Electronic Supplementary Information

Highly selective carbon dioxide uptake by a microporous kgm-pillared metal-organic framework with acylamide groups

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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. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400 II CHNS/O analyzer. 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. Thermal gravimetric analyses (TGA) were performed under N_2 atmosphere (100 ml/min) with a heating rate of 5 °C/min using a 2960 SDT thermogravimetric analyzer. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 ADVANCE X-ray diffractometer with Cu Kα radiation.

2. Synthesis of the ligand

The organic linker 5-(nicotinamido)isophthalic acid (H$_2$NAIP) was prepared according to the literature method[1-2] and characterized by IR and ^{1}H NMR.

Preparation of 5-(nicotinamido)isophthalic acid (H$_2$NAIP): A mixture of nicotinic acid (3.7 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 %. Selected IR (KBr, cm^{-1}): 3494, 3437, 3301, 3119, 3077, 2900, 2797, 1838, 1703, 1652, 1616, 1597, 1564, 1483, 1448, 1415, 1332, 1294, 1224, 1140, 1120, 1097, 1043, 995, 960, 881, 845, 762. ^{1}H NMR (600MHz, DMSO-d_6, δ ppm): 13.35 (s, 2H, COO$\underline{H}$), 10.81 (s, 1H, CON$\underline{H}$), 9.16 (d, J=1.8 Hz, 1H, Ar$\underline{H}$), 8.80 (d×d, J=3 Hz, J=1.8 Hz, 1H, Ar$\underline{H}$), 8.67(d, J=1.8 Hz, 2H, Ar$\underline{H}$), 8.35~8.37 (d×t, J=7.8 Hz, J=3.6 Hz, 1H, Ar$\underline{H}$), 8.24 (t, J=1.8 Hz, 1H, Ar$\underline{H}$), 7.60~7.62 (m, 1H, Ar$\underline{H}$).

3. Synthesis of NJFU-1[C$_{14}$H$_8$CuN$_2$O$_5$·x(solv)]

A mixture of Cu(NO$_3$)$_2$·3H$_2$O (10 mg, 0.04 mmol), H$_2$NAIP (10 mg, 0.04 mmol), HNO$_3$ (30 μl, 16 mol/L) and DMF/ethanol/H$_2$O (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 65 °C for 48 h. After cooling to the room temperature, the Aquamarine hexagonal crystals were obtained. The crystals of NJFU-1 were filtered and washed with fresh solution of DMF/ethanol/H$_2$O (3:3:0.5 in volume). Yield: ~ 53 % based on the ligand. Anal. Calcd for [C14H8CuN2O5]: C, 48.30; H, 2.30; N, 8.05; Found: C, 47.99; H, 2.78; N, 8,12. Selected IR (KBr, cm^{-1}): 3432, 3075, 2929, 1663, 1595, 1558, 1421, 1374, 1289, 1254, 1194, 1150, 1097, 1049, 1031, 915, 887, 801, 775, 730, 700.

4. X-ray Structure Determination

Single crystal suitable for X-ray structure determination were selected and sealed in a capillary under a microscope. The X-ray diffraction intensity data were measured on a Bruker Smart Apex CCD diffractometer at room temperature 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 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[3] 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 NJFU-1 have been deposited in CSD database, and labeled as 981374. 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 NJFU-1.

Identification code	NJFU-1
CCDC number	981374
Empirical formula	C14 H8 Cu N2 O5
Formula weight	347.77
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Hexagonal
Space group	R -3 c
a	18.431(17) Å
b	18.431(17) Å
c	69.911(15) Å
α	90°
β	90°
γ	120°
Volume	20567(7) Å^3
Z	36
Density (calculated)	1.011 g cm^{-3}
Absorption coefficient	0.971 mm^{-1}
F(000)	6300
Crystal size	0.18 ×0.14 × 0.07 mm
Theta range for data collection	1.73 to 25.00 °.
Limiting indices	-21<=h<=20, -21<=k<=21, -83<=l<=80
Reflections collected unique	36383 / 4039 [R(int) = 0.0633]
Completeness	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.934 and 0.849
Refinement method	Full-matrix least-squares on F^2
Data /restraints / parameters	4040 / 17 / 199
Goodness-of-fit on F^2	1.183
Final R indices [I>2sigma(I)]	R1 = 0.0642, wR2 [a] = 0.1905
R indices (all data)	R1 = 0.0744, wR2 [a] = 0.1993
Largest diff. peak and hole	1.008 and -0.926 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 S1. The ^{1}H NMR spectrum of 5-(nicotinamido)isophthalic acid (H$_2$NAIP).

Figure S2. The photograph of the single crystals of NJFU-1.

Figure S3. PXRD patterns of NJFU-1: the simulated (black), as-synthesized (red), acetone-exchanged (cyan) and activated (blue).
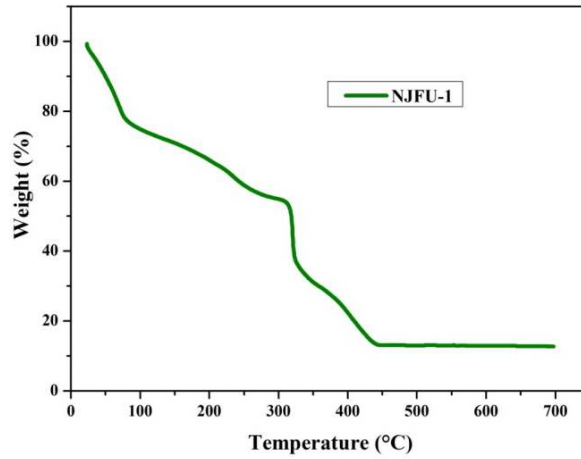
Figure S4. TGA data of as-synthesized sample of NJFU-1.
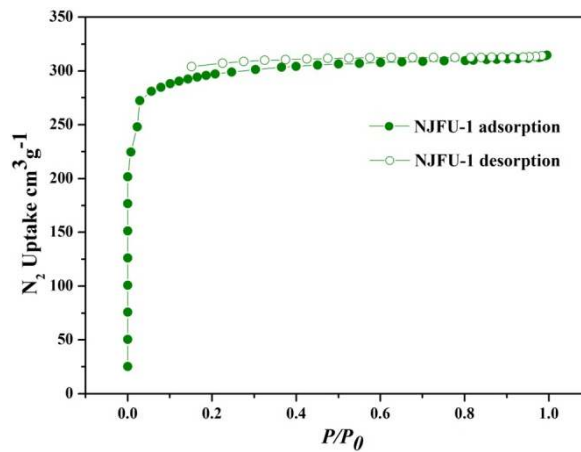
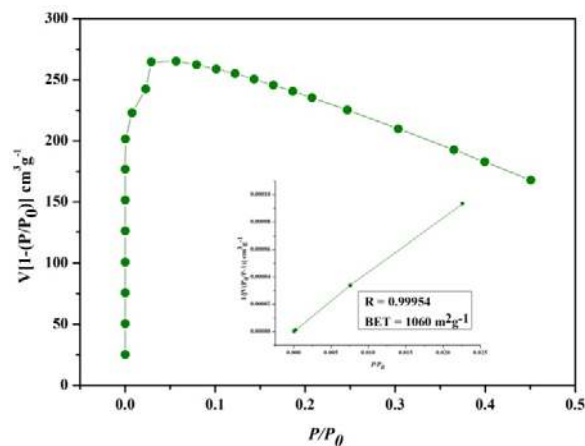**Figure S5.** Nitrogen sorption isotherm at 77 K. Adsorption (filled circles), desorption (open circles).

Figure S6. Plot of the linear region for the BET equation, which satisfies the second consistency criteria for application of the BET theory: (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.
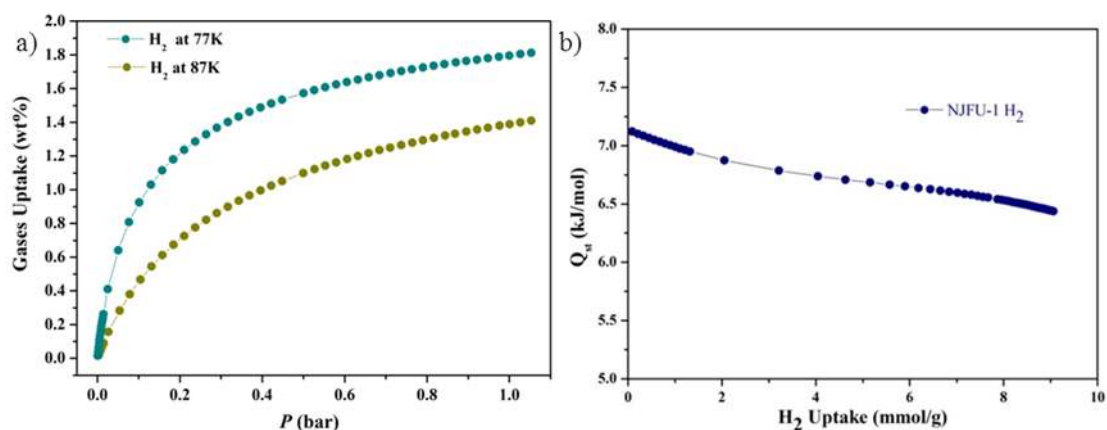
Figure S7. a) The H_2 adsorption isotherms in the low pressure range (0−1 bar), 77 K (dark cyan), 87 K (dark yellow). b) The H_2 isosteric adsorption enthalpies for NJFU-1 calculated from the adsorption at 87 K and 77 K through the virial method.
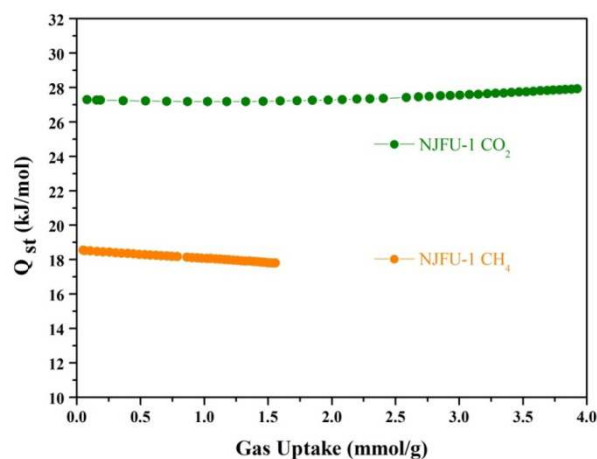

Figure S8. The CO_2 and CH_4 isosteric adsorption enthalpies for NJFU-1 caculated from the adsorption at 298 K and 273 K through the virial method.
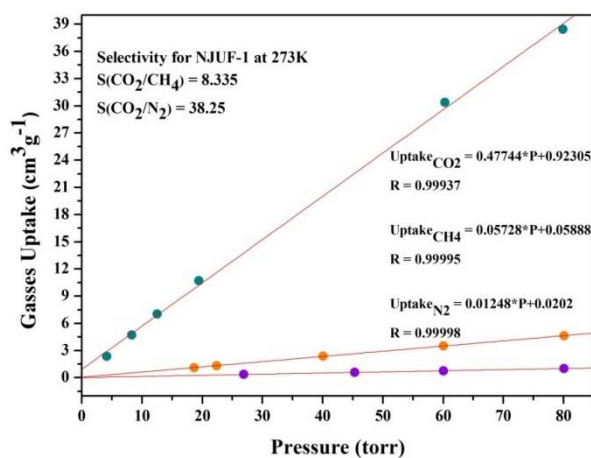

Figure S9. The fitting initial slope for CO_2, CH_4 and N_2 isotherms for NJFU-1 collected at 273 K (R = related coefficient). The calculated selectivity of CO_2/CH_4 and CO_2/N_2 is about 8.34 and 38.3, respectively.
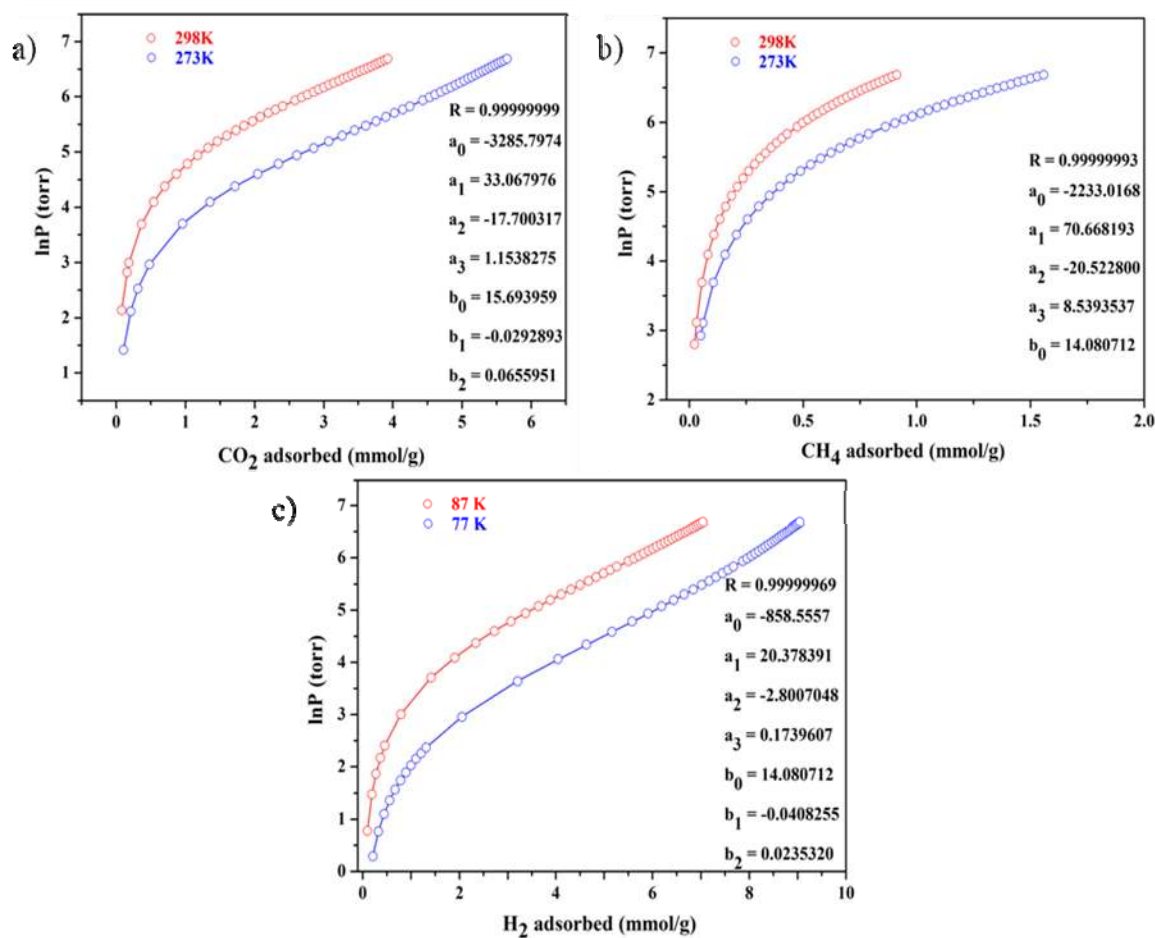
Figure S10. The gas isotherms (red and blue symbols, respectively) and the corresponding virial equation fits (red and blue lines, respectively) for NJFU-1. (a-b): CO_2 and CH_4 at 273 K and 298 K; (c): H_2 at 77 K and 87 K.

Reference

[1] J. J. Ferreiro, J. G. De La Campa, A. E. Lozano, J. D. Abajo, *J. Polym. Sci. A: Polym. Chem.*, 2005, **43**, 5300.

[2] A. E. Lozano, J. G. De La Campa, J. D. Abajo, *Polymer*, 1995, **36**, 1113.

[3] A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.