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Electronic Supplementary Information

Pore Space Partition via Secondary Metal Ions Entrapped by Pyrimidine Hooks: Influences on Structural Flexibility and Carbon Dioxide Capture

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Section S1. Experimental Section

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. ^{1}H NMR spectra were recorded on a Bruker AVANCE III 600 MHz spectrometer with tetramethylsilane as an internal reference. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 ADVANCE X-ray diffractometer with Cu/Kα radiation. Gas sorption measurements were conducted using a Micrometritics ASAP 2020 surface area and pore size analyzer up to saturated pressure at different temperatures.

2. Synthesis of the ligand

The ligand of 5-(nicotinamido)isophthalic acid (H_2NAIP) was prepared according to literature and characterized by ^{1}H NMR and IR.

H_2NAIP: ^{1}H NMR (600 MHz, DMSO-d_6, δ ppm): 13.30 (s, 2H, COO$\underline{\mathrm{H}}$), 10.77 (s, 1H, CON$\underline{\mathrm{H}}$), 9.14 (d, J = 1.8 Hz, 1H, Ar$\underline{\mathrm{H}}$), 8.78 (d × d, J = 4.8 Hz, J = 1.8 Hz, 1H, Ar$\underline{\mathrm{H}}$), 8.66 (d, J = 1.2 Hz, 2H, Ar$\underline{\mathrm{H}}$), 8.33~8.35 (d × t, J = 7.8 Hz, J = 1.8 Hz, 1H, Ar$\underline{\mathrm{H}}$), 8.23 (t, J = 1.2 Hz, 1H, Ar$\underline{\mathrm{H}}$), 7.58~7.60 (d × d, J = 7.8 Hz, J = 4.8 Hz, 1H, Ar$\underline{\mathrm{H}}$). Selected IR (KBr, cm^{-1}): 3500, 3442, 3304, 3121, 3085, 2903, 2801, 1732, 1707, 1652, 1617, 1596, 1567, 1486, 1448, 1418, 1392, 1333, 1294, 1224, 1123, 1100, 1049, 962, 910, 883, 843, 762, 717, 700.

Preparation of 5-(pyrimidin-5-amido) isophthalic acid (H_2PCIP): A mixture of pyrimidine-5-carboxylic acid (5 g, 0.04 mol), freshly distilled thionyl chloride (12 mL, 0.16 mol), and a few drops of DMF was heated to reflux for 12 h. Excess thionyl chloride was removed by distillation under reduced pressure and the resulting white powder was used as such. To this was added 5-aminoisophthalic acid (9.1 g, 0.05 mol), DMA (50 mL), and N,N-dimethyl-4-aminopyridine (0.12 g, 0.001 mol), after which the solution was stirred in ice bath for 12 h. The resultant mixture was poured into water, and the precipitate that formed was filtered off, extracted with hot water several times and dried in vacuum at 40℃. Yield: 70 %. ^{1}H NMR (600MHz, DMSO-d_6, δ ppm): 13.35 (s, 2H, COO$\underline{\mathrm{H}}$), 10.94 (s, 1H, CON$\underline{\mathrm{H}}$), 9.39 (s, 1H, Ar$\underline{\mathrm{H}}$), 9.32 (s, 2H, Ar$\underline{\mathrm{H}}$), 8.64 (d, J = 1.8 Hz, 2H, Ar$\underline{\mathrm{H}}$), 8.25 (t, J = 1.8 Hz, 1H, Ar$\underline{\mathrm{H}}$). Selected IR (KBr, cm^{-1}): 3471, 3165, 3071, 2976, 2923, 1867, 1700, 1613, 1587, 1561, 1444, 1413, 1334, 1293, 1254, 1195, 1174, 1086, 1051, 960, 923, 882, 801, 760, 710.

3. Synthesis of HHU-2 $[Cu_{4/3}(PCIP)\cdot(NO_3)_{2/3}\cdot(H_2O)_{1/3}]_n\cdot x(solv)$

A mixture of $Cu(NO_3)_2\cdot 3H_2O$ (10 mg, 0.04 mmol), H_2PCIP (10 mg, 0.04 mmol), HNO_3 (30 μl, 16 mol/L) and DMF/ethanol/H_2O (3: 3: 0.5 in volume) (2 mL) was stirred for 10 min in air and sealed in a 20 mL Teflon-lined autoclave, which was heated at 60 °C for 24 h. After cooling to the room temperature, the blue hexagonal-plate-shaped crystals were obtained. The crystals of HHU-2 were filtered and washed with fresh DMF. Yield: ~ 60 % based on the ligand. Selected IR (KBr, cm^{-1}): 3434, 3260, 3063, 2976, 2928, 2866, 1668, 1591, 1566, 1417, 1375, 1295, 1254, 1197, 1169, 1095, 1050, 1001, 974, 918, 890, 805, 776, 729, 715.

4. Synthesis of NJFU-1 $[Cu(NAIP)]_n\cdot x(solv)$

A mixture of $Cu(NO_3)_2\cdot 3H_2O$ (10 mg, 0.04 mmol), H_2NAIP (10 mg, 0.04 mmol), HNO_3 (30 μl, 16 mol/L) and DMF/ethanol/H_2O (3: 3: 0.5 in volume) (2 mL) was stirred for 10 min in air and sealed in a 20 mL Teflon-lined autoclave, which was heated at 60 °C for 24 h. After cooling to the room temperature, the blue hexagonal-plate-shaped crystals were obtained. The crystals of NJFU-1 were filtered and washed with fresh DMF. Yield: ~ 60 % based on the ligand. Selected IR (KBr, cm^{-1}): 3449, 3074, 2929, 1665, 1591, 1566, 1421, 1375, 1293, 1253, 1198, 1153, 1103, 1050, 1033, 975, 917, 889, 827, 801, 777, 731, 700.

5. Sample activation

The solvent-exchanged sample was prepared by immersing the as-synthesized HHU-2 or NJFU-1 in methanol for 3 days to remove the nonvolatile solvates (DMF and water), and the extract was decanted every 8 hours and fresh methanol was replaced. The completely activated sample was obtained by heating the solvent-exchanged sample at 60 °C under a dynamic high vacuum for 24 hours. During this time, the pale blue sample of HHU-2 changed to a jewelry-blue color indicative of the presence of unsaturated metal Cu^{II} sites, and the green sample of NJFU-1 remains green (Figure S1).

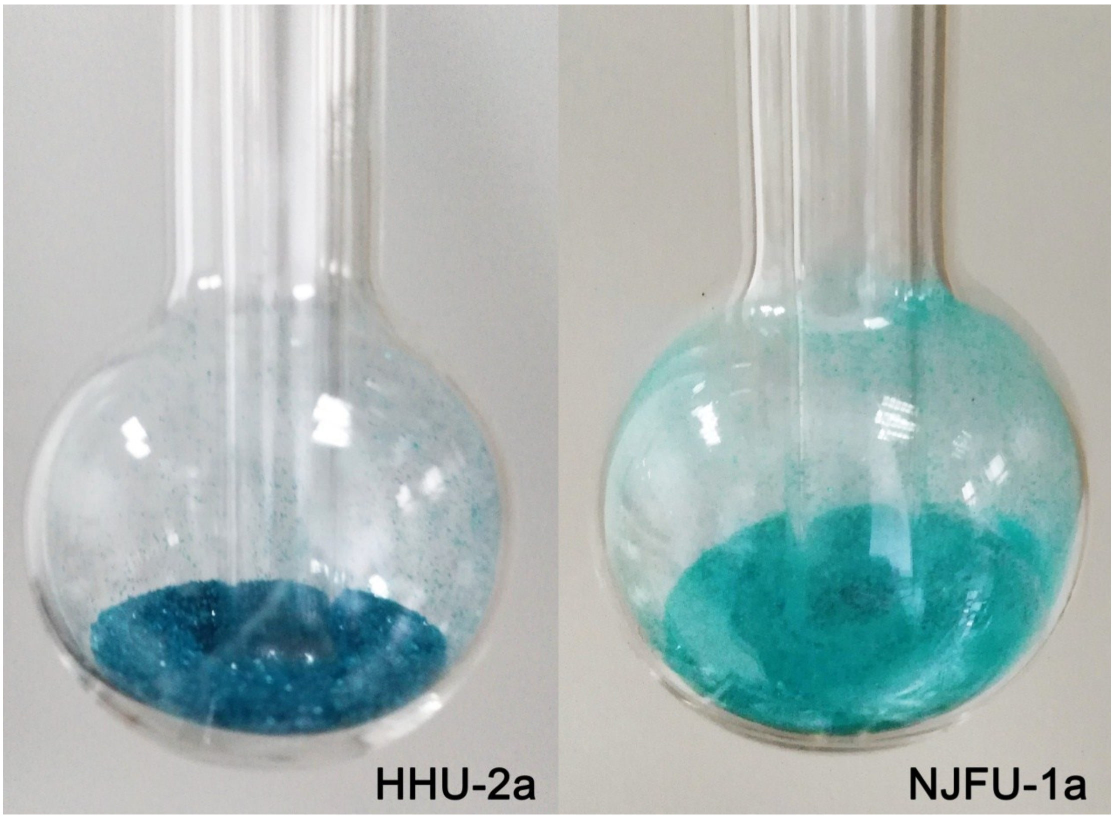

Figure S1 Pictures of HHU-2a and NJFU-1a.

HHU-2a: Selected IR (KBr, cm–1): 3421, 3267, 3078, 2976, 1670, 1623, 1556, 1415, 1370, 1294, 1246, 1194, 1168, 1110, 1043, 1001, 972, 923, 887, 775, 724.

NJFU-1a: Selected IR (KBr, cm–1): 3434, 3099, 2969, 2921, 1621, 1559, 1477, 1422, 1372, 1289, 1247, 1198, 1150, 1121, 1109, 1046, 974, 883, 826, 776, 731, 720.

Section S2. Crystal Structure

The X-ray diffraction intensity data were measured on a Bruker Apex II diffractometer at 173 K using graphite monochromated Mo/Kα radiation (λ = 0.71073 Å). 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-2016 package. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms were placed in calculated positions with isotropic displacement parameters set to 1.2 × U_{eq} of the attached atom. The unit cell includes a large region of disordered solvent molecules, which could not be modeled as discrete atomic sites. We employed PLATON/SQUEEZE 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. Crystal data and refinement conditions are shown in Table S1. The crystal data for HHU-2 have been deposited in CSD database, and labeled as 1450125. Copies of the data can be obtained, free of charge, on application to the CCDC (e-mail: deposit@ccdc.cam.ac.uk).

Table S1. Crystal data and structure refinement for HHU-2.

Identification code	**HHU-2**
CCDC number	1450125
Empirical formula	$C_{13}H_{7.67}Cu_{1.33}N_{3.67}O_{7.33}$
Formula weight	417.29
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Trigonal
Space group	R -3 m
a	18.672(3) Å
b	18.672(3) Å
c	35.448(2) Å
α	90°
β	90°
γ	120°
Volume	10703(4) Å^3
Z	18
Density (calculated)	1.165 g cm^{-3}
Absorption coefficient	1.240 mm^{-1}
F(000)	3756
Crystal size	0.28 ×0.24 × 0.22 mm
Theta range for data collection	2.181 to 26.983 °
Limiting indices	-23<=h<=23, -23<=k<=19, -43<=l<=45
Reflections collected unique	51927 / 2852 [R(int) = 0.0093]
Completeness	100 %
Absorption correction	multi-scan
Max. and min. transmission	0.761 and 0.714
Refinement method	Full-matrix least-squares on F^2
Data /restraints / parameters	2852 / 0 / 166
Goodness-of-fit on F^2	0.964
Final R indices [I>2sigma(I)]	R1 = 0.0326, wR2 ^{a} = 0.0973
R indices (all data)	R1 = 0.0406, wR2 ^{a} = 0.0988
Largest diff. peak and hole	0.258 and -0.726 e. Å^{-3}

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

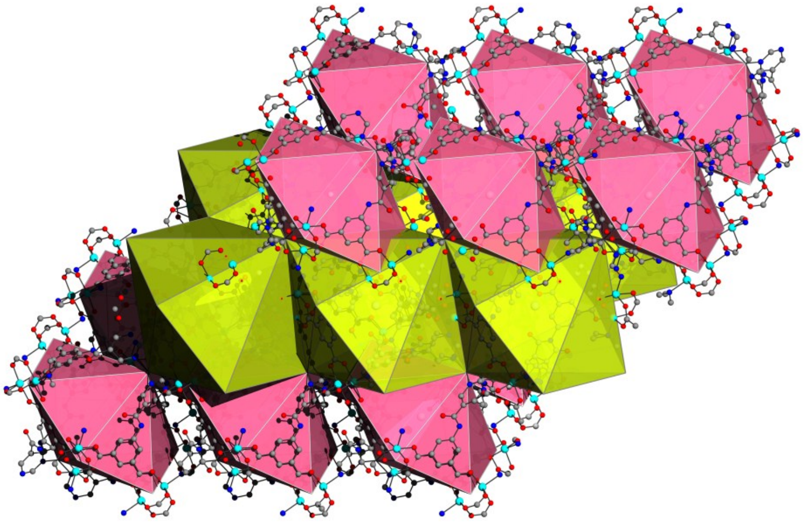

Figure S2 The packing mode of the two kinds of cages in HHU-2.

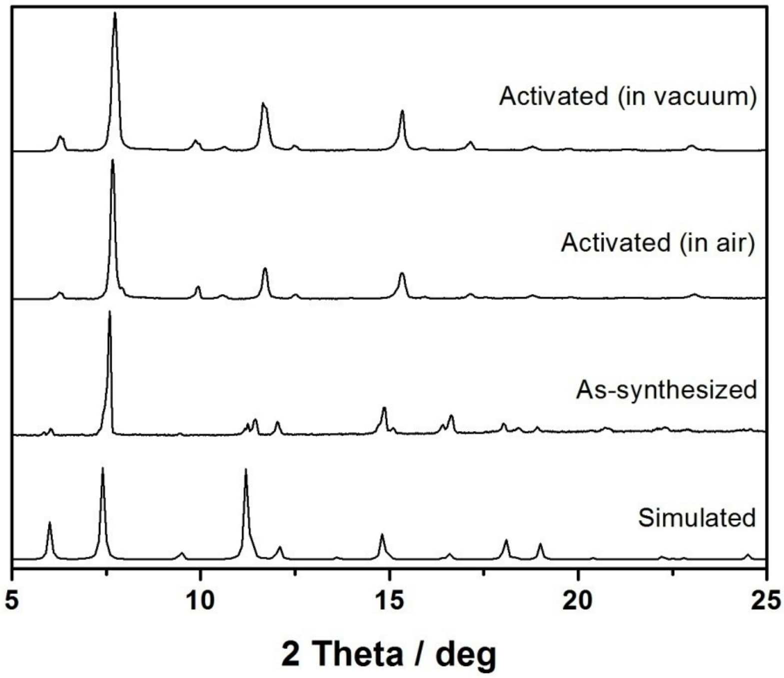

Figure S3 PXRD patterns for HHU-2.

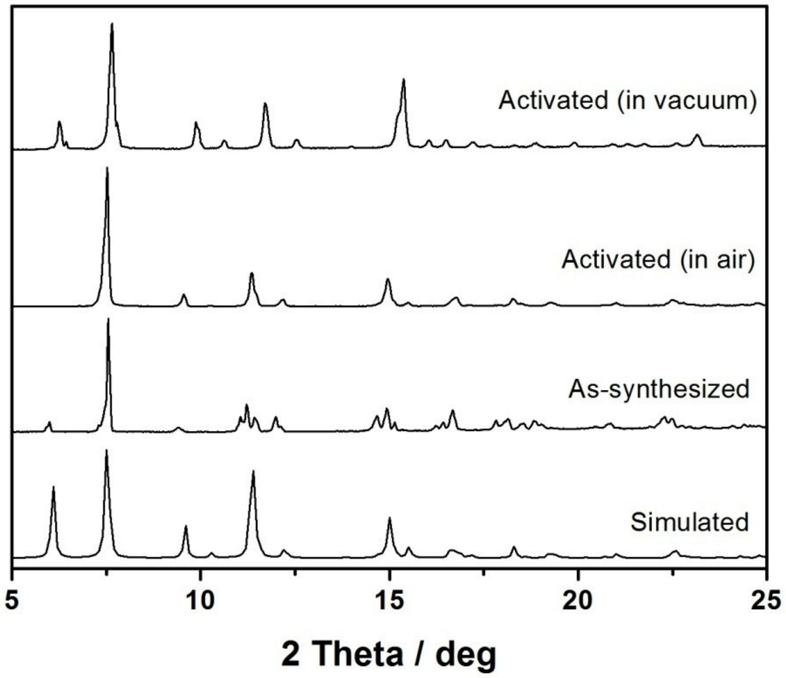

Figure S4 PXRD patterns for NJFU-1.

Section S3. BET Surface Area Analyses

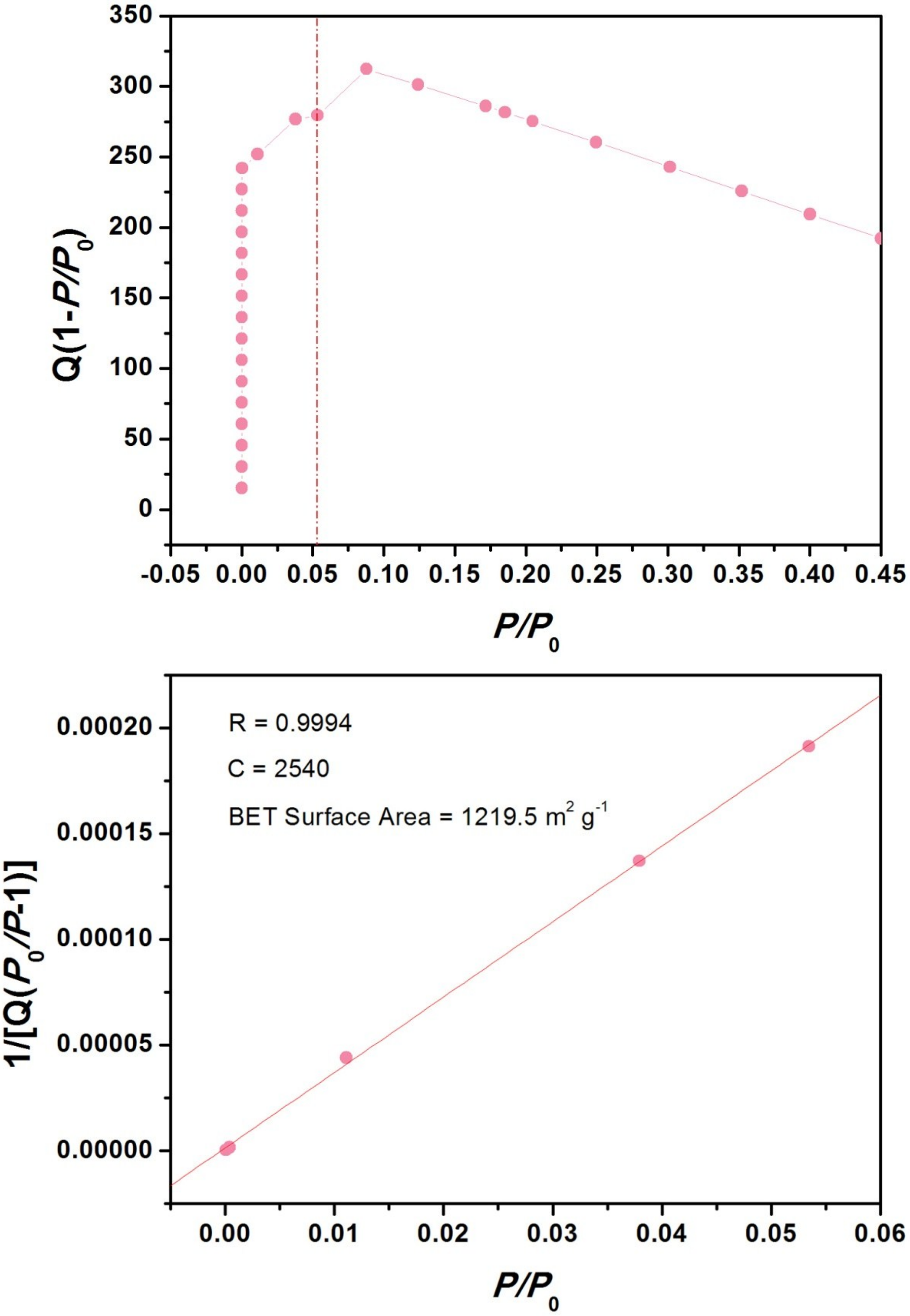

Figure S5 Top: Q(1-P/P_0) vs. P/P_0 for simulated N_2 isotherm of NJFU-1a. Only the range below P/P_0 = 0.06 satisfies the first consistency criterion for application of the BET theory. Bottom: Plot of the linear region for the BET equation, which satisfies the second criterion for application of the BET theory.

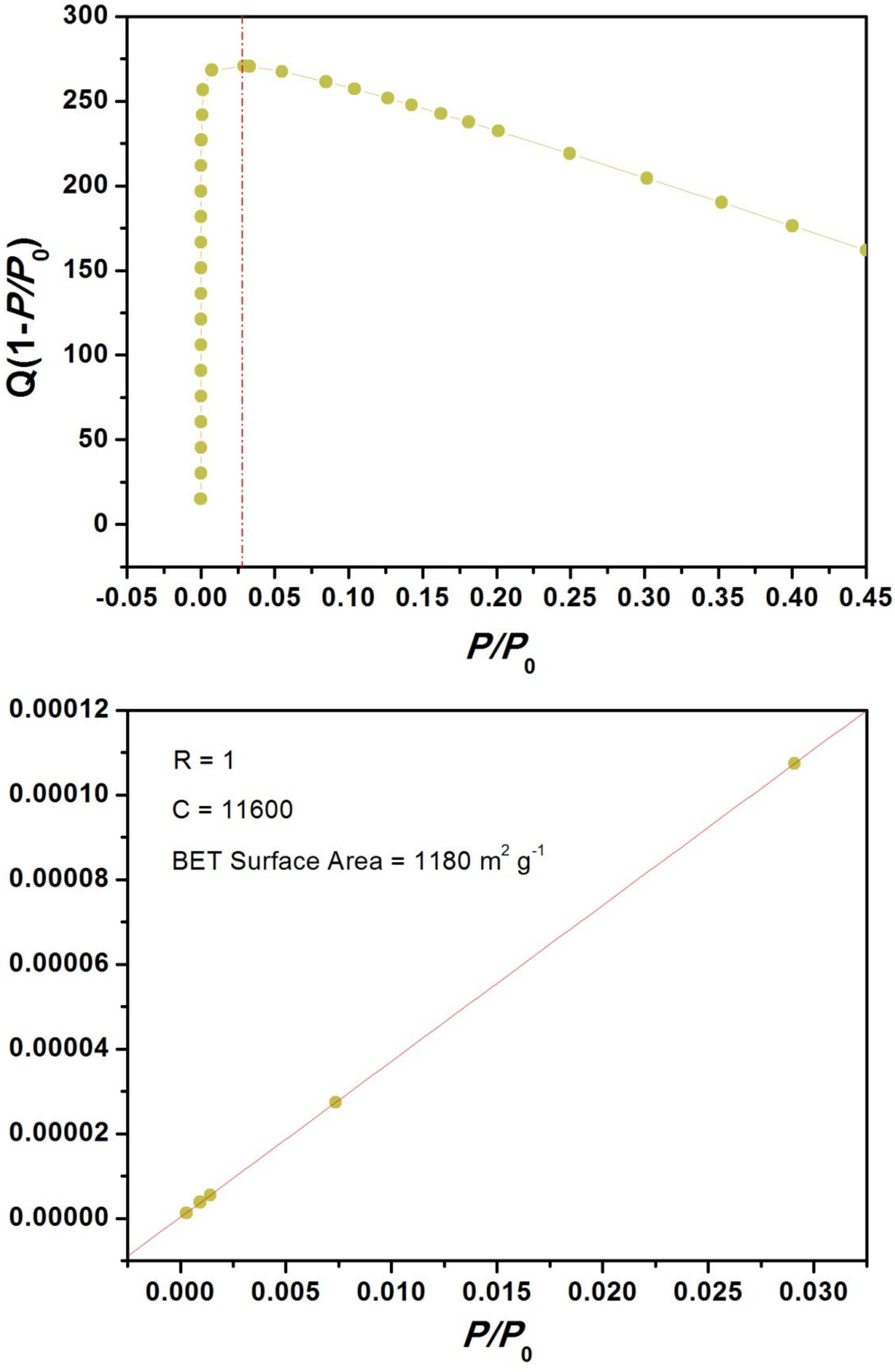

Figure S6 Top: Q(1-P/P_0) vs. P/P_0 for simulated N_2 isotherm of HHU-2a. Only the range below P/P_0 = 0.03 satisfies the first consistency criterion for application of the BET theory. Bottom: Plot of the linear region for the BET equation, which satisfies the second criterion for application of the BET theory.

Section S4. Langmuir Surface Area Analysis

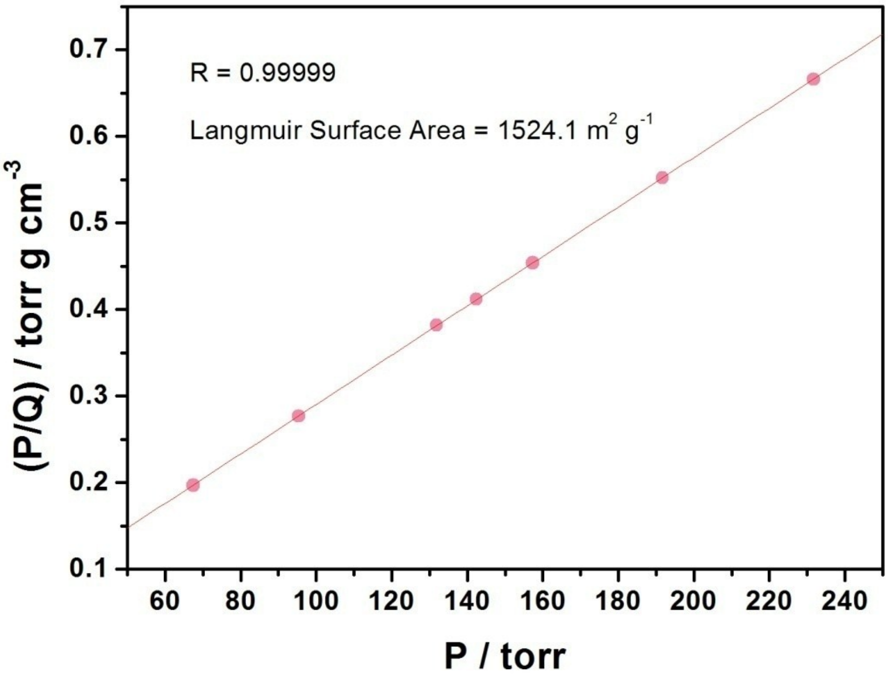

Figure S7 Langmuir equation fitting curve for NJFU-1a's N_2 isotherm (adsorption branch data points, P/P_0 = 0.1 – 0.3)

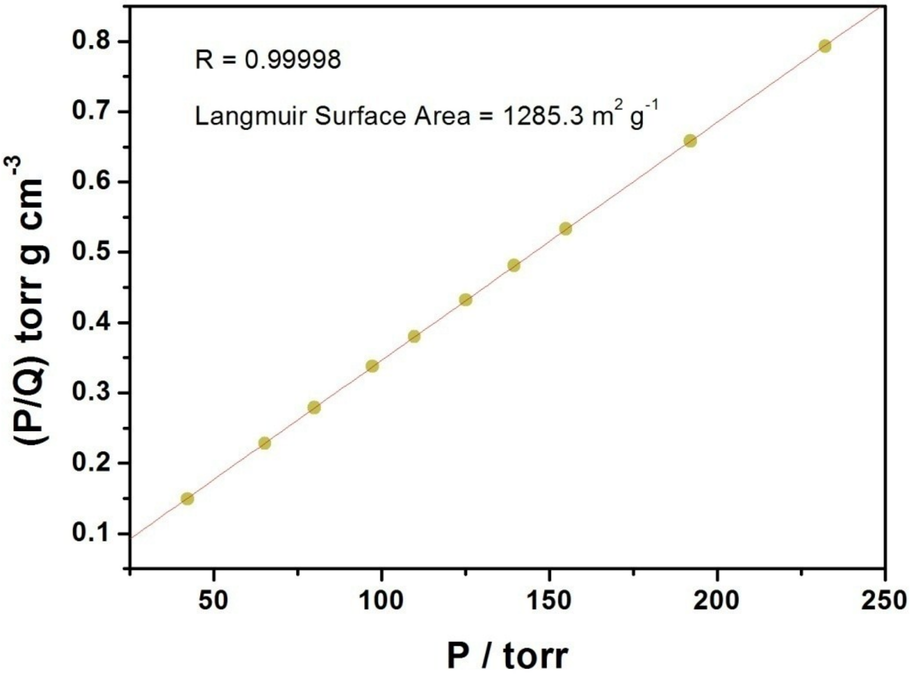

Figure S8 Langmuir equation fitting curve for HHU-2a's N_2 isotherm (adsorption branch data points, P/P_0 = 0.1 – 0.3)

Section S5. CO_2 Adsorption Isotherms

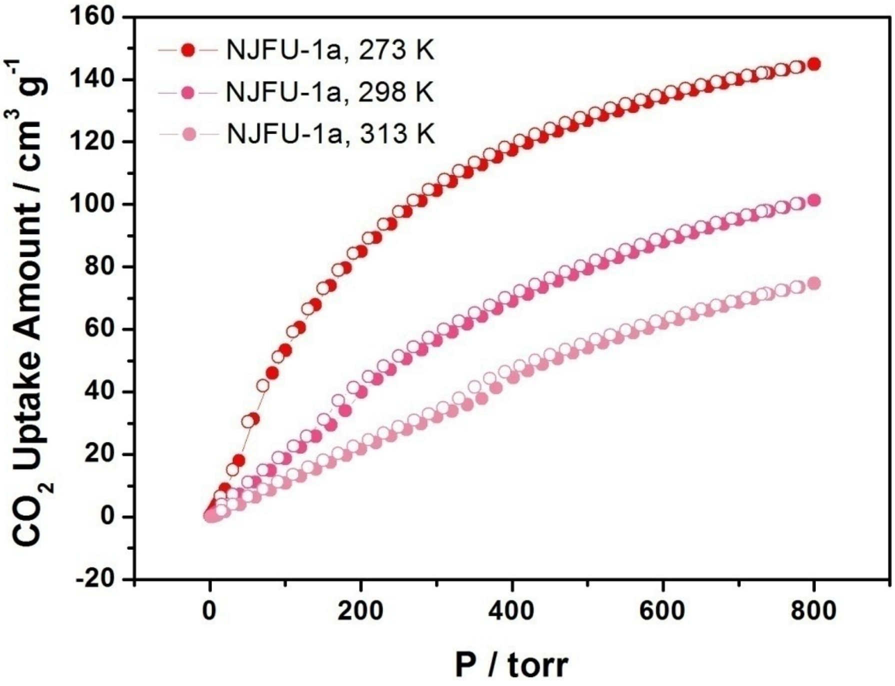

Figure S9 CO_2 isotherms for NJFU-1a at 273 K, 298 K and 313 K

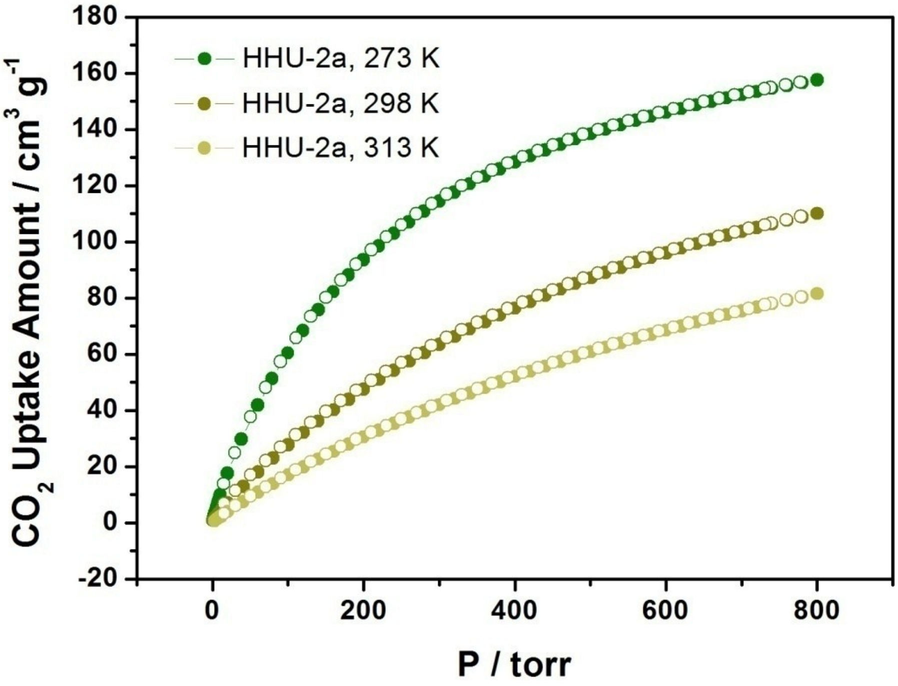

Figure S10 CO_2 isotherms for HHU-2a at 273 K, 298 K and 313 K

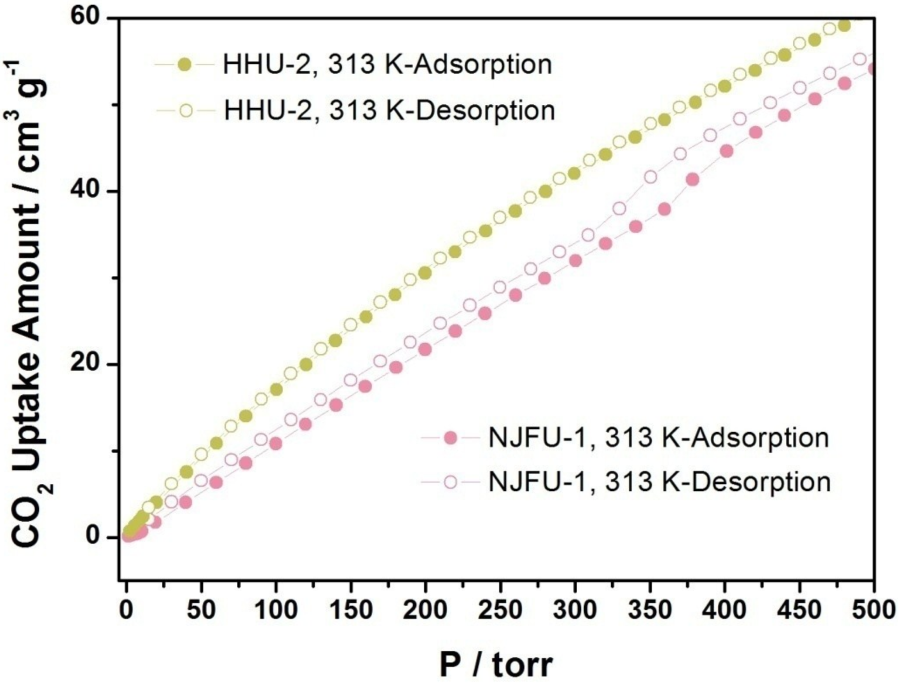

Figure S11 CO_2 isotherms for NJFU-1a and HHU-2a at 313 K under low pressure range (0 ~ 500 torr)

Section S6. Estimation of the Isosteric Heats of Gas Adsorption

A virial-type expression comprising the temperature-independent parameters a_i and b_i was employed to calculate the enthalpies of adsorption for CO_2 (at 273 and 298 K). The data were fitted using the equation:

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

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_i 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).

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

Here, Q_{st} is the coverage-dependent isosteric heat of adsorption and R is the universal gas constant.

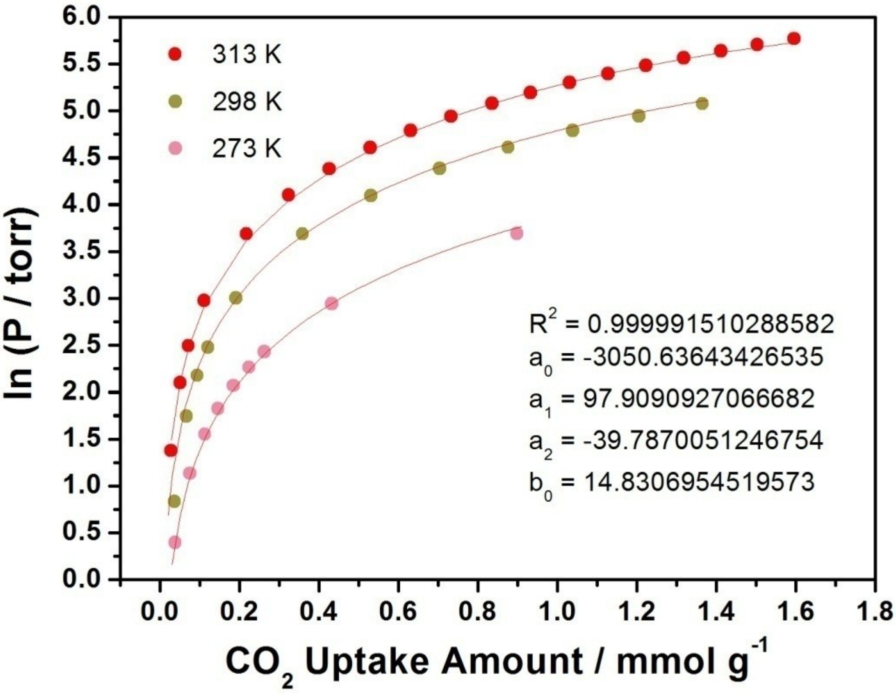

Figure S12 The details of virial equation (solid lines) fitting to the experimental CO_2 adsorption data (symbols) for NJFU-1a.

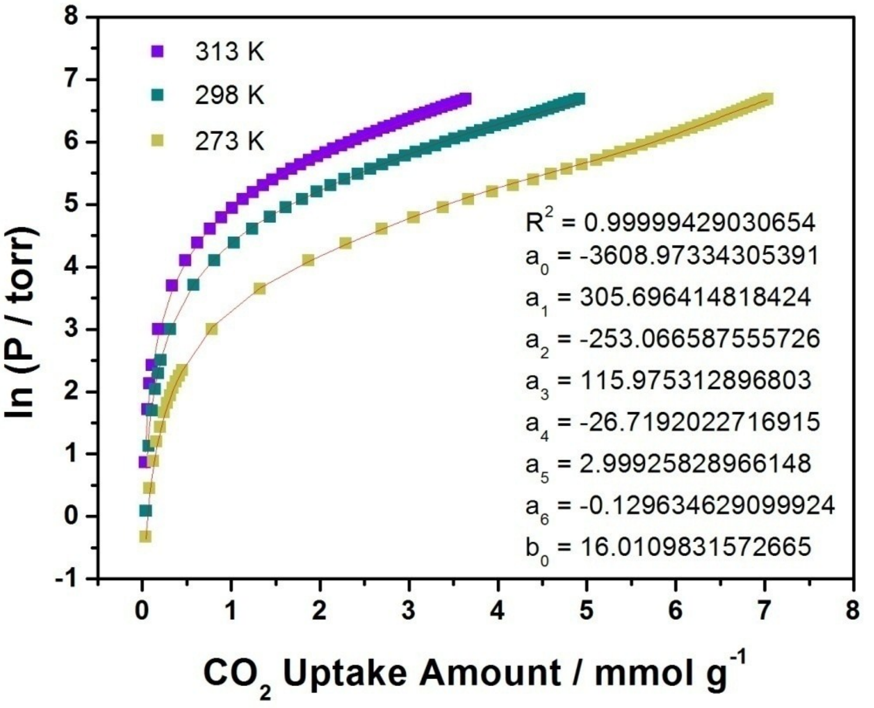

Figure S13 The details of virial equation (solid lines) fitting to the experimental CO_2 adsorption data (symbols) for HHU-2a.

Section S7. Thermal Analysis

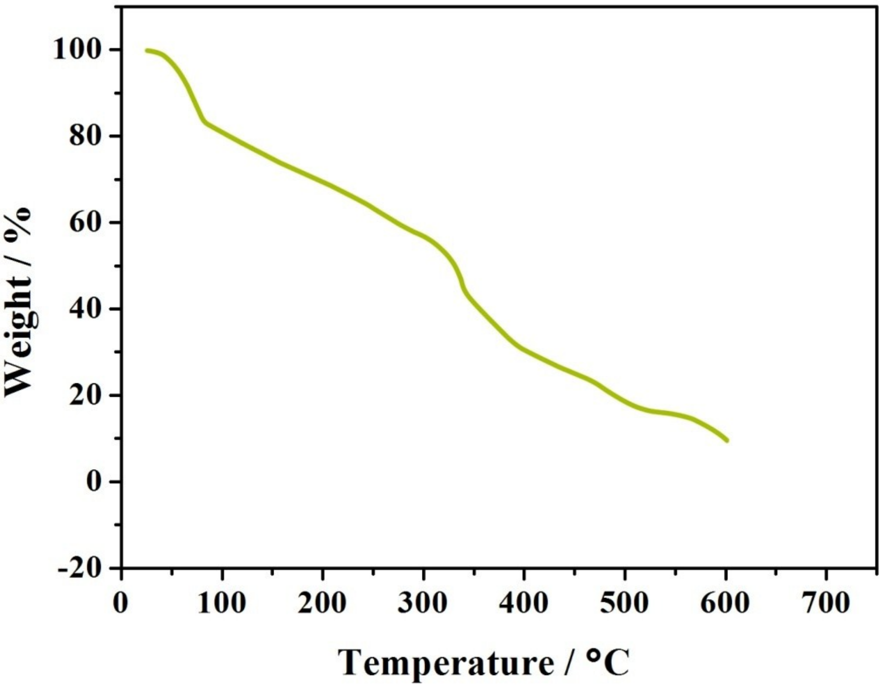

Figure S14 TG curve of HHU-2.

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