Supporting Information for the Manuscript:

Solvent-induced Secondary Building Unit (SBU) Variations in a Series of

Cu(II) Metal−Organic Frameworks Derived from a Bifunctional Ligand

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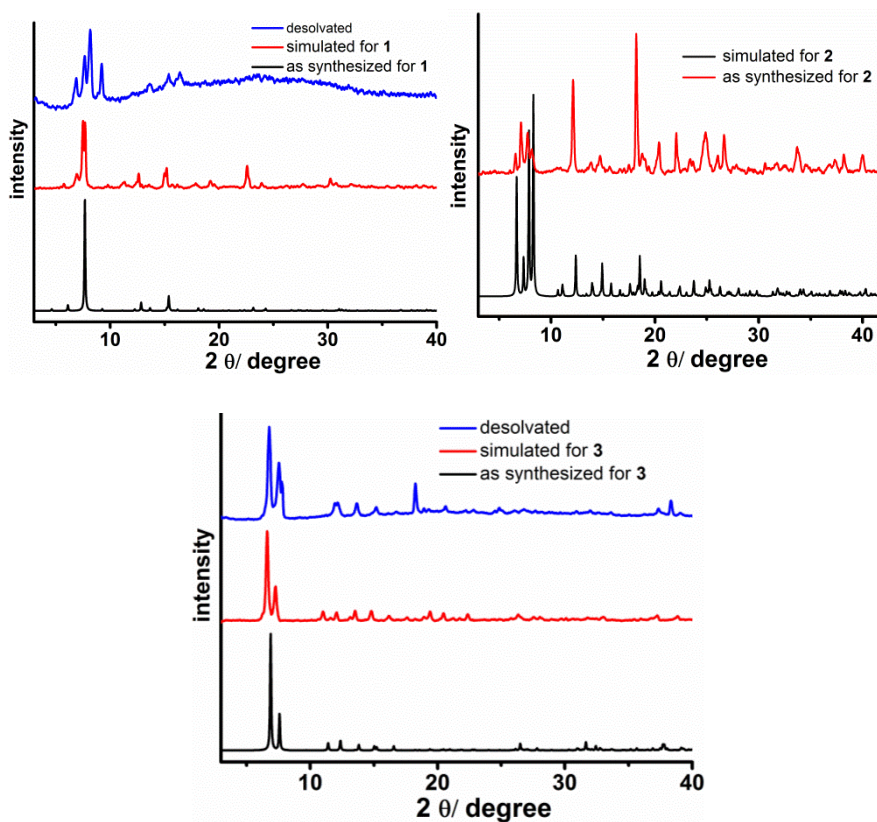Author for correspondence: mvbasten@nankai.edu.cn

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Fig. S1. Experimental (red) and simulated (black) PXRD patterns of complexes. **1−3**.
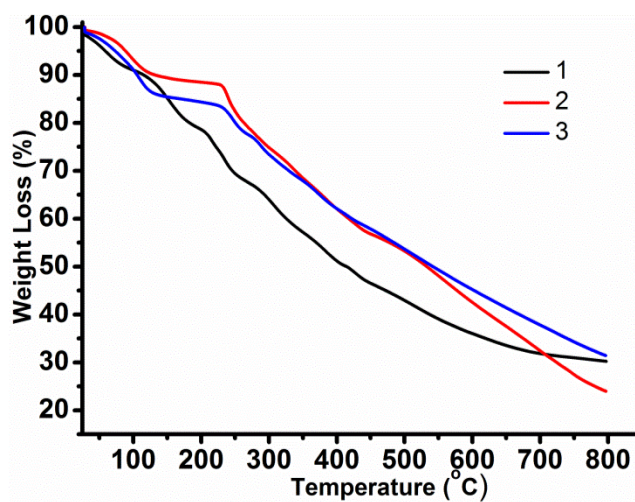

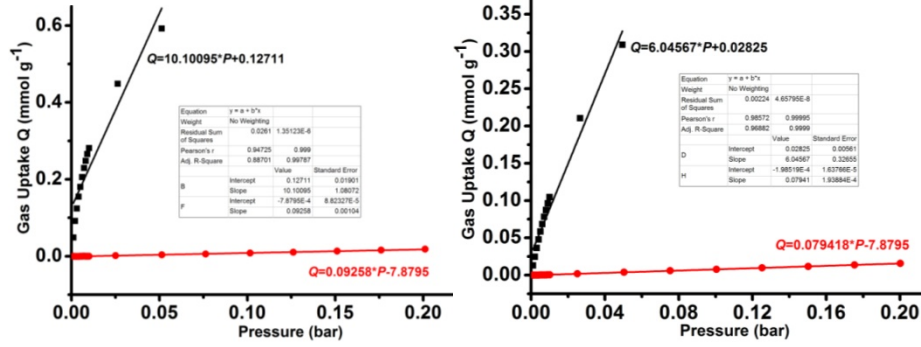**Fig. S2.** Thermogravimetric curves of **1-3**.

Fig. S3 Linear fitting of the low-pressure region of CO_2 (black) and N_2 (red) adsorption isotherms of **3** measured at 273 and 298 K, respectively.

Analysis of Gas Adsorption Isotherms:

The carbon dioxide adsorption isotherms of **3** are fitted to the Langmuir-Freundlich according to the literature.[1] An accurate fit was obtained by using this equation which results a precise prediction over the quantity of gas adsorbed at saturation. A variant of the Clausius-Clapeyron equation was used to calculate enthalpy of adsorption.

$$ln\frac{P_1}{P_2} = \Delta H_{ads} \times \frac{T_2 - T_1}{R \times T_2 \times T_1} \quad \text{(I)}$$

where T_1 and T_2 are the two isotherm temperatures (273 and 298 K), P_1 and P_2 are pressures at T_1 and T_2, respectively, for a given uptake, and R is the universal gas constant (R = 8.3147 J / (K·mol)). Pressure as a function of the amount of gas adsorbed was determined using the Langmuir-Freundlich fit for the isotherms.

$$\frac{q_i}{q} = \frac{bp^{(1/t)}}{1 + bp^{(1/t)}} \quad \text{(II)}$$

Where q_i = the amount adsorbed, q = the amount adsorbed at saturation, p = pressure,

$$p = \left(\dfrac{\dfrac{q_i}{q}}{b - b\dfrac{q_i}{q}}\right)^t \quad (III)$$

b and t = constants. The equation (II) rearranges to:

$$\Delta H_{ads} = \frac{RT_1 T_2}{T_2 - T_1} \times ln\boxed{ro}\left(\frac{P_1}{P_2}\right) \quad (IV)$$
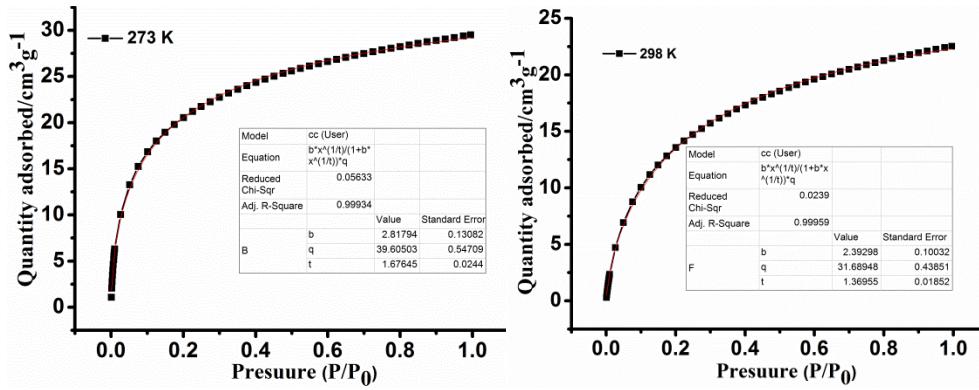

Fig. S4. CO_2 adsorption isotherm for **3** at 273 K and 298 K. The red solid line represents the best fit to the data using the Langmuir-Freundlich equation, as described above.

IAST Adsorption Selectivity Calculation

The ideal adsorbed solution theory (IAST) was adopted based upon the experimental single gas adsorption measurements as described in the main text, including carbon dioxide and nitrogen at 273 K and 298 K, which is commonly used to predict binary mixture adsorption selectivity. Using the pure component isotherm fits, the adsorption selectivity is defined by:

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

Where q_i is the amount of i adsorbed and p_i is the partial pressure of i in the mixture fits.

We use the following written codes to simulate the adsorption selectivity of CO_2 over

N_2.

28   # No. of Pressure Point

0.2, 0.8   # Molar fraction of binary mixture (y1 and y2, y1 + y2 = 1)

100, 200, 300, 400, 500, 600, 700, 800, 900, 1000, 2000, 3000, 4000, 5000, 6000,

7000, 8000, 9000, 10000, 20000, 30000, 40000, 50000, 60000, 70000, 80000, 90000,

100000   #The unit is same parameter b, Pa

a1, a2   # fitting parameter Nsat for both component (Unit: mmol/g)

b1, b2   # fitting parameter b for both component (Unit: kPa-1)

Selectivity Data of CO_2:N_2 (15:85) at 298K

	A(X)	B(Y)	C(Y)	D(Y)	E(Y)	F(Y)
Long Name	Pressure	N1	N2	x1	x2	Selectivity
Units	Pa	mmol/g	mmol/g			
Comments						
Sparklines						
1	100	0.02985	0.00142	0.95459	0.04541	84.07596
2	200	0.05964	0.00284	0.95457	0.04543	84.045
3	300	0.08935	0.00425	0.95455	0.04545	84.01405
4	400	0.11898	0.00567	0.95454	0.04546	83.98336
5	500	0.14855	0.00708	0.95452	0.04548	83.95245
6	600	0.17805	0.00849	0.95451	0.0455	83.92157
7	700	0.20747	0.00989	0.95449	0.04551	83.89094
8	800	0.23683	0.0113	0.95447	0.04553	83.86033
9	900	0.26611	0.0127	0.95446	0.04554	83.82952
10	1000	0.29533	0.0141	0.95444	0.04556	83.79895
11	2000	0.58367	0.02796	0.95428	0.04572	83.49492
12	3000	0.86527	0.0416	0.95413	0.04587	83.19457
13	4000	1.14036	0.05502	0.95397	0.04603	82.89785
14	5000	1.40917	0.06824	0.95381	0.04619	82.60471
15	6000	1.67189	0.08124	0.95366	0.04634	82.31532
16	7000	1.92875	0.09405	0.9535	0.0465	82.02917
17	8000	2.17993	0.10667	0.95335	0.04665	81.74646
18	9000	2.42561	0.1191	0.9532	0.0468	81.46712
19	10000	2.66597	0.13134	0.95305	0.04695	81.1911
20	20000	4.8112	0.24486	0.95157	0.04843	78.594
21	30000	6.57389	0.34483	0.95016	0.04984	76.25754
22	40000	8.04737	0.43418	0.94881	0.05119	74.13814
23	50000	9.29693	0.51505	0.94751	0.05249	72.2018
24	60000	10.36962	0.589	0.94625	0.05375	70.4221
25	70000	11.30017	0.6572	0.94504	0.05496	68.77774
26	80000	12.1148	0.72057	0.94386	0.05614	67.25135
27	90000	12.83368	0.77982	0.94272	0.05728	65.82862
28	100000	13.47254	0.83554	0.9416	0.0584	64.49779

Table **S1**. Selected Bond Lengths (Å) and Bond Angles (°) for **1**

Cu(1)-N(3)#1	2.015(8)	N(3)#1-Cu(1)-N(3)#2	90.4(5)
Cu(1)-N(3)#2	2.015(8)	N(3)#1-Cu(1)-N(3)#3	89.6(5)
Cu(1)-N(3)#3	2.015(8)	N(3)#2-Cu(1)-N(3)#3	180.0(4)
Cu(1)-N(3)	2.015(8)	N(3)#1-Cu(1)-N(3)	179.997(1)
Cu(1)-Cl(3)	2.642(4)	N(3)#2-Cu(1)-N(3)	89.6(5)
Cu(1)-Cl(3)#1	2.642(4)	N(3)#3-Cu(1)-N(3)	90.4(5)
Cu(2)-O(2)#4	1.946(13)	N(3)#1-Cu(1)-Cl(3)	89.4(2)
Cu(2)-O(2)#5	1.946(13)	N(3)#2-Cu(1)-Cl(3)	90.6(2)
Cu(2)-O(2)#6	1.946(13)	N(3)#3-Cu(1)-Cl(3)	89.4(2)
Cu(2)-O(2)	1.946(13)	N(3)-Cu(1)-Cl(3)	90.6(2)
Cu(2)-Cl(1)	2.216(5)	N(3)#1-Cu(1)-Cl(3)#1	90.6(2)
Cu(2)-Cu(2)#7	2.661(11)	N(3)#2-Cu(1)-Cl(3)#1	89.4(2)
Cl(3)-Cu(1)#8	2.642(4)	N(3)#3-Cu(1)-Cl(3)#1	90.6(2)
Cl(3)-Cu(1)-Cl(3)#1	180.0	O(2)#4-Cu(2)-O(2)#5	84.3(10)
O(2)#4-Cu(2)-O(2)#6	94.4(10)	O(2)#5-Cu(2)-O(2)#6	167.5(13)
O(2)#4-Cu(2)-O(2)	167.5(13)	O(2)#5-Cu(2)-O(2)	94.4(10)
O(2)#6-Cu(2)-O(2)	84.2(10)	O(2)#4-Cu(2)-Cl(1)	96.2(7)
O(2)#5-Cu(2)-Cl(1)	96.2(7)	O(2)#6-Cu(2)-Cl(1)	96.2(7)
O(2)-Cu(2)-Cl(1)	96.2(7)	O(2)#4-Cu(2)-Cu(2)#7	83.8(7)
O(2)#5-Cu(2)-Cu(2)#7	83.8(7)	Cl(1)-Cu(2)-Cu(2)#7	180.0(13)
O(2)#6-Cu(2)-Cu(2)#7	83.8(7)	Cu(1)#8-Cl(3)-Cu(1)	84.29(1)
O(2)-Cu(2)-Cu(2)#7	83.8(7)		

Symmetry transformations used to generate equivalent atoms: 1): -x+1/2,-y+1/2,-z+1;

2) x,y,-z+1; 3): -x+1/2,-y+1/2,z; 4) x,-y,-z; 5): x,y,-z; 6): x,-y,z; 7): -x,-y,-z; 8):

x+1/2,-y+1/2,-z+1

Table **S2**. Selected Bond Lengths (Å) and Bond Angles (°) for **2**

Cu(1)-O(5)#1	1.953(6)	O(5)#1-Cu(1)-O(5)#2	91.9(4)
Cu(1)-O(5)#2	1.953(6)	O(5)#1-Cu(1)-O(3)#3	167.9(2)
Cu(1)-O(3)#3	1.972(6)	O(5)#2-Cu(1)-O(3)#3	88.2(3)
Cu(1)-O(3)#4	1.972(6)	O(5)#1-Cu(1)-O(3)#4	88.2(3)
Cu(1)-Cl(4)	2.390(3)	O(5)#2-Cu(1)-O(3)#4	167.9(2)
Cu(1)-Cu(1)#5	2.640(2)	O(3)#3-Cu(1)-O(3)#4	89.2(4)
Cu(2)-N(7)	1.963(6)	O(5)#1-Cu(1)-Cl(4)	92.17(18)
Cu(2)-N(7)#6	1.963(6)	O(5)#2-Cu(1)-Cl(4)	92.17(18)
Cu(2)-O(2)	2.032(7)	O(3)#3-Cu(1)-Cl(4)	99.87(18)

Cu(2)-Cl(4)	2.280(3)	O(3)#4-Cu(1)-Cl(4)	99.87(18)
Cu(2)-O(1)	2.481(11)	O(5)#1-Cu(1)-Cu(1)#5	80.02(17)
Cu(2)-Cl(1)	2.5943(14)	O(5)#2-Cu(1)-Cu(1)#5	80.02(17)
Cu(3)-N(9)	1.948(7)	O(3)#3-Cu(1)-Cu(1)#5	88.13(17)
Cu(3)-N(3)	1.960(7)	O(3)#4-Cu(1)-Cu(1)#5	88.13(17)
Cu(3)-O(2)	2.028(4)	Cl(4)-Cu(1)-Cu(1)#5	
Cu(3)-Cl(2)	2.276(3)	168.70(11)	
Cu(3)-O(0AA)#7	2.450(16)	N(7)-Cu(2)-N(7)#6	173.9(4)
O(2)-Cu(3)#	62.027(4)	N(7)-Cu(2)-O(2)	89.51(18)
N(9)-Cu(3)-Cl(2)	91.3(2)	N(7)#6-Cu(2)-O(2)	89.51(18)
N(3)-Cu(3)-Cl(2)	91.4(2)	N(7)-Cu(2)-Cl(4)	91.06(18)
O(2)-Cu(3)-Cl(2)	172.8(2)	N(7)#6-Cu(2)-Cl(4)	91.06(18)
N(9)-Cu(3)-O(0AA)#7	86.9(5)	O(2)-Cu(2)-Cl(4)	168.7(3)
N(3)-Cu(3)-O(0AA)#7	90.6(5)	N(7)-Cu(2)-O(1)	87.0(2)
O(2)-Cu(3)-O(0AA)#7	98.4(5)	N(7)#6-Cu(2)-O(1)	87.0(2)
Cl(2)-Cu(3)-O(0AA)#7	88.8(5)	O(2)-Cu(2)-O(1)	94.0(3)
Cu(2)-Cl(4)-Cu(1)	120.53(12)	Cl(4)-Cu(2)-O(1)	97.3(3)
Cu(3)#6-O(2)-Cu(3)	112.9(4)	N(7)-Cu(2)-Cl(1)	92.8(2)
Cu(3)#6-O(2)-Cu(2)	109.3(2)	N(7)#6-Cu(2)-Cl(1)	92.8(2)
Cu(3)-O(2)-Cu(2)	109.3(2)	O(2)-Cu(2)-Cl(1)	76.7(2)
C(17)-N(7)-N(9)	107.7(6)	Cl(4)-Cu(2)-Cl(1)	92.01(8)
C(17)-N(7)-Cu(2)	132.2(6)	O(1)-Cu(2)-Cl(1)	170.7(3)
N(9)-N(7)-Cu(2)	120.0(5)	N(9)-Cu(3)-N(3)	176.3(3)
C(31)-N(9)-N(7)	107.2(7)	N(9)-Cu(3)-O(2)	89.9(3)
C(31)-N(9)-Cu(3)	133.1(6)	N(3)-Cu(3)-O(2)	87.7(3)
		N(7)-N(9)-Cu(3)	119.6(5)

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

Table **S3**. Selected Bond Lengths (Å) and Bond Angles (º) for **3**

Cu(1)-O(3)	1.937(3)	O(3)-Cu(1)-O(5)	173.57(15)
Cu(1)-O(5)	1.942(3)	O(3)-Cu(1)-O(8)	96.95(14)
Cu(1)-O(8)	1.976(4)	O(5)-Cu(1)-O(8)	84.65(14)
Cu(1)-N(6)	1.990(4)	O(3)-Cu(1)-N(6)	88.32(16)
Cu(1)-Cl(6)	2.5637(13)	O(5)-Cu(1)-N(6)	88.73(15)
Cu(1)-Cu(3)	2.8509(8)	O(8)-Cu(1)-N(6)	165.87(15)
Cu(3)-O(1)	1.914(3)	O(3)-Cu(1)-Cl(6)	93.45(11)
Cu(3)-O(5)	1.919(4)	O(5)-Cu(1)-Cl(6)	92.31(10)
Cu(3)-O(8)	1.993(3)	O(8)-Cu(1)-Cl(6)	101.63(10)
Cu(3)-N(1)	2.001(4)	N(6)-Cu(1)-Cl(6)	91.08(12)
Cu(6)-O(5)#1	1.908(3)	O(3)-Cu(1)-Cu(3)	137.56(11)

Cu(6)-O(8)	1.945(3)	O(5)-Cu(1)-Cu(3)	42.08(11)
Cu(6)-O(2)	1.969(3)	O(8)-Cu(1)-Cu(3)	44.33(10)
Cu(6)-O(4)	1.995(4)	N(6)-Cu(1)-Cu(3)	125.51(11)
Cu(6)-Cl(6)#1	2.7502(13)	Cl(6)-Cu(1)-Cu(3)	108.82(4)
Cu(8)-O(5)#2	1.927(3)	O(1)-Cu(3)-O(5)	172.71(15)
Cu(8)-N(21)	1.989(4)	O(1)-Cu(3)-O(8)	94.01(15)
Cu(8)-N(9)	2.005(4)	O(5)-Cu(3)-O(8)	84.80(13)
Cu(8)-Cl(1)	2.2458(13)	O(1)-Cu(3)-N(1)	93.25(16)
Cl(6)-Cu(6)#3	2.7502(13)	O(5)-Cu(3)-N(1)	89.12(15)
O(8)-Cu(6)-O(2)	94.48(14)	O(8)-Cu(3)-N(1)	168.30(16)
O(5)#1-Cu(6)-O(4)	89.21(15)	O(1)-Cu(3)-Cu(1)	137.46(11)
O(8)-Cu(6)-O(4)	94.24(14)	O(5)-Cu(3)-Cu(1)	42.71(9)
O(2)-Cu(6)-O(4)	143.40(15)	O(8)-Cu(3)-Cu(1)	43.86(10)
O(5)#1-Cu(6)-Cl(6)#1	87.49(10)	N(1)-Cu(3)-Cu(1)	127.35(12)
O(8)-Cu(6)-Cl(6)#1	80.99(10)	O(5)#1-Cu(6)-O(8)	168.38(14)
O(2)-Cu(6)-Cl(6)#1	116.27(11)	O(5)#1-Cu(6)-O(2)	89.28(14)
O(4)-Cu(6)-Cl(6)#1	100.19(11)	O(5)#2-Cu(8)-Cl(1)	178.18(12)
O(5)#2-Cu(8)-N(21)	86.79(15)	N(21)-Cu(8)-Cl(1)	92.01(12)
O(5)#2-Cu(8)-N(9)	89.86(16)	N(9)-Cu(8)-Cl(1)	91.38(12)
N(21)-Cu(8)-N(9)	176.28(17)	Cu(1)-Cl(6)-Cu(6)#3	71.83(3)
C(34)-O(2)-Cu(6)	126.5(3)		

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

References.

(1) Yang, R. T. Gas Separation by Adsorption Processes, Butterworth, Boston, 1997.