Electronic Supplementary Information

Distortable functionalized ligand implantation in ultra-microporous MOFs for efficient C_2H_2 purification

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Table S1 The crystal data and structure refinements for four Ni-MOFs.

Compound	SNNU-501	SNNU-502	SNNU-503	SNNU-504
Empirical formula	$C_{42}H_{25}Ni_3O_{18}P_2$	$C_{52}H_{35}N_2Ni_3O_{16}P_2$	$C_{57}H_{47}N_7Ni_3O_{16}P_2$	$C_{54}H_{34}N_6Ni_3O_{16}P_2$
Formula weight	1055.69	1179.87	1324.08	1260.94
Temperature/K	209(2)	153.00	193.00	153.00
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	*Pnma*	*Pnma*	*Pnma*	*Pnma*
a/Å	26.9465(11)	25.673(3)	26.2459(12)	30.911(3)
b/Å	23.1262(10)	25.550(3)	24.2568(11)	25.023(2)
c/Å	18.4887(9)	15.0211(5)	16.8482(7)	13.8644(13)
α/°	90	90	90	90
β/°	90	90	90	90
γ/°	90	90	90	90
V/Å^3	11521.6(9)	9853.0(19)	10726.3(8)	10724.2(18)
Z	4	4	4	4
ρ_{calc} g/cm^3	0.609	0.797	0.820	0.781
μ/mm^{-1}	0.542	1.297	3.259	1.224
F(000)	2040.0	2386.4	2720.0	2568.0
Reflections collected	68506	87398	63685	80681
Independent reflections	10441[R_{int} = 0.1015, R_{sigma} = 0.1017]	9234 [R_{int} = 0.0416, R_{sigma} = 0.0202]	10105 [R_{int} = 0.1035, R_{sigma} = 0.0654]	9512 [R_{int} = 0.0549, R_{sigma} = 0.0279]
Goodness-of-fit on F^2	0.911	1.022	0.977	1.057
Final *R* indexes [I>=2σ (I)]	R_1 = 0.0937, wR_2 = 0.2408	R_1 = 0.0536, wR_2 = 0.1803	R_1 = 0.0706, wR_2 = 0.2080	R_1 = 0.0878, wR_2 = 0.2575
Final *R* indexes [all data]	R_1 = 0.1388, wR_2 = 0.2626	R_1 = 0.0542, wR_2 = 0.1810	R_1 = 0.1029, wR_2 = 0.2334	R_1 = 0.0985, wR_2 = 0.2724

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table S2 The selected bond length (Å) for four compounds.

SNNU-501		SNNU-502		SNNU-503		SNNU-504	
Atom-Atom	Length/Å	Atom-Atom	Length/Å	Atom-Atom	Length/Å	Atom-Atom	Length/Å

Ni3-O10	1.989(4)	Ni1-O9	1.9961(17)	Ni1-O2	2.042(3)	Ni1-O1	1.995(3)
Ni3-O1	2.081(4)	Ni1-O1	2.0337(17)	Ni1-O3	2.050(3)	Ni1-O5	2.035(4)
Ni3-O8	2.028(4)	Ni1-O6	2.0296(19)	Ni1-O9	1.994(4)	Ni1-O8	2.022(4)
Ni3-O9	2.185(8)	Ni1-N2^{4}	2.107(3)	Ni1-N6	2.135(5)	Ni1-N1	2.088(6)
Ni2-O4	2.109(4)	Ni2-O9	1.9970(19)	Ni2-O1	2.059(3)	Ni2-O1	2.001(3)
Ni2-O7	2.089(4)	Ni2-O5	2.0491(17)	Ni2-O5	2.054(4)	Ni2-O2	2.043(3)
Ni2-O6	2.130(7)	Ni2-O7	2.0421(17)	Ni2-O8	2.106(7)	Ni2-O9	2.061(3)
Ni1-O2	2.095(4)	Ni2-O8	2.105(3)	Ni2-O9	2.006(4)	Ni2-N6	2.089(5)
Ni1-O10	1.998(5)	Ni3-O9	2.0048(18)	Ni2-O4	2.070(3)	Ni3-O1	1.987(3)
Ni1-O3	2.070(4)	Ni3-O2	2.0361(18)	Ni2-O6	2.063(3)	Ni3-O3	2.015(4)
Ni1-O11	2.308(9)	Ni3-N1	2.094(3)	Ni2-O9	2.000(4)	Ni3-O4	2.118(5)
		Ni3-O4	2.0236(19)	Ni2-N1	2.097(5)	Ni3-O6	2.034(3)

Table S3 The selected bond angles (°) for SNNU-501 and SNNU-502.

SNNU-501		**SNNU-502**	
Atom-Atom-Atom	**Angle/°**	**Atom-Atom-Atom**	**Angle/°**
O10-Ni3-O1	94.36(16)	O1-Ni1-O9	91.12(6)
O10-Ni3-O8	93.29(16)	O1-Ni1-O1	94.92(12)
O10-Ni3-O1	179.1(2)	O6-Ni1-O9	93.94(7)
O1^{1}-Ni3-O1^{2}	89.4(3)	O6-Ni1-O1^{1}	87.33(9)
O1-Ni3-O9	85.03(19)	O6-Ni1-O1^{2}	174.43(8)
O8-Ni3-O1^{2}	89.7(2)	O6^{3}-Ni1-O6	89.99(14)
O8-Ni3-O1^{1}	172.34(18)	N2^{4}-Ni1-O9	176.95(10)
O8^{3}-Ni3-O8	90.0(3)	N2^{4}-Ni1-O1^{1}	86.82(7)
O8-Ni3-O9	87.32(18)	N2^{4}-Ni1-O6	88.22(8)
O4^{4}-Ni2-O4^{5}	90.6(2)	O5-Ni2-O9	94.07(6)
O4^{4}-Ni2-O6	86.15(19)	O5^{6}-Ni2-O5^{5}	91.24(11)
O4^{5}-Ni2-O6	86.15(18)	O7-Ni2-O9	92.88(7)
O10-Ni2-O4	93.06(14)	O7^{3}-Ni2-O5^{6}	89.32(8)
O10-Ni2-O7	92.77(15)	O7^{3}-Ni2-O5^{5}	172.97(8)
O10-Ni2-O6	178.9(3)	O7^{3}-Ni2-O7	89.27(11)
O7-Ni2-O4^{4}	90.01(15)	O8-Ni2-O9	179.22(10)
O7-Ni2-O4^{4}	174.11(17)	O8-Ni2-O5	85.39(8)
O7^{3}-Ni2-O4^{5}	174.11(16)	O8-Ni2-O7	87.67(8)
O7-Ni2-O7^{3}	88.8(2)	O2-Ni3-O9	94.01(6)
O7-Ni2-O6	88.03(19)	O2^{2}-Ni3-O2^{1}	93.92(12)
O2^{1}-Ni1-O2^{2}	89.8(2)	N1-Ni3-O9	178.26(9)
O2-Ni1-O11	82.85(18)	N1-Ni3-O2	87.18(7)
O10-Ni1-O2	95.22(15)	O4-Ni3-O9	91.56(7)

O10-Ni1-O3	93.03(16)	O4^{5}-Ni3-O2^{2}	174.33(8)
O10-Ni1-O11	177.3(2)	O4^{5}-Ni3-O2^{1}	86.77(10)
O3^{5}-Ni1-O2^{2}	89.03(17)	O4-Ni3-N1	87.23(8)
O3^{4}-Ni1-O2^{2}	171.74(17)	O4^{6}-Ni3-O4^{5}	91.99(16)
O3^{4}-Ni1-O3^{5}	91.0(3)		
O3-Ni1-O11	88.89(18)		

^{1}+X,1/2-Y,+Z; ^{2}1-X,-1/2+Y,1-Z; ^{3}1-X,1-Y,1-Z; ^{4}1/2+X,+Y,1/2-Z; ^{5}1/2-X,-1/2+Y,-1/2+Z; ^{6}1/2-X,1-Y,-1/2+Z.

Table S4 The selected bond angles (°) for SNNU-503 and SNNU-504.

SNNU-503		**SNNU-504**	
Atom-Atom-Atom	**Angle/°**	**Atom-Atom-Atom**	**Angle/°**
O2^{1}-Ni1-O2	91.3(2)	O1-Ni1-O5	92.85(12)
O2-Ni1O3^{2}	173.23(12)	O1-Ni1-O8	92.77(13)
O2-Ni1O3^{3}	89.58(15)	O1-Ni1-N1^{5}	178.6(2)
O2-Ni1-N6^{4}	86.43(13)	O5^{1}-Ni1-O5^{2}	92.3(2)
O3^{2}-Ni1-O3^{3}	88.8(2)	O5-Ni1-N1^{5}	86.21(16)
O3-Ni1-N6^{4}	86.93(14)	O8^{4}-Ni1-O5^{1}	88.1(2)
O9-Ni1-O2	93.08(12)	O8^{3}-Ni1-O5^{1}	174.33(16)
O9-Ni1-O3	93.57(13)	O8^{3}-Ni1-O8^{4}	90.9(3)
O9-Ni1-N6^{4}	179.29(19)	O8^{4}-Ni1-N1^{5}	88.18(16)
O1^{1}-Ni2-O1	92.72(19)	O1-Ni2-O2	94.20(11)
O1^{1}-Ni2-O8	85.6(3)	O1-Ni2-O9	91.82(11)
O1-Ni2-O8	87.0(3)	O1-Ni2-N6	176.72(16)
O5^{6}-Ni2-O1	173.34(14)	O2-Ni2-O2^{6}	88.48(19)
O5^{5}-Ni2-O1	87.06(15)	O2-Ni2-O9^{4}	173.97(14)
O5^{5}-Ni2-O5^{6}	92.4(2)	O2-Ni2-O9^{3}	90.74(14)
O5^{6}-Ni2-O8	87.8(3)	O2-Ni2-N6	88.15(13)
O5^{5}-Ni2-O8	86.4(3)	O9^{4}-Ni2-O9^{3}	89.4(2)
O9-Ni2-O1	94.05(12)	O9^{4}-Ni2-N6	85.85(13)
O9-Ni2-O5	92.60(14)	O9^{3}-Ni2-N6	85.85(14)
O9-Ni2-O8	178.9(4)	O1-Ni3-O3	90.94(13)
O4-Ni3-N1	87.05(13)	O1-Ni3-O4	177.1(2)
O6^{6}-Ni3-O4^{2}	172.61(13)	O1-Ni3-O6	95.21(12)
O6^{6}-Ni3-O4^{3}	89.63(13)	O3-Ni3-O3^{6}	92.2(4)
O6^{5}-Ni3-O6^{6}	90.82(17)	O3-Ni3-O4	87.06(16)
O6-Ni3-N1	85.63(13)	O3^{6}-Ni3-O6^{2}	173.81(16)
O9-Ni3-O4	93.86(12)	O3-Ni3-O6^{2}	87.1(2)
O9-Ni3-O6	93.48(12)	O6-Ni3-O4	86.77(15)
O9-Ni3-N1	178.73(18)	O6^{1}-Ni3-O6^{2}	93.0(2)

^{1}+X,1/2-Y,+Z; ^{2}1-X,-1/2+Y,1-Z; ^{3}1-X,1-Y,1-Z; ^{4}1/2+X,+Y,1/2-Z; ^{5}1/2-X,-1/2+Y,-1/2+Z; ^{6}1/2-X,1-Y,-1/2+Z

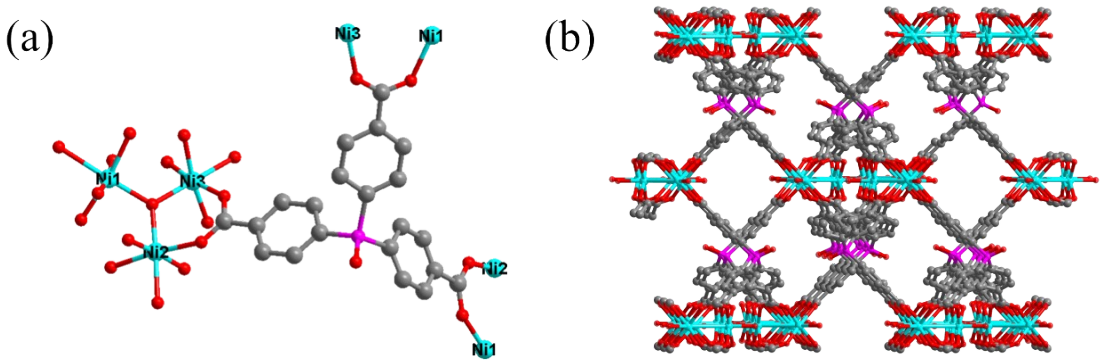

Fig. S1 The structure of SNNU-501: (a) asymmetric unit; (b) 3D structure.

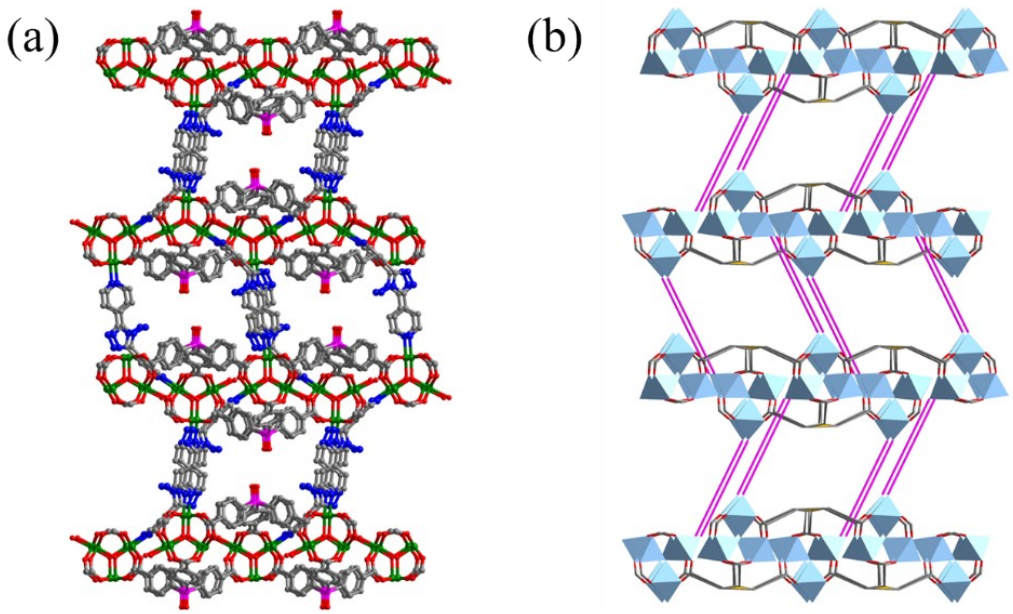

Fig. S2 The pillar-layer structure of SNNU-504 along the b axis.

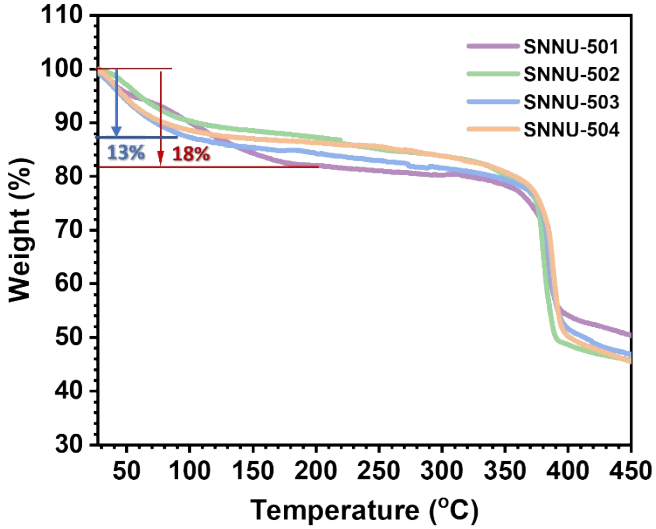

Fig. S3 TGA curves of four compounds.

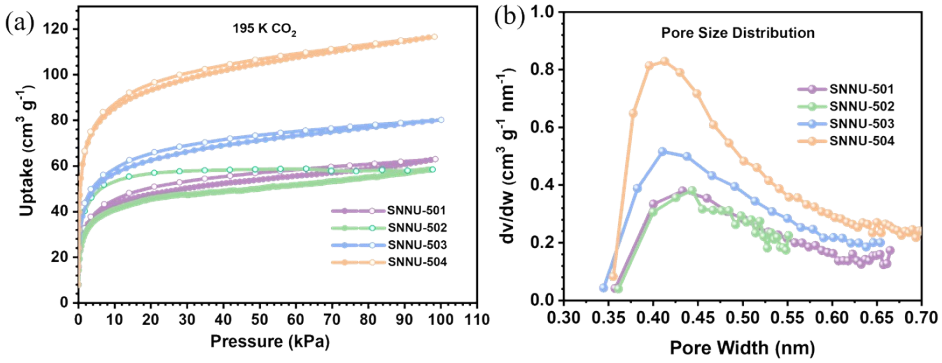

Fig. S4 (a) The CO_2 adsorption isotherms at 195 K, under ambient pressure; (b) the pore size distributions.

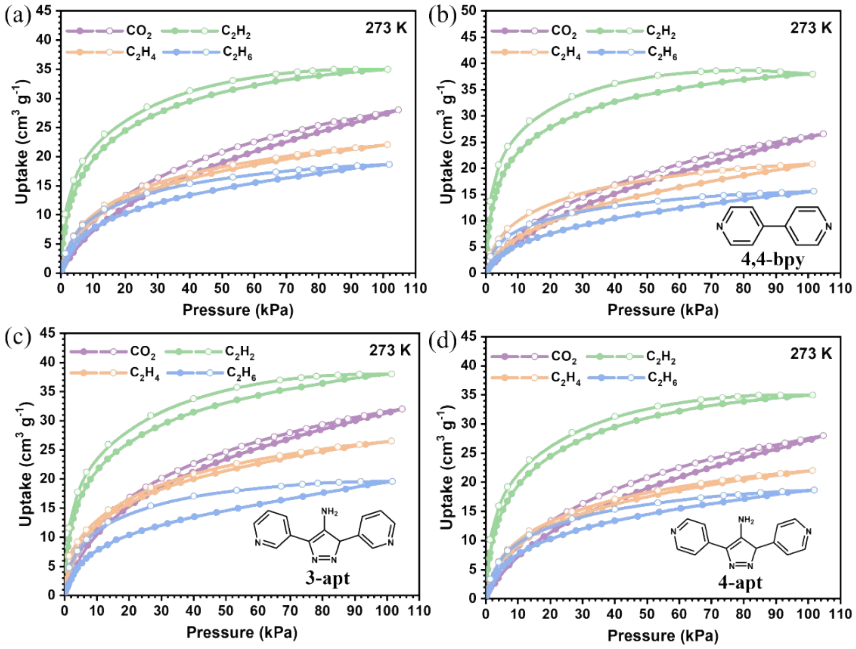

Fig. S5 The gas adsorption curves at 273 K: (a) SNNU-501; (b) SNNU-502; (c) SNNU-503; (d) SNNU-504.

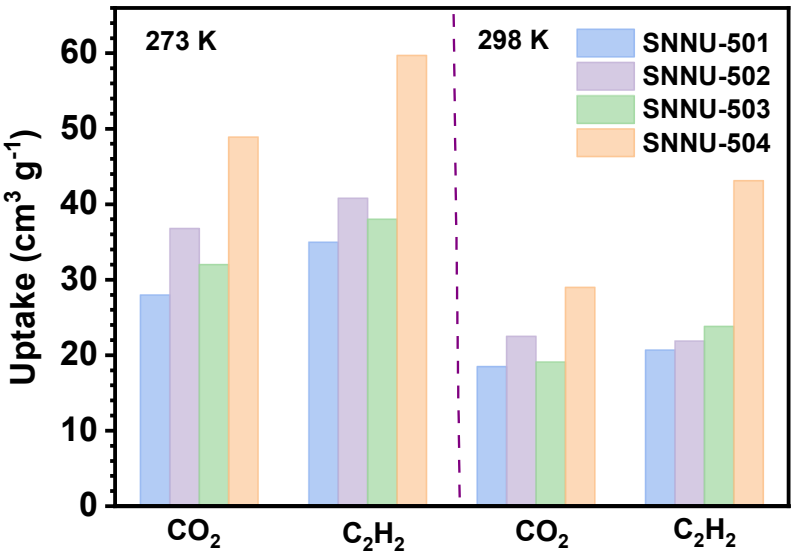

Fig. S6 The uptakes for C_2H_2 and CO_2 at different temperature under 1 bar.

Adsorption enthalpy calculation -- Virial equation

$$ln\,P = ln\,N + \frac{1}{T}\sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i \quad \text{.....e1}$$

$$Q_{st} = -R\sum_{i=0}^{m} a_i N^i \quad \text{.....e2}$$

Where P is the pressure, N is the adsorption amount, T is the temperature, m and N determine the number of terms needed to adequately describe the isotherm.

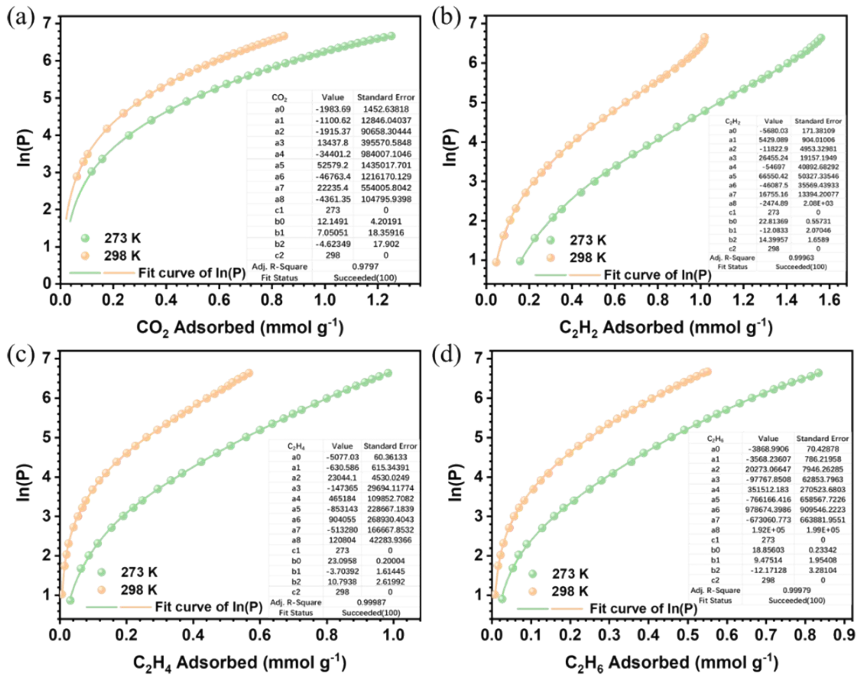

Fig. S7 The fitting parameters by the virial equation in SNNU-501.

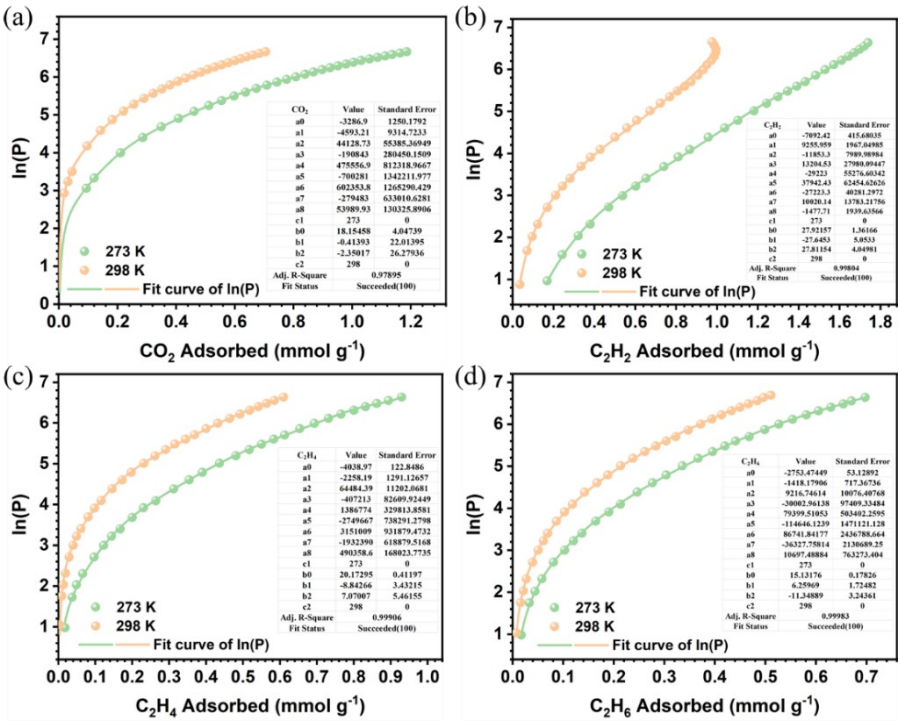

Fig. S8 The fitting parameters by the virial equation in SNNU-502.

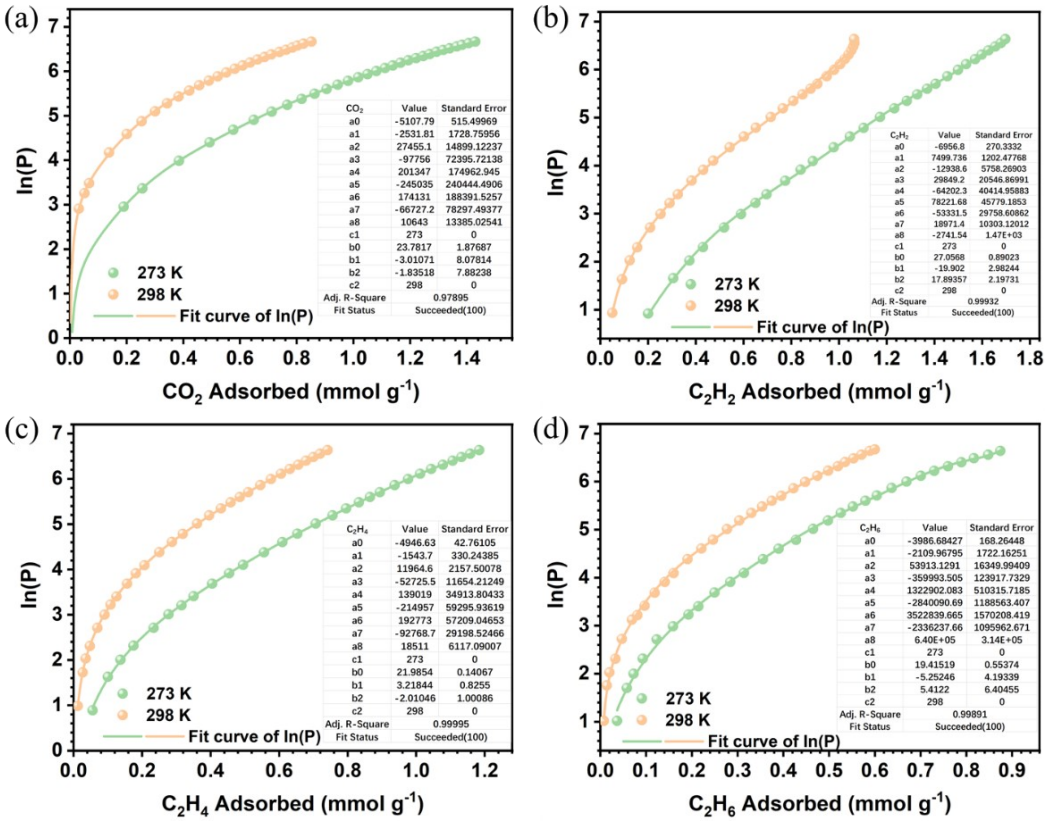

Fig. S9 The fitting parameters by the virial equation in SNNU-503.

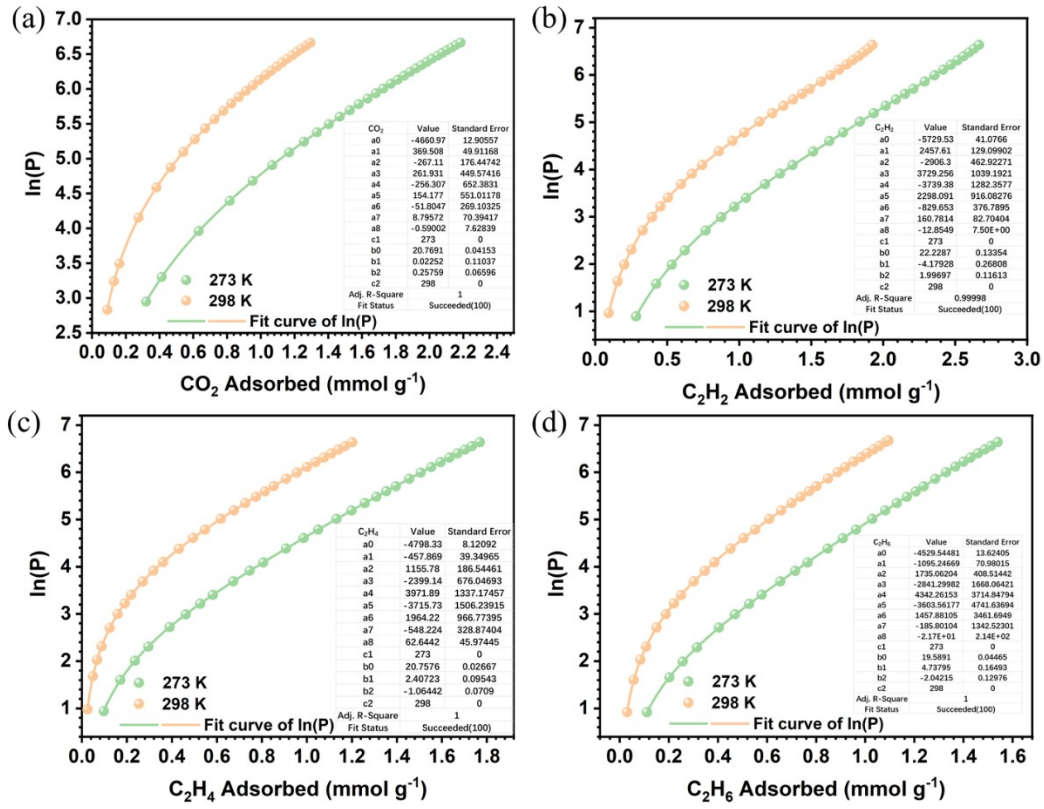

Fig. S10 The fitting parameters by the virial equation in SNNU-504.

Calculation of ideal adsorption solution theory (IAST)

Langmuir−Freundlich (LF)：

$$q = q_m * \frac{b * p^{1/n}}{1 + b * p^{1/n}} \quad \text{.....e3}$$

Where p is the pressure when the volume gas is in equilibrium with the adsorption phase (kPa), q is the adsorption capacity per unit mass of the adsorbent (mmol g^{-1}), q_m is the saturation capacity of the site (mmol g^{-1}), b is the affinity coefficient of the site (1/kPa), and n represents the deviation from the ideal homogeneous surface.

Separation ratio calculation：

$$S_{A/B} = \frac{x_A / y_A}{x_B / y_B} \quad \text{.....e4}$$

Where *x*i and *y*i are the molar fractions of components i (i = A and B) in the adsorption phase and bulk phase, respectively. Note that in the Henry system, $S_{A/B}$ is the same ratio as the Henry constant for both species.

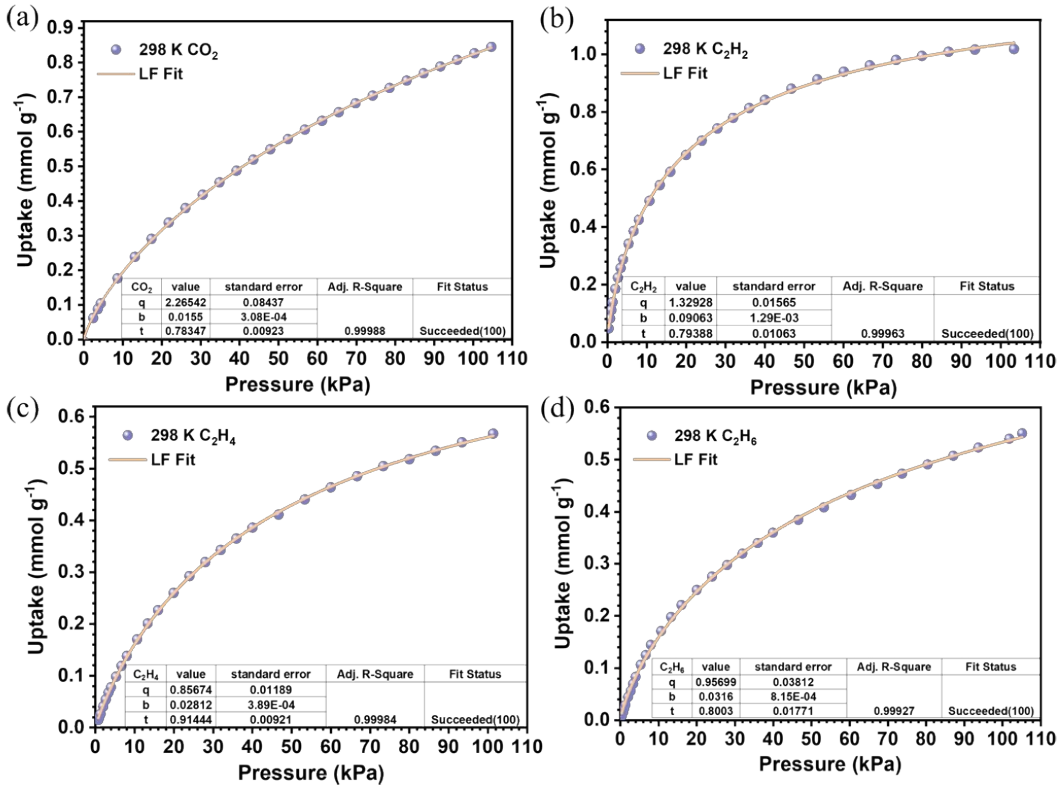

Fig. S11 LF fitting parameters for the adsorption by SNNU-501 at 298 K.

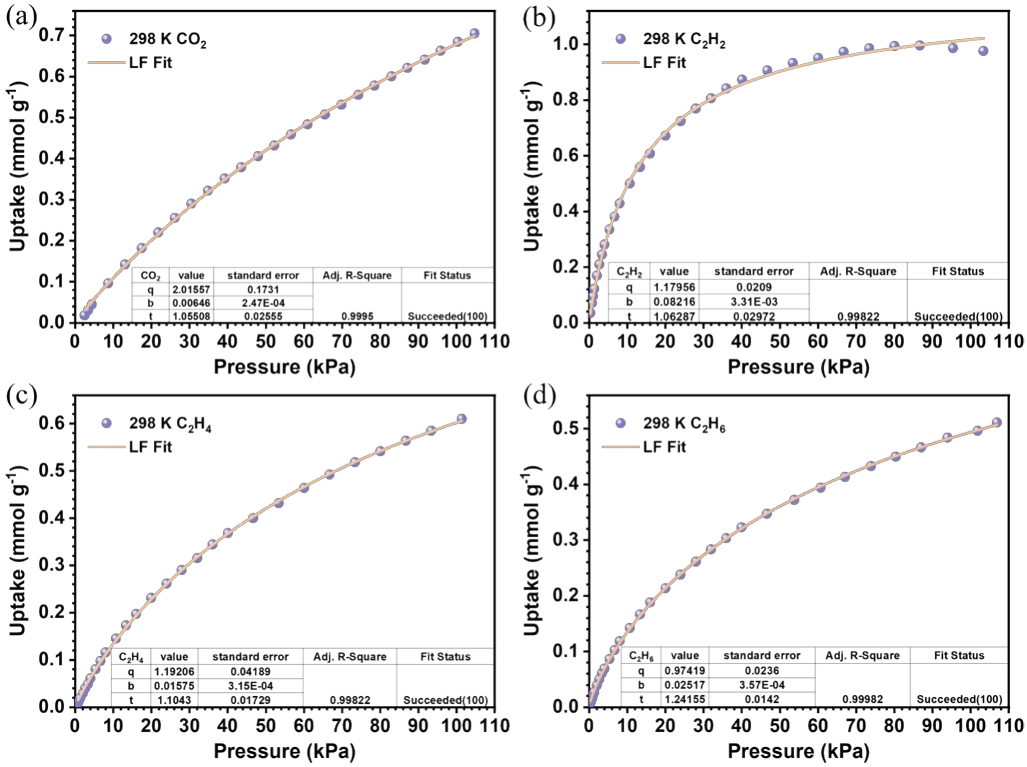

Fig. S12 LF fitting parameters for the adsorption by SNNU-502 at 298 K.

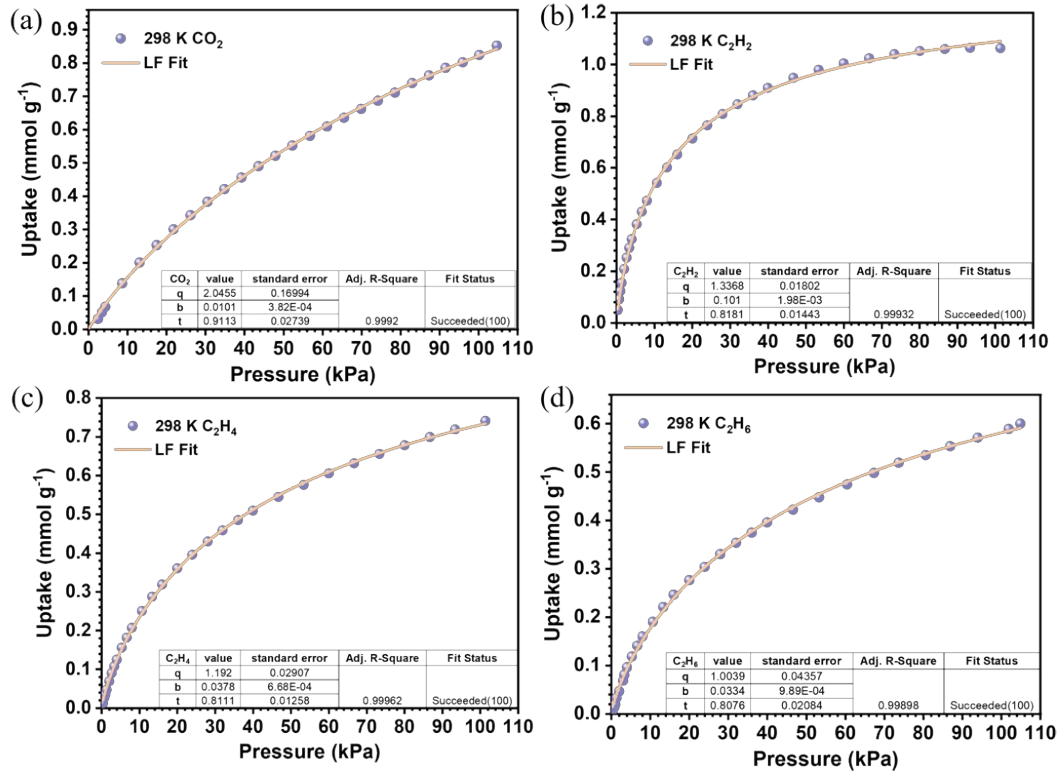

Fig. S13 LF fitting parameters for the adsorption by SNNU-503 at 298 K.

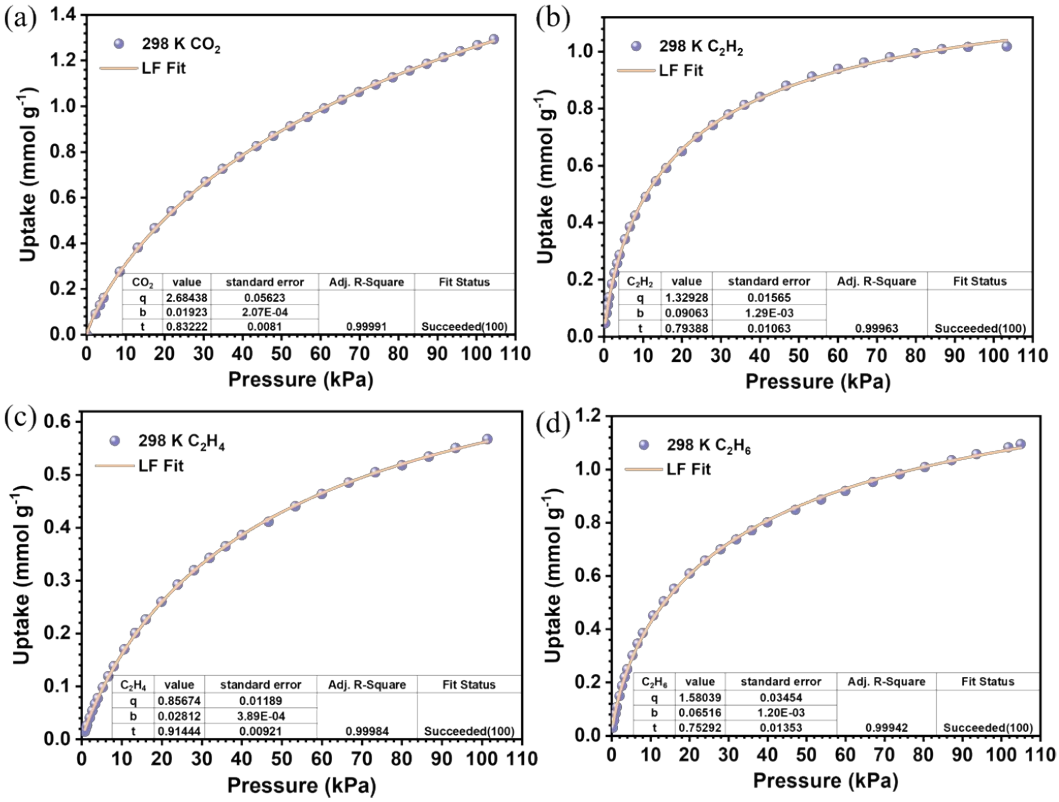

Fig. S14 LF fitting parameters for the adsorption by SNNU-504 at 298 K.

Table S5 Selective separation ratio of four compounds at 298 K, 1 bar for equimolar quantity C_2H_x/CO_2 mixture.

	SNNU-501	SNNU-502	SNNU-503	SNNU-504
C_2H_2/CO_2	3.34	4.22	4.46	4.55
C_2H_4/CO_2	/	/	1.33	1.33
C_2H_6/CO_2	/	/	/	1.28

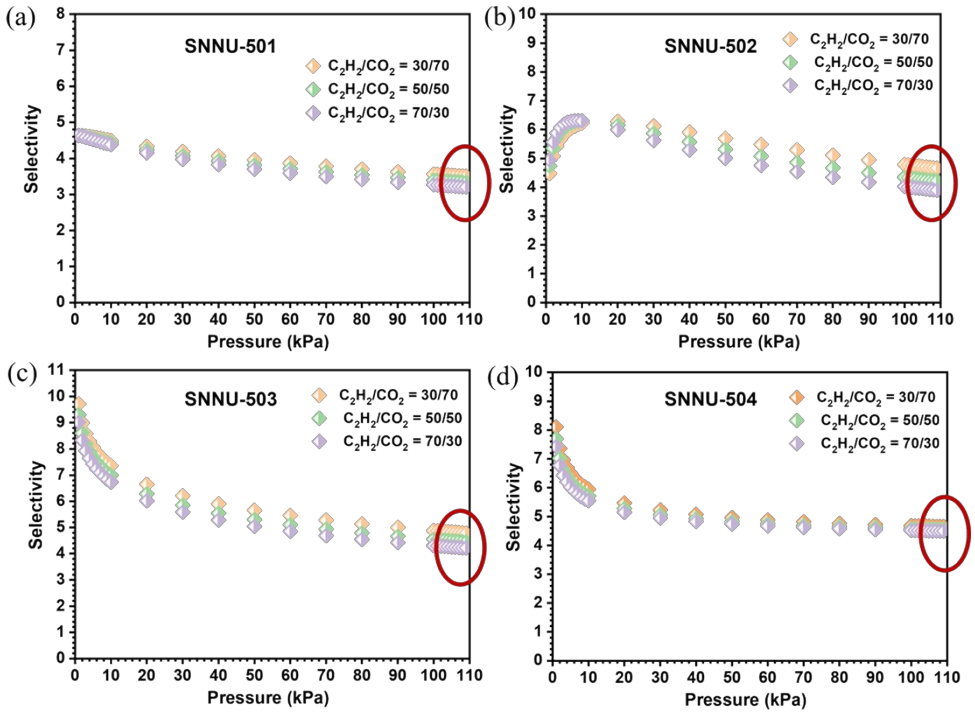

Fig. S15 Selective separation ratio of four compounds for C_2H_2/CO_2 with different component at 298 K.

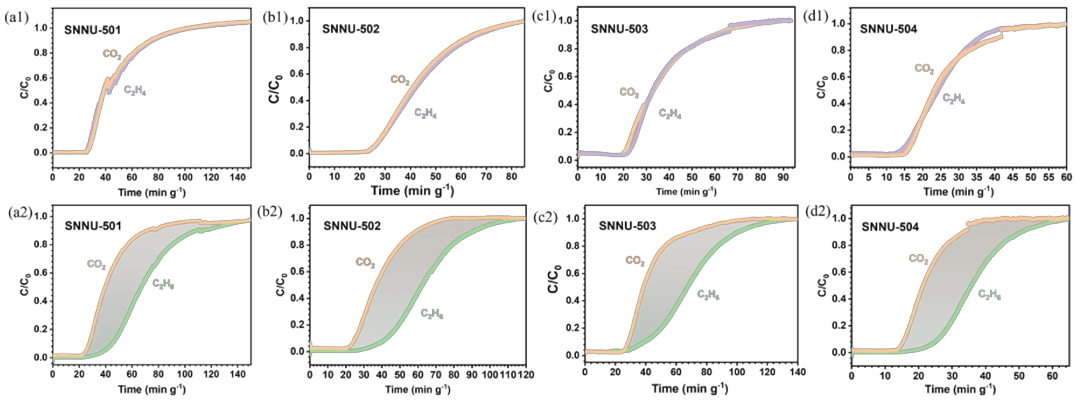

Fig. S16 Breakthrough curves of C_2H_4/CO_2 (top) and C_2H_6/CO_2 (bottom) for four compounds at 298 K, under 1 bar with a gas flow rate of 2 mL min^{-1}: (a) SNNU-501; (b) SNNU-502; (c) SNNU-503; (d) SNNU-504.

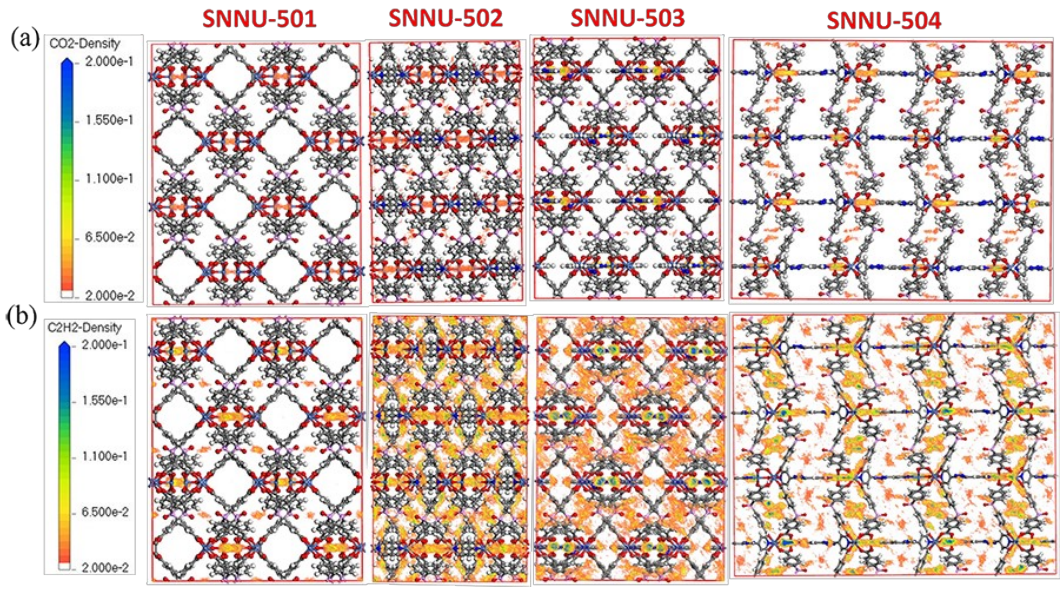

Fig. S17 The density distributions of CO_2 (a) and C_2H_2 (b) molecules in SNNU-501/502/503/504 skeleton at 298 K and 1 bar.

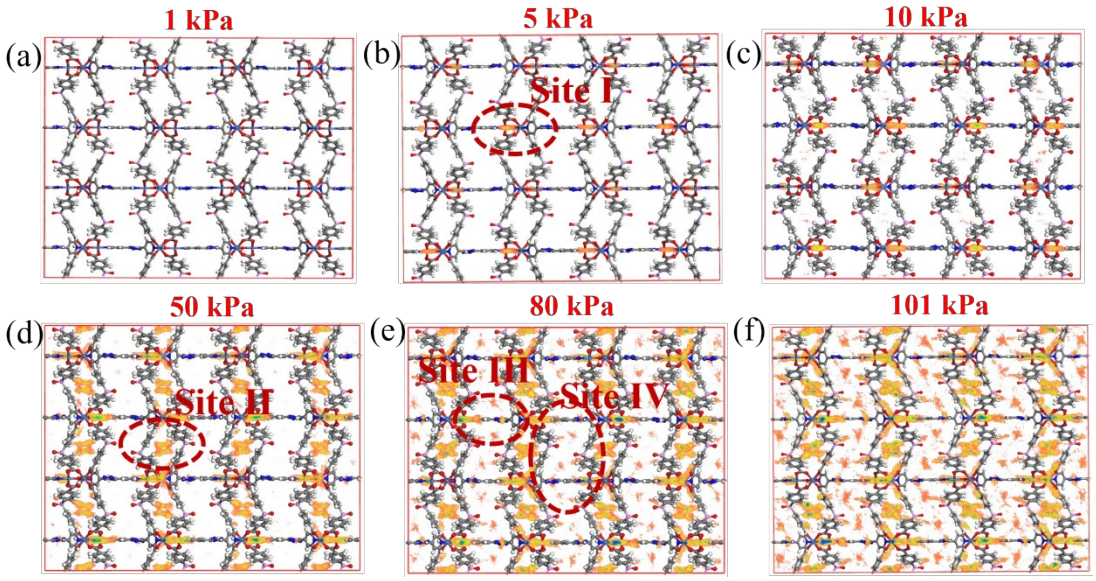

Fig. S18 The density distributions of C_2H_2 molecules in the SNNU-504 at 298 K under different pressure, respectively (a) 1 kPa; (b) 5 kPa; (c) 10 kPa; (d) 50 kPa; (e) 80 kPa; (f) 101 kPa.