Supporting Information

Four new 3D metal–organic frameworks constructed by the asymmetrical pentacarboxylate: gas sorption behaviour and magnetic properties

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Table S1 Selected bond lengths (Å) and bond angles (º) for **1-4.**

Complex **1**			
Cu(1)-O(1)	1.942(4)	Cu(1)-O(1)#2	1.942(4)
Cu(1)-O(2)#1	1.950(4)	Cu(1)-O(2)#3	1.950(4)
Cu(1)-O(1WA)	2.194(18)	O(1WB)-Cu(1)	2.16(3)
O(1)-Cu(1)-O(1)#2	88.9(2)	O(1) -Cu(1)-O(2)#3	88.64(18)
O(1)#2-Cu(1)-O(2)#1	88.64(18)	O(1)-Cu(1)- O(2)#1	167.33(19)
O(1)#2-Cu(1)-O(2)#3	167.33(19)	O(1) -Cu(1)-O(1WB)	90.9(16)
O(1)#2-Cu(1)-O(1WA)	104.0(14)	O(2)#3-Cu(1)-O(1WA)	88.7(15)
O(1)-Cu(1)-O(1WA)	104.0(14)	O(2)#1-Cu(1)-O(2)#3	91.0(2)

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

Complex **2**			
Co(1)-O(1)	1.976(3)	Co(2)-O(5)#4	2.167(3)
Co(1)-O(4)#1	1.990(2)	Co(2)-O(6)#4	2.173(3)
Co(1)-O(8)#2	1.956(3)	Co(2)-O(7)#2	2.106(3)
Co(1)-O(10)#3	1.974(2)	Co(2)-O(9)#3	2.087(3)
Co(2)-O(2)	2.030(3)	Co(2)-O(11)	2.099(5)
Co(2)-O(11A)	2.087(10)	O(7)-Co(2)#7	2.106(3)
O(4)-Co(1)#5	1.990(2)	O(8)-Co(1)#7	1.956(3)
O(5)-Co(2)#6	2.167(3)	O(9)-Co(2)#3	2.087(2)
O(6)-Co(2)#6	2.173(3)	O(10)-Co(1)#3	1.974(2)
O(1)-Co(1)-O(4)#1	102.45(12)	O(5)#4-Co(2)-O(6)#4	59.83(12)
O(8)#2-Co(1)-O(1)	99.28(15)	O(7)#2-Co(2)-O(5)#4	82.92(11)

O(8)#2-Co(1)-O(4)#1	99.11(11)	O(7)#2-Co(2)-O(6)#4	85.27(13)
O(8)#2-Co(1)-O(10)#3	134.58(12)	O(9)#3-Co(2)-O(5)#4	98.24(11)
O(10)#3-Co(1)-O(1)	104.02(12)	O(9)#3-Co(2)-O(6)#4	157.96(12)
O(10)#3-Co(1)-O(4)#1	112.88(11)	O(9)#3-Co(2)-O(7)#2	94.60(12)
O(2)-Co(2)-O(5)#4	157.45(12)	O(9)#3-Co(2)-O(11)	94.7(2)
O(2)-Co(2)-O(6)#4	97.65(13)	O(11)-Co(2)-O(5)#4	97.4(2)
O(2)-Co(2)-O(7)#2	94.93(13)	O(11)-Co(2)-O(6)#4	86.7(2)
O(2)-Co(2)-O(9)#3	104.31(11)	O(11)-Co(2)-O(7)#2	170.5(2)
O(2)-Co(2)-O(11)	81.1(2)	O(11A)-Co(2)-O(5)#4	83.8(4)
O(2)-Co(2)-O(11A)	102.2(4)	O(11A)-Co(2)-O(6)#4	98.8(3)
O(11A)-Co(2)-O(9)#3	74.9(4)	O(11A)-Co(2)-O(7)#2	161.7(5)

Symmetrical codes: #1 x+1, y, z; #2 x+1/2, -y+1/2, z+1/2; #3 -x+2, -y+1, -z+1; #4 –x+3/2, y+1/2, -z+3/2; #5 x-1, y, z; #6 -x+3/2, y-1/2, -z+3/2; #7 x-1/2, -y+1/2, z-1/2.

Complex **3**

Co(1)-O(2)	2.018(7)	Co(2)-O(10)#3	2.054(7)
Co(1)-O(4)#1	2.042(7)	O(4)-Co(1)#5	2.042(7)
Co(1)-O(5)#2	2.207(7)	O(4)-Co(2)#5	2.042(7)
Co(1)-O(6)#2	2.095(7)	O(5)-Co(1)#6	2.207(7)
Co(1)-O(9)#3	2.042(7)	O(6)-Co(1)#6	2.095(6)
Co(2)-O(1)	2.033(8)	O(7)-Co(2)#4 O(8)-	2.204(8)
Co(2)-O(11)	2.142(9)	Co(2)#4	2.159(6)
Co(2)-O(4)#1	2.110(7)	O(9)-Co(1)#3	2.042(7)
Co(2)-O(7)#4	2.204(8)	O(10)-Co(2)#3	2.054(7)
Co(2)-O(8)#4	2.159(6)	O(10)#3-Co(2)-O(7)#4	105.6(3)
O(2)-Co(1)-O(4)#1	105.9(3)	O(10)#3-Co(2)-O(8)#4	165.1(3)
O(2)-Co(1)-O(5)#2	91.7(3)	O(11)-Co(2)-O(7)#4	90.9(3)
O(2)-Co(1)-O(6)#2	102.3(3)	O(11)-Co(2)-O(8)#4	95.8(3)
O(2)-Co(1)-O(9)#3	96.3(3)	O(4)#1-Co(2)-O(11)	91.9(3)
O(4)#1-Co(1)-O(5)#2	92.9(3)	O(4)#1-Co(2)-O(7)#4	159.2(3)
O(4)#1-Co(1)-O(6)#2	142.0(3)	O(4)#1-Co(2)-O(8)#4	99.5(3)
O(4)#1-Co(1)-O(9)#3	100.6(3)	O(8)#4-Co(2)-O(7)#4	59.7(3)
O(6)#2-Co(1)-O(5)#2	61.1(3)	O(1)-Co(2)-O(8)#4	83.8(3)
O(9)#3-Co(1)-O(5)#2	161.6(3)	O(1)-Co(2)-O(10)#3	93.3(3)
O(9)#3-Co(1)-O(6)#2	100.9(3)	O(10)#3-Co(2)-O(11)	86.7(4)
O(1)-Co(2)-O(11)	178.1(3)	O(10)#3-Co(2)-O(4)#1	95.1(3)
O(1)-Co(2)-O(4)#1	90.0(3)		

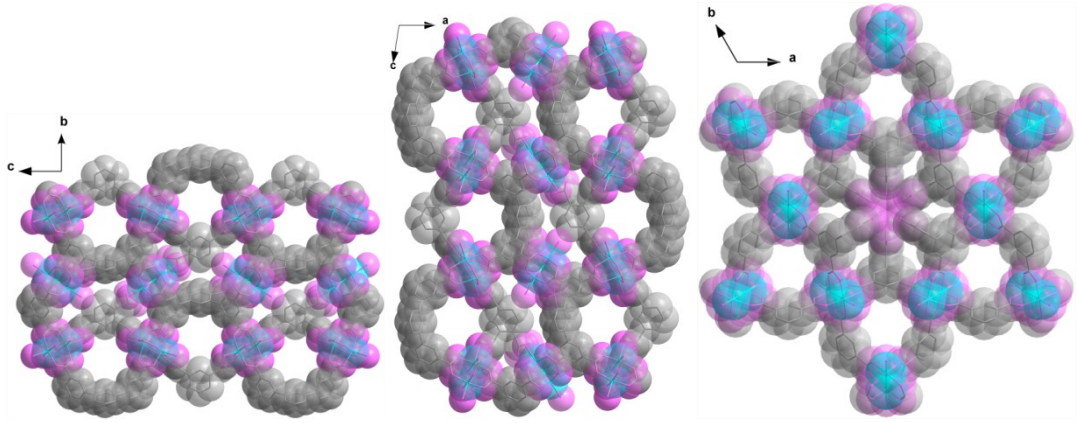
Symmetrical codes: #1 x, y+1, z; #2 -x+1, y+1/2, -z+3/2; #3 -x+1, -y+2, -z+1; #4 -x, -y+2, -z+1; #5 x, y-1, z; #6 –x+1, y-1/2, -z+3/2.

Complex **4**

Mn(1)-O(1)	2.170(2)	Mn(1)-O(4)#1	2.152(2)
Mn(1)-O(1W)	2.200(2)	Mn(1)-O(1W)	2.200(2)

Mn(2)-O(6)#5	2.123(2)	Mn(1)-O(11)	2.193(3)
Mn(1)-O(5)#2	2.125(2)	Mn(2)-O(10)	2.209(3)
Mn(1)-O(7)#3	2.221(2)	O(3)-Mn(2)#7	2.109(2)
Mn(2)-O(3)#4	2.109(2)	O(4)-Mn(1)#8	2.152(2)
Mn(2)-O(7)#6	2.188(2)	O(5)-Mn(1)#2	2.124(2)
Mn(2)-O(9)	2.236(2)	O(7)-Mn(1)#3	2.222(2)
O(6)-Mn(2)#6	2.124(2)	O(3)#4-Mn(2)-O(9)	93.76(9)
O(7)-Mn(2)#5	2.188(2)	O(3)#4-Mn(2)-O(10)	149.36(10)
O(5)#2-Mn(1)-O(7)#3	84.55(9)	O(6)#5-Mn(2)-O(7)#6	105.14(8)
O(5)#2-Mn(1)-O(11)	93.86(11)	O(6)#5-Mn(2)-O(9)	98.04(10)
O(11)-Mn(1)-O(1W)	91.92(10)	O(6)#5-Mn(2)-O(10)	94.61(11)
O(11)-Mn(1)-O(7)#3	172.71(9)	O(7)#6-Mn(2)-O(9)	146.82(9)
O(3)#4-Mn(2)-O(6)#5	101.60(10)	O(7)#6-Mn(2)-O(10)	96.21(9)
O(3)#4-Mn(2)-O(7)#6	104.25(9)	O(10)-Mn(2)-O(9)	58.03(9)
O(4)#1-Mn(1)-O(1)	170.62(9)	O(1)-Mn(1)-O(1W)	89.77(9)
O(4)#1-Mn(1)-O(1W)	84.93(9)	O(1)-Mn(1)-O(7)#3	99.83(8)
O(4)#1-Mn(1)-O(7)#3	87.88(9)	O(1)-Mn(1)-O(11)	87.32(10)
O(4)#1-Mn(1)-O(11)	85.14(10)	O(5)#2-Mn(1)-O(4)#1	94.18(10)
O(5)#2-Mn(1)-O(1)	91.87(9)		
O(5)#2-Mn(1)-O(1W)	174.06(9)		

Symmetrical codes: #1 x+1, y, z; #2 -x+2, -y+1, -z+2; #3 -x+2, -y, -z+2; #4 x, -y+1/2, z-1/2; #5 -x+1, y-1/2, -z+3/2; #6 -x+1, y+1/2, -z+3/2; #7 x, -y+1/2, z+1/2; #8 x-1, y, z.



(a)

Fig. S1 3D microporous framework of **1** and the different shapes of channels along a, b and c-axis. All the H atoms and guest molecules are omitted for clarity.

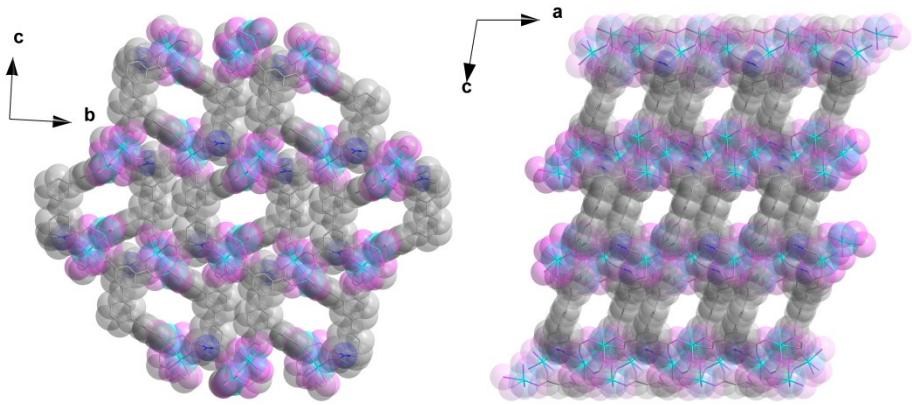
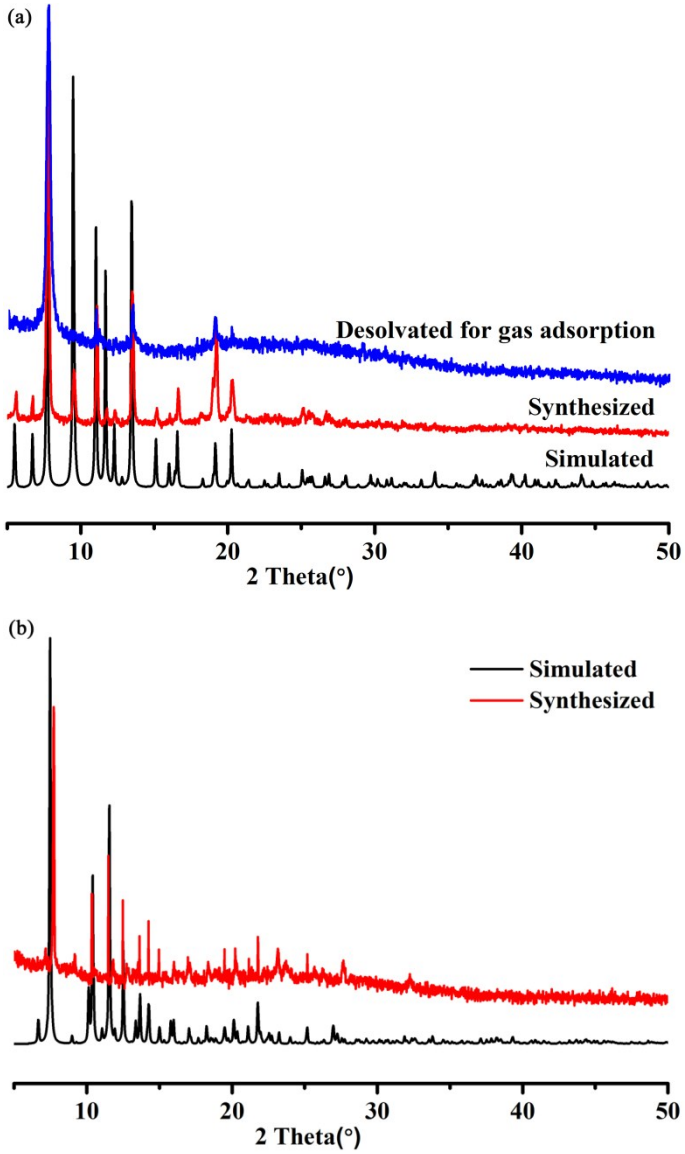


Fig. S2 3D microporous framework of **2** and the different shapes of channels along a-axis and b-axis. All the H atoms and guest molecules are omitted for clarity.



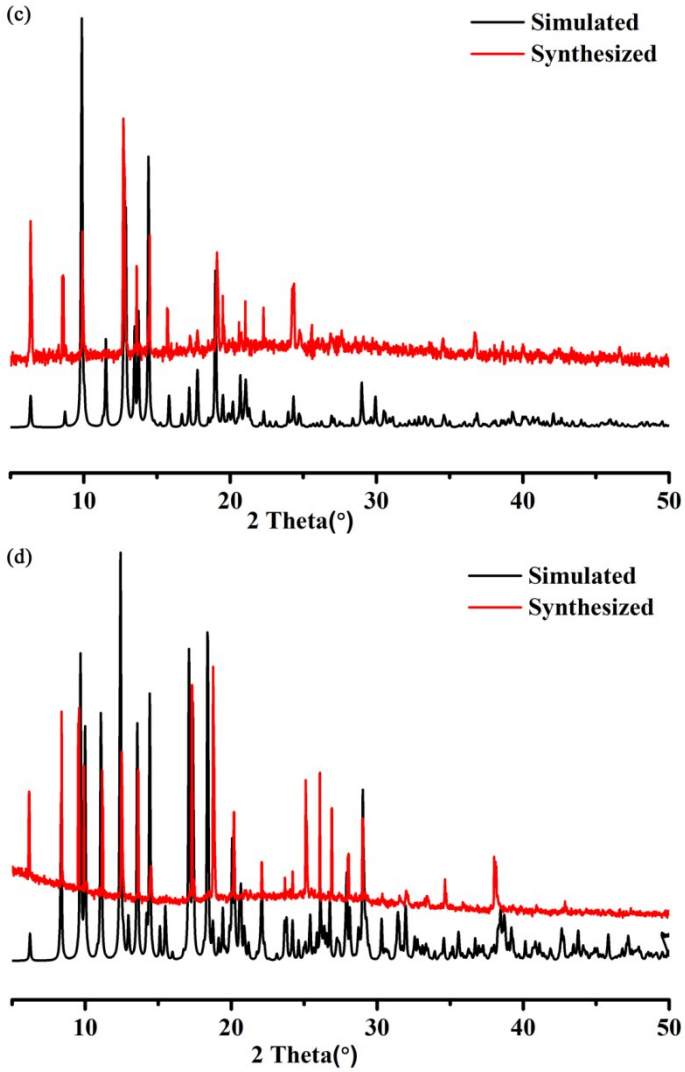
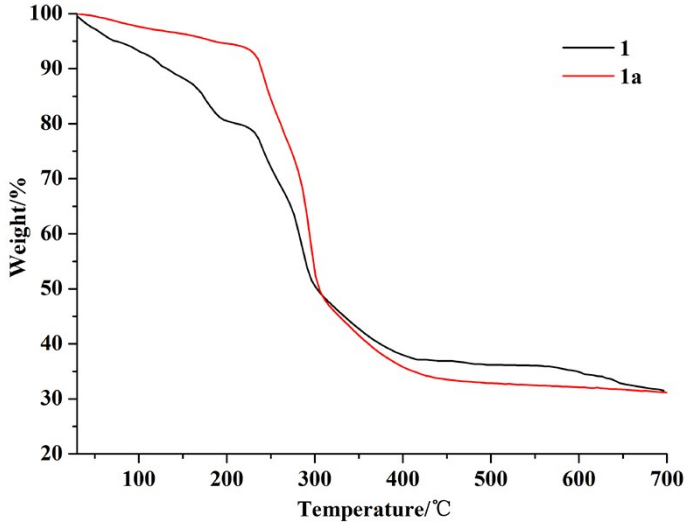


Fig. S3 PXRD patterns of **1-4** in (a-d) simulated from the X-ray single-crystal structure, experimental samples and desolvated samples.



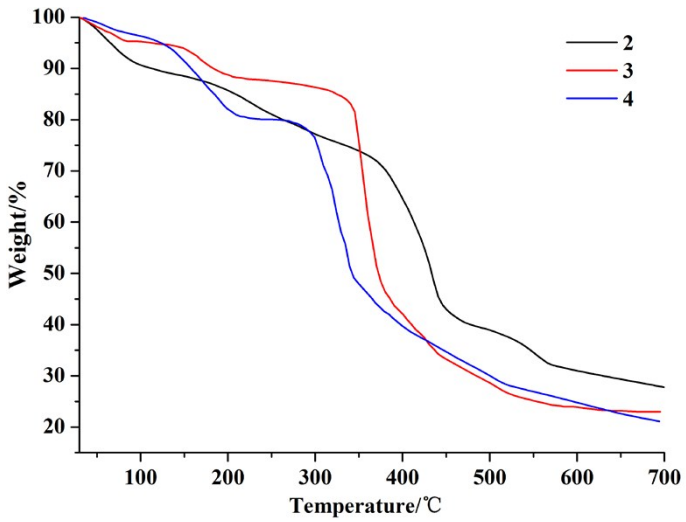


Fig. S4 TGA plots of complexes **1-4.**

IAST adsorption selectivity calculation

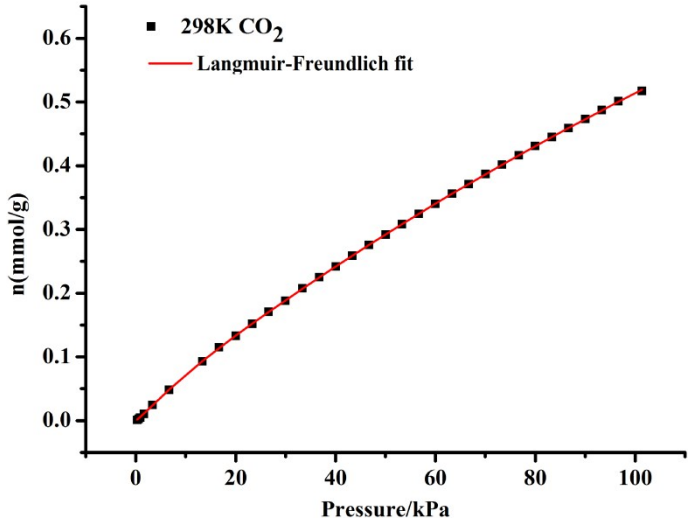
The experimental isotherm data for pure CO_2 and CH_4 (measured at 273 and 298 K) were fitted using a Langmuir-Freundlich (L-F) model

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

Where q and p are adsorbed amounts and pressures of component i, respectively. The adsorption selectivities for binary mixtures of 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.



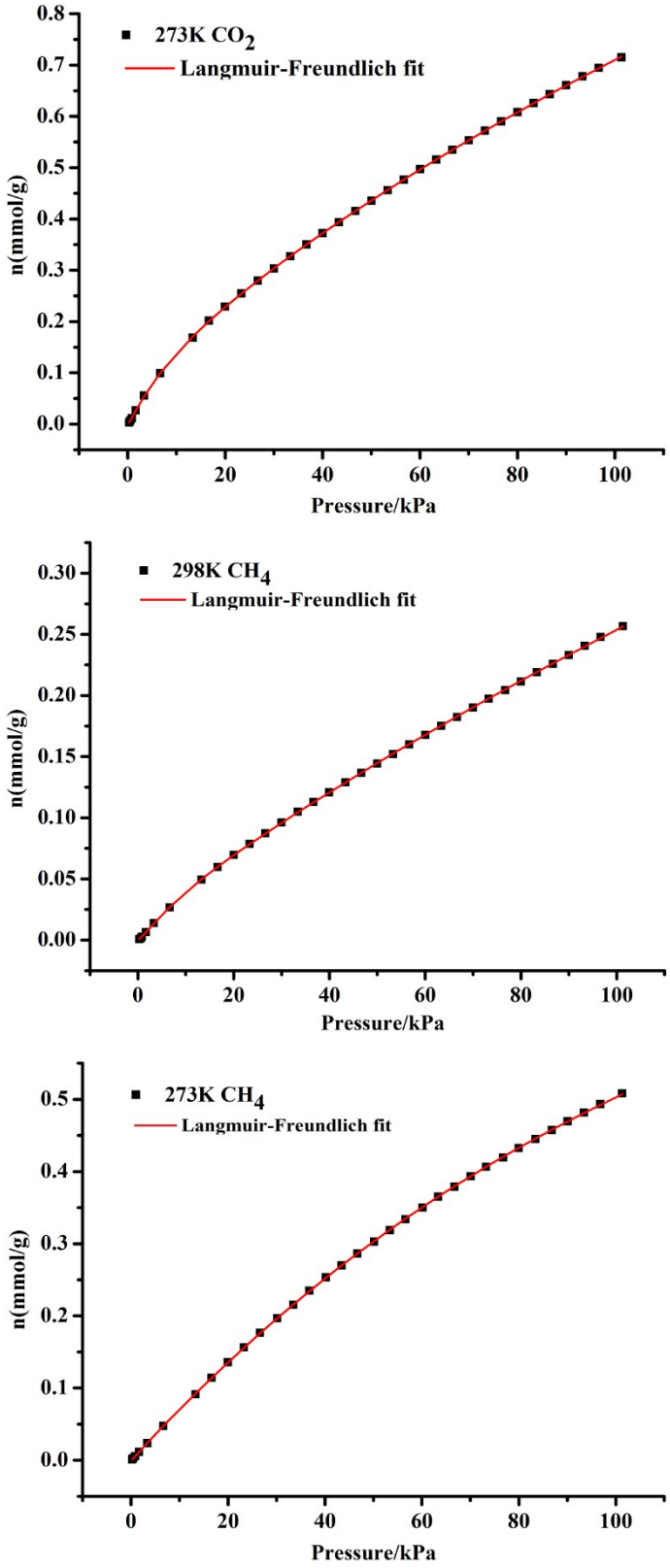
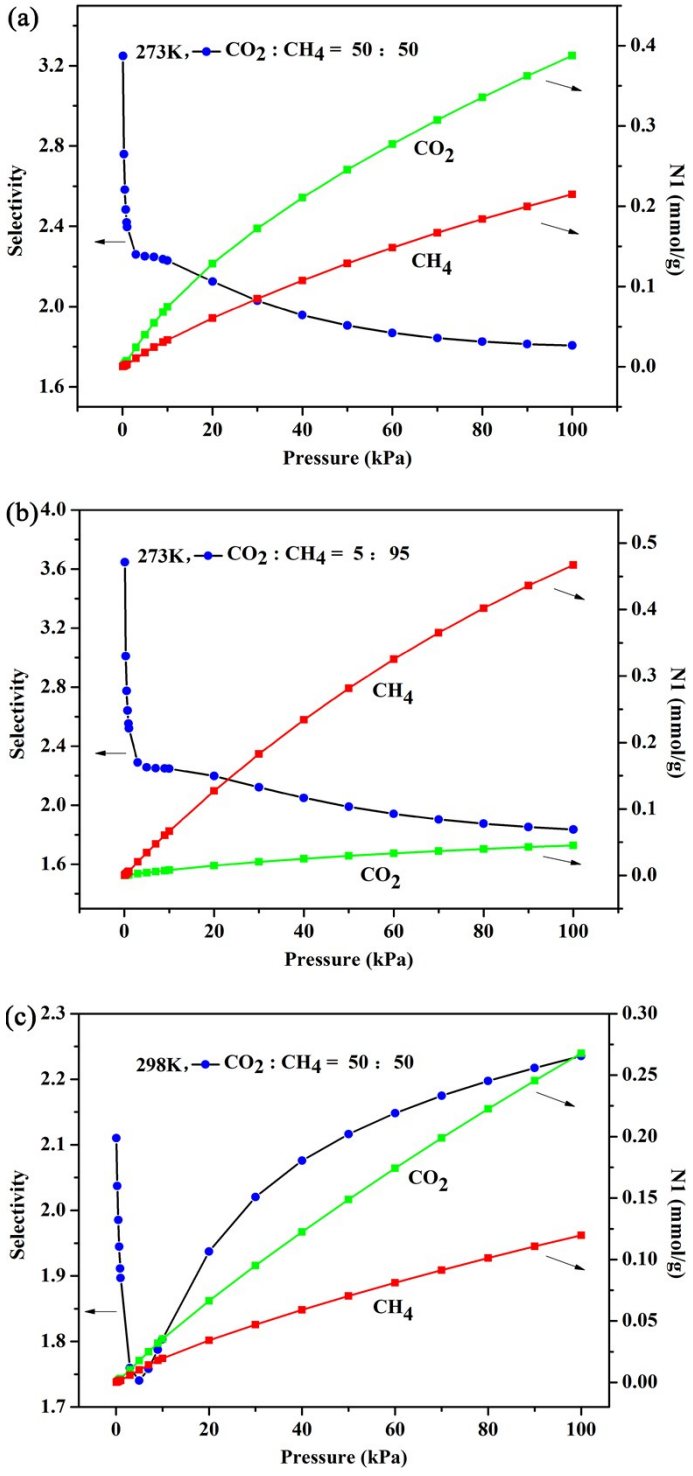


Fig. S5 CO_2 adsorption isotherms of **1a** at 298K with fitting by L-F model: a = 2.50728, b = 0.000245, c =1.00205, Chi^2 = 4.94 $\times 10^{-7}$, R^2 = 0.99998; CO_2 adsorption isotherms of **1a** at 273K with fitting by L-F model: a = 3.36251, b = 0.00292, c =0.94909, Chi^2 = 8.84 $\times 10^{-7}$, R^2 = 0.99999; CH_4 adsorption isotherms of **1a** at 298K with fitting by L-F model: a = 1.7084, b = 0.00161, c = 0.99718, Chi^2

= 2.08 ×10^{-7}, R^2 = 0.99997; CH_4 adsorption isotherms of **1a** at 273K with fitting by L-F model: a = 1.16981, b = 0.004, c = 1.12694, Chi^2 = 4.22 ×10^{-7}, R^2 = 0.99999.



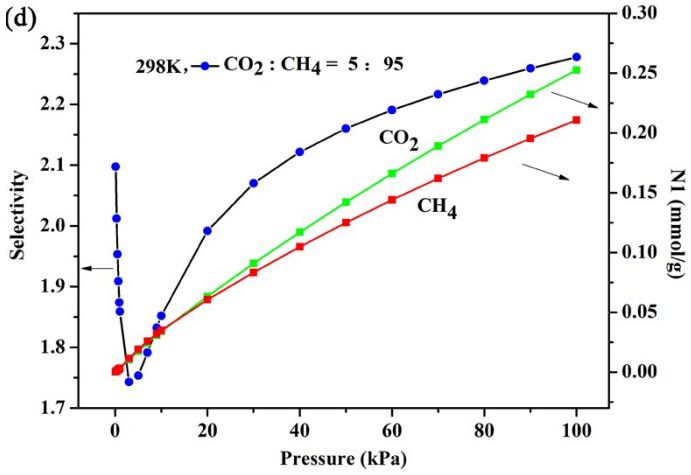


Fig. S6 IAST adsorption selectivity of **1a** for the CO_2/CH_4 mixtures with different components at 273 and 298 K.

Calculation of sorption heat for CO_2 uptake using Virial 2 model

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

The above equation was applied to fit the combined CO_2 isotherm data for desolvated **1** 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.

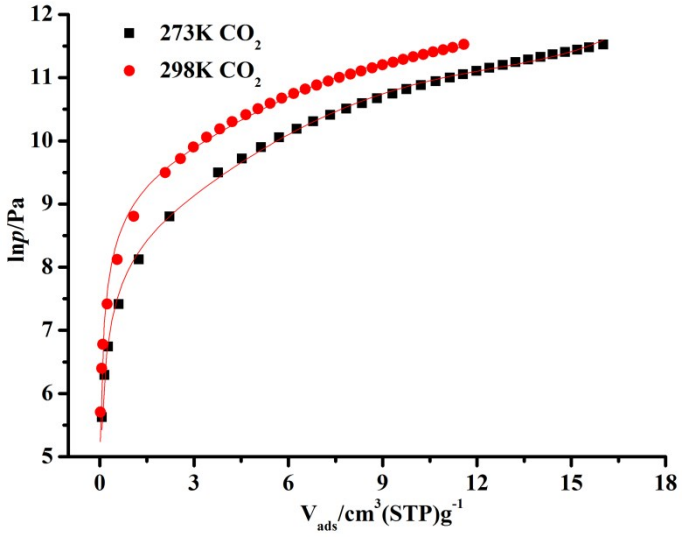


Fig. S7 Virial analysis of the CO_2 adsorption data at 273 and 298 K for **1**. Fitting results: a0= -3070.23, a1 = 207.49, a2 = 2.10, a3 = -1.16, a4 = 0.04, Chi^2 = 0.00931, R^2 = 0.9962.

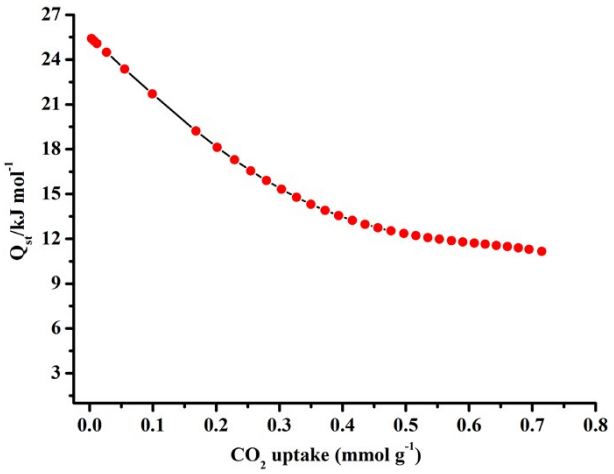
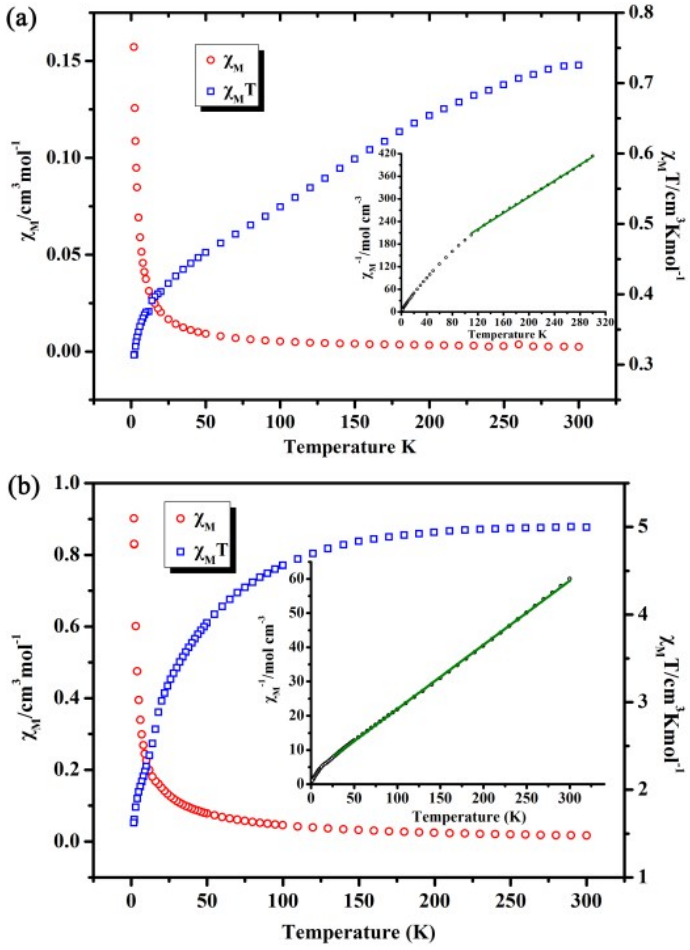


Fig. S8 Isosteric heat of CO_2 adsorption for **1a** estimated by the virial equation from the adsorption isotherms at 273 and 298 K.



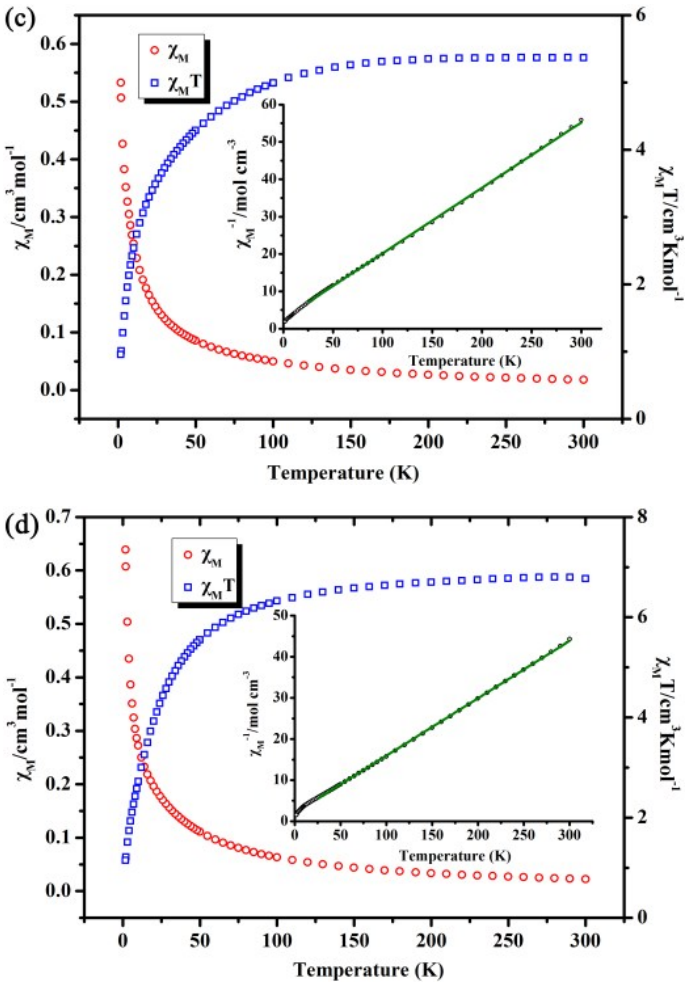
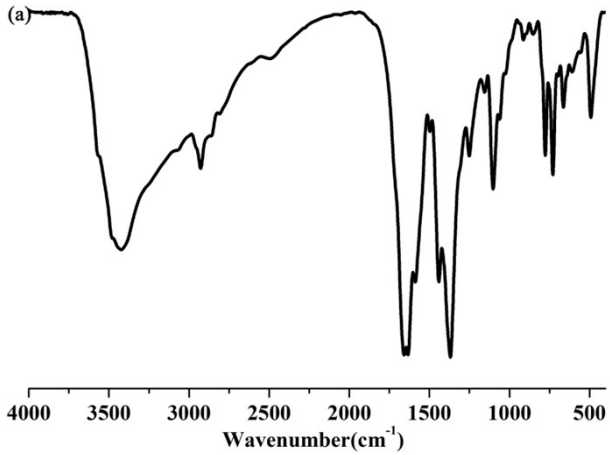


Fig. S9 The $\chi_M T$, χ_M, and $1/\chi_M$ vs. T plots of **1-4** in (a-d), respectively. The green line represents the fits.



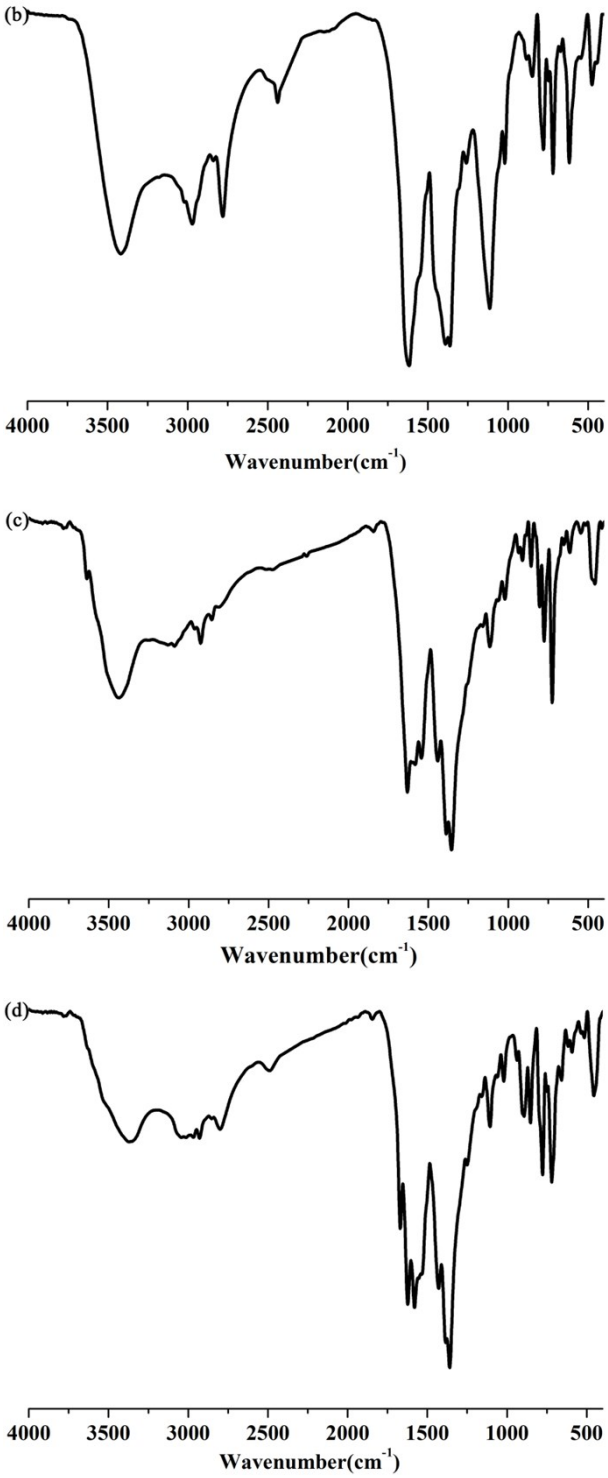


Fig. S10 IR spectra of the as-synthesized **1-4** in (a-d).