Electronic Supplementary Information (ESI) for:

Microporous Rod Metal-Organic Frameworks with Diverse Zn/Cd-Triazolate Ribbons as Secondary Building Units for CO_2 Uptake and Selective Adsorption of Hydrocarbons

Jian-Wei Zhang, Man-Cheng Hu,* Shu-Ni Li, Yu-Cheng Jiang, and Quan-Guo Zhai*

Key Laboratory of Macromolecular Science of Shaanxi Province,

School of Chemistry & Chemical Engineering,

Shaanxi Normal University, Xi'an, Shaanxi, 710062, P. R. China

*To whom correspondence should be addressed:

E-mail: zhaiqg@snnu.edu.cn (Q.-G. Zhai)

hmch@snnu.edu.cn (M.-C. Hu)

Table S1. Crystal data and structure refinements for **SNNU-21**, **-22**, and **-23**.

Compound	**SNNU-21**	**SNNU-22**	**SNNU-23**
Empirical formula	$C_{40}H_{32}Cd_5N_{20}O_{16}$	$C_{32}H_{29}Cd_4N_9O_{14}$	$C_{40}H_{24}Zn_5N_{12}O_{16}$
Formula weight	1610.91	1213.28	1255.56
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Ibca*	*Pbcn*	*Imma*
a(Å)	17.4956(8)	37.9410(6)	9.4770(8)
b(Å)	29.4158(11)	19.9026(4)	34.800(3)
c(Å)	35.2708(14)	14.3533(3)	25.010(2)
α (deg)	90	90	90
β (deg)	90	90	90
γ (deg)	90	90	90
Volume(Å^3)	18152.0(13)	10838.5(4)	8248.4(12)
Z	8	8	4
$d_{calcd.}$ (g·cm^{-3})	1.179	1.486	1.011
μ(mm^{-1})	6.298	1.604	1.481
F(000)	15260	4703	2504
Reflections collected/unique	26904 / 5908	46730 / 11067	20894 / 3944
R_{int}	0.0656	0.0566	0.1520
Data/restraints/parameters	5908/0/366	11067/0/516	3944 / 0 / 200
GOF on F^2	0.953	1.141	1.090
R_1[a], wR_2[b] [I > 2σ(I)]	0.0628, 0.1668	0.0763, 0.1523	0.0648, 0.1446
R_1[a], wR_2[b] (all data)	0.0851, 0.1768	0.0905, 0.1572	0.1637, 0.1541

[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. Selected bond lengths (Å) and angles (°) for **SNNU-21**.

Cd(1)-N(9)	2.199(8)	N(9)-Cd(1)-N(7)	98.6(3)
Cd(1)-O(8)	2.497(6)	O(7)-Cd(1)-O(8)	145.1(3)
Cd(1)-O(7)	2.486(8)	O(5)-Cd(1)-O(8)	134.8(3)
Cd(1)-O(5)	2.308(8)	O(1)-Cd(1)-O(8)	55.1(2)
Cd(1)-O(1)	2.240(8)	N(7)-Cd(1)-O(8)	86.5(2)
Cd(1)-N(7)	2.223(8)	N(9)-Cd(1)-O(8)	82.7(2)
Cd(2)-O(8)	2.492(6)	O(5)-Cd(1)-O(7)	54.2(3)
Cd(2)-N(10)	2.337(7)	O(1)-Cd(1)-O(7)	92.2(3)
Cd(2)-N(5)	2.277(7)	N(9)-Cd(1)-O(1)	129.7(3)
Cd(3)-N(6)	2.242(8)	N(7)-Cd(1)-O(7)	90.9(3)
Cd(3)-N(8)	2.226(7)	N(9)-Cd(1)-O(7)	132.0(3)
Cd(3)-O(2)	2.288(9)	O(1)-Cd(1)-O(5)	99.3(3)
Cd(3)-O(6)	2.329(7)	N(7)-Cd(1)-O(5)	138.6(3)
Cd(3)-O(4)	2.389(7)	N(9)-Cd(1)-O(5)	91.8(3)
Cd(3)-O(3)	2.435(8)	N(7)-Cd(1)-O(1)	104.2(4)
N(6)-Cd(3)-O(2)	101.0(4)	N(5)#1-Cd(2)-N(5)	162.9(4)
N(6)-Cd(3)-N(8)	100.5(3)	N(10)-Cd(2)-O(8)#1	169.6(2)
N(8)-Cd(3)-O(4)	146.9(3)	N(5)-Cd(2)-O(8)	82.4(2)
N(8)-Cd(3)-O(6)	100.4(3)	N(5)-Cd(2)-N(10)	97.5(3)
N(8)-Cd(3)-O(2)	93.2(3)	N(5)-Cd(2)-N(10)#1	92.6(2)
O(8)#1-Cd(2)-O(8)	88.1(3)	N(10)-Cd(2)-N(10)#1	107.5(4)
N(6)-Cd(3)-O(4)	96.1(3)	N(5)-Cd(2)-O(8)#1	85.3(2)
N(6)-Cd(3)-O(3)	142.8(3)	N(10)-Cd(2)-O(8)	82.3(2)
O(2)-Cd(3)-O(4)	55.3(3)	O(2)-Cd(3)-O(6)	160.0(4)
O(6)-Cd(3)-O(3)	54.6(3)	N(6)-Cd(3)-O(6)	90.9(3)
O(6)-Cd(3)-O(4)	107.8(3)	O(4)-Cd(3)-O(3)	83.8(3)
N(8)-Cd(3)-O(3)	99.3(3)	O(2)-Cd(3)-O(3)	109.0(4)

Symmetry codes: #1: - x + 3/2, y, - z + 1.

Table S3. Selected bond lengths (Å) and angles (°) for **SNNU-22**.

Cd(1)-N(3)#1	2.215(8)	N(3)#1-Cd(1)-N(8)#2	113.1(3)
Cd(1)-N(8)#2	2.208(8)	N(3)#1-Cd(1)-O(7)	97.5(3)
Cd(1)-O(7)	2.284(9)	N(8)#2-Cd(1)-O(7)	149.3(3)
Cd(1)-O(8)	2.349(12)	N(3)#1-Cd(1)-O(8)	81.9(4)
Cd(1)-O(3)	2.362(14)	N(8)#2-Cd(1)-O(8)	95.8(4)
Cd(1)-O(10)	2.428(9)	O(7)-Cd(1)-O(8)	90.8(5)
Cd(2)-N(7)	2.181(7)	N(3)#1-Cd(1)-O(3)	87.7(5)
Cd(2)-N(2)#3	2.218(7)	N(8)#2-Cd(1)-O(3)	87.9(5)
Cd(2)-O(6)#4	2.328(7)	O(7)-Cd(1)-O(3)	90.8(6)
Cd(2)-O(4)#5	2.340(6)	O(8)-Cd(1)-O(3)	169.6(5)
Cd(2)-O(2)#3	2.343(7)	N(3)#1-Cd(1)-O(10)	151.9(3)
Cd(2)-O(14)	2.360(7)	N(8)#2-Cd(1)-O(10)	94.7(3)
Cd(3)-O(13)	2.227(6)	O(7)-Cd(1)-O(10)	55.1(3)
Cd(3)-N(1)	2.232(9)	O(8)-Cd(1)-O(10)	91.2(4)
Cd(3)-O(12)	2.323(6)	O(3)-Cd(1)-O(10)	98.2(5)
Cd(3)-O(5)	2.331(6)	N(7)-Cd(2)-N(2)#3	177.1(3)
Cd(3)-O(4)#6	2.357(6)	N(7)-Cd(2)-O(6)#4	88.3(3)
Cd(3)-O(1)#6	2.469(7)	N(2)#3-Cd(2)-O(6)#4	93.3(3)
Cd(4)-O(11)	2.249(6)	N(7)-Cd(2)-O(4)#5	94.3(3)
Cd(4)-N(6)	2.266(8)	N(2)#3-Cd(2)-O(4)#5	87.2(3)
Cd(4)-O(9)#4	2.279(6)	O(6)#4-Cd(2)-O(4)#5	114.5(2)
Cd(4)-O(5)	2.333(7)	N(7)-Cd(2)-O(2)#3	88.4(3)
Cd(4)-O(14)	2.460(6)	N(2)#3-Cd(2)-O(2)#3	89.5(3)
Cd(4)-O(12)	2.487(6)	N(7)-Cd(2)-O(14)	87.3(3)
Cd(4)-O(6)#4	2.574(7)	N(2)#3-Cd(2)-O(14)	90.9(3)
O(12)-Cd(3)-O(1)#6	89.6(2)	O(6)#4-Cd(2)-O(14)	72.5(2)
O(5)-Cd(3)-O(1)#6	161.7(2)	O(4)#5-Cd(2)-O(14)	172.8(2)
O(4)#6-Cd(3)-O(1)#6	53.6(2)	O(2)#3-Cd(2)-O(14)	94.5(3)
O(11)-Cd(4)-N(6)	92.0(3)	O(6)#4-Cd(2)-O(2)#3	166.7(3)
O(11)-Cd(4)-O(9)#4	100.5(3)	O(4)#5-Cd(2) O(2)#3	78.6(2)
O(5)-Cd(4)-O(14)	85.7(2)	O(13)-Cd(3)-N(1)	92.0(3)
O(9)#4-Cd(4)-O(14)	120.4(2)	O(13)-Cd(3)-O(12)	86.2(2)
N(6)-Cd(4)-O(14)	84.1(2)	O(13)-Cd(3)-O(5)	90.4(3)
O(11)-Cd(4)-O(14)	139.0(2)	N(1)-Cd(3)-O(12)	176.3(3)
O(9)#4-Cd(4)-O(5)	97.7(2)	N(1)-Cd(3)-O(5)	101.3(3)
N(6)-Cd(4)-O(5)	168.2(3)	O(12)-Cd(3)-O(5)	82.0(2)
N(6)-Cd(4)-O(9)#4	92.6(3)	O(13)-Cd(3)-O(4)#6	158.7(3)
O(11)-Cd(4)-O(5)	91.8(2)	N(1)-Cd(3)-O(4)#6	89.3(3)
O(11)-Cd(4)-O(12)	86.8(2)	O(12)-Cd(3)-O(4)#6	91.2(2)
O(5)-Cd(4)-O(12)	78.6(2)	O(5)-Cd(3)-O(4)#6	110.2(2)
N(6)-Cd(4)-O(12)	90.5(3)	O(13)-Cd(3)-O(1)#6	105.2(3)
O(9)#4-Cd(4)-O(12)	171.9(2)	N(1)-Cd(3)-O(1)#6	87.8(3)
O(14)-Cd(4)-O(12)	52.5(2)	O(11)-Cd(4)-O(6)#4	153.8(2)
O(9)#4-Cd(4)-O(6)#4	53.7(2)	N(6)-Cd(4)-O(6)#4	85.3(2)
O(14)-Cd(4)-O(6)#4	66.7(2)	O(5)-Cd(4)-O(6)#4	96.1(2)
O(12)-Cd(4)-O(6)#4	119.2(2)		

Symmetry codes: #1: -x + 1, y, -z + 1/2; #2: -x + 1, y, -z + 3/2; #3: -x + 1/2, -y + 1/2, z + 1/2; #4: -x + 1/2, y - 1/2, z; #5: x, -y, z + 1/2; #6: -x + 1/2, y + 1/2, z.

Table S4. Selected bond lengths (Å) and angles (°) for **SNNU-23**.

Zn(1)-O(1)	1.923(7)	O(1)-Zn(1)-N(1)#1	113.2(2)
Zn(1)-N(1)	1.982(7)	N(1)-Zn(1)-N(1)#1	96.0(4)
Zn(1)-N(1)#1	1.982(7)	O(1)-Zn(1)-O(7)#1	106.0(3)
Zn(1)-O(7)#1	2.238(12)	N(1)-Zn(1)-O(7)#1	91.0(3)
Zn(1)-O(7)	2.238(12)	N(1)#1-Zn(1)-O(7)#1	133.2(3)
Zn(3)-O(3)	1.964(8)	O(1)-Zn(1)-O(7)	106.0(3)
Zn(3)-N(3)#2	1.966(7)	N(1)-Zn(1)-O(7)	133.2(3)
Zn(3)-N(3)#3	1.966(7)	N(1)#1-Zn(1)-O(7)	91.0(3)
Zn(3)-O(5)	1.990(10)	O(7)#1-Zn(1)-O(7)	53.4(5)
Zn(2)-N(2)#1	2.111(7)	O(3)-Zn(3)-N(3)#2	114.3(2)
Zn(2)-N(2)#4	2.111(7)	O(3)-Zn(3)-N(3)#3	114.3(2)
Zn(2)-N(2)	2.111(7)	N(3)#2-Zn(3)-N(3)#3	106.7(3)
Zn(2)-N(2)#5	2.111(7)	O(3)-Zn(3)-O(5)	101.3(4)
Zn(2)-O(2)	2.167(8)	N(3)#2-Zn(3)-O(5)	110.1(3)
Zn(2)-O(2)#5	2.167(8)	N(3)#3-Zn(3)-O(5)	110.1(3)
O(1)-Zn(1)-N(1)	113.2(2)	N(2)#1-Zn(2)-N(2)#4	180.0(2)
N(2)#1-Zn(2)-N(2)	89.7(4)	N(2)#4-Zn(2)-N(2)	90.3(4)
N(2)#1-Zn(2)-N(2)#5	90.3(4)	N(2)#4-Zn(2)-N(2)#5	89.7(4)
N(2)-Zn(2)-N(2)#5	180.0(5)	N(2)#1-Zn(2)-O(2)	91.4(2)
N(2)#4-Zn(2)-O(2)	88.6(2)	N(2)-Zn(2)-O(2)	91.4(2)
N(2)#5-Zn(2)-O(2)	88.6(2)	N(2)#1-Zn(2)-O(2)#5	88.6(2)
N(2)#4-Zn(2)-O(2)#5	91.4(2)	N(2)-Zn(2)-O(2)#5	88.6(2)
N(2)#5-Zn(2)-O(2)#5	91.4(2)	O(2)-Zn(2)-O(2)#5	180.0(4)

Symmetry codes: #1: -x, y, z; #2: –x + 1/2, -y, z + 1/2; #3: x - 1/2, -y, z + 1/2; #4: x, -y, -z; #5: -x, -y, -z.

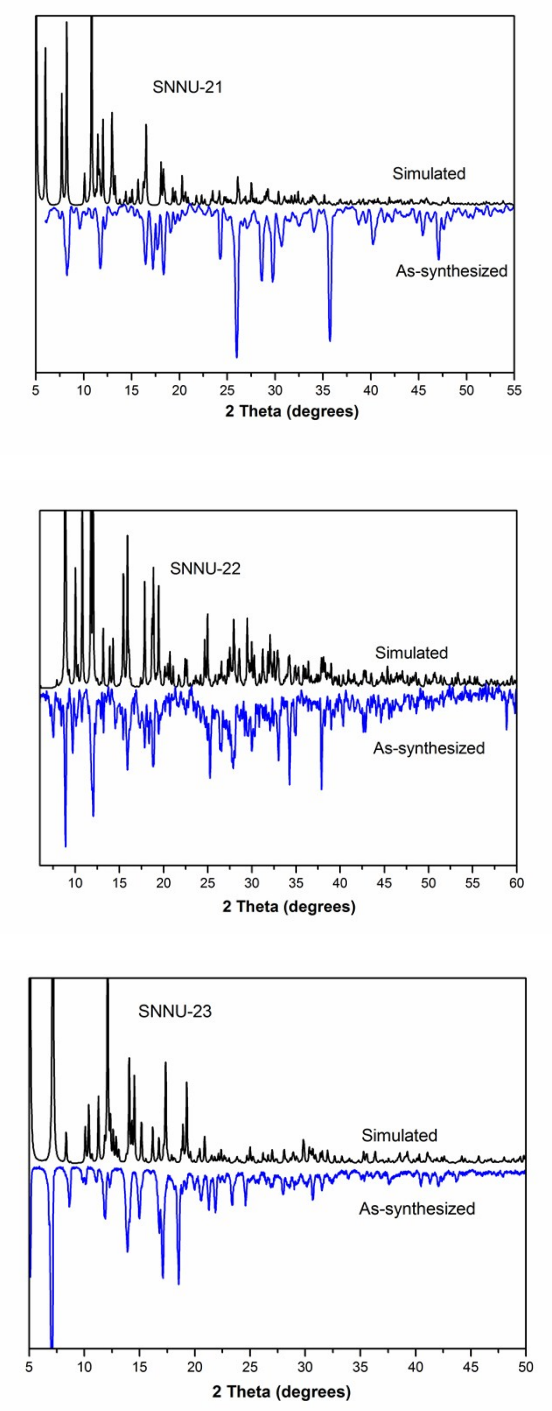
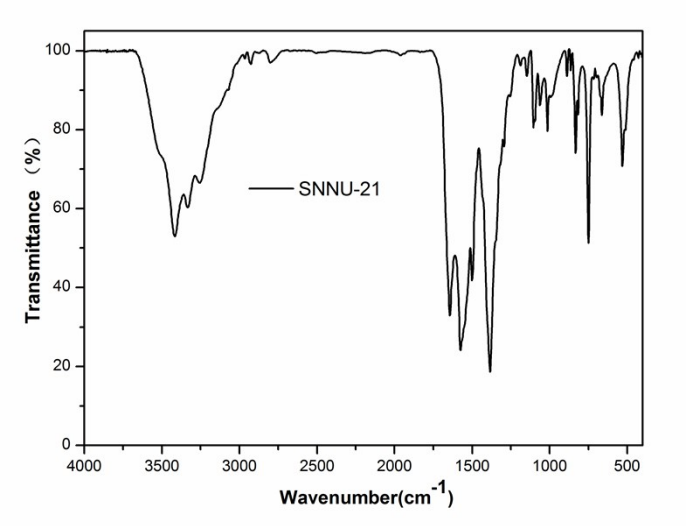
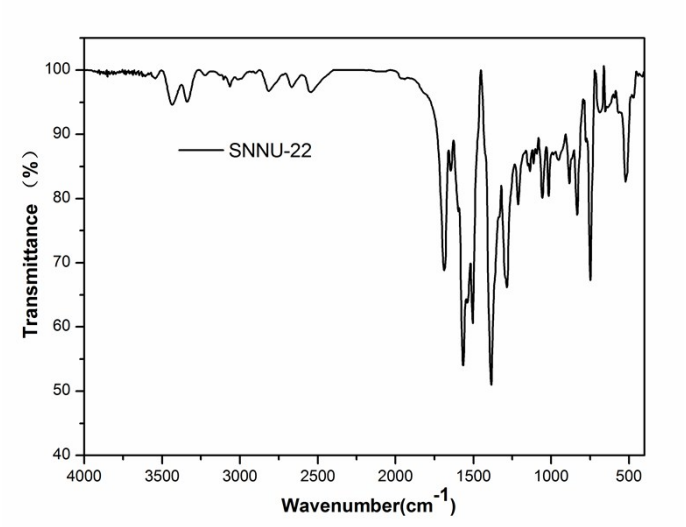


Figure S1. PXRD patterns for **SNNU-21**, **-22** and **-23**.





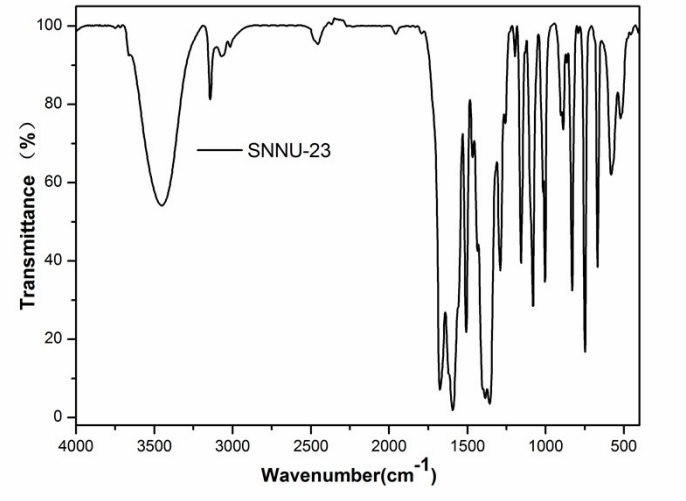


Figure S2. FT-IR spectra for **SNNU-21**, **-22** and **-23**.

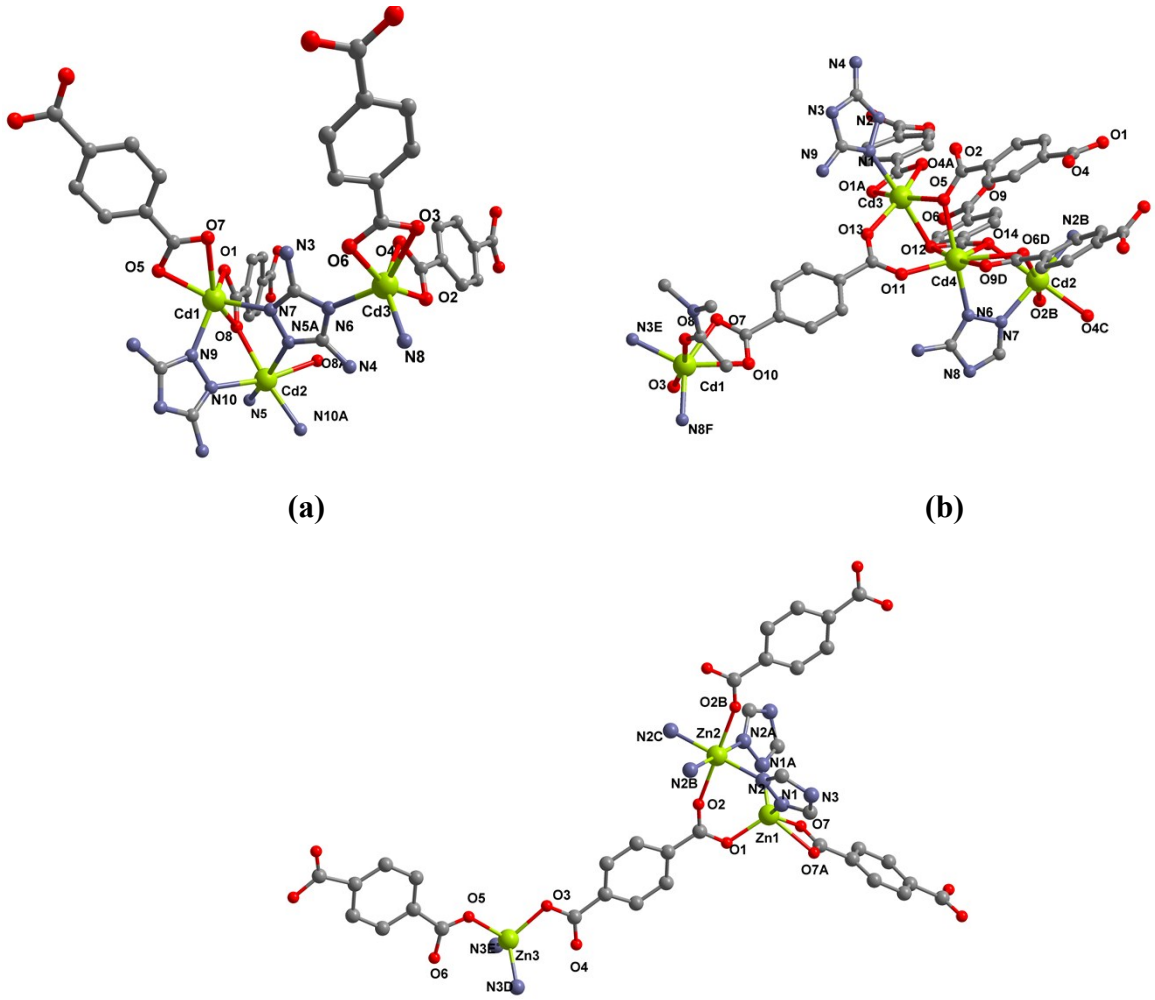


Figure S3. The coordination environments of **SNNU-21** (a), **SNNU-22** (b) and **SNNU-23** (c).

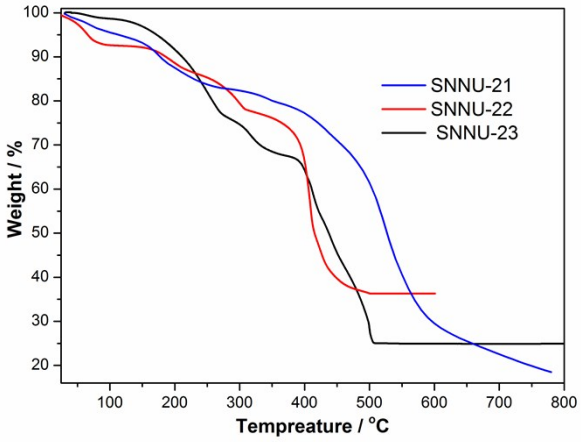
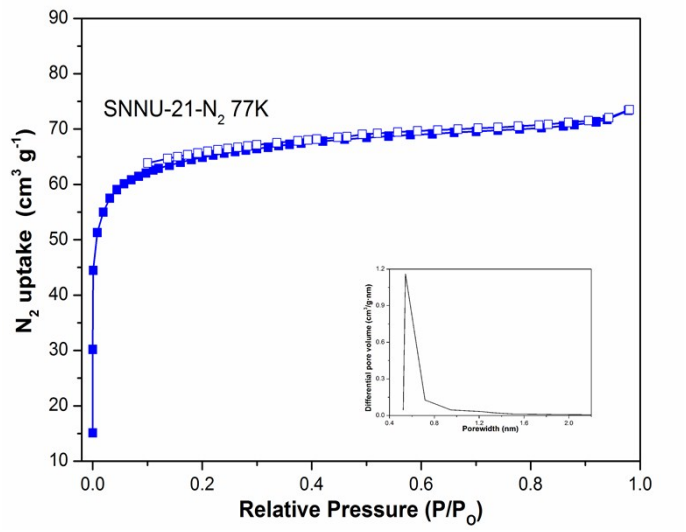
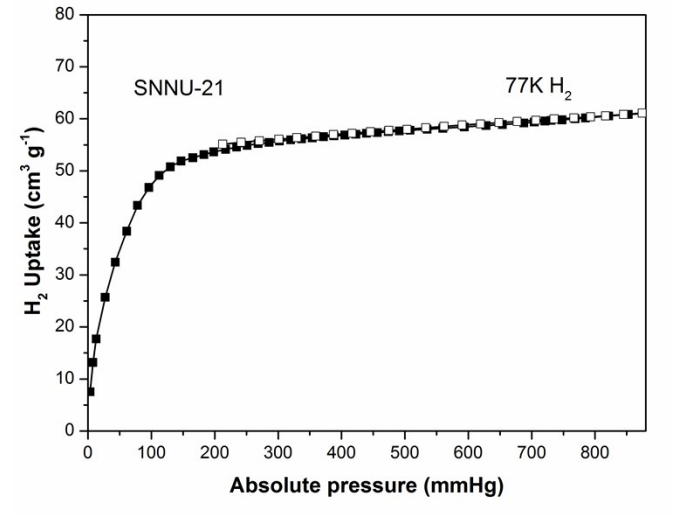


Figure S4. TGA curves for **SNNU-21**, **-22** and **-23**.





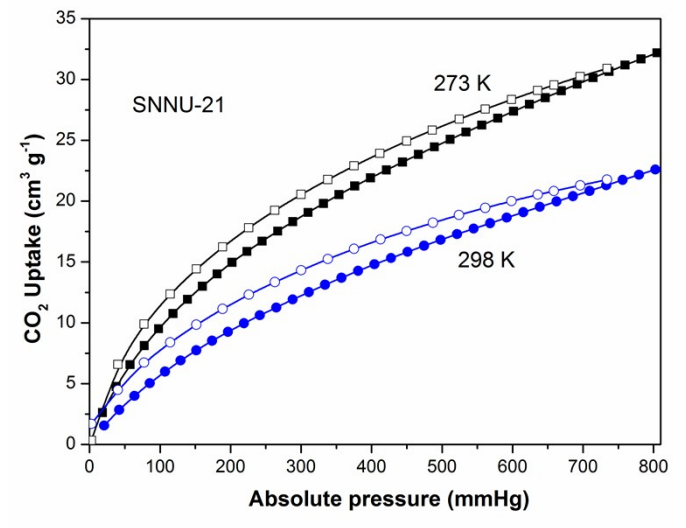


Figure S5. N_2, H_2 and CO_2 adsorption and desorption isotherms for **SNNU-21**.

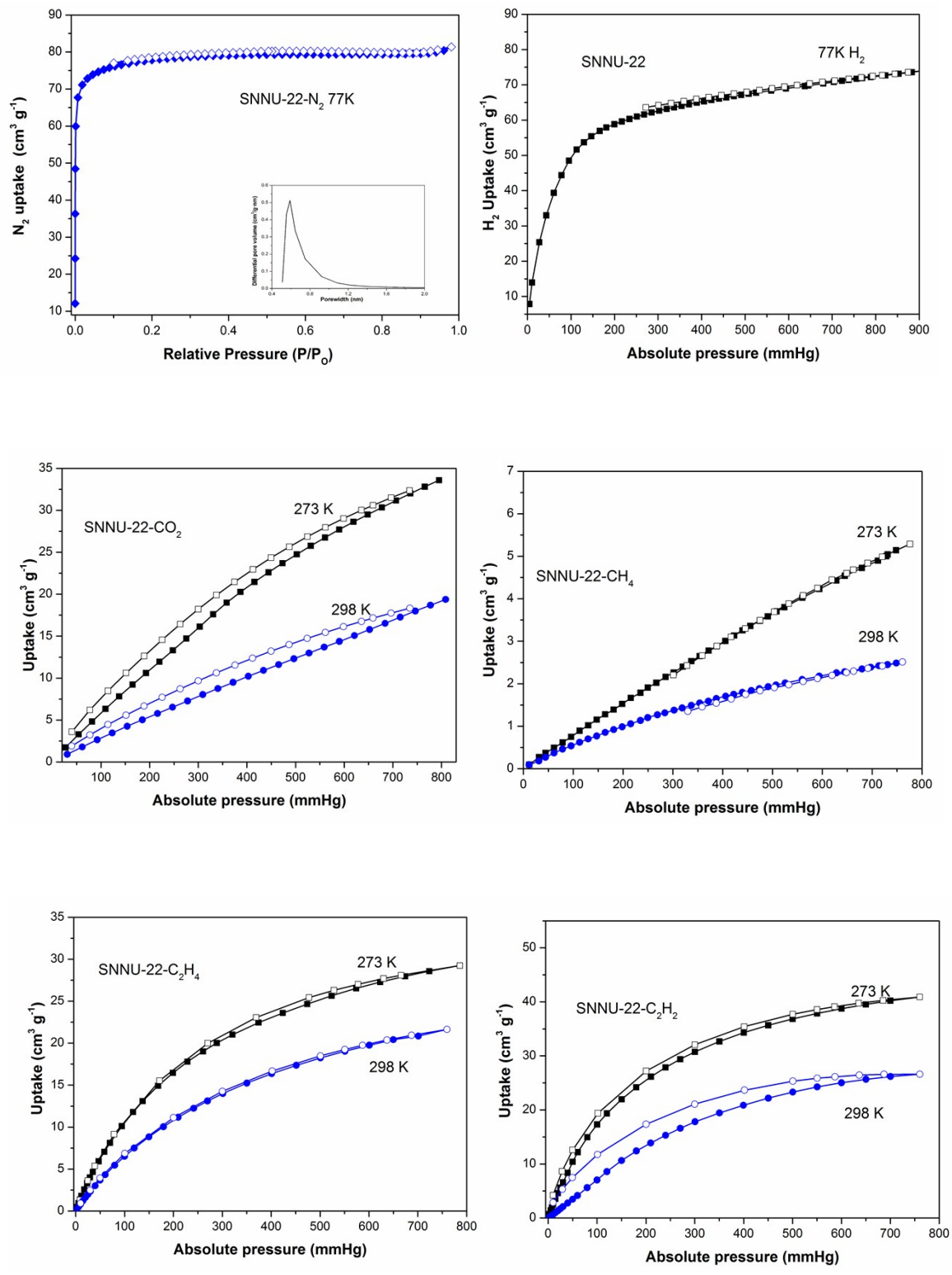


Figure S6. N_2, H_2, CO_2, CH_4, C_2H_4 and C_2H_2 adsorption and desorption isotherms for **SNNU-22**.

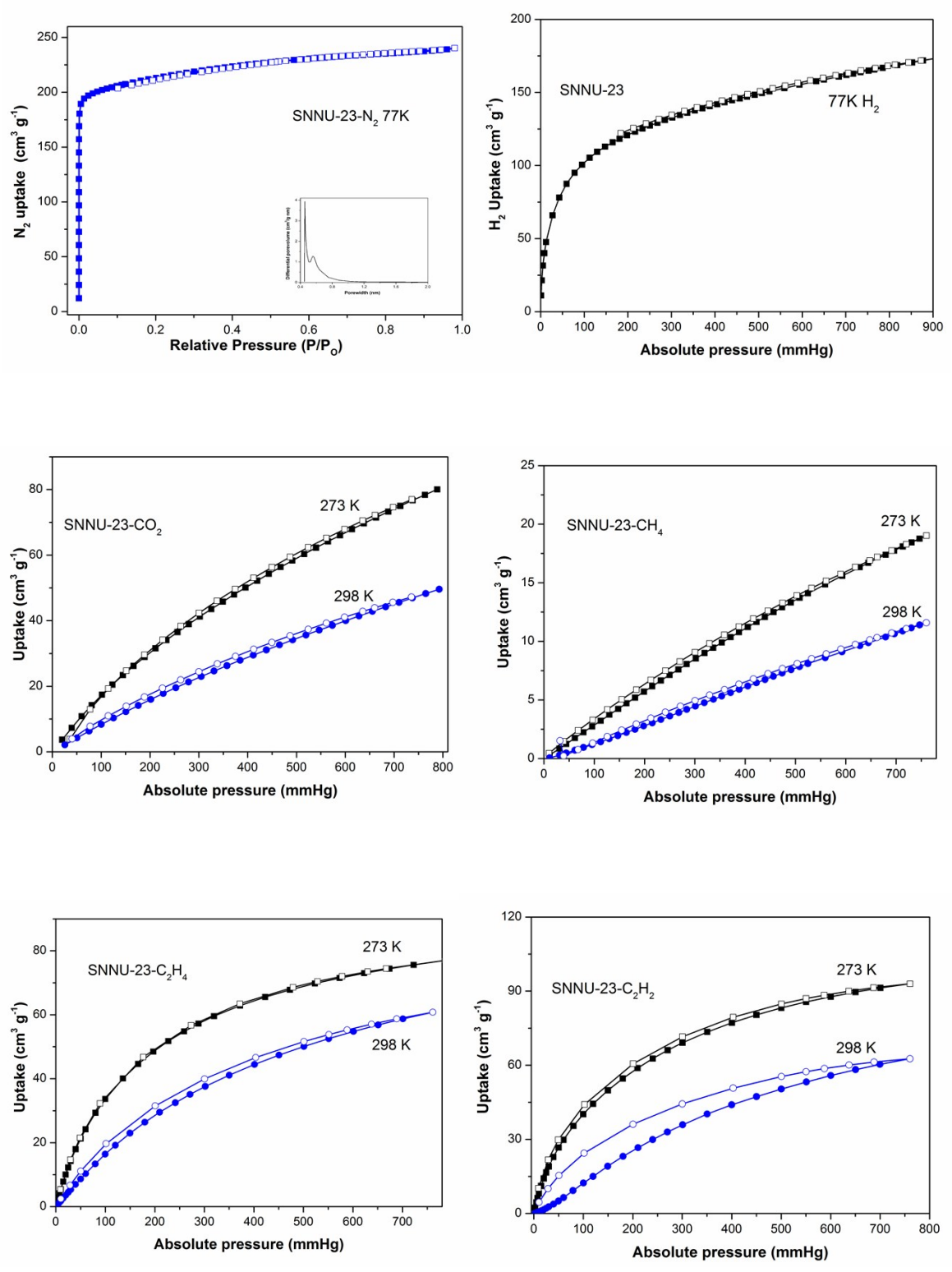


Figure S7. N_2, H_2, CO_2, CH_4, C_2H_4 and C_2H_2 adsorption and desorption isotherms for **SNNU-23**.

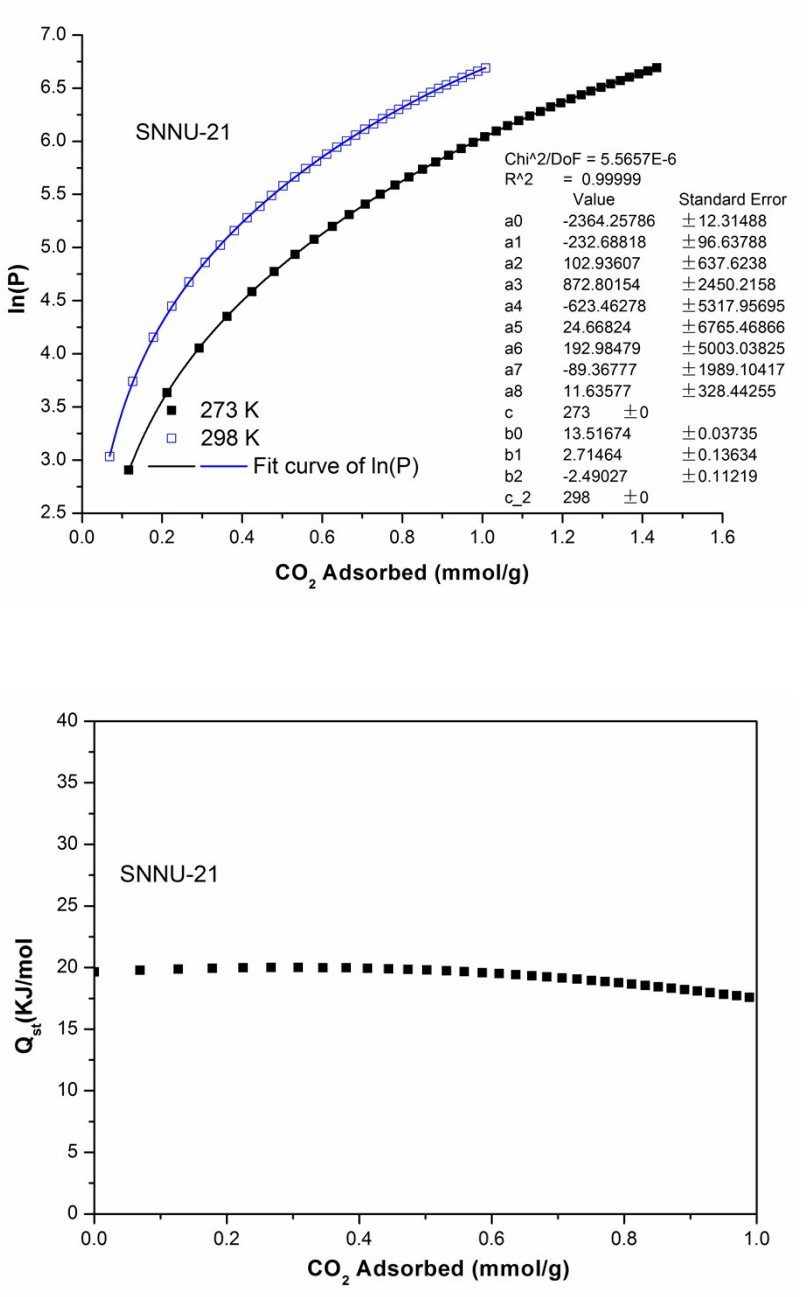


Figure S8. Fitted CO_2 adsorption isotherms of **SNNU-21** measured at 273 K and 298 K (top), and the isosteric heats of adsorption (Q_{st}) (bottom).

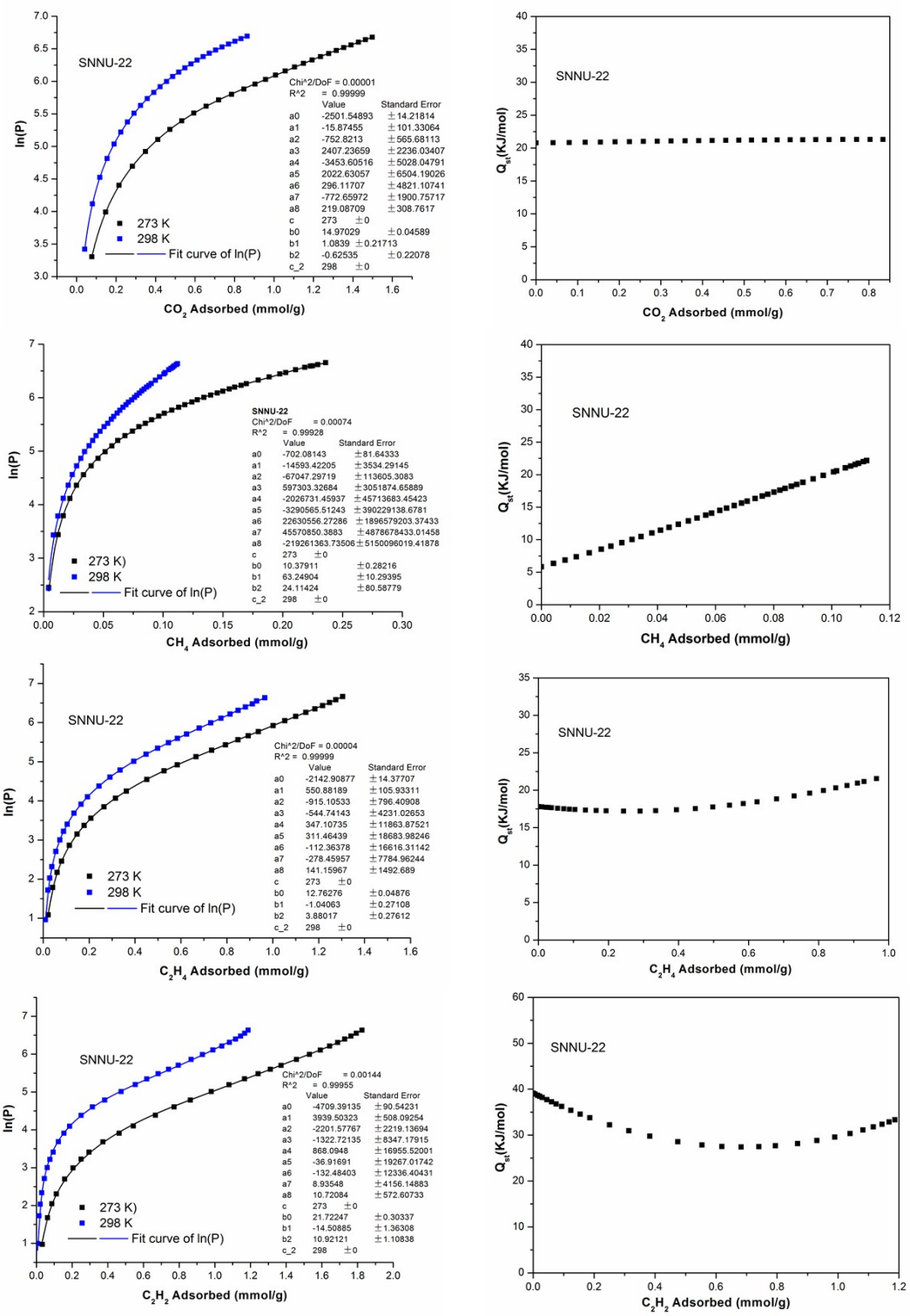


Figure S9. Fitted gas adsorption isotherms of **SNNU-22** measured at 273 K and 298 K (Left), and their corresponding isosteric heats of adsorption (Q_{st}) (Right).

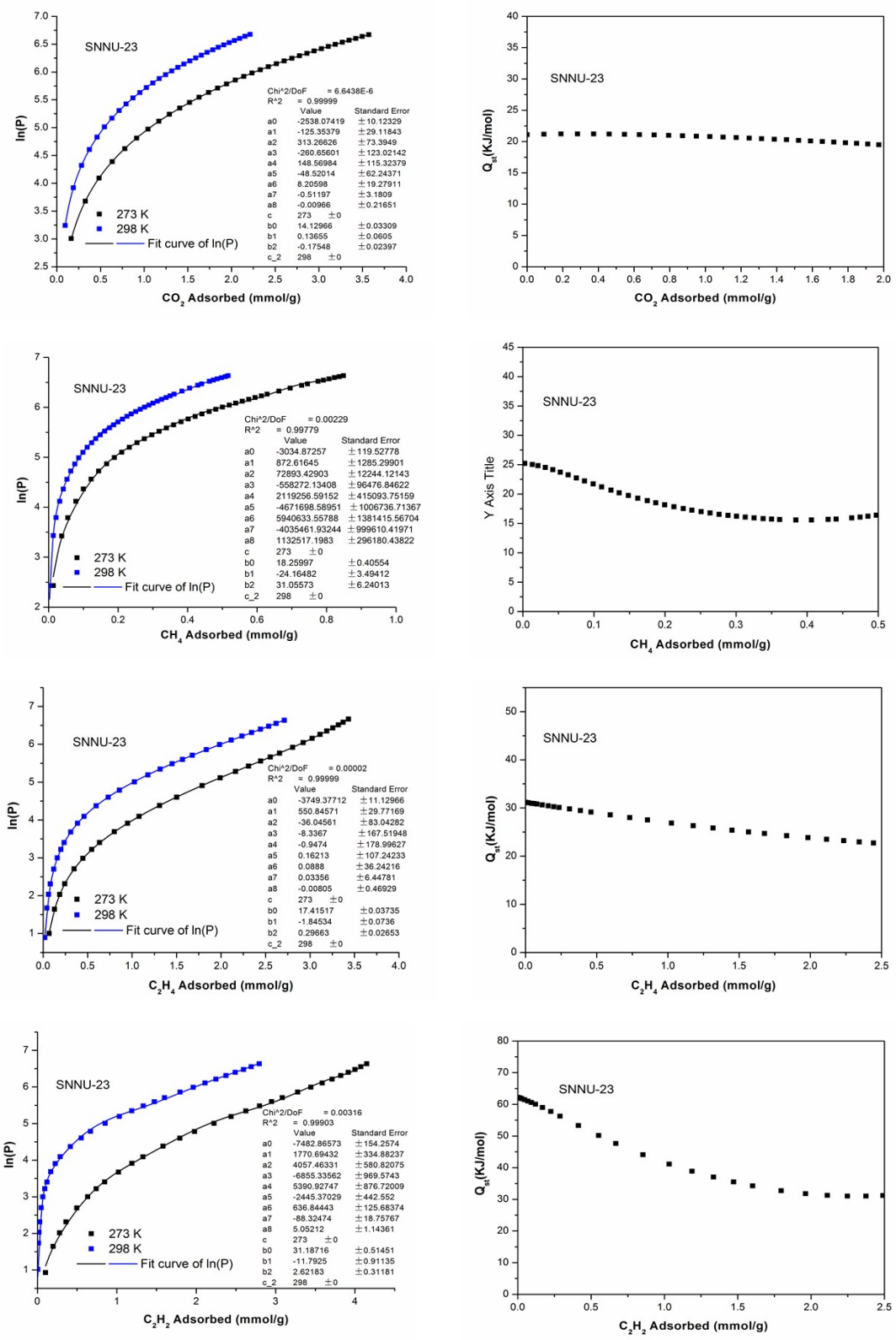


Figure S10. Fitted gas adsorption isotherms of **SNNU-23** measured at 273 K and 298 K (Left), and their corresponding isosteric heats of adsorption (Q_{st}) (Right).

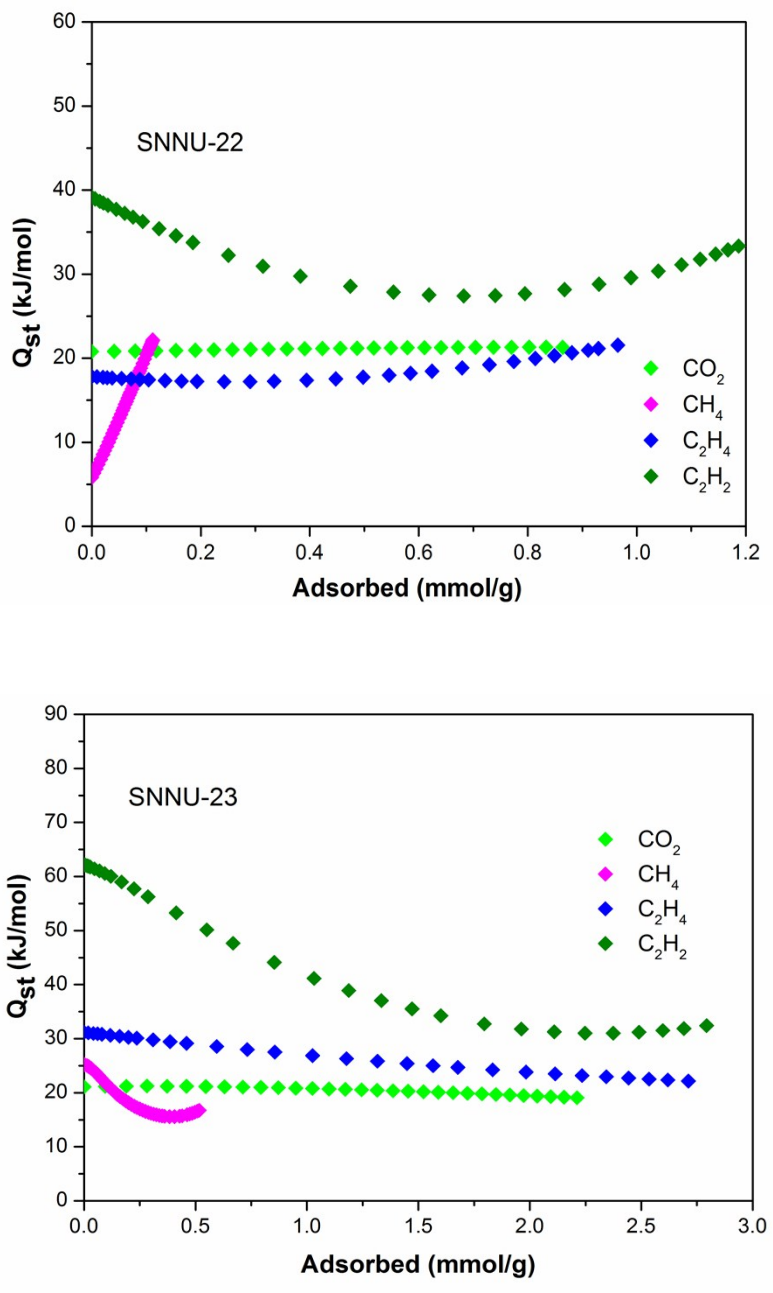


Figure S11. Comparisons of the isosteric heats of adsorption (Q_{st}) for **SNNU-22** and **-23**.

Ideal Adsorbed Solution Theory.

To perform the integrations required by IAST, the single-component isotherms should be fitted by a proper model. Several isotherm models were tested to fit the experimental pure isotherms for CO_2, C_2H_2, and C_2H_4 and CH_4 of **SNNU-22/-23**, and the Langmuir–Freundlich (LF) equation were found to the best fit to the experimental data:

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

where p is the pressure of the bulk gas at equilibrium with the adsorbed phase (kPa), q is the adsorbed amount per mass of adsorbent (mmol g^{-1}), q_m is the saturation capacities of site (mmol g^{-1}), b is the affinity coefficients of site (1/kPa), and n represent the deviations from an ideal homogeneous surface. The correlation coefficients (R^2) values for all of the fitted isotherms were over 0.999. Hence, the fitted isotherm parameters were applied to perform the necessary integrations in IAST.

Based on the above equation parameters of pure gas adsorption, we used the IAST model to investigate the separation of CO_2/ CH_4, C_2H_2/CH_4 and C_2H_4/CH_4. The adsorption selectivity is defined by

$$s_{A/B} = \frac{x_A / y_A}{x_B / y_B}$$

Where x_i and y_i are the mole fractions of component i (i = A, B) in the adsorbed and bulk phases, respectively. Note that in the Henry regime $S_{A/B}$ is identical to the ratio of the Henry constants of the two species.

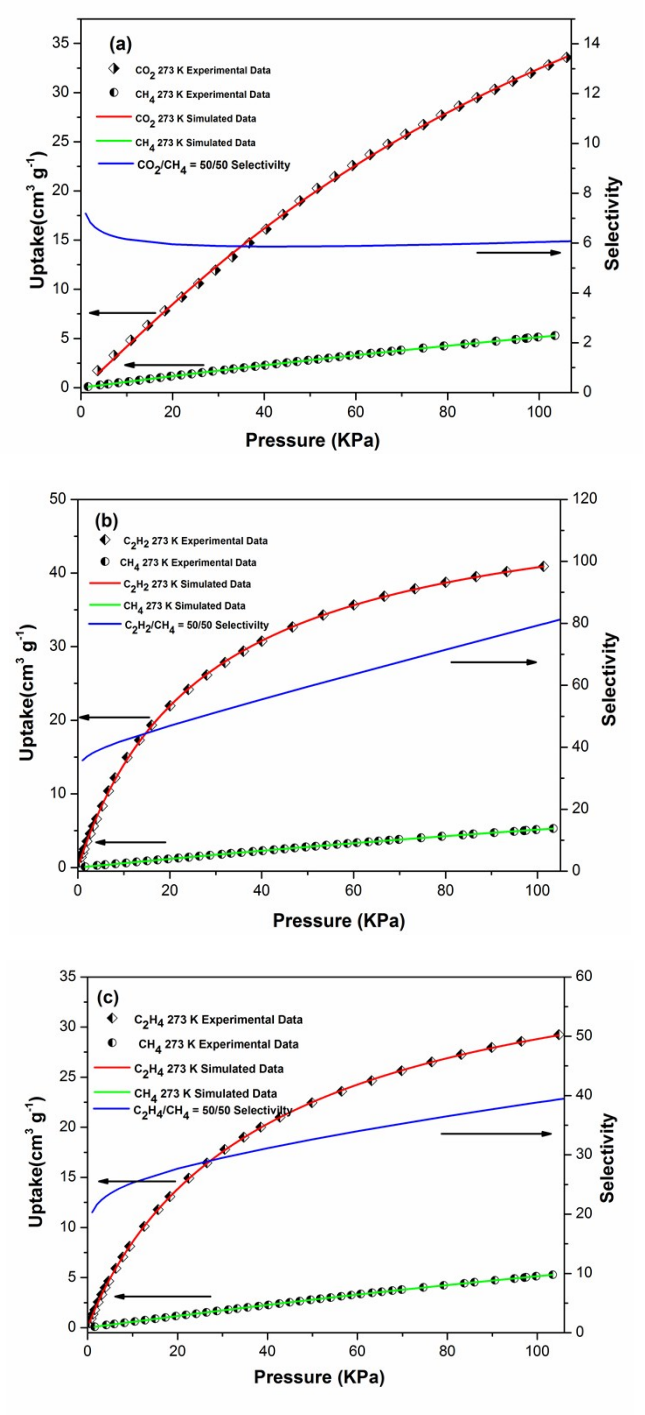


Figure S12. Comparison of experimental isotherms and simulated isotherms (Left *Y* axis), and mixture adsorption selectivity predicted by IAST (Right *Y* axis) of **SNNU-22** for equimolar binary-mixture at 273 K: (a) CO_2/CH_4, (b) C_2H_2/CH_4 and (c) C_2H_4/CH_4.

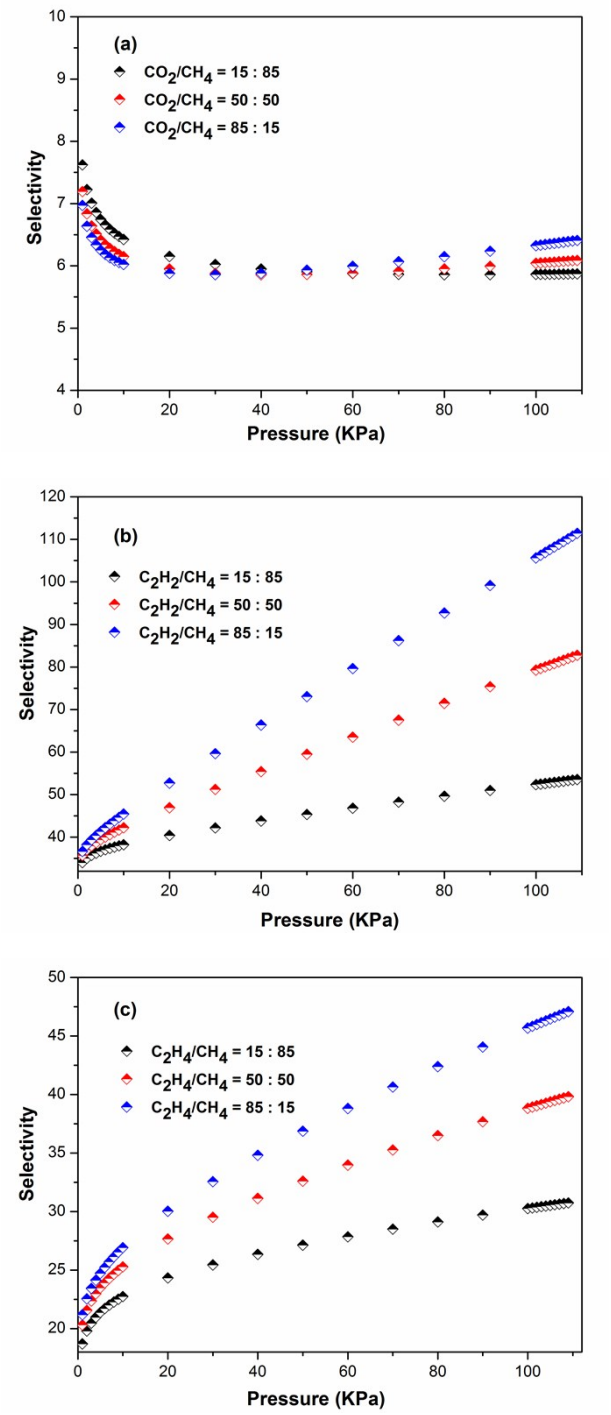


Figure S13. Three different composition selectivity predicted by IAST of **SNNU-22** for binary mixture at 273 K (15 : 85 black; 50: 50 red; and 85 : 15 blue).

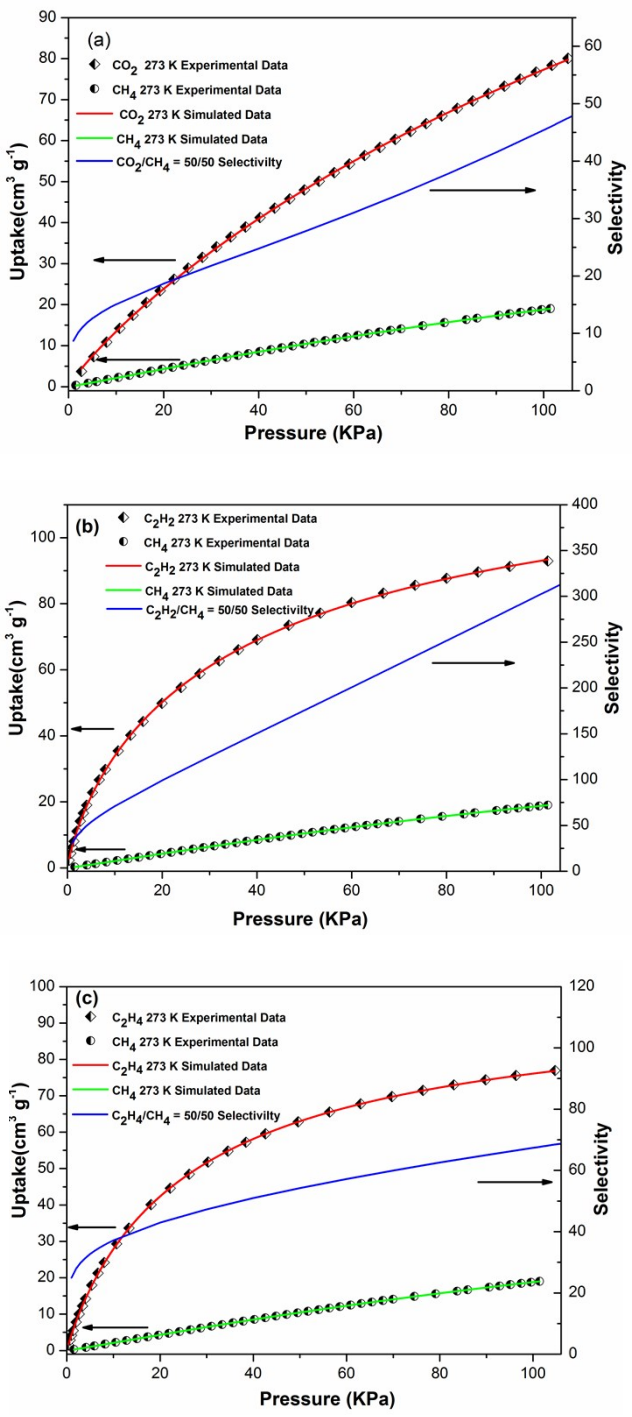


Figure S14. Comparison of experimental isotherms and simulated isotherms (Left *Y* axis), and mixture adsorption selectivity predicted by IAST (Right *Y* axis) of **SNNU-23** for equimolar binary- mixture at 273 K: (a) CO_2/CH_4, (b) C_2H_2/CH_4 and (c) C_2H_4/CH_4.

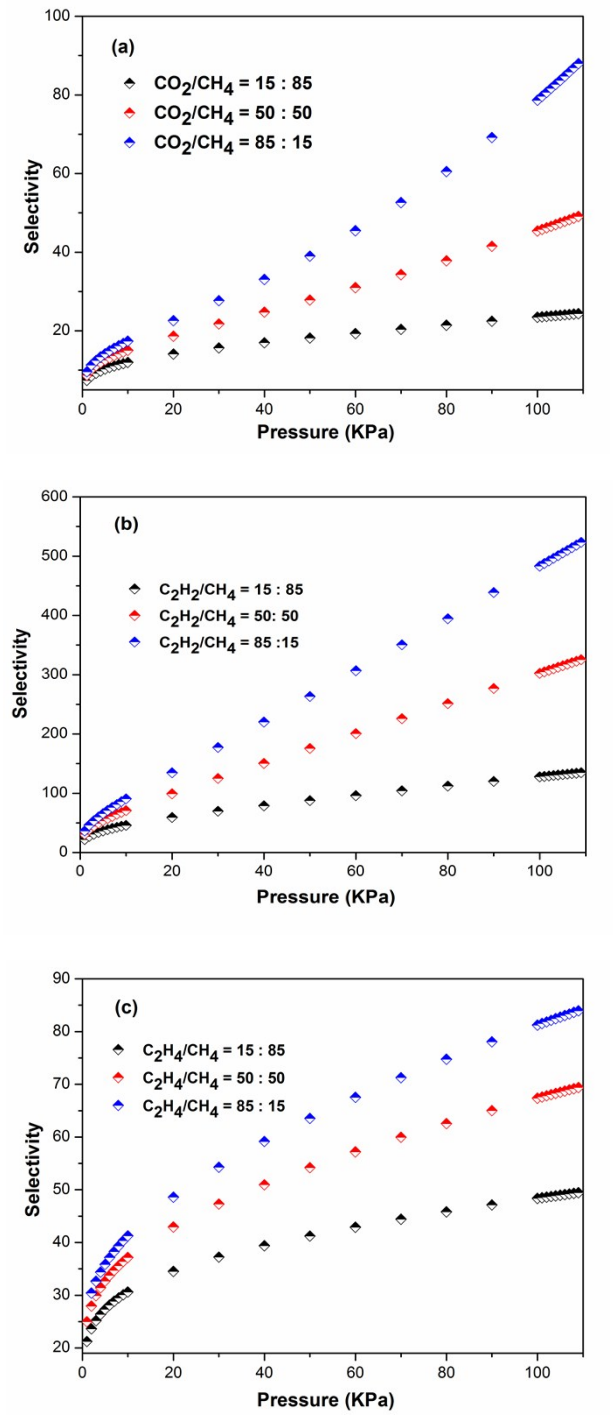


Figure S15. Three different composition selectivity predicted by IAST of **SNNU-23** for binary mixture at 273 K (15 : 85 black; 50: 50 red; and 85 : 15 blue).

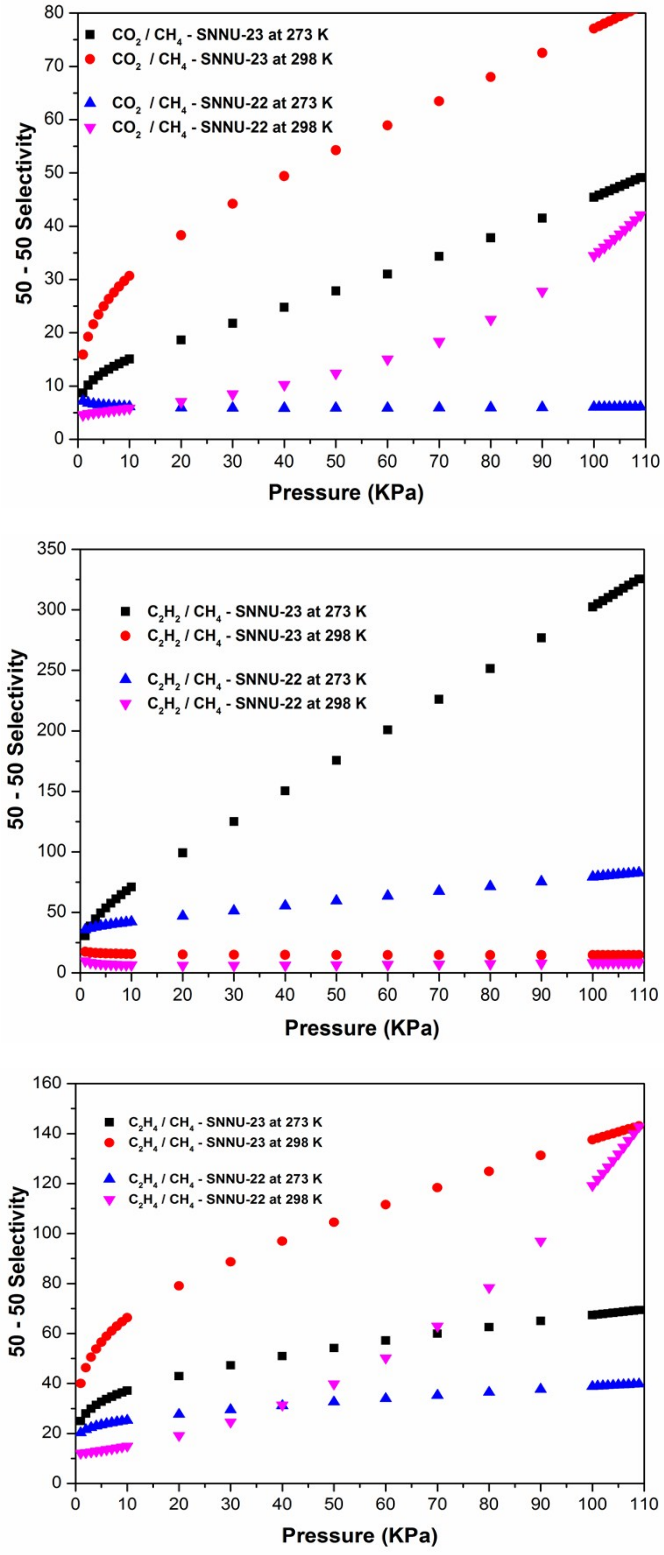


Figure S16. The comparisons of CO_2, C_2H_2 and C_2H_4 over CH_4 selectivity for an equimolar binary-mixture at 273 K and 298 K calculated by IAST for **SNNU-22/-23**.