Structural Diversity, Gas Adsorption and Magnetic Property of Three Coordination Polymers based on Rigid Multicarboxylate Ligand

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Table S1. Crystallographic data of 1 - 3

Complexes	**1**	**2**	**3**
Empirical formula	$C_{65}H_{48}Co_2N_9O_{14}$	$C_{62}H_{50}Co_4N_4O_{26}$	$C_{106}H_{73}Co_6N_{12}O_{22}$
Formula weight	1296.98	1502.78	2220.34
Temperature/K	150.0	150.15	298.15
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	P2/c	$P2_1/n$	$Pca2_1$
a/Å	10.3720(3)	10.2987(6)	33.5570(11)
b/Å	16.8173(4)	16.1185(9)	15.8380(5)
c/Å	16.8664(4)	17.2403(10)	20.0331(6)
α/°	90	90	90
β/°	98.4820(10)	97.391(2)	90
γ/°	90	90	90
Volume/Å^3	2909.81(13)	2838.1(3)	10647.1(6)
Z	2	2	4
D_c /g·cm^{-3}	1.480	1.759	1.385
μ/mm^{-1}	0.648	1.248	0.987
F(000)	1334.0	1532.0	4523.0
2θ range for data collection	4.652 to 52.794	4.722 to 50.754	4.458 to 52.924
Index ranges	-12 ≤ h ≤ 12, -21 ≤ k ≤ 21, -21 ≤ l ≤ 17	-12 ≤ h ≤ 12, -19 ≤ k ≤ 19, -20 ≤ l ≤ 20	-41 ≤ h ≤ 41, -19 ≤ k ≤ 19, -25 ≤ l ≤ 22

Reflections collected	47972	29277	114929
Independent reflections	5918 [R_{int} = 0.0586]	5187 [R_{int} = 0.1049]	21258 [R_{int} = 0.1035]
Data/restraints/parameters	5918/33/426	5187/0/437	21258/557/1479
Goodness-of-fit on F^2	1.031	1.174	1.005
Final R indexes [I>=2σ (I)]	R_1 = 0.0731, wR_2 = 0.1580	R_1 = 0.0709, wR_2 = 0.1178	R_1 = 0.0544, wR_2 = 0.1178
Final R indexes [all data]	R_1 = 0.0823, wR_2 = 0.1613	R_1 = 0.1136, wR_2 = 0.1351	R_1 = 0.1131, wR_2 = 0.1400
Largest diff. peak/hole / e $Å^{-3}$	0.72/-0.75	0.55/-0.56	0.61/-0.63
CCDC number	1899104	1899102	1899108

Table S2: Selected bond lengths (Å) and angles (°) for 1-3

1

Co1-O1[1]	2.081(3)	Co1-O1	2.081(3)	Co1-O6	2.182(3)
Co1-O6[1]	2.182(3)	Co1-N3[1]	2.111(4)	Co1-N3	2.111(4)
Co2-O3	2.016(3)	Co1-O3[2]	2.016(3)	Co1-N1	2.051(4)
Co1-N1[2]	2.052(4)	O1[1]-Co1-O1	176.82(19)	O1[1]-Co1-O6	88.92(13)
O6-Co1-O6[1]	84.42(19)	O1-Co1-O6	88.72(13)	O1-Co1-N3	88.02(14)
N3-Co1-O6[1]	90.63(14)	N3[1]-Co1-O6	90.63(14)	N3-Co1-O6	174.12(15)
N3-Co1-N3[1]	94.5(2)	O3[2]-Co2-O3	150.0(2)	O3[2]-Co2-N1	107.49(15)
O3-Co2-N1	91.84(14)	O3-Co2-N1[2]	107.49(15)	N1-Co2-N1[2]	99.9(2)

Symmetry codes: [1]1-X,+Y,1.5-Z; [2]2-X,+Y,0.5-Z

2

Co1-O1[1]	2.095(4)	Co1-O3	2.111(4)	Co1-O8	2.063(4)
Co2-O2	2.124(4)	Co2-O1	2.030(4)	Co2-O9	2.020(4)
Co2-O10	2.086(4)	Co2-O6[4]	2.307(4)	O1-Co1-O1[1]	84.09(15)
O1[1]-Co1-O3	91.75(16)	O1-Co1-O3	96.50(15)	O1-Co1-O8	95.23(16)
O1-Co1-O1[3]	178.15(17)	O3-Co1-O1[3]	82.43(16)	O8-Co1-O3	89.56(17)
O8-Co1-O1[3]	86.29(17)	O11[2]-Co1-O3	116.11(16)	O9-Co2-O2	88.53(18)
O1-Co2-O4[3]	94.24(16)	O2-Co2-O6[4]	81.55(15)	O1-Co2-O2	99.97(15)
O9-Co2-O1	99.94(16)	O9-Co2-O6[4]	85.61(16)	O9-Co2-O10	164.50(17)
O10-Co2-O2	88.00(16)	O10-Co2-O4[3]	89.99(16)	O10-Co2-O6[4]	78.93(15)

Symmetry codes: [1]1+X, Y, Z; [2]1-X, +Y, -Z; [3]1/2+X, -1/2-Y, 1/2+Z; [4]0.5-X, -0.5+Y, -0.5-Z

3

Co1-O1	2.093(6)	Co1-O10[1]	2.144(7)	Co1-N4	2.072(9)
Co2-O3	2.170(7)	Co2-O4	2.107(8)	Co2-O6	2.067(7)
Co2-O9	2.204(7)	Co2-N5	2.068(12)	Co3-O4	2.028(6)
Co3-O5	2.048(7)	Co3-N8[4]	2.228(8)	Co3-N12[3]	2.112(7)
Co4-O4	1.915(7)	Co4-O7	1.950(7)	Co4-O8	1.963(6)

Co5-O11	1.927(7)	Co5-O12	1.952(6)	Co6-O12	2.039(6)
Co6-N9	2.107(7)	Co6-O13	2.080(7)	O1-Co1-O10[1]	178.4(3)
O1-Co1-O19[2]	90.5(3)	N4-Co1-O1	88.6(3)	N4-Co1-O12[1]	164.4(4)
O3-Co2-O9	90.2(3)	O4-Co2-O3	99.6(3)	O4-Co2-O9	80.1(3)
O6-Co2-O9	174.8(3)	O6-Co2-N5	96.2(3)	N5-Co2-O4	165.5(4)
N5-Co2-O9	88.0(3)	N5-Co2-O15[2]	87.3(3)	O4-Co3-O5	92.9(3)
O4-Co3-O16[2]	91.6(3)	O5-Co3-O16[2]	94.8(3)	O4-Co3-N8[4]	87.5(3)
O4-Co3-N12[3]	175.5(3)	O4-Co4-O7	115.2(3)	O4-Co4-O8	96.0(3)
O7-Co4-O8	112.0(3)	O11-Co5-O12	113.4(3)	O11-Co5-O18[5]	104.1(3)
O12-Co6-O13	92.7(3)	O12-Co6-O2[7]	88.1(3)	O12-Co6-N9	173.3(3)

Symmetry codes: [1]+X,-1+Y,+Z; [2]0.5+X,1-Y,+Z; [3]1-X,1-Y,-1/2+Z; [4]+X,+Y,-1+Z; [5]1/2-X,+Y,1/2+Z; [6]-1/2+X,2-Y,+Z; [7]1/2-X,Y,0.5+Z; [8]-0.5+X,1-Y,Z; [9]-0.5+X,1-Y,1+Z

Table S3. Comparison of CO2 separation performances at 1 atm and 298 K of 3 and selected other CPs. (CO_2/CH_4 = 0.5/0.5)

No.	CPs	Selectivity	Ref.
1	$[Zn_2(btec)(btzmb)]_n \cdot 8nH_2O$	28.6	1
2	$\{[Cu_{0.5}(bpdado)_{0.5}(bpa)_{0.5}]\cdot 3H_2O\}_n$	18.9	2
3	$\{[Cu_{0.5}(bpdado)_{0.5}(bpe)_{0.5}]\cdot 3H_2O\}_n$	15.4	2
4	this work of 3	14.2	
5	UiO-66-AD10	9.29	3
6	JLU-Liu6	6.8	4

References:

[1] Y. P. Zhao, Y. Li, C. Y. Cui, Y. Xiao, R. Li, S. H. Wang, F. K. Zheng, G. C. Guo, *Inorg. Chem*., 2016, **55**, 7335−7340.

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[3] E. E. Moushi, A. Kourtellaris, I. Spanopoulos, M. J. Manos, G. S. Papaefstathiou, P. N. Trikalitis, A. J. Tasiopoulos, *Cryst. Growth Des.* 2015, **15**, 185−193.

[4] D. Wang, T. Zhao, Y. Cao, S. Yao, G. Li, Q. Huo, Y. Liu, *Chem. Commun*., 2014, **50**, 8648 – 8650.

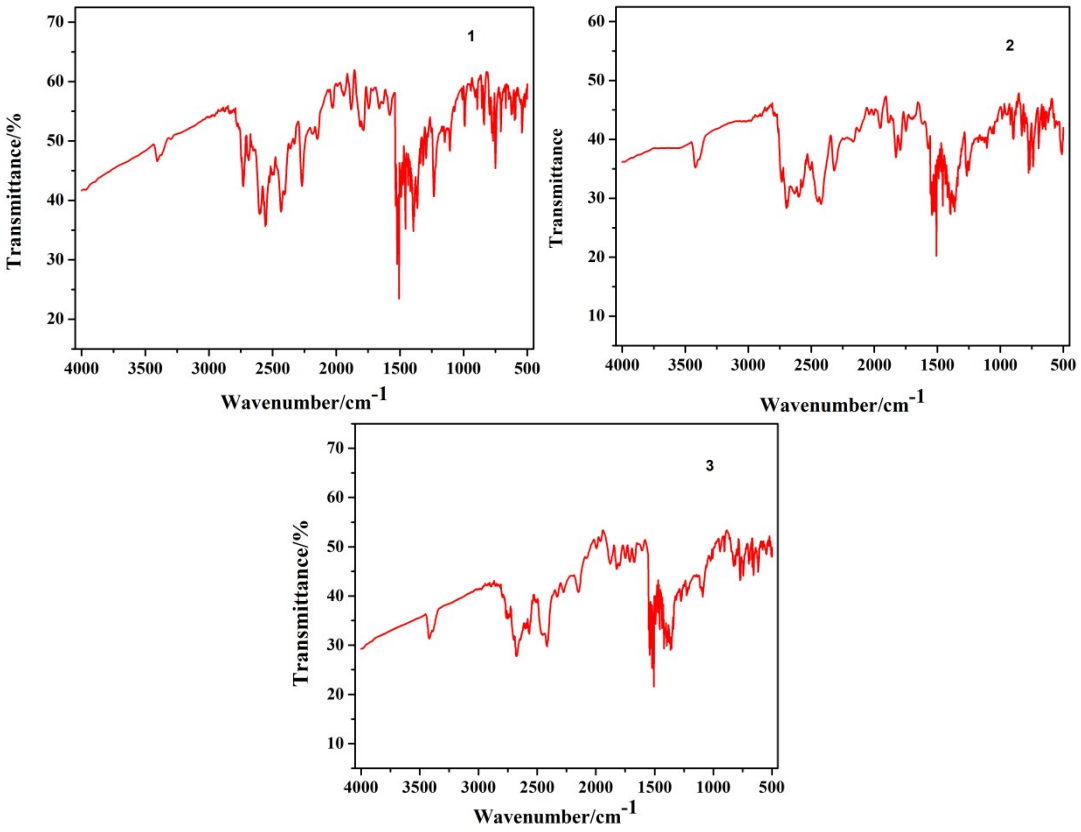

Fig. S1 :IR spectrum of 1-3

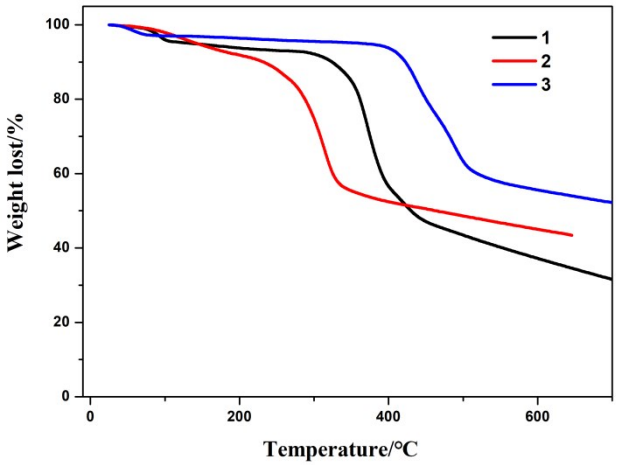

Fig. S2. Thermogravimetric analysis of 1-3

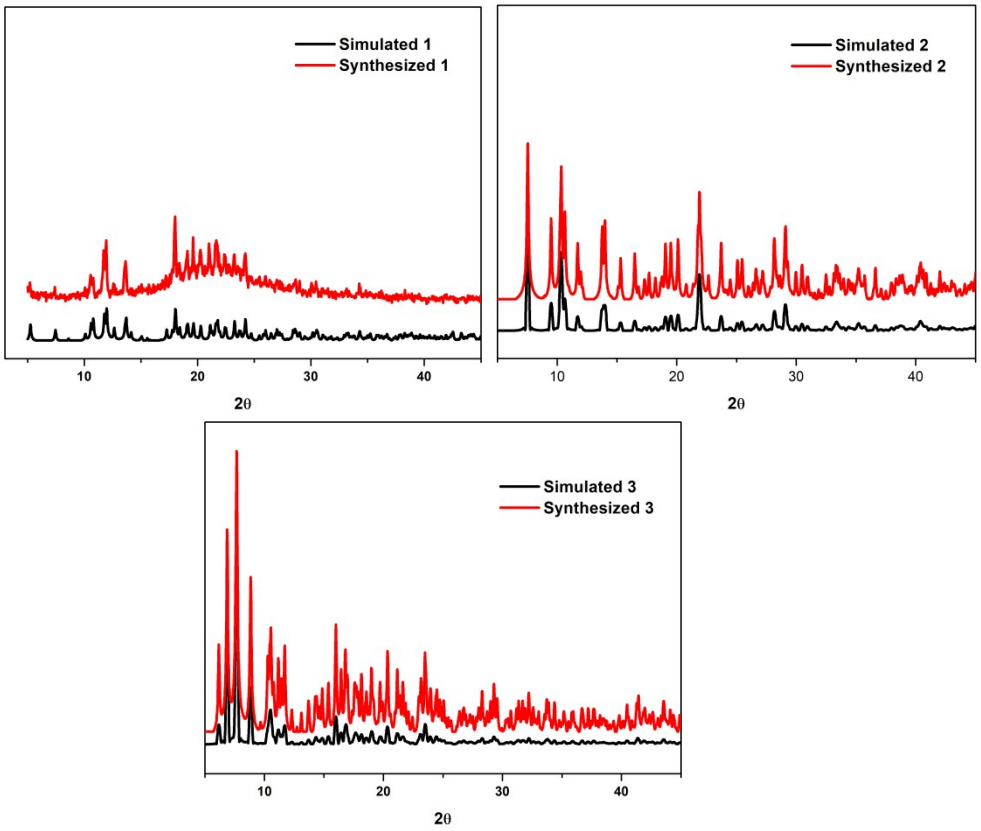

Fig. S3. The powder XRD pattern and the simulated one from the single-crystal diffraction data for 1-3.

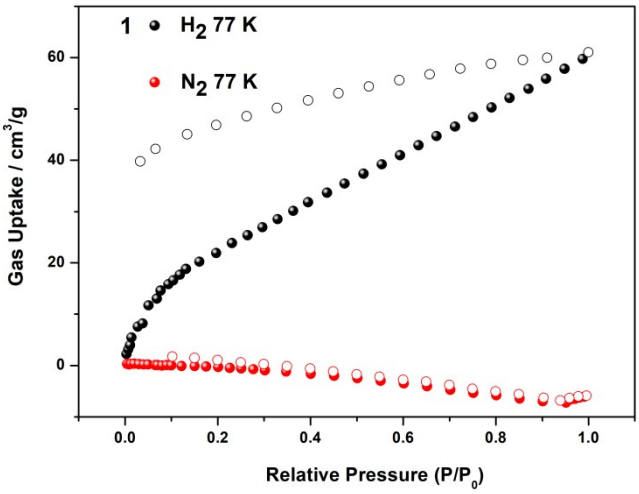

Fig. S4. Gas adsorption−desorption isotherm of H_2 and N_2 for 1.

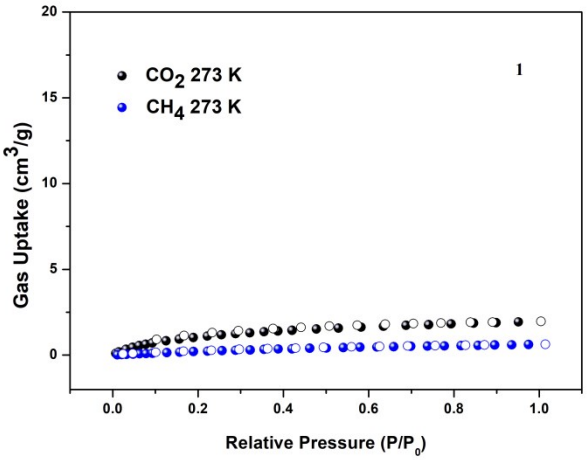

Fig. S5. Gas adsorption−desorption isotherm of CO_2 and CH_4 for 1

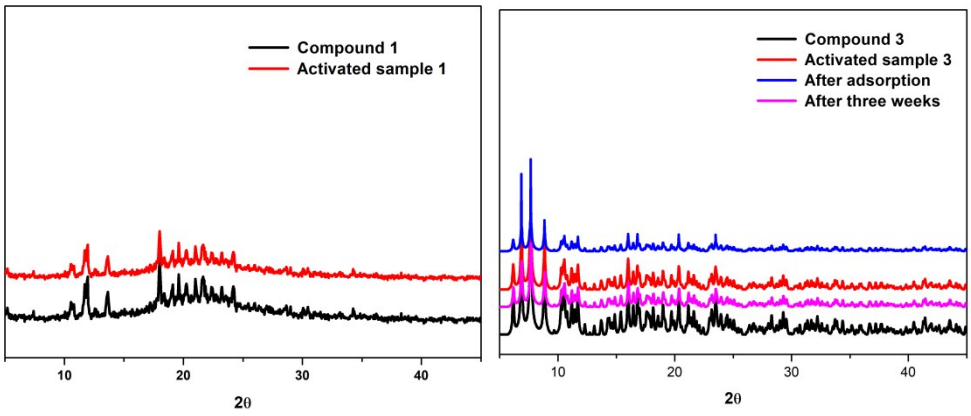

Fig. S6. PXRD patterns of 1 and 3, activated sample, and after CO_2 adsorption.

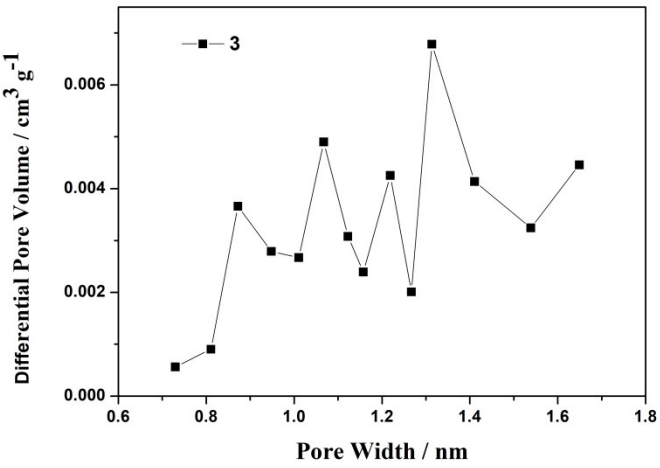

Fig. S7. the pore size distributions of 3

CO_2/CH_4 Selectivity Prediction via IAST

The experimental isotherm data for pure CO_2 and CH_4 (measured at 298 K) were fitted using a Langmuir-Freundlich (L-F) model:

$$N = a \times \frac{bp^c}{1+bp^c} \qquad (1)$$

Here, *a* is saturation capacity, *b* and *c* are constant.

The adsorption selectivities, S_{ads}, for binary mixtures of CO_2/CH_4, defined by (Equation 2):

$$S_{ads} = \frac{x_i / x_j}{y_i / y_j} \qquad (2)$$

S_{ads}: adsorption selectivity

x_i: the mole fractions of component i in the adsorbed phases

y_i: the mole fractions of component i in the bulk phases

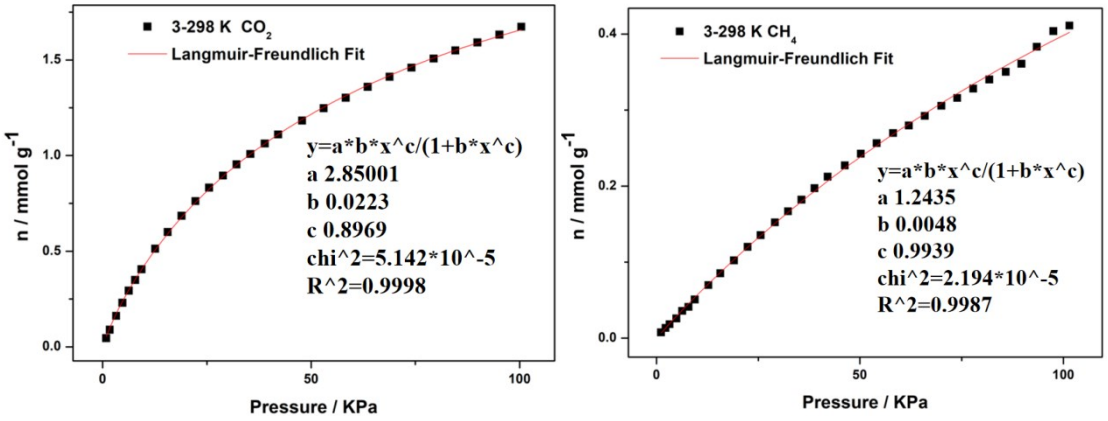

Figure S8. Langmuir-Freundlich fitting of CO_2 and CH_4 adsorption isotherms of 3 at 298 K.

Calculation of sorption heat for CO_2 and CH_4 uptake using the virial equation

$$\ln P = \ln N + \frac{1}{T}\sum_{i=0}^{m} ai\, N^i + \sum_{i=0}^{n} bi\, N^i$$

$$Q_{st} = -R\sum_{i=0}^{m} ai\, N^i$$

The above equation were applied to fit the combined CO_2 isotherm data for **3** at 273 and 298 K, where *P* is the pressure, *N* is the adsorbed amount, *T* is thetemperature, *ai*

and *bi* are virial coefficients, and *m* and *n* are the number of coefficients used to describe the isotherms. Q_{st} is the coverage-dependent enthalpy of adsorption and *R* is the universal gas constant.

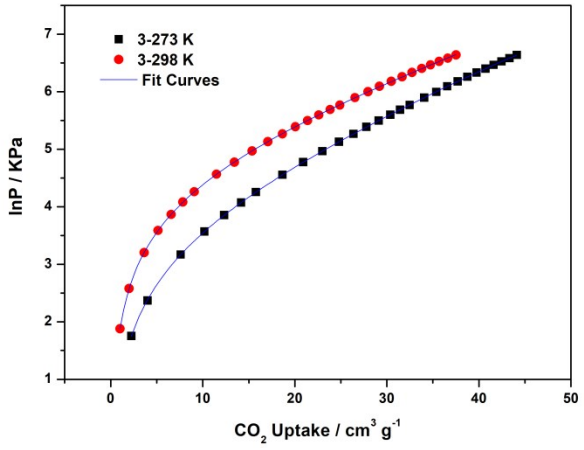

Figure S9. Virial analysis of the CO_2 sorption data for **3** (a0 = -3210.626, a1 = 47.5769, a2 = 0.10472, a3 = -0.01198, a4 = 2.5673×10^{-4} , a5 = -2.2116×10^{-6}, b0 = 12.61921, b1 = -0.14429, b2 = 7.62082×10^{-4} , Chi^2 = 1.60976×10^{-5}, R^2 = 0.999)

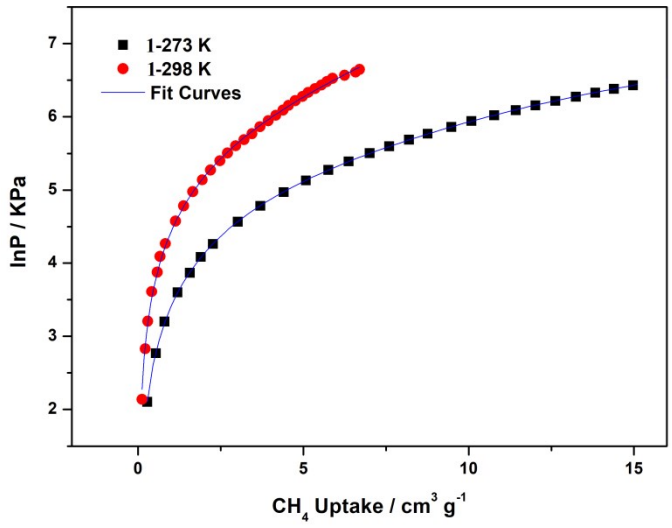

Figure S10. Virial analysis of the CH_4 sorption data for **3** (a0 = -3260.281, a1 = -51.943, a2 = -10.301, a3 = 0.2968, a4 = -0.018 , a5 = 3.835×10^{-4}, b0 = 15.3143, b1 = 0.2351, b2 = 0.0301 , Chi^2 = 8.9147×10^{-4}, R^2 = 0.999)

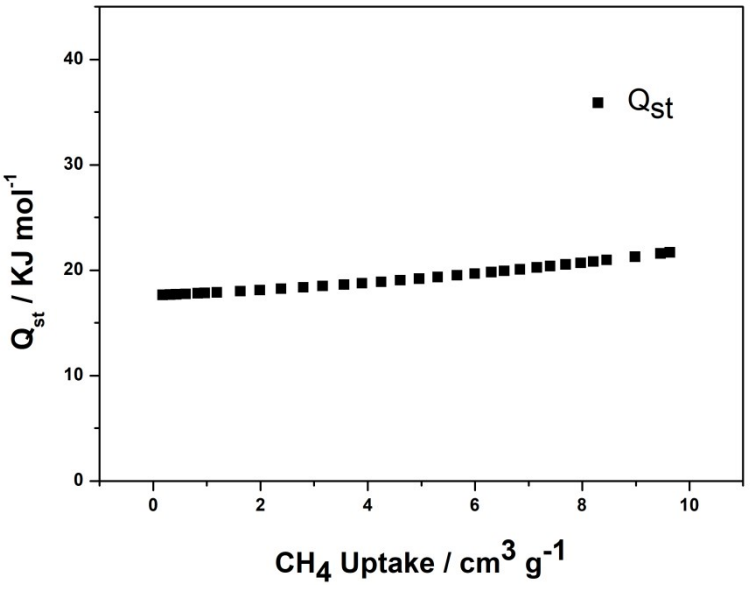

Figure S11. The Qst of 3 for CH_4 at 298 K

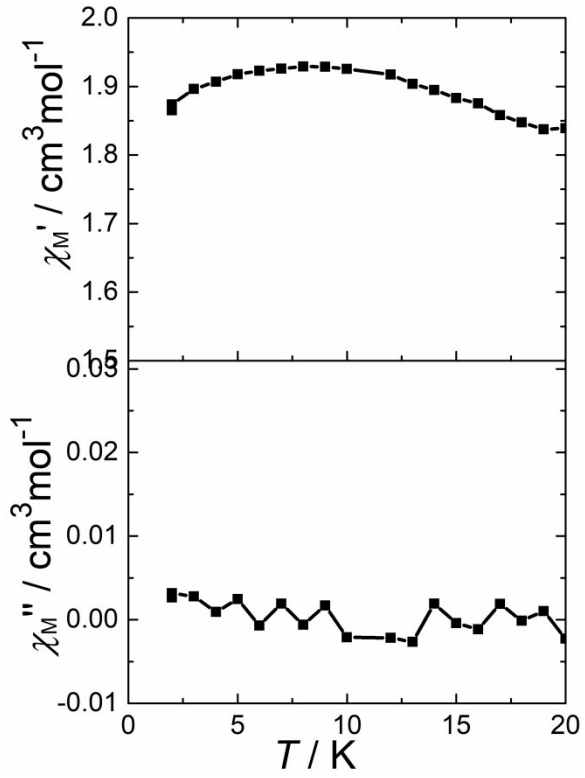

Figure S12. Temperature dependence of χ_M for 2 at 2 Oe ac and 0 Oe dc.