Electronic Supporting Information

Construction of two novel non-penetrating Co-MOFs derived from designed 2,4,6-tri(2,4-dicarboxyphenyl) pyridine: synthesis, structure and gas adsorption properties

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Table S1. Selected Bond Length (Å) and Angles (°) for Co-MOF 1-2

Co-MOF 1			
Co(1)-O(5)#1	2.020(4)	Co(1)-O(1)	1.970(5)
Co(1)-O(5)#2	2.020(4)	Co(2)-O(8)#3	1.935(4)
Co(1)-O(7)#3	2.068(5)	Co(2)-O(8)#4	1.935(4)
Co(1)-O(7)#4	2.068(5)	Co(2)-O(2)	1.923(5)
O(5)#1-Co(1)-O(5)#2	89.8(3)	O(1)-Co(1)-O(7)#4	103.3(2)
O(7)#4-Co(1)-O(7)#3	91.2(4)	O(8)#3-Co(2)-O(8)#4	114.8(3)
O(1)-Co(1)-O(5)#2	95.12(18)	O(2)-Co(2)-O(8)#4	114.74(17)
O(1)-Co(1)-O(5)#1	95.12(18)	O(2)-Co(2)-O(8)#3	114.74(17)
O(1)-Co(1)-O(7)#3	103.3(2)		
Symmetry code: #1 -x+1,-y+1,-z+2; #2 y,x,-z+2; #3 -x+y+1/3,-x+2/3,z-1/3; #4 x+1/3,x-y+2/3,z-1/3; #5 -y+2/3,x-y+1/3,z+1/3; #6 -y+1,-x+1,z for Co-MOF **1**.			
Co-MOF 2			
Co(1)-O(3)	2.093(3)	Co(2)-O(15)	2.083(3)
Co(1)-O(4)	2.084(3)	Co(3)-O(2)	2.136(3)
Co(1)-O(5)	2.096(3)	Co(3)-O(2)#1	2.136(3)
Co(1)-O(6)#1	2.145(3)	Co(3)-O(3)	2.057(2)
Co(1)-O(10)#2	2.087(3)	Co(3)-O(3)#1	2.057(2)

Co(1)-O(16)	2.111(3)	Co(3)-O(17)	2.136(3)
Co(2)-O(1)	2.060(3)	Co(3)-O(17)#1	2.136(3)
Co(2)-O(3)	2.080(3)	Co(4)-O(4)	1.976(3)
Co(2)-O(4)	2.138(3)	Co(4)-O(9)#2	1.993(3)
Co(2)-O(7)#1	2.114(3)	Co(4)-O(11)#3	1.977(3)
Co(2)-O(14)	2.115(3)	Co(4)-O(13)#4	2.019(3)
O(3)-Co(1)-O(5)	96.22(10)	O(14)-Co(2)-O(4)	176.15(12)
O(3)-Co(1)-O(6)#1	87.11(11)	O(15)-Co(2)-O(4)	96.95(12)
O(3)-Co(1)-O(16)	87.99(11)	O(15)-Co(2)-O(7)#1	88.36(13)
O(4)-Co(1)-O(3)	87.25(10)	O(15)-Co(2)-O(14)	86.72(13)
O(4)-Co(1)-O(5)	89.92(11)	O(2)-Co(3)-O(2)#1	180.00(7)
O(4)-Co(1)-O(6)#1	85.15(12)	O(2)-Co(3)-O(17)	89.72(11)
O(4)-Co(1)-O(10)#2	97.13(11)	O(2)-Co(3)-O(17)#1	90.28(11)
O(4)-Co(1)-O(16)	173.75(12)	O(2)#1-Co(3)-O(17)	90.28(11)
O(5)-Co(1)-O(6)#1	173.93(13)	O(2)#1-Co(3)-O(17)#1	89.72(11)
O(5)-Co(1)-O(16)	94.62(13)	O(3)-Co(3)-O(2)	95.68(10)
O(10)#2-Co(1)-O(3)	175.46(11)	O(3)#1-Co(3)-O(2)	84.32(10)
O(10)#2-Co(1)-O(5)	85.01(11)	O(3)#1-Co(3)-O(2)#1	95.68(10)
O(10)#2-Co(1)-O(6)#1	92.06(12)	O(3)-Co(3)-O(2)#1	84.32(10)
O(10)#2-Co(1)-O(16)	87.56(12)	O(3)-Co(3)-O(3)#1	180
O(16)-Co(1)-O(6)#1	90.56(14)	O(3)-Co(3)-O(17)	93.88(10)
O(1)-Co(2)-O(3)	93.63(11)	O(3)#1-Co(3)-O(17)	86.12(10)
O(1)-Co(2)-O(4)	86.97(12)	O(3)#1-Co(3)-O(17)#1	93.88(10)
O(1)-Co(2)-O(7)#1	173.54(12)	O(3)-Co(3)-O(17)#1	86.12(10)
O(1)-Co(2)-O(14)	94.34(14)	O(17)-Co(3)-O(17)#1	180.00(15)
O(1)-Co(2)-O(15)	88.10(13)	O(4)-Co(4)-O(9)#2	111.22(11)
O(3)-Co(2)-O(4)	86.19(10)	O(4)-Co(4)-O(11)#3	109.52(14)
O(3)-Co(2)-O(7)#1	90.19(11)	O(4)-Co(4)-O(13)#4	128.22(13)
O(3)-Co(2)-O(14)	90.11(11)	O(9)#2-Co(4)-O(13)#4	100.01(12)
O(3)-Co(2)-O(15)	176.50(13)	O(11)#3-Co(4)-O(9)#2	93.71(13)
O(7)#1-Co(2)-O(4)	88.10(11)	O(11)#3-Co(4)-O(13)#4	108.43(14)
O(7)#1-Co(2)-O(14)	90.86(13)		

Symmetry code: #1 -x+1/2,-y+3/2,-z+1; #2 -x+1/2,-y+5/2,-z+1; #3 -x+1/2,y+1/2,-z+1/2; #4 x-1/2,-y+3/2,z-1/2; #5 -x+1/2,y-1/2,-z+1/2; #6 x+1/2,-y+3/2,z+1/2 for Co-MOF **2**.

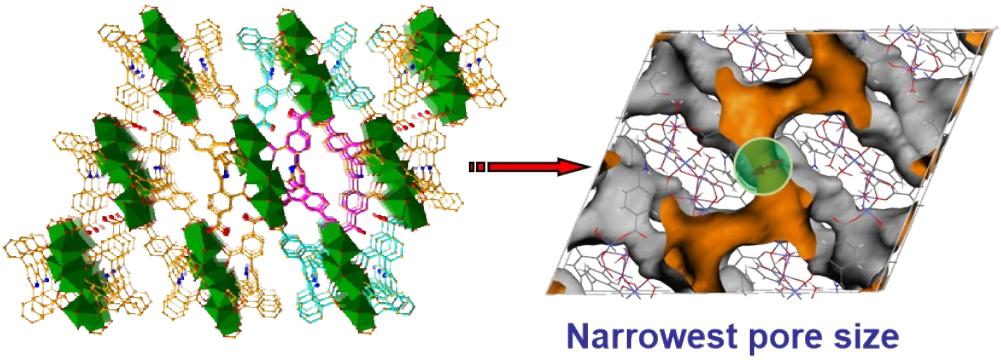
Table S2. A comparison of various MOF materials used for selective adsorption for C_2H_2 and CO_2 over CH_4.

MOF materials	IAST calculated selectivity		Ref.
	C_2H_2/CH_4	CO_2/CH_4	
$[(CH_3)_2NH_2][Zn_{1.5}(\mu_3\text{-}O)_{0.5}(F\text{-}tzba)_{1.25}(bpy)_{0.25}(\mu_2\text{-}$	14.4	4.2	22a

$F)_{0.5}]\cdot 2DMF\cdot 2H_2O$			
$\{[(Me_2NH_2)_{0.5}][Cu_{0.75}(L)_{0.5}(DMA)_{0.375}]\cdot H_2O\}_n$		8.3	22d
$\{[Cu_4(L)_2(H_2O)_4]\cdot 4DMF\cdot 8H_2O\}_n$		3.2	22d
$\{[Cu_4(L)_2(ATZ)_2(H_2O)]\cdot 5DMF\cdot 5H_2O\}_n$		7.2	22d
ZJNU-26	19	4.3	23a
Sc-ABTC	14.7		23b
$\{[Co_6(\mu_3\text{-}OH)_4(Ina)_8](H_2O)_{10}(DMA)_2\}_n$	9.6		22c
ZJU-19	42.2	6.4	23c
MOF-505	~8.9		23d
ZJNU-15	37.7	5.0	23e
ZJNU-119	62.9	28.6	22b
NOTT-108	~6.3		23d
HNUST-2	~4.3		23d
Co-MOF 1	25.43	11.33	This work
Co-MOF 2	32.71	11.42	This work

Table S3. Results of the ICP analyses obtained for MOF materials of Co-MOF **1-2**.

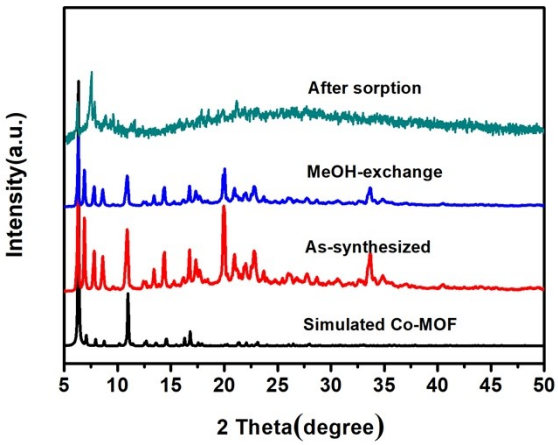
	Total sample quality(mg)	The expected amount of Li^+ ion (ppm)	The expected amount of Zn^{2+} ion (ppm)	The ratio of Li^+:Zn^{2+} in sample	The expected ratio in cation exchange with Li^+
Co-MOF **1**	6.10	0.397	4.50	1 : 11.34	1 : 8.48
Co-MOF **2**	6.38	0.37	11.6	1 : 31.35	1 : 29.71



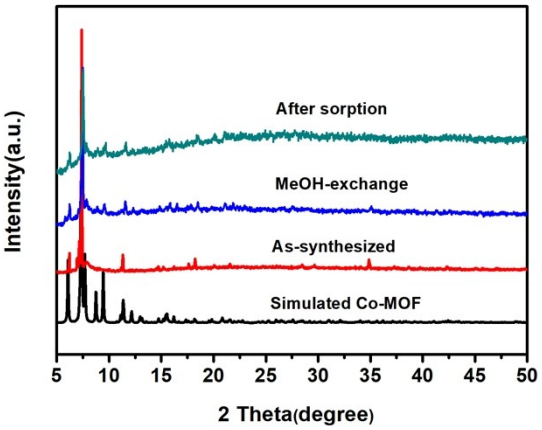
(a) **(b)**

Figure S1. (a) The linkage of the $Co_7(COO)_{12}$ cluster with eight adjacent cores; (b) A

channel diagram distorted in the b-direction of Co-MOF **2**.

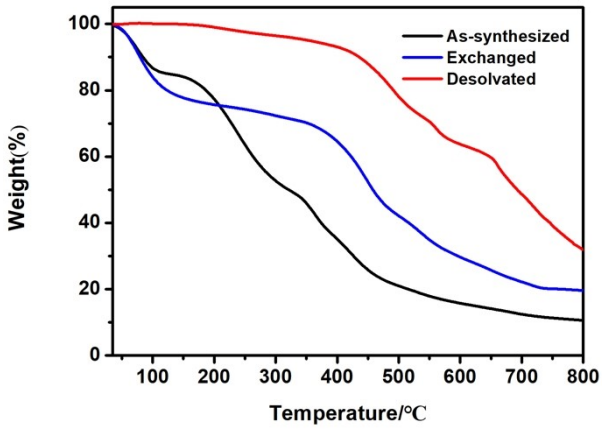


(a)

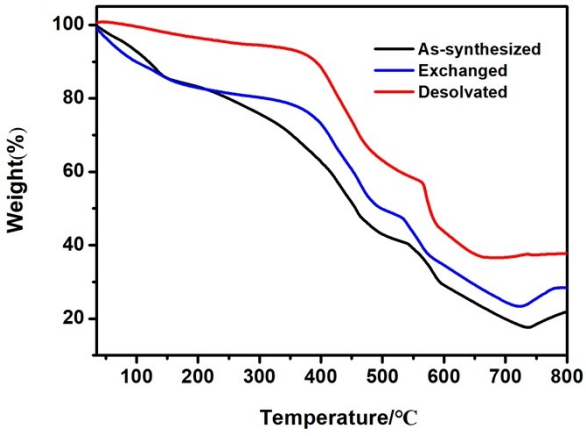


(b)

Figure S2. (a) and (b) correspond to the PXRD patterns for Co-MOF **1** and Co-MOF **2**: simulated, as-synthesized, exchanged and activated samples.

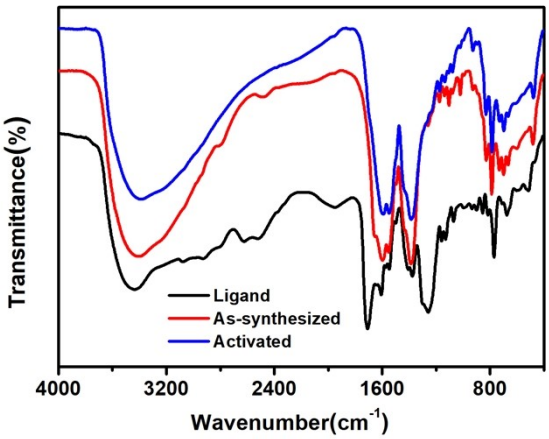


(a)

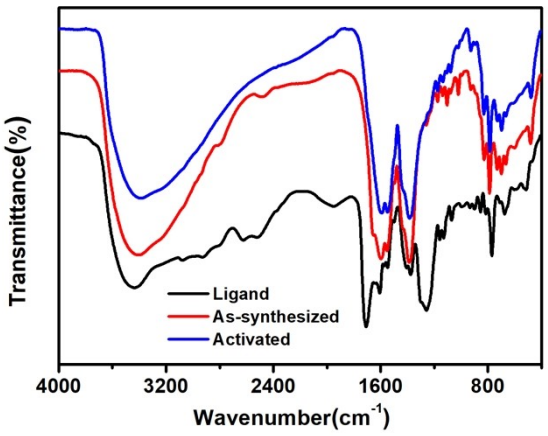


(b)

Figure S3. (a) and (b) correspond to the TGA for Co-MOF **1** and Co-MOF **2**: as-synthesized, exchanged and desolvated samples.



(a)



(b)

Figure S4. (a) and (b) correspond to the Infrared Spectra of H_6tdp ligand, as-

synthesized and activated samples of Co-MOF **1** and Co-MOF **2**.

IAST adsorption selectivity calculation

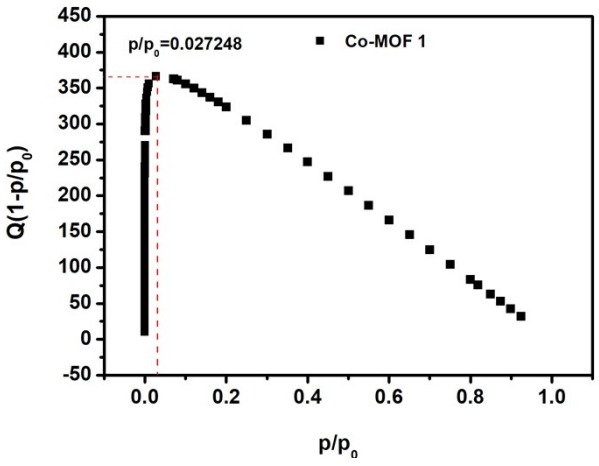
The experimental isotherm data for pure C_2H_2, CO_2, C_2H_4, and CH_4 (measured at 298 K) were fitted using a Langmuir-Freundlich (L-F) model.

$$q = \frac{a * b * p^c}{1 + b * p^c}$$

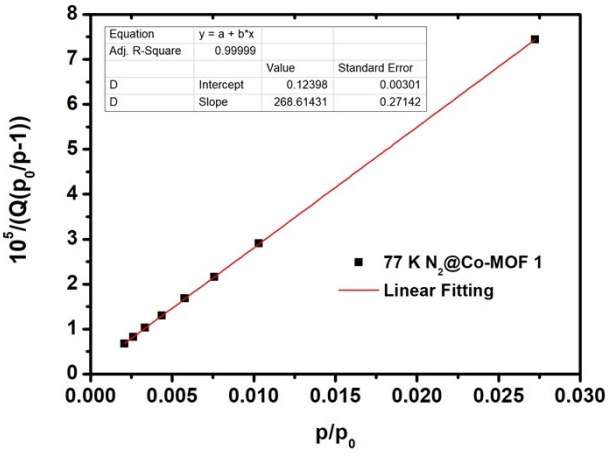
Where q and p are adsorbed amounts and pressures of component i, respectively. The adsorption selectivities for binary mixtures of C_2H_2/CH_4, C_2H_4/CH_4, CO_2/CH_4 at 273 and 298 K, defined by

$$S_{ads} = (q_1 / q_2) / (p_1 / p_2)$$

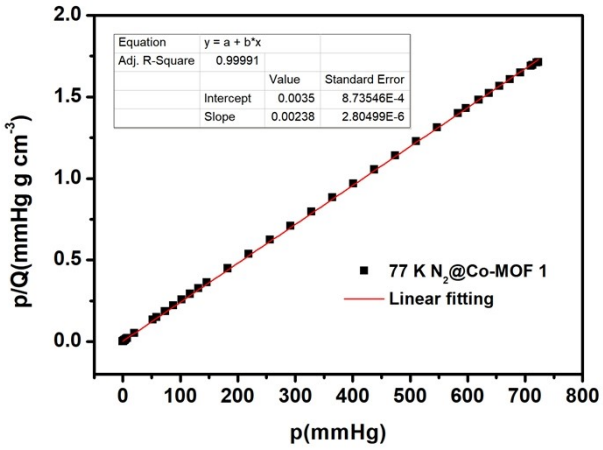
Where qi is the amount of i adsorbed and pi is the partial pressure of i in the mixture.



(a)



(b)



(c)

S_{BET}=1/(0.124×10^{-6}+268.61)×10^5/22414×6.023×10^{23}×0.162×10^{-18}=1620.64 m^2 g^{-1}

$S_{Langmuir}$=(1/0.00238)/22414×6.023×10^{23}×0.162×10^{-18}=1829.08 m^2 g^{-1}

BET constant C=1+268.61/0.124×10^5×10^{-6}=217.62

$$(P/P_0)_{nm} = \frac{1}{\sqrt{C}+1} = 0.063484$$

Figure S5. (a) The consistency plot, (b) BET surface area plot, and (c) Langmuir surface area plot for Co-MOF **1**.

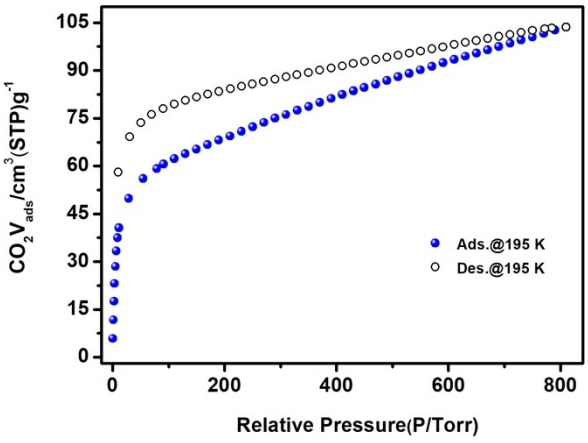
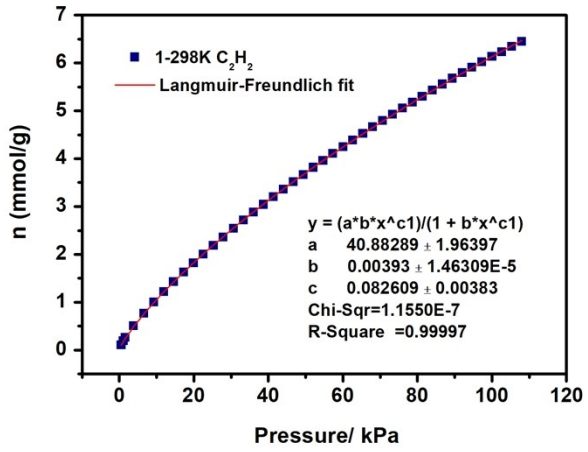
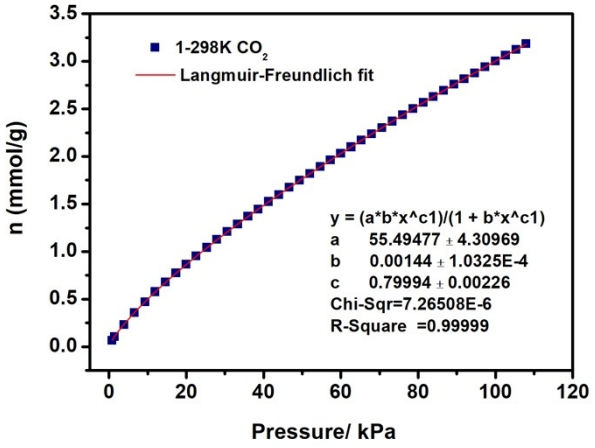


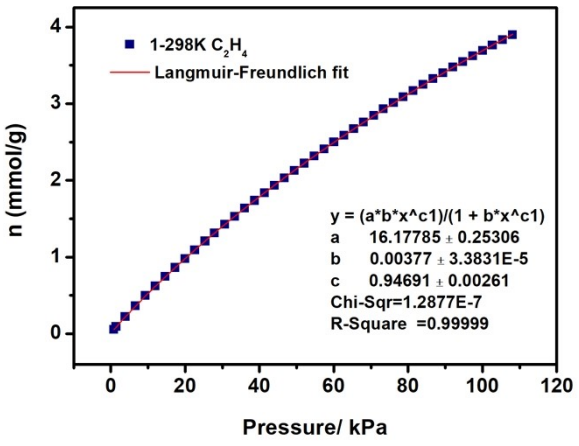
Figure S6. CO_2 adsorption and desorption isotherm curves of Co-MOF **2** at 195 K.


1-298K C2H2
Langmuir-Freundlich fit
y = (a*b*x^c1)/(1 + b*x^c1)
a 40.88289 ± 1.96397
b 0.00393 ± 1.46309E-5
c 0.082609 ± 0.00383
Chi-Sqr=1.1550E-7
R-Square =0.99997
n (mmol/g)
Pressure/ kPa

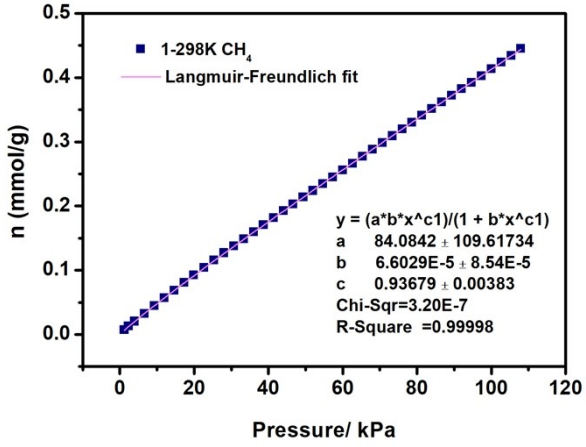
(a)


1-298K CO2
Langmuir-Freundlich fit
y = (a*b*x^c1)/(1 + b*x^c1)
a 55.49477 ± 4.30969
b 0.00144 ± 1.0325E-4
c 0.79994 ± 0.00226
Chi-Sqr=7.26508E-6
R-Square =0.99999
n (mmol/g)
Pressure/ kPa

(b)

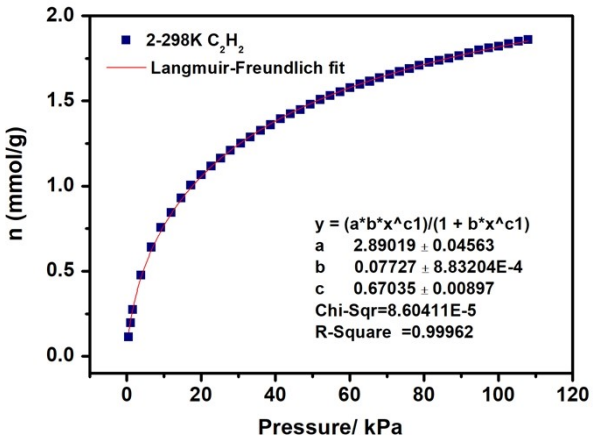

1-298K C2H4
Langmuir-Freundlich fit
y = (a*b*x^c1)/(1 + b*x^c1)
a 16.17785 ± 0.25306
b 0.00377 ± 3.3831E-5
c 0.94691 ± 0.00261
Chi-Sqr=1.2877E-7
R-Square =0.99999
n (mmol/g)
Pressure/ kPa

(c)

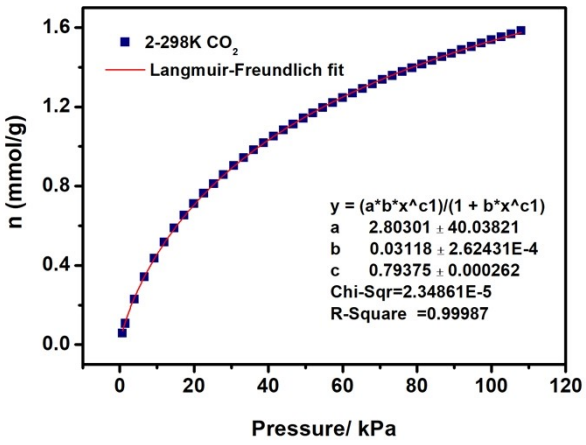


(d)

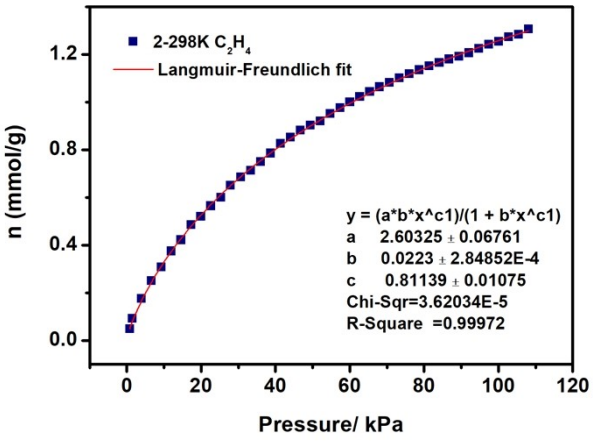
Figure S7. (a), (b), (c) and (d) correspond to the C_2H_2, CO_2, C_2H_4, CH_4 adsorption isotherms of Co-MOF **1** at 298 K with fitting by L-F model.



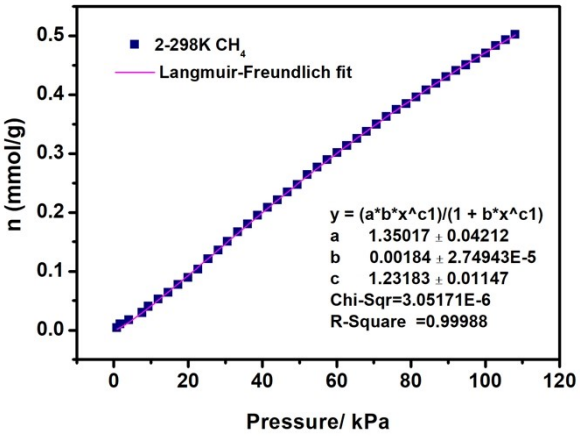
(a)



(b)



(c)



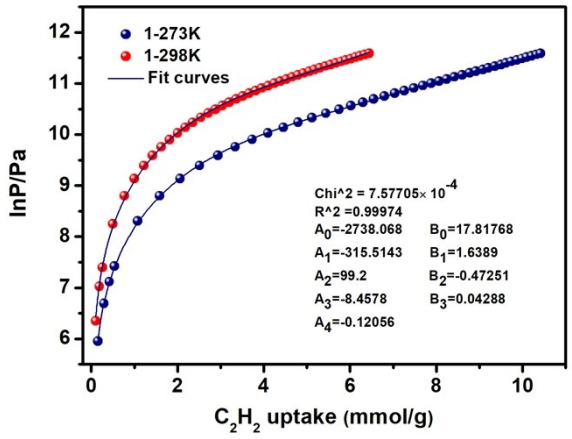
(d)

Figure S8. (a), (b), (c) and (d) correspond to the C_2H_2, CO_2, C_2H_4, CH_4 isotherms of Co-MOF **2** at 298 K with fitting by L-F model.

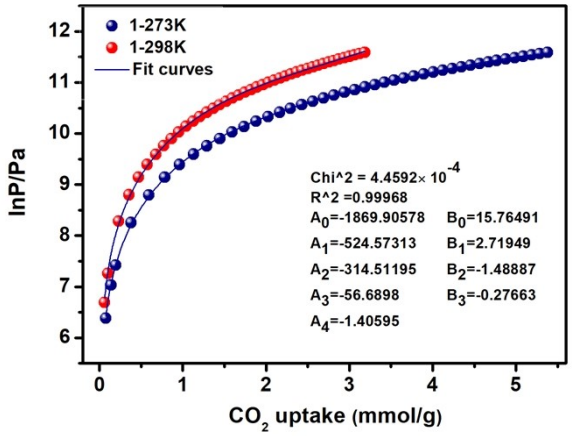
Calculation of sorption heat for C_2H_2 and CO_2 uptakes using Virial II model

The above equation was applied to fit the C_2H_2, C_2H_4 and CO_2 adsorption isotherm data for desolvated Co-MOF **1** and Co-MOF **2** at 273 and 298 K, where P is the pressure, N is the adsorbed amount, T is the temperature, 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.

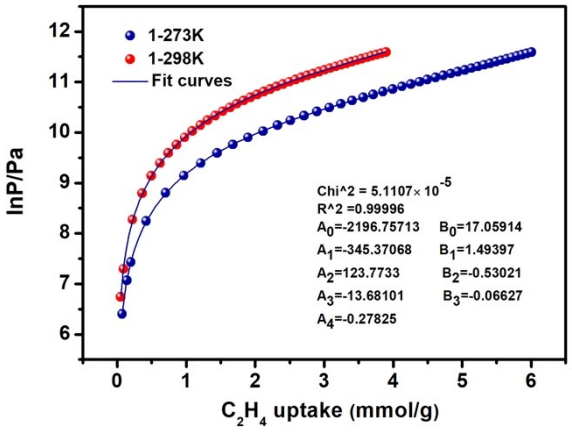
$$\ln P = \ln N + 1/T \sum_{i=0}^{m} aiN^i + \sum_{i=0}^{n} biN^i Q_{st} = -R \sum_{i=0}^{m} aiN^i$$



(a)

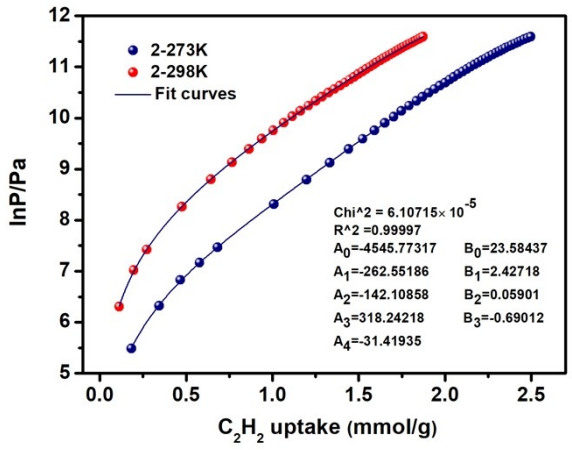


(b)

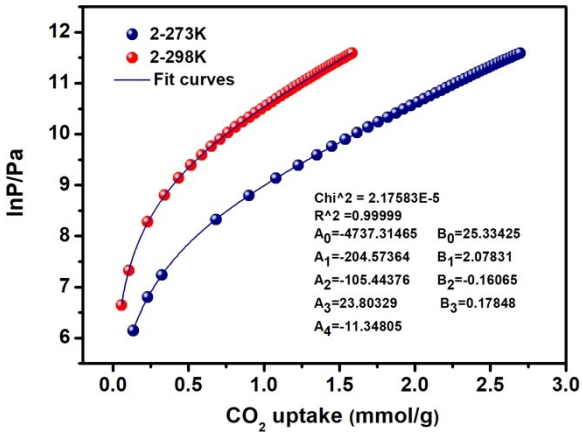


(c)

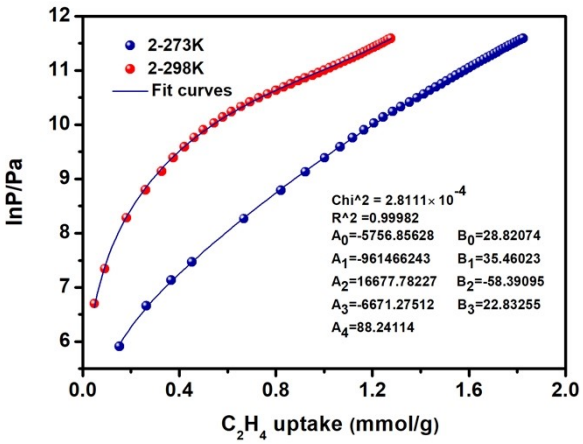
Figure S9. (a), (b) and (c) correspond to the Virial analysis of the C_2H_2, CO_2, C_2H_4 adsorption data at 298 K and 273 K for Co-MOF **1**.



(a)



(b)



(c)

Figure S10. (a), (b) and (c) correspond to the Virial analysis of the C_2H_2, CO_2, C_2H_4 adsorption data at 298 K and 273 K for Co-MOF **2**.