Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Two new MOFs based on 5-((4-carboxypyridin-2-yl)oxy) isophthalic acid displaying the unique selective CO_2 gas adsorption and Magnetic properties†

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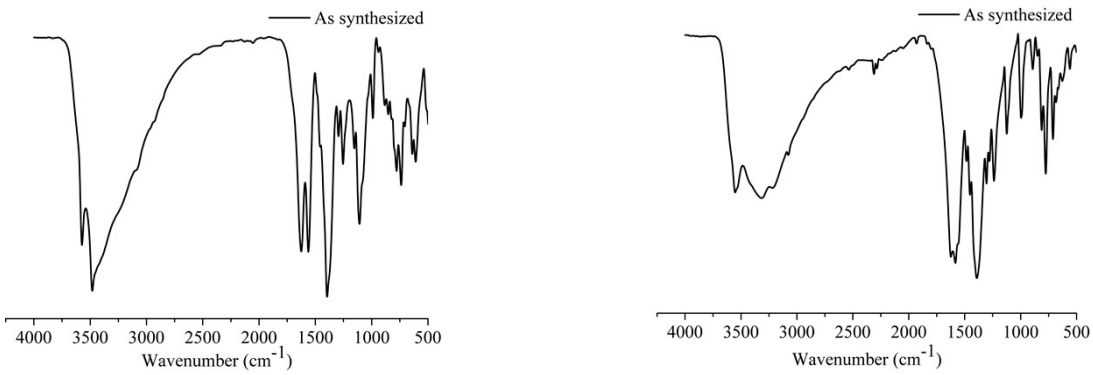


(a) (b)

Fig. S1 The FTIR spectra of **1** (a) and **2** (b).

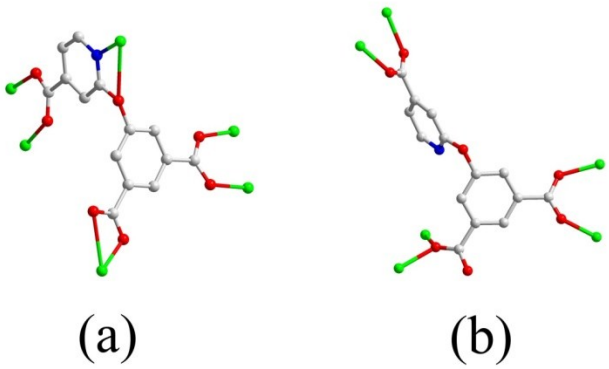
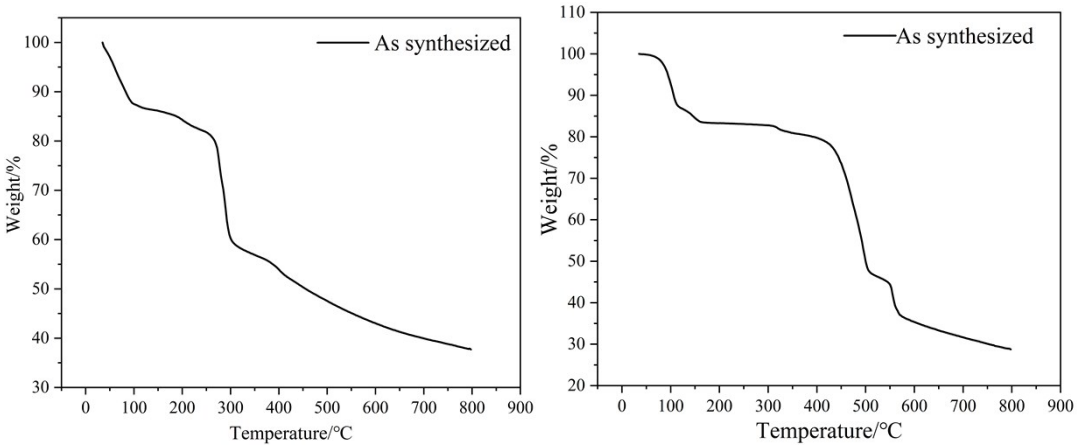
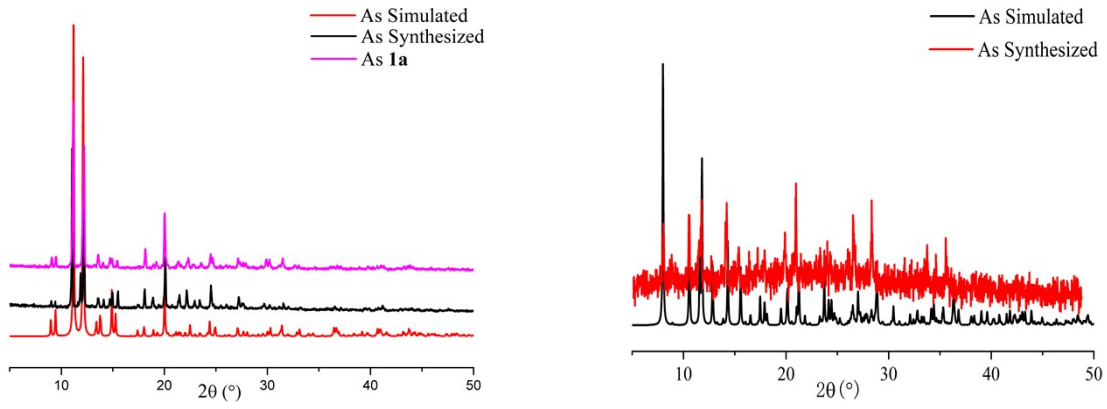


Fig. S2 The coordination modes of L^{3-} ligands.



(a) (b)

Fig. S3 TGA curves for **1** (a) and **2** (b).



(a) (b)

Fig. S4 PXRD patterns of the as-synthesized products **1** (a) and **2** (b).

IAST adsorption selectivity calculation.

The experimental isotherm data for pure CO_2, and CH_4 were fitted using a dual Langmuir-Freundlich (L-F) model:

$$q = \frac{a_1 * b_1 * p^{1/c1}}{1 + b_1 * p^{1/c1}} + \frac{a_2 * b_2 * p^{1/c2}}{1 + b_1 * p^{1/c1}}$$

Where q and p are adsorbed amounts and the pressure of component , respectively.

The adsorption selectivities for binary mixtures of CO_2/CH_4, defined by

$$S_{i/j} = \frac{x_i * y_j}{x_j * y_i}$$

were respectively calculated using the Ideal Adsorption Solution Theory (IAST) of Myers and Prausnitz. Where xi is the mole fraction of component i in the adsorbed phase and yi is the mole fraction of component i in the bulk.

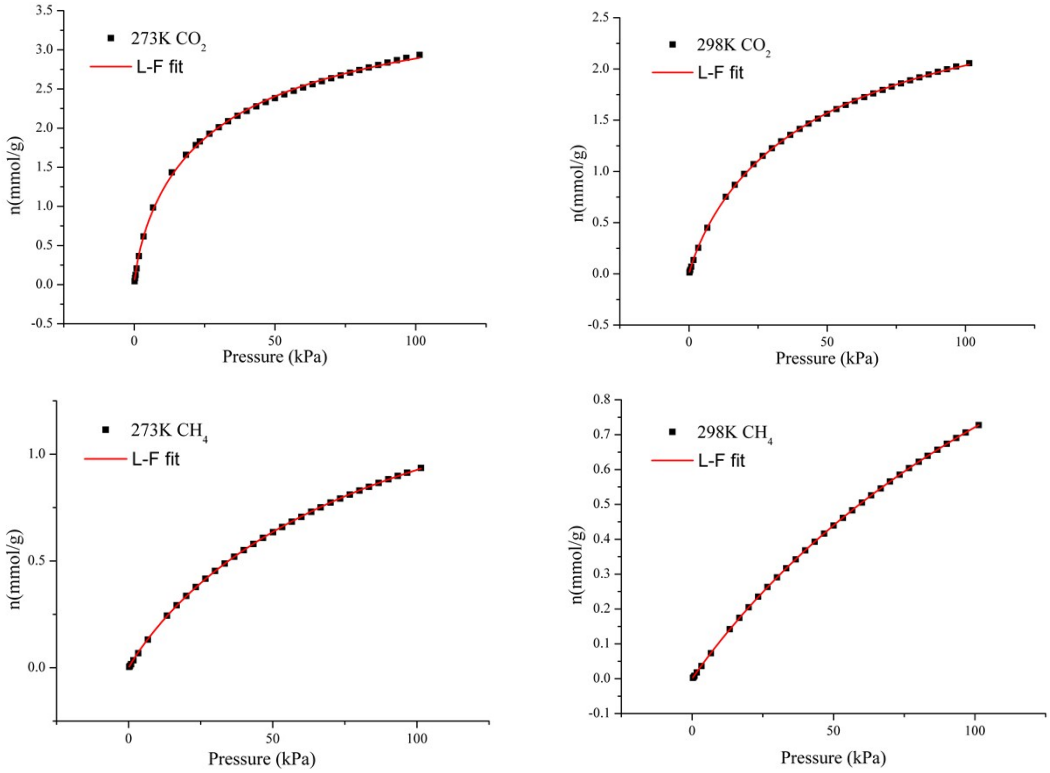


Fig. S5 CO_2 adsorption isotherms of **1a** at 273 K with fitting by L-F model: a =4.02817, b = 0.07094, c =0.77666, Chi^2 = 0.01498, R^2 = 0.99944; CO_2 adsorption isotherms of **1a** at 298 K with fitting by L-F model: a = 3.13065, b =0.03163, c =0.88432, Chi^2 = 0.00179, R^2 = 0.99987; CH_4 adsorption isotherms of **1a** at 273 K with fitting by L-F model: a = 1.83444, b = 0.01315, c = 0.94514, Chi^2 = 1.19341E-4, R^2 = 0.99996; CH_4 adsorption isotherms of **1a** at 298 K with fitting by L-F model: a = 2.1113, b = 0.00566, c = 0.98122, Chi^2 = 2.21927E-5, R^2 = 0.99999.

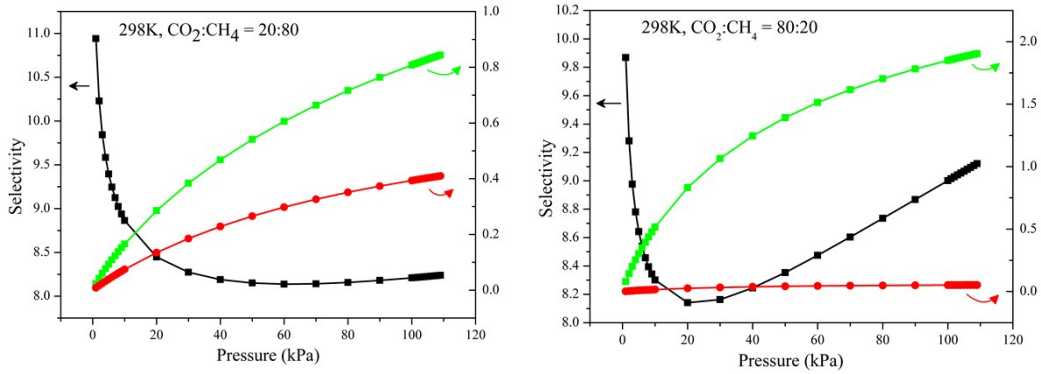


Fig. S6 IAST adsorption selectivity of **1a** for equimolar mixtures of CO_2 and CH_4 at 298 K.

Calculation of sorption heat for CO_2 and CH_4 uptake using Virial 2 model.

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

The above virial expression was used to fit the combined isotherm data for **1a** at 273 and 298 K, where P is the pressure, N is the adsorbed amount, T is the temperature, a_i and b_i 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.

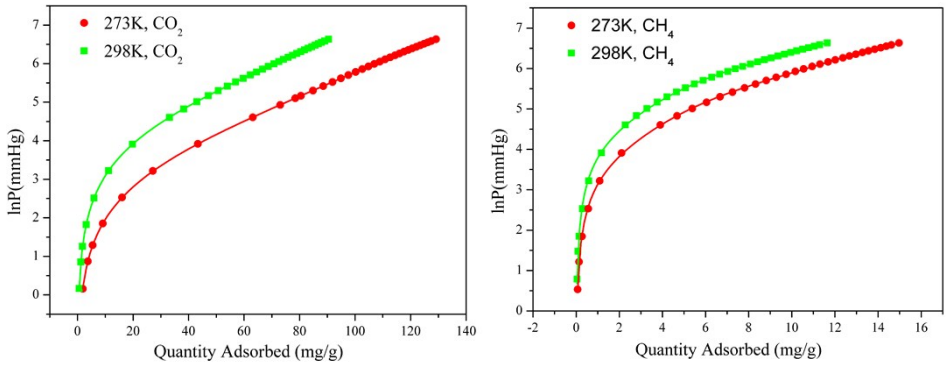


Fig. S7 (a) CO_2 adsorption isotherms for **1a** with fitting by Virial 2 model. Fitting results: a0 = –3726.36715, a1 = 5.59175, a2 = -0.07487, a3 = -2.16198E-5, b0 = 13.16416, b1 = -0.00583, b2 = –2.65363E-4, Chi^2 = 2.03079E-5, R^2 = 0.99999. (b) CH_4 adsorption isotherms for 1a with fitting by Virial 2 model. Fitting results: a0 = 2222.01658, a1 = -117.24684, a2 = 22.02785, a3 = -3.18084, b0 = -4.22443, b1 = 0.23254, b2 =-6.91796E-4, Chi^2 =7.40906E-4, R^2 = 0.99971.

Table S1 Selected bond lengths [Å] and angles [°] for **1** and **2**.

Complex **1**

Cu(1)-O(2)#1	1.967(2)	O(2)#1-Cu(1)-O(1A)#1	54.7(4)
Cu(1)-O(2)	1.968(2)	O(2)-Cu(1)-O(1A)#1	88.7(5)
Cu(1)-O(1)	2.60(3)	O(1)#1-Cu(1)-O(1)	120.0(10)
Cu(1)-O(1)#1	2.60(3)	O(1A)-Cu(1)-O(1A)#1	129.6(10)
Cu(1)-O(1A)#1	2.57(3)	O(6)#3-Cu(2)-Cu(2)#2	81.11(6)
Cu(1)-O(1A)	2.57(3)	O(6)#3-Cu(2)-O(7)#4	167.61(9)
Cu(2)-Cu(2)#2	2.6560(7)	O(6)#3-Cu(2)-O(8)	96.37(10)
Cu(2)-O(6)#3	1.961(2)	O(4)-Cu(2)-Cu(2)#2	82.19(6)
Cu(2)-O(4)	1.943(2)	O(4)-Cu(2)-O(6)#3	89.81(10)

Cu(2)-O(7)#4	1.961(2)	O(4)-Cu(2)-O(7)#4	88.98(10)
Cu(2)-O(3)#2	1.9535(19)	O(4)-Cu(2)-O(3)#2	167.48(8)
Cu(2)-O(8)	2.139(2)	O(4)-Cu(2)-O(8)	95.38(10)
O(2)#1-Cu(1)-O(2)	90.28(13)	O(7)#4-Cu(2)-Cu(2)#2	86.51(7)
O(2)-Cu(1)-O(1)#1	81.1(5)	O(7)#4-Cu(2)-O(8)	96.02(10)
O(2)-Cu(1)-O(1)	56.6(5)	O(3)#2-Cu(2)-Cu(2)#2	85.34(6)
O(2)#1-Cu(1)-O(1)#1	56.6(5)	O(3)#2-Cu(2)-O(6)#3	89.30(10)
O(2)#1-Cu(1)-O(1)	81.1(5)	O(3)#2-Cu(2)-O(7)#4	89.21(10)
O(2)-Cu(1)-O(1A)	54.7(4)	O(3)#2-Cu(2)-O(8)	97.13(9)
O(2)#1-Cu(1)-O(1A)	88.7(5)	O(8)-Cu(2)-Cu(2)#2	176.47(8)

Symmetry transformations used to generate equivalent atoms: #1 -x+2, y, -z+1/2; #2 -x+2, -y, -z+1; #3 -x+3/2, -y+1/2, -z+1; #4 x+1/2, y-1/2, z; #5 x-1/2, y+1/2, z.

Complex **2**

Co(2)-O(1)	2.0283(12)	O(5)#2-Co(2)-O(10)	83.39(6)
Co(2)-O(2)	2.0303(13)	O(5)#2-Co(2)-O(7)#1	91.09(5)
Co(2)-O(9)	2.1770(14)	O(1)-Co(1)-O(1)#3	81.94(5)
Co(2)-O(10)	2.1062(13)	O(1)-Co(1)-O(6)#5	174.57(5)
Co(2)-O(7)#1	2.2451(13)	O(1)#3-Co(1)-O(6)#5	100.17(5)
Co(2)-O(5)#2	2.0467(13)	O(1)-Co(1)-N(2)	93.27(6)
Co(1)-O(1)#3	2.1176(13)	O(1)#3-Co(1)-N(2)	173.16(6)
Co(1)-O(1)	2.0824(12)	O(1)#3-Co(1)-O(13)	173.16(6)
Co(1)-O(3)	2.0553(13)	O(1)-Co(1)-O(13)	93.27(6)
Co(1)-O(7)#4	2.0743(12)	O(3)-Co(1)-O(1)#3	93.77(5)
Co(1)-O(6)#5	2.1593(13)	O(3)-Co(1)-O(1)	102.47(5)
Co(1)-N(2)	2.1358(19)	O(3)-Co(1)-O(7)#4	163.77(5)
Co(1)-O(13)	2.1358(19)	O(3)-Co(1)-O(6)#5	82.45(5)
O(1)-Co(2)-O(2)	98.17(5)	O(3)-Co(1)-N(2)	92.02(7)
O(1)-Co(2)-O(9)	93.21(5)	O(3)-Co(1)-O(13)	92.02(7)
O(1)-Co(2)-O(10)	177.28(5)	O(7)#4-Co(1)-O(1)	91.73(5)
O(1)-Co(2)-O(7)#1	78.33(5)	O(7)#4-Co(1)-O(1)#3	80.34(5)
O(1)-Co(2)-O(5)#2	95.37(5)	O(7)#4-Co(1)-O(6)#5	83.73(5)
O(2)-Co(2)-O(9)	96.43(6)	O(7)#4-Co(1)-N(2)	95.00(7)
O(2)-Co(2)-O(10)	83.02(5)	O(7)#4-Co(1)-O(13)	95.00(7)
O(2)-Co(2)-O(7)#1	90.18(5)	N(2)-Co(1)-O(6)#5	84.19(7)
O(2)-Co(2)-O(5)#2	166.37(6)	O(13)-Co(1)-O(6)#5	84.19(7)
O(9)-Co(2)-O(7)#1	169.96(5)	Co(2)-O(1)-Co(1)	117.99(6)
O(10)-Co(2)-O(9)	89.09(6)	Co(2)-O(1)-Co(1)#3	97.68(5)

O(10)-Co(2)-O(7)#1	99.25(5)	Co(1)-O(1)-Co(1)#3	98.06(5)
O(5)#2-Co(2)-O(9)	84.27(6)	Co(1)#6-O(7)-Co(2)#1	92.49(5)

Symmetry transformations used to generate equivalent atoms: #1 -x, -y+1, -z; #2 x+1, y, z-1; #3 -x+1, -y+2, -z; #4 x+1, y+1, z; #5 -x, -y+2, -z+1; #6 x-1, y-1, z;#7 x-1, y, z+1.

Table S2. Comparison of CO_2/CH_4 selectivity calculated by IAST method for the equimolar mixture at 1 atm and 298 K of **1a** with the selected MOFs.

MOFs	selectivity	ref
MPM-1-TIFSIX	20.3	1
Cu-TDPDA	13.8	2
$[H_2N(Me)_2]_2[Zn_4(L)_2(H_2O)_{1.5}]\cdot 5DMF\cdot H_2O$	12.0	3
$[Cu(bpy)_2(SiF_6)]$	10.5	4
Mg-MOF-74	11.5	5
PCN-307	8.8	6
$[Cu_{1.5}(L)(H_2O)]\cdot 2H_2O$	**8.6**	**This work**
ZIF-93	8.2	7
UiO-66-AD4	8.0	8
PCN-306	7.5	6
SNU-151′	7.2	9
Zr-UiO-67AcOH	6.8	10
ZIF-100	5.9	11
ZJU-60	5.5	12
MOF-177	4.4	13
dia-7i-1-Co	4.1, 4.0[a]	14
DMOF	3.2	15

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