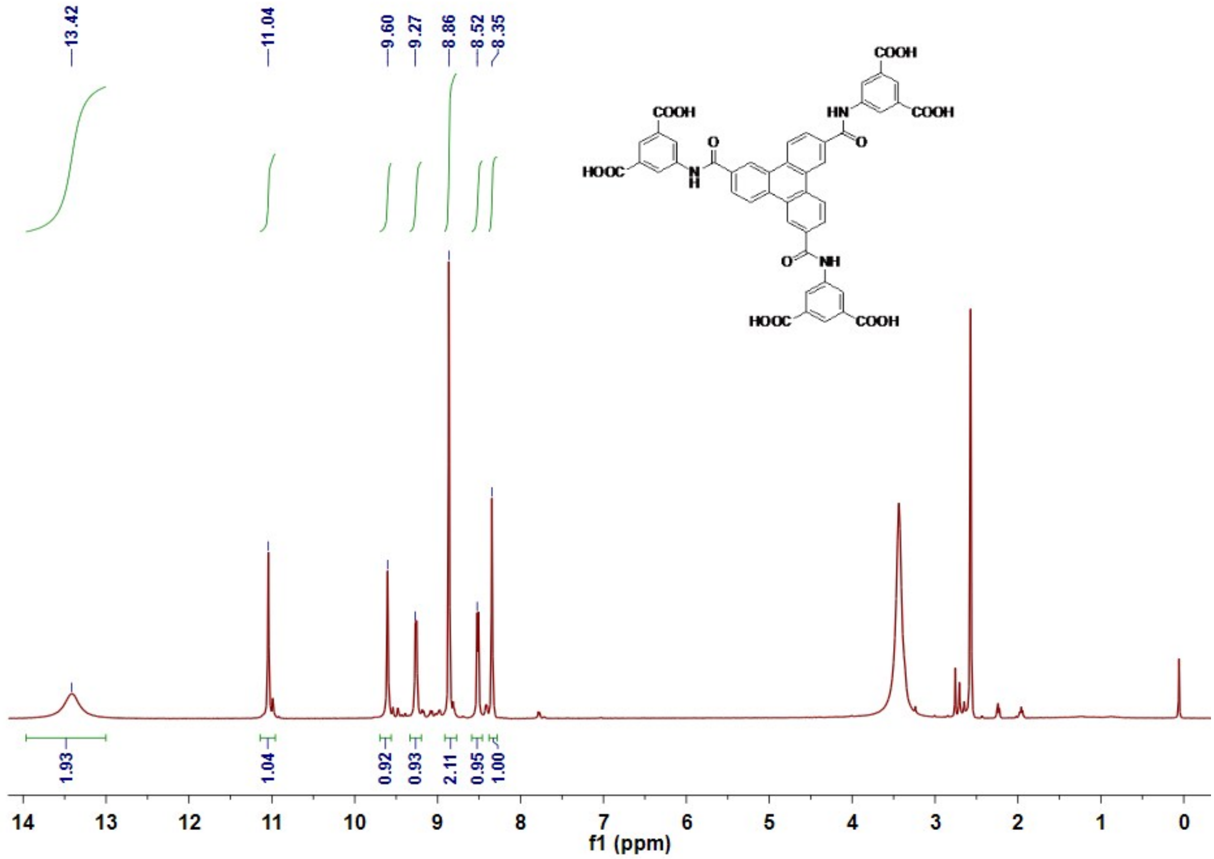

Fig. S1. ^{1}H NMR spectrum of the Linker TTTT in DMSO-d_6 (500 MHz).

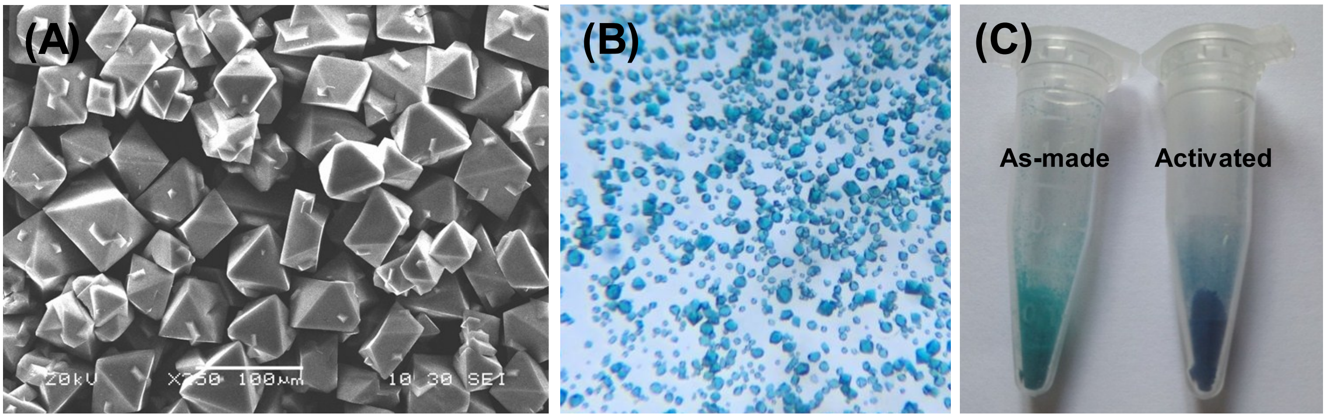

Fig. S2. (A) A representative SEM image of as-synthesized **HNUST-5**. (B) Photographic image of as-synthesized **HNUST-5**, the crystal size has been magnified about 80 times. (C) Visual color change of **HNUST-5** upon activation.

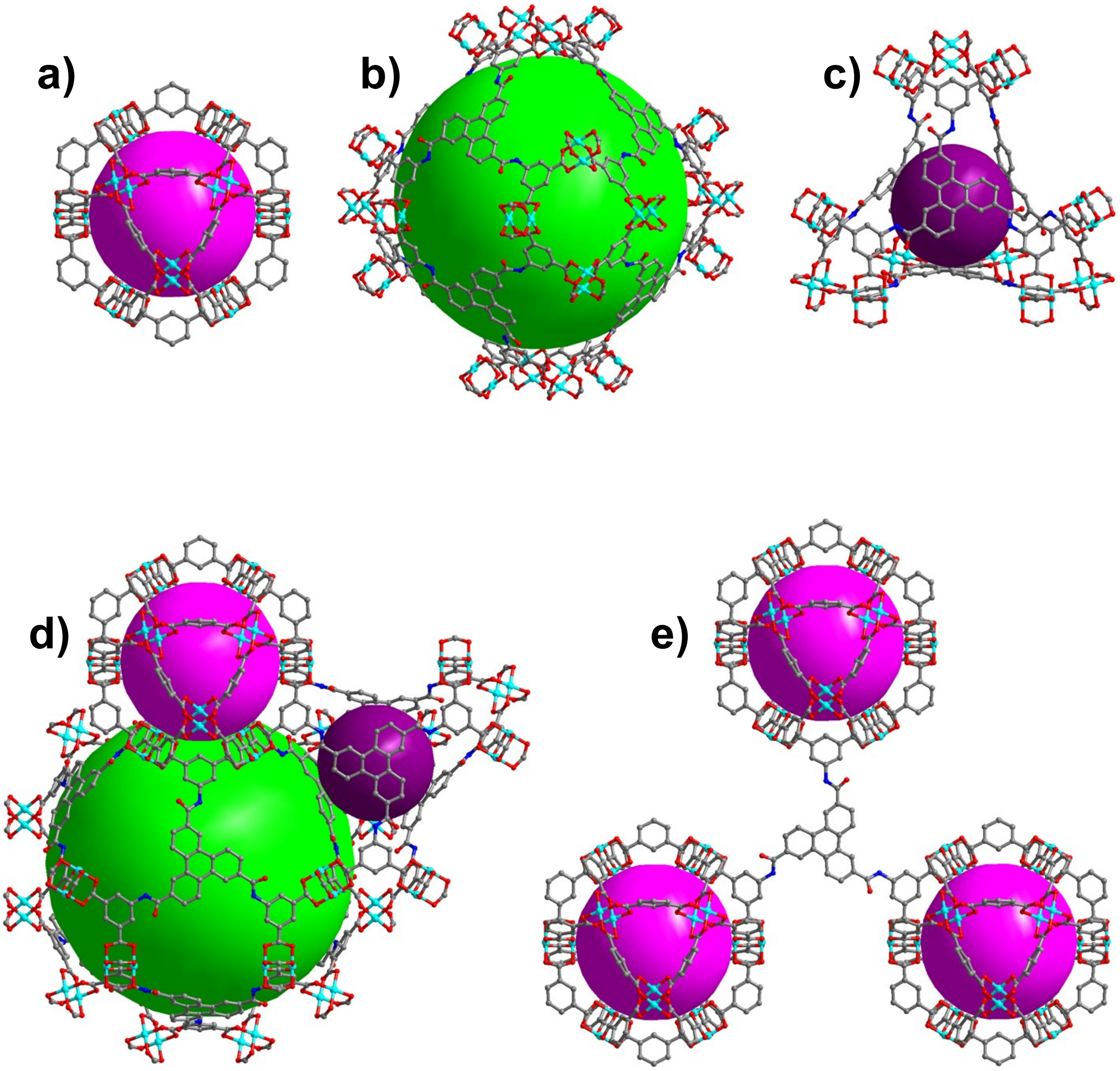

Fig. S3. Crystal structure of MOF **HNUST-5**. a-d) Three types of polyhedra (cuboctahedron, cub-Oh; truncated tetrahedron, T-Td and truncated octahedron, T-Oh), e) a portion of structure of the (3, 24)-connected *rht*-type framework. Coordinated water molecules have been omitted for clarity.

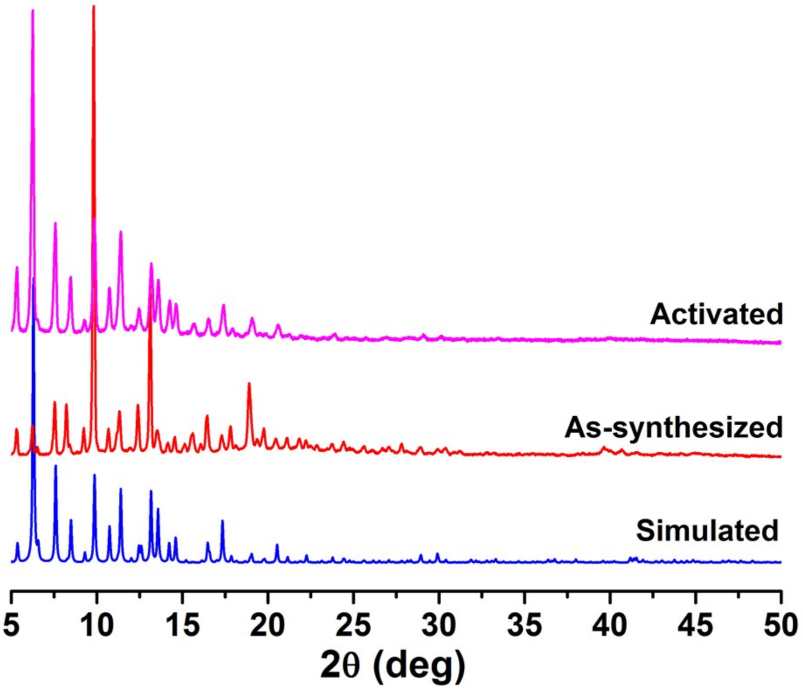

Fig. S4. PXRD patterns of **HNUST-5**, simulated (blue), as-synthesized (red) and activated (magent).

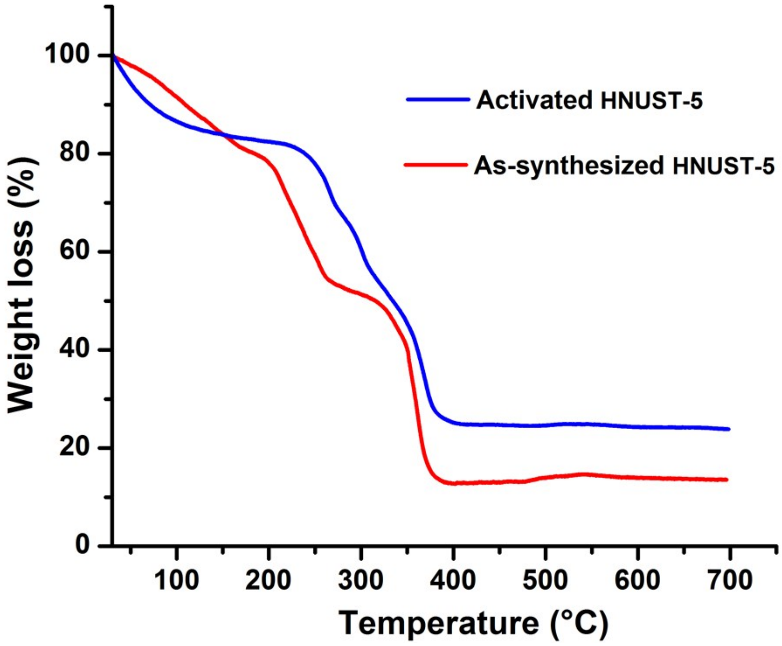

Fig. S5. TGA curve of the as-synthesized and activated **HNUST-5**, recorded under N_2 flow with a heating rate of 5 °C /min.

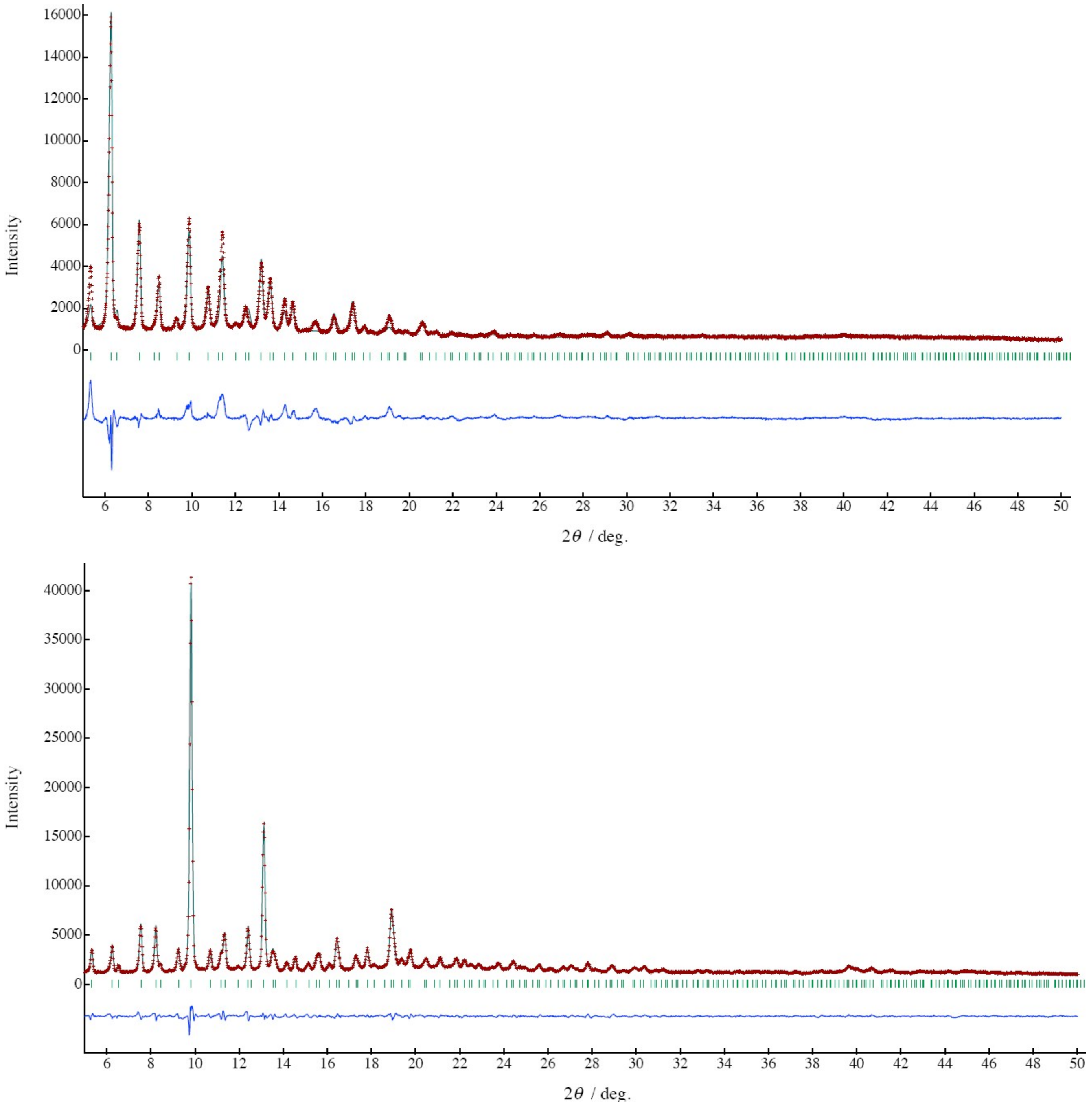

Fig. S6. The results of Rietveld analysis of evacuated (upper) and Le Bail analysis for the as-synthesized (down) **HNUST-5**. Red line gives the experimental data, olive line gives the calculated curve, and the blue line the difference. Vertical bars mark the allowed Bragg positions. The wavelength of an incident X-ray is 1.5418 Å and temperature is 303 K. Refined parameters and reliability factors are as follows: Cubic, *Fm-3m*, a = 46.542(2) Å, V = 100817(13) Å^3, R_p = 3.469 and R_{wp}= 4.556.

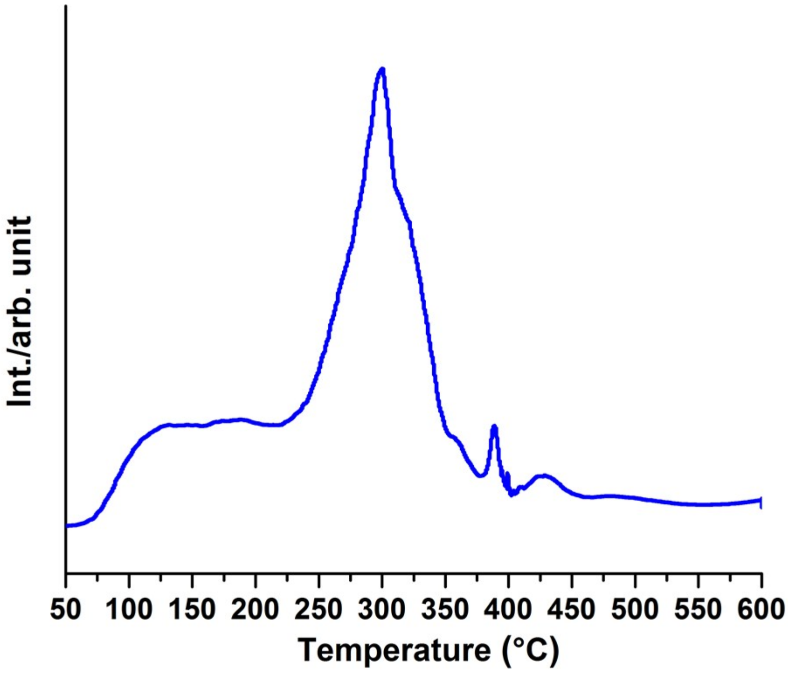

Fig. S7. NH_3-TPD profile of **HNUST-5**.

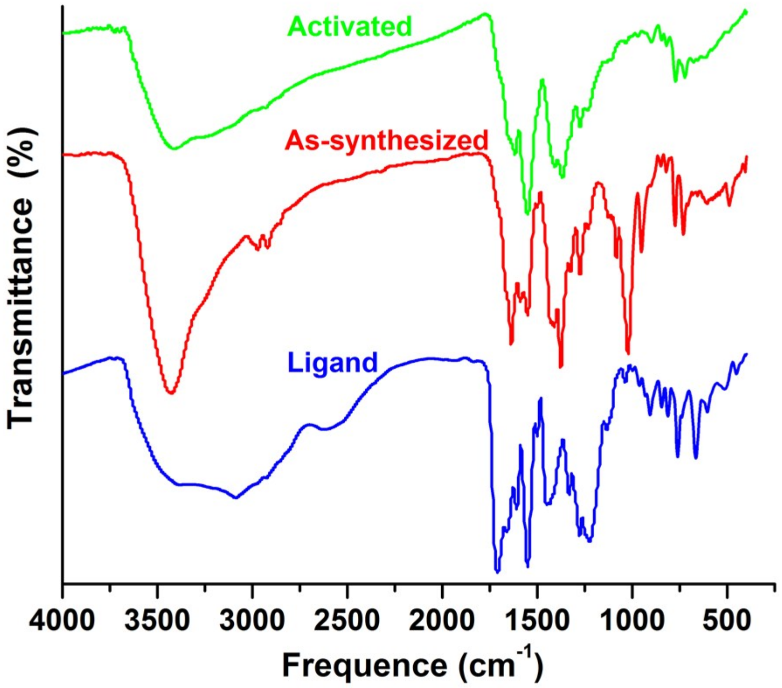

Fig. S8. Infrared spectra of the ligand TTTT, as-synthesized and activated **HNUST-5**. Note the absence of the vibration frequencies of the solvent DMF, DMSO and acetone molecules in the activated samples.

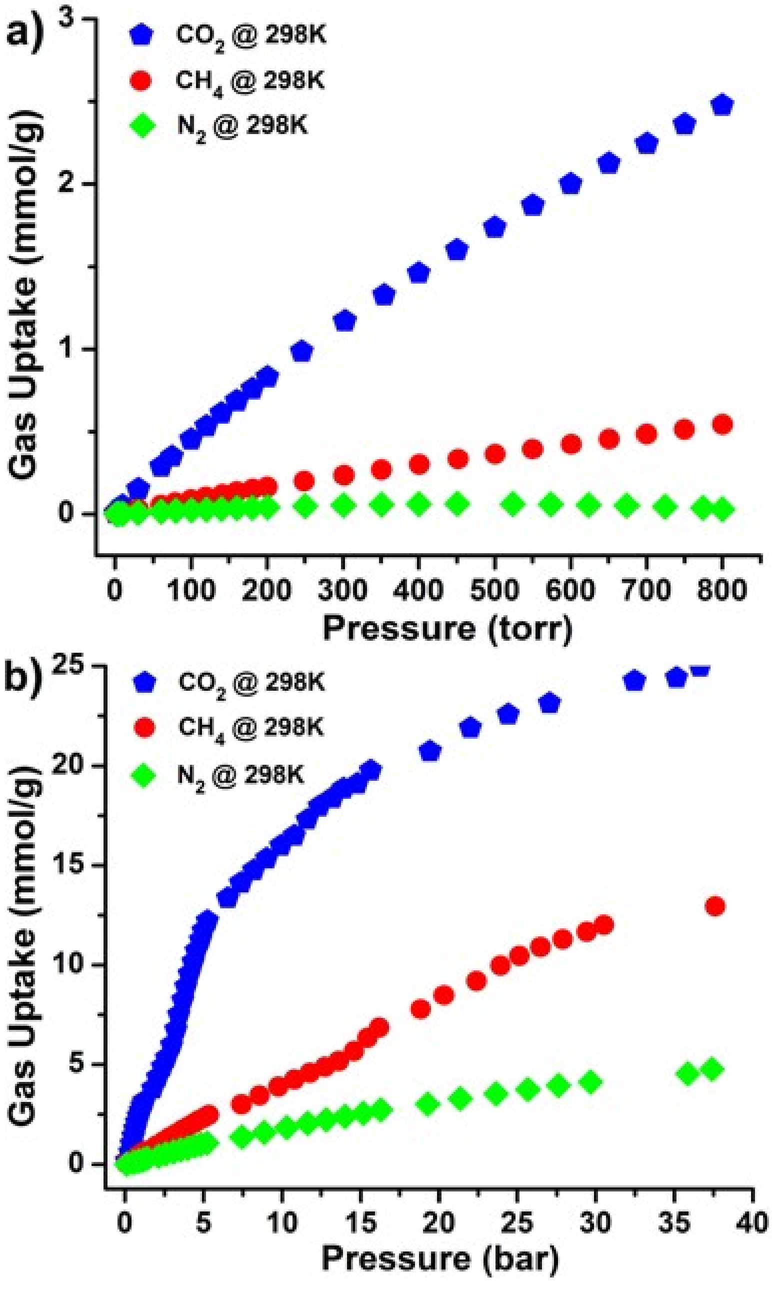

Fig. S9. Low- and high-pressure gas (CO_2, CH_4 and N_2) sorption isotherms of **HNUST-5** at 298 K.

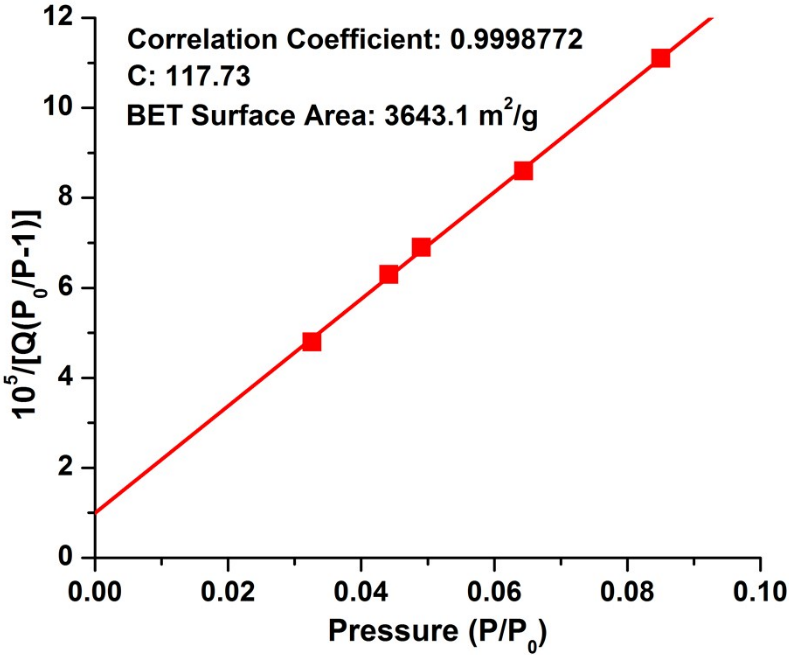

Fig. S10. BET plots for **HNUST-5** calculated from the N_2 adsorption isotherm at 77 K in the chosen range ($P/P_0 = 0.02 – 0.1$).

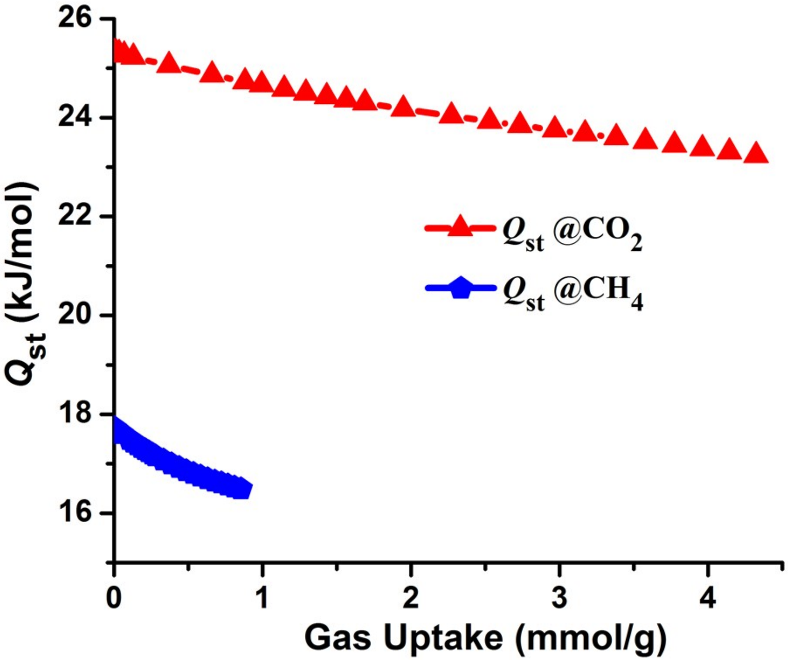

Fig. S11. The CO_2 and CH_4 isosteric adsorption enthalpies of **HNUST-5** calculated from the adsorptions at two different temperatures (298 K and 273 K) through the Virial method.

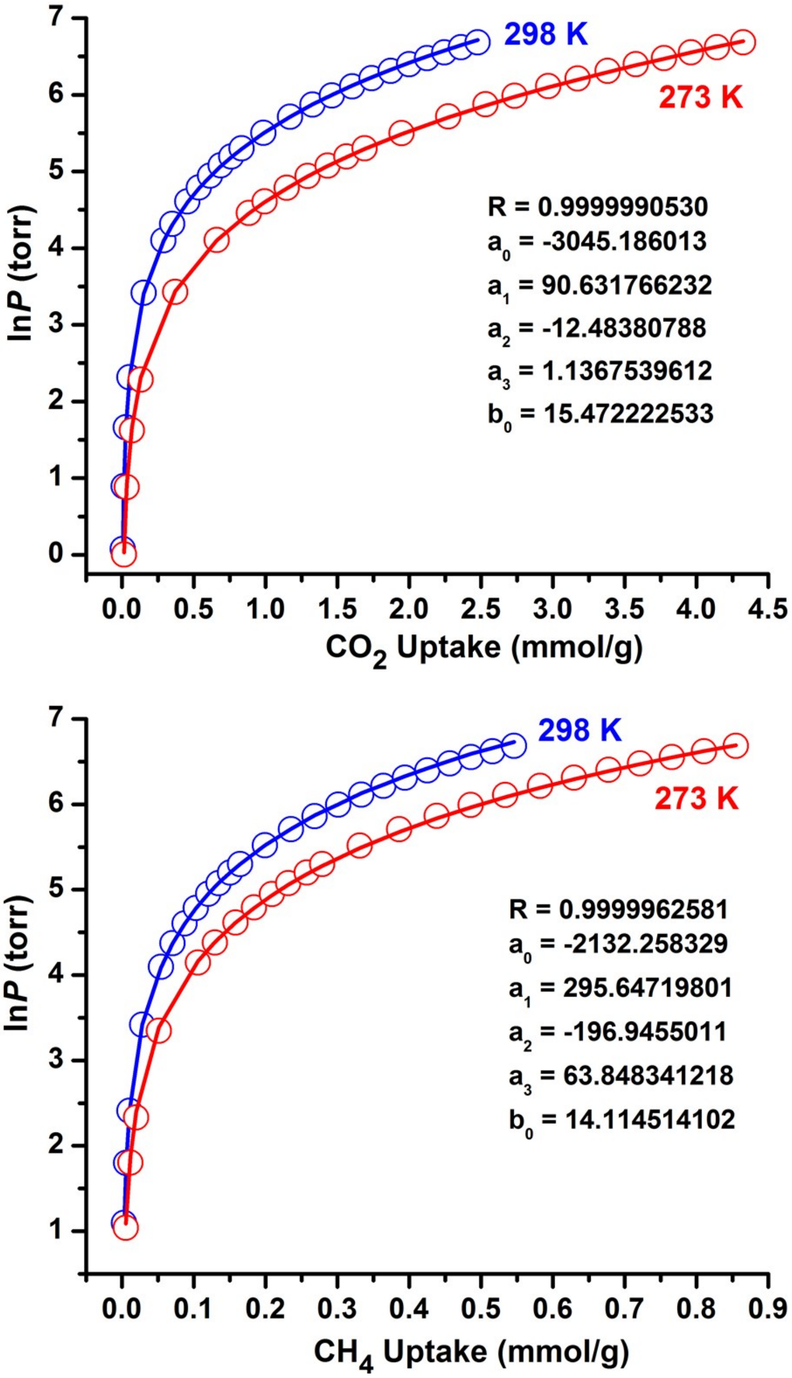

Fig. S12. Details of Virial equation (solid lines) fitting to the experimental gas adsorption data (symbols) for **HNUST-5** collected at 273 K and 298 K, respectively. CO_2 gas (upper); CH_4 gas (down).

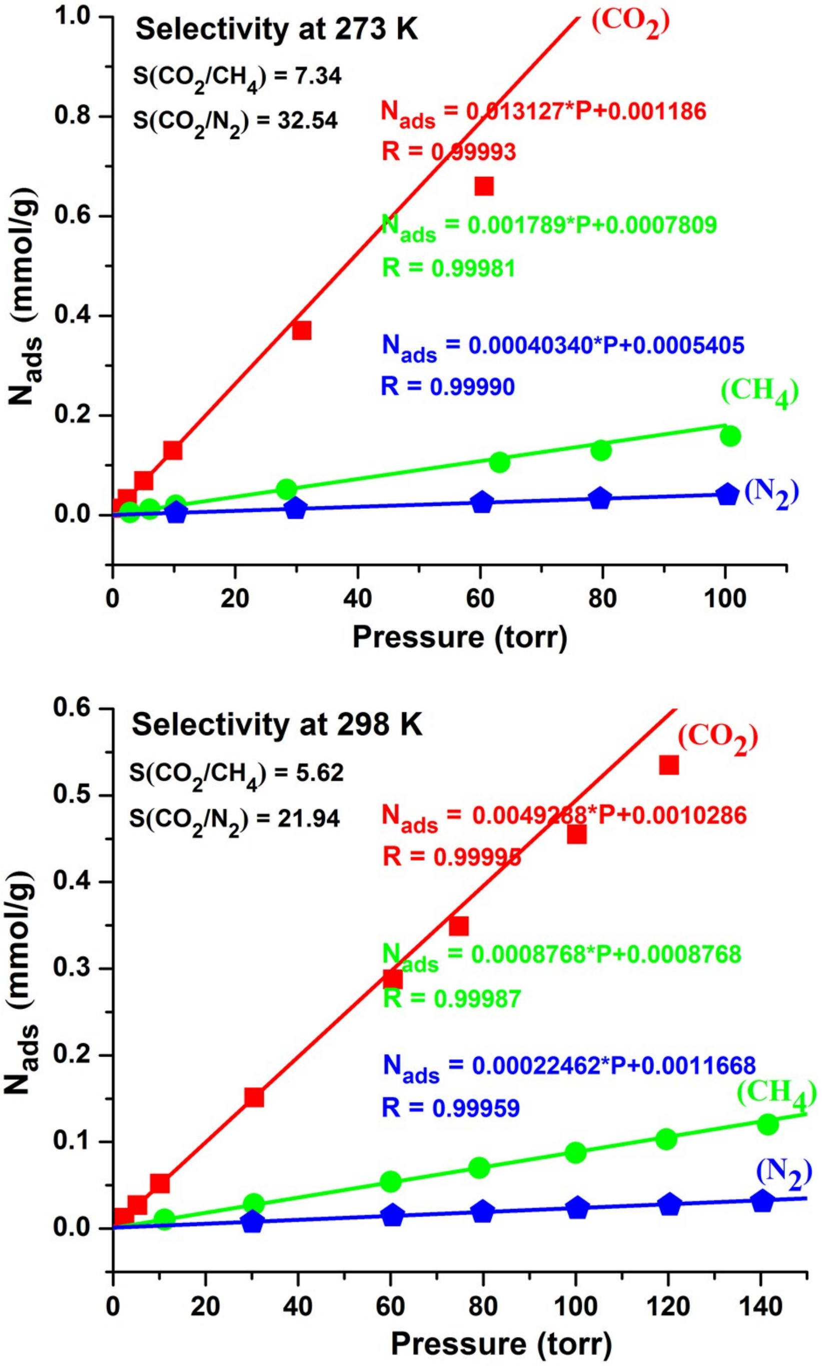

Fig. S13. The fitting initial slope for CO_2, CH_4 and N_2 isotherms for **HNUST-5** collected at 273 K and 298 K, respectively (N_{ads} = gas uptake; R = related coefficient). The calculated selectivity of CO_2/CH_4 and CO_2/N_2 is 7.3, 32.5 and 5.6, 21.9 at 273 K and 298 K, respectively.

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