Electronic Supplementary Information (ESI)

for

Two New Metal-Organic Frameworks Based on Tetrazole-Heterocyclic Ligands Accompanied by In-Situ Ligand Formation

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Table S1. Crystal data and structure refinement parameters for **1** and **2**.

	1	**2**
chemical formula	$C_{18}H_{10}N_{10}O_8Zn_2$	$C_{18}H_8N_{10}O_8Cd_2$
formula weight	625.14	717.16
crystal system	Tetragonal	Monoclinic
space group	*Aba*2	*C*2/*c*
a/Å	17.8735(9)	22.552(5)
b/Å	20.9554(14)	22.119(4)
c/Å	20.7462(13)	19.125(4)
β/(°)	90	114.67(3)
V/Å^3	7770.4(8)	8669(3)
Z	8	8
D/g cm^{-3}	1.069	1.099
T/K	173(2)	293(2)
μ/mm^{-1}	1.276	1.018
F(000)	2496	2768
R^a [$I > 2\sigma(I)$]	0.0813	0.0934
wR^b [all data]	0.2230	0.3189
GOF on F^2	1.053	1.018

[a] $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$; [b] $R_w = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma w(F_o^2)^2]^{1/2}$.

Table S2. Selected bond distances (Å) and angles (deg) for **1.**

Zn(1)#1-O(5)#2	1.923(9)	Zn(1)-N(6)	2.022(13)
Zn(1)-O(3)#1	1.886(11)	Zn(1)-N(4)	2.062(12)
Zn(2)-O(1)	1.909(9)	Zn(2)-N(8)#4	2.084(12)
Zn(2)-O(1)#2	1.909(9)	Zn(2)-N(8)#3	2.084(12)
Zn(3)-N(2) #6	2.023(12)	Zn(3)-N(2)	2.023(12)
Zn(3)-O(8)#4	1.925(12)	Zn(3)-O(8)#5	1.925(12)
O(3)#1-Zn(1)-O(5)#2	113.9(5)	O(5)#2-Zn(1)-N(4)	101.5(4)
O(1)#3-Zn(2)-O(1)	127.5(6)	O(1)#3-Zn(2)-N(8)#4	100.2(4)
O(1)-Zn(2)-N(8)#5	100.2(4)	O(1)#3-Zn(2)-N(8)#5	109.5(4)
O(8)#6-Zn(3)-O(8)#5	107.7(13)	O(1)-Zn(2)-N(8)#4	109.5(4)
N(6)-Zn(1)-N(4)	105.9(5)	O(5)#2-Zn(1)-N(6)	111.6(5)
N(8)#4-Zn(2)-N(8)#5	109.5(7)	O(8)#6-Zn(3)-N(2)	100.3(6)
N(2)-Zn(3)-N(2)#7	107.6(7)	O(8)#4-Zn(3)-N(2)	121.2(5)
O(8)#6-Zn(3)-N(2)#7	121.2(5)	O(8)#5-Zn(3)-N(2)#7	100.3(6)
O(3)#1-Zn(1)-N(6)	122.2(5)	O(3)#1-Zn(1)-N(4)	98.0(5)

Symmetry codes:

#1 x+1/2,-y+3/2,z+0 #2 x-1/2,-y+3/2,z+0 #3 -x,-y+2,z #4 x-1/2,-y+2,z+1/2

#5 -x+1/2,y,z+1/2 #6 -x+3/2,y,z+1/2 #7 -x+1,-y+2,z

Table S3. Selected bond distances (Å) and angles (deg) for **2.**

O(5)-Cd(3)	2.372(8)	Cd(1)-O(1)	2.358(7)
O(6)-Cd(3)	2.372(8)	O(3)-Cd(2)#3	2.321(7)
O(7)-Cd(1)#2	2.358(7)	N(9)-Cd(1)#1	2.246(8)
O(8)-Cd(1)#2	2.440(7)	N(7)-Cd(3)	2.226(8)
O(4)-Cd(2)#3	2.391(7)	Cd(1)-N(2)	2.269(7)
Cd(1)-O(2)	2.369(8)	Cd(2)-N(4)	2.261(8)
Cd(2)-N(4) #4	2.261(8)	O(3)#6-Cd(2)-O(4)#7	97.6(3)
O(7)#5-Cd(1)-O(1)	88.7(3)	N(9)#4-Cd(1)-N(2)	95.7(3)
O(7)#5-Cd(1)-O(2)	96.7(3)	N(4)-Cd(2)-N(4)#8	99.2(4)
O(1)-Cd(1)-O(2)	55.9(3)	N(7)-Cd(3)-N(7)#9	96.6(5)
O(7)#5-Cd(1)-O(8)#5	55.2(3)	N(9)#4-Cd(1)-O(7)#5	145.3(3)
O(1)-Cd(1)-O(8)#5	86.7(3)	N(2)-Cd(1)-O(7)#5	95.2(3)
O(2)-Cd(1)-O(8)#5	135.4(3)	N(9)#4-Cd(1)-O(1)	92.2(3)
O(3)#6-Cd(2)-O(3)#7	90.1(4)	N(2)-Cd(1)-O(1)	159.7(3)
O(3)#7-Cd(2)-O(4)#7	54.5(3)	N(9)#4-Cd(1)-O(2)	112.4(3)
O(3)#6-Cd(2)-O(4)#6	54.5(3)	N(2)-Cd(1)-O(2)	103.8(3)
O(4)#7-Cd(2)-O(4)#8	135.4(3)	N(9)#4-Cd(1)-O(8)#5	90.2(3)
O(6)-Cd(3)-O(6)#9	88.9(5)	N(2)-Cd(1)-O(8)#5	111.8(3)
O(6)-Cd(3)-O(5)#9	91.3(3)	N(4)-Cd(2)-O(3)#7	95.6(3)
O(6)#9-Cd(3)-O(5)	91.3(3)	O(6)-Cd(3)-O(5)	54.5(3)
O(6)#9-Cd(3)-O(5)#9	54.5(3)	O(3)#7-Cd(2)-O(4)#6	97.6(3)
O(5)#9-Cd(3)-O(5)	133.9(4)	N(4)-Cd(2)-O(4)#6	90.4(3)
N(4)-Cd(2)-O(3)#6	144.9(3)	N(4)#8-Cd(2)-O(3)#6	95.6(3)
N(4)#8-Cd(2)-O(4)#7	90.4(3)	N(4)#8-Cd(2)-O(3)#7	144.9(3)
N(4)-Cd(2)-O(4)#7	113.9(3)	N(4)#8-Cd(2)-O(4)#6	113.9(3)
N(7)#9-Cd(3)-O(5)#9	103.8(3)	N(7)-Cd(3)-O(6)	158.3(3)
N(7)#9-Cd(3)-O(5)	106.4(3)	N(7) -Cd(3)-O(5)	103.8(3)

N(7)#9-Cd(3)-O(6)#9	158.3(3)	N(7)#9-Cd(3)-O(6)	91.2(3)
N(7)-Cd(3)-O(5)#9	106.4(3)	N(7) -Cd(3)-O(6)#9	91.2(3)

Symmetry codes:

#1 x,-y+1,z-1/2 #2 x-1/2,-y+1/2,z-1/2 #3 x+1/2,y+1/2,z #4 x,-y+1,z+1/2

#5 x+1/2,-y+1/2,z+1/2 #6 -x,y,-z+1/2 #7 x-1/2,y-1/2,z #8 -x+1/2,y-1/2,-z+1/2

#9 -x,y,-z-1/2

Table S4. Gas-adsorption data for **1a**.

Gas	Temperature and Pressure	Amounts of gas adsorb		
		wt%	cm^3/g	mmol/g
N_2	77 K and 773 mmHg	0.004	0.03	0.001
	273 K and 770 mmHg	0.65	5.21	0.23
	298 K and 771 mmHg	0.31	2.49	0.11
CO_2	195 K and 738 mmHg	22.88	116.47	5.20
	273 K and 771 mmHg	10.45	53.18	2.37
	298 K and 770 mmHg	7.73	39.34	1.76
CH_4	273 K and 770 mmHg	1.40	19.56	0.87
	298 K and 770 mmHg	0.80	11.18	0.50

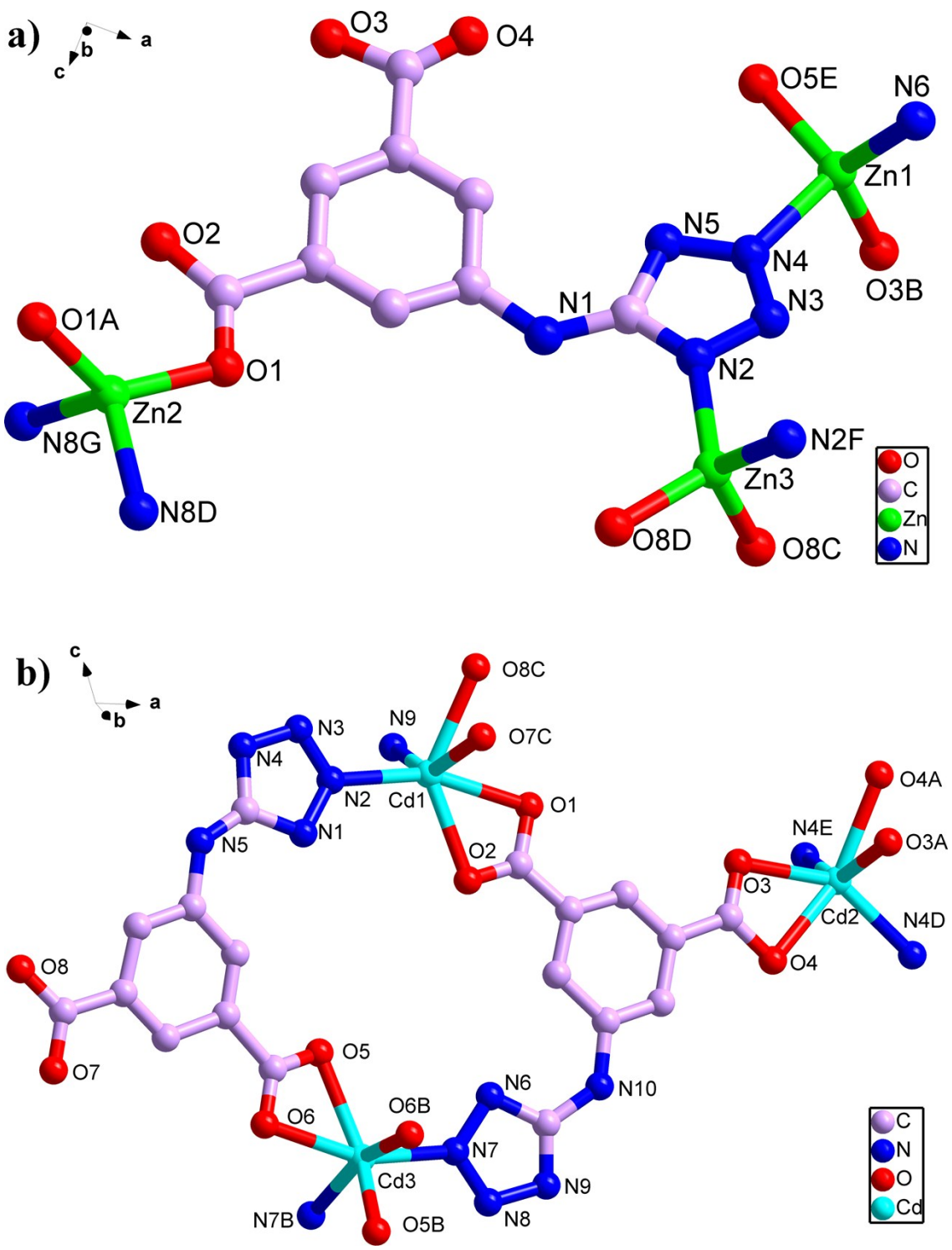

Figure S1. The coordination environments of **1**(a) and **2**(b). Hydrogen atoms are omitted for clarity.For **1**(a), A, B, C, D, E, F and G indicate symmetry operators –x, 2-y, z; 0.5+x, 1.5-y, z; 1.5-x, y, 0.5+z; -0.5+x, 2-y, 0.5+z; -0.5+x, 1.5-y, z; 1-x, 2-y, z; 0.5-x, y, 0.5+z, respectively. For **2**(b), A, B, C, D and E indicate symmetry operators 1-x, y, 2.5-z; -x, y, 1.5-z; 0.5+x, 0.5-y, 0.5+z; 0.5+x, 0.5+y, z; 0.5-x, 0.5+y, 2.5-z, respectively.

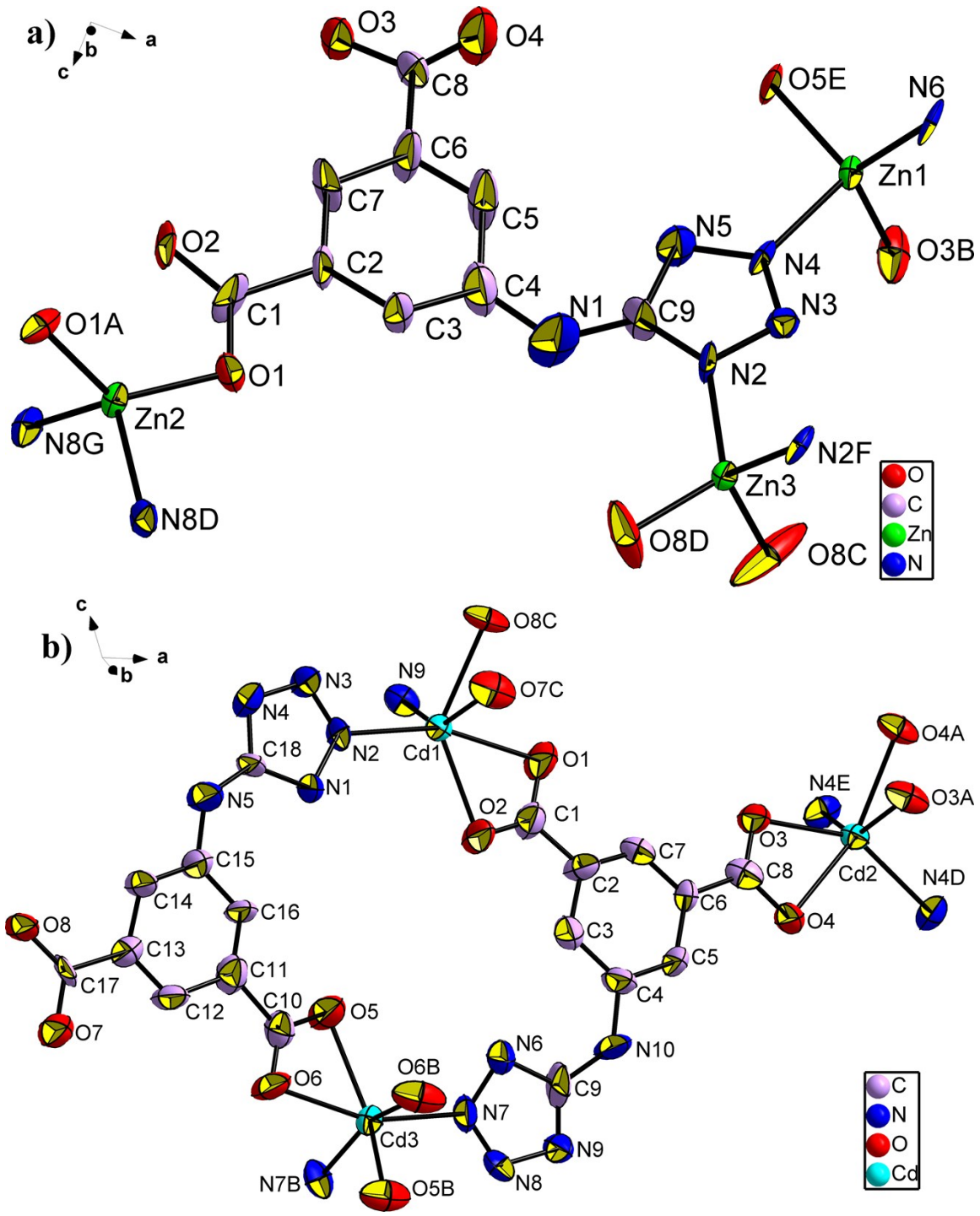

Figure S2 The structures of the $[Zn_2(HL)_2]$ of **1**(a) and complex $[Cd_2(HL)_2]$ of **2**(b). Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. For **1**(a), A, B, C, D, E, F and G indicate symmetry operators –x, 2-y, z; 0.5+x, 1.5-y, z; 1.5-x, y, 0.5+z; -0.5+x, 2-y, 0.5+z; -0.5+x, 1.5-y, z; 1-x, 2-y, z; 0.5-x, y, 0.5+z, respectively. For **2**(b), A, B, C, D and E indicate symmetry operators 1-x, y, 2.5-z; -x, y, 1.5-z; 0.5+x, 0.5-y, 0.5+z; 0.5+x, 0.5+y, z; 0.5-x, 0.5+y, 2.5-z, respectively.

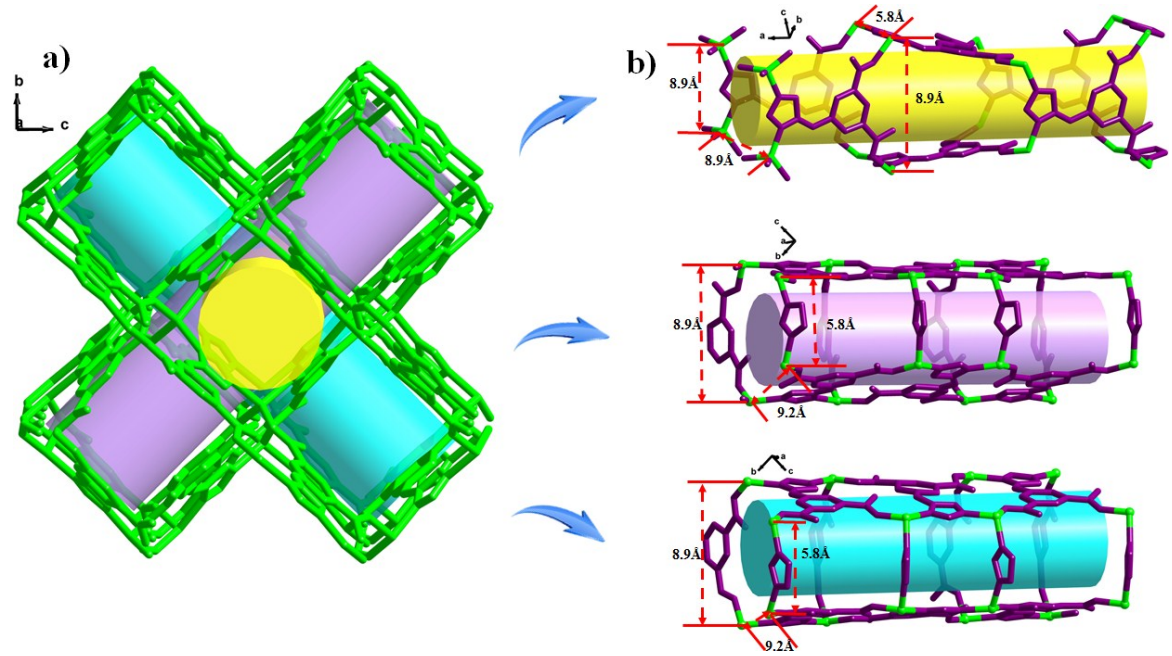

Figure S3. The crystal structure of **1.** a) 3D framework showing open 3D intersecting channel system; b) Three types of channels from different directions. The light green represent Zn(II) centers, and the violet represent the ligand HL^{2-}. H atoms and solvent molecules are omitted for clarity.

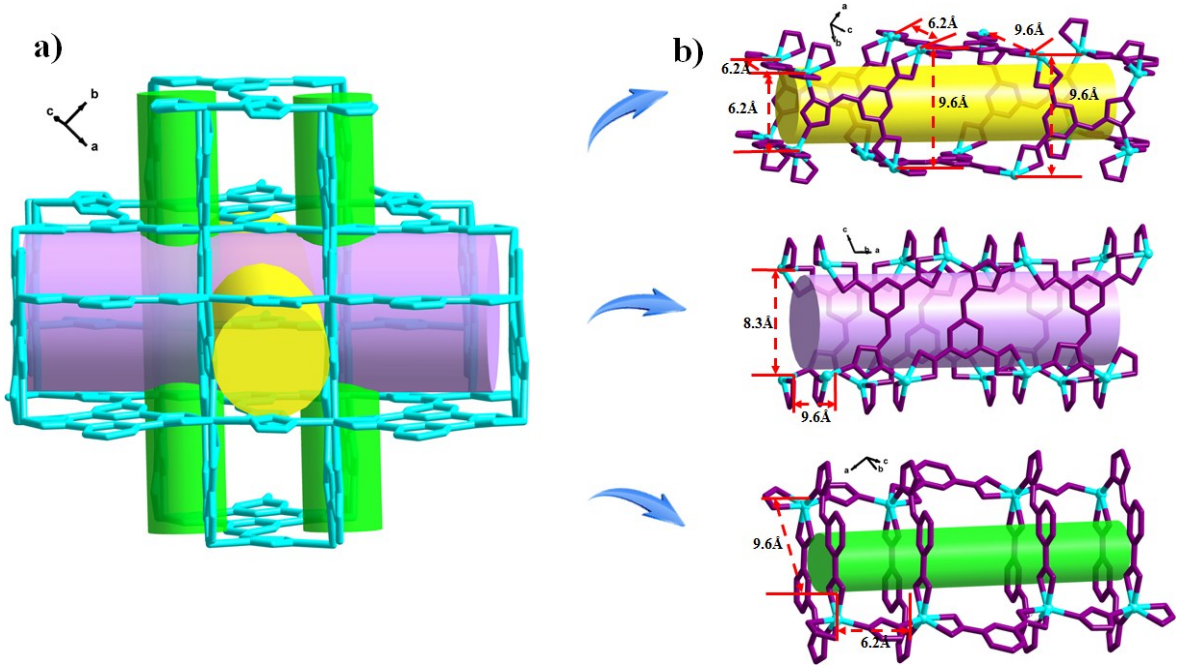

Figure S4. The crystal structure of **2.** a) 3D framework showing open 3D intersecting channel system; b) Three types of channels from different directions. The bright blue represent Cd(II) centers, and the violet represent the ligand L^{3-}. H atoms and solvent molecules are omitted for clarity.

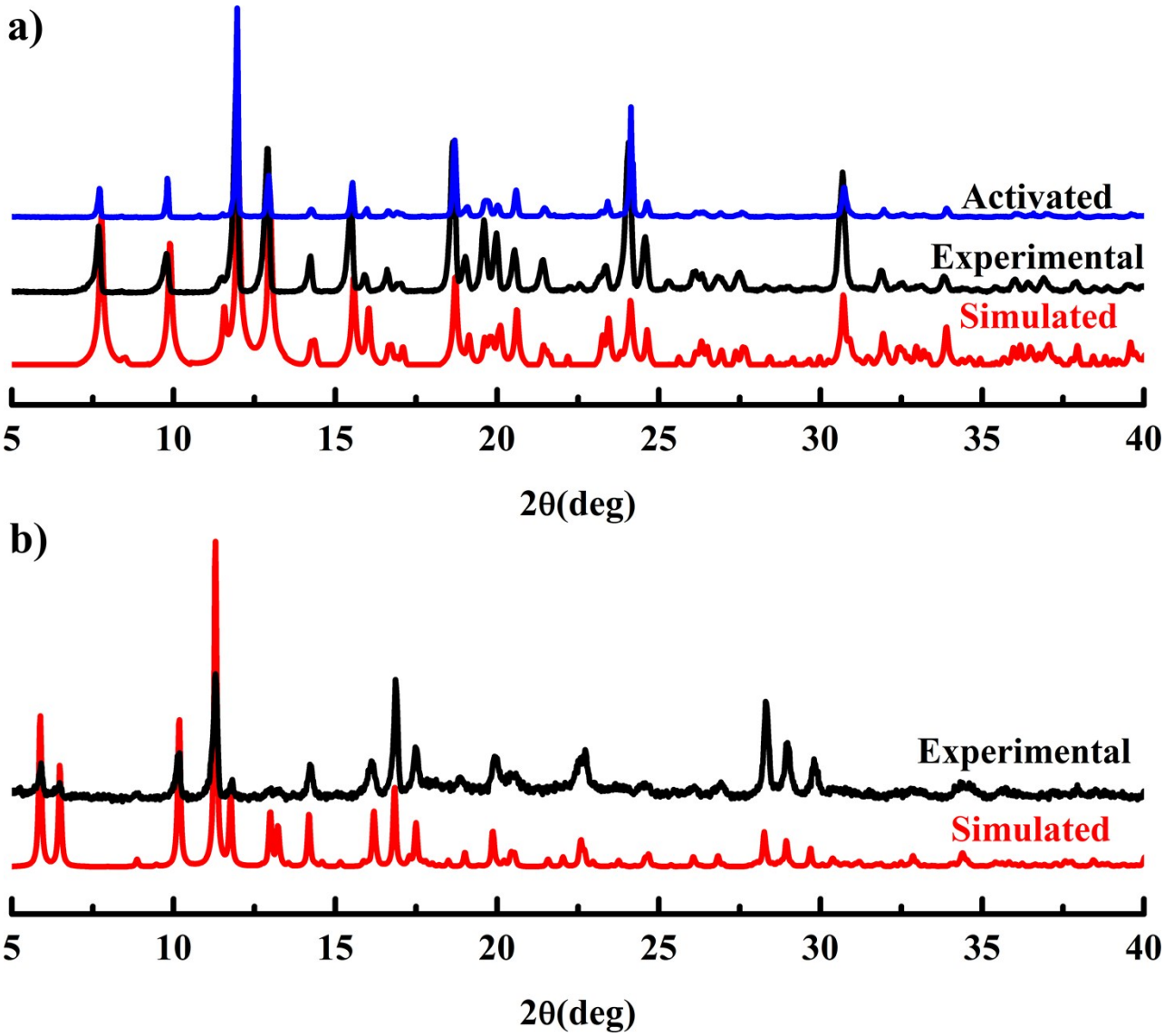

Figure S5. Power X-ray diffraction(PXRD) patterns for **1**(a) and **2**(b).

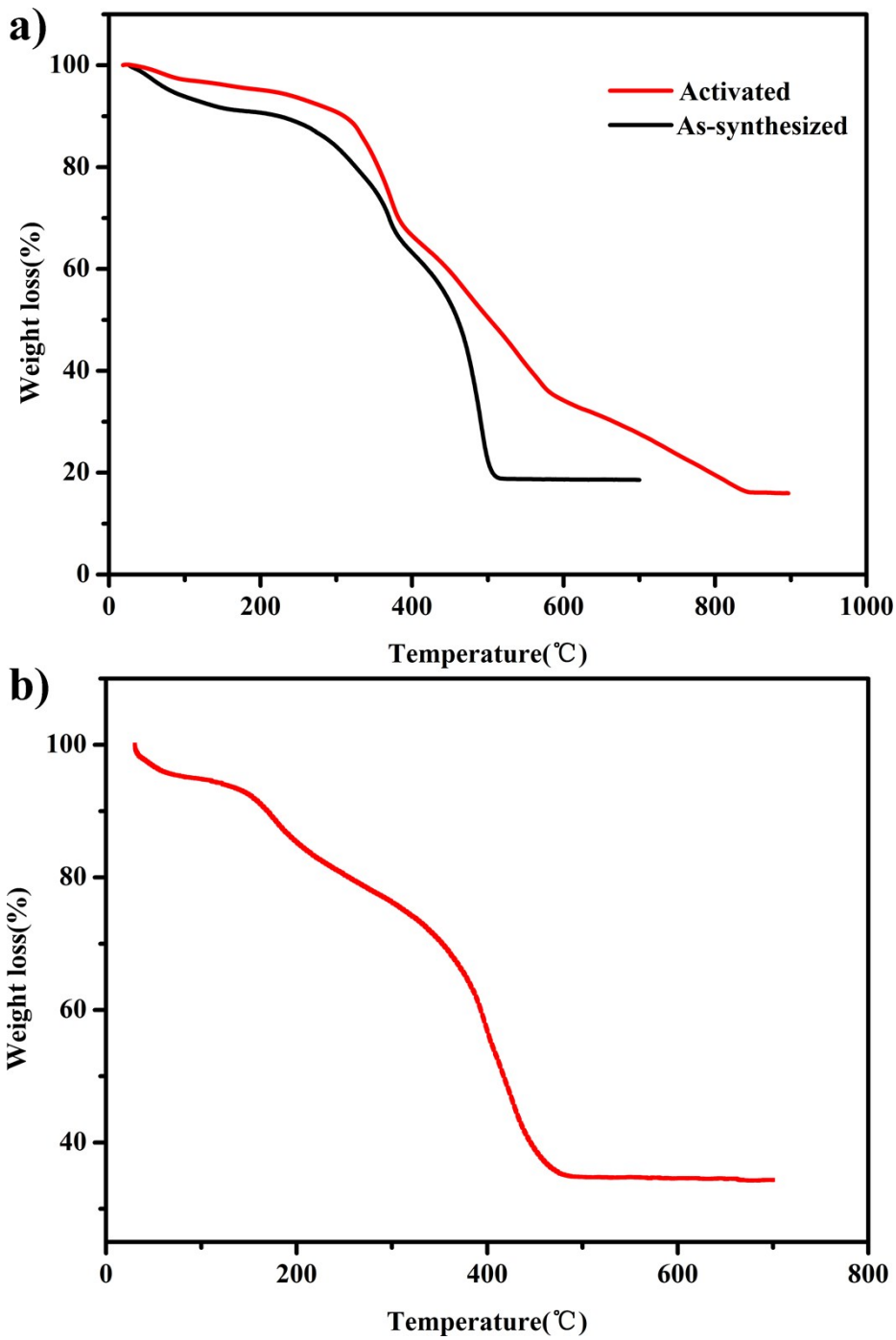

Figure S6. Thermogravimetric analyses (TGA) curves for **1** (a) and **2** (b).

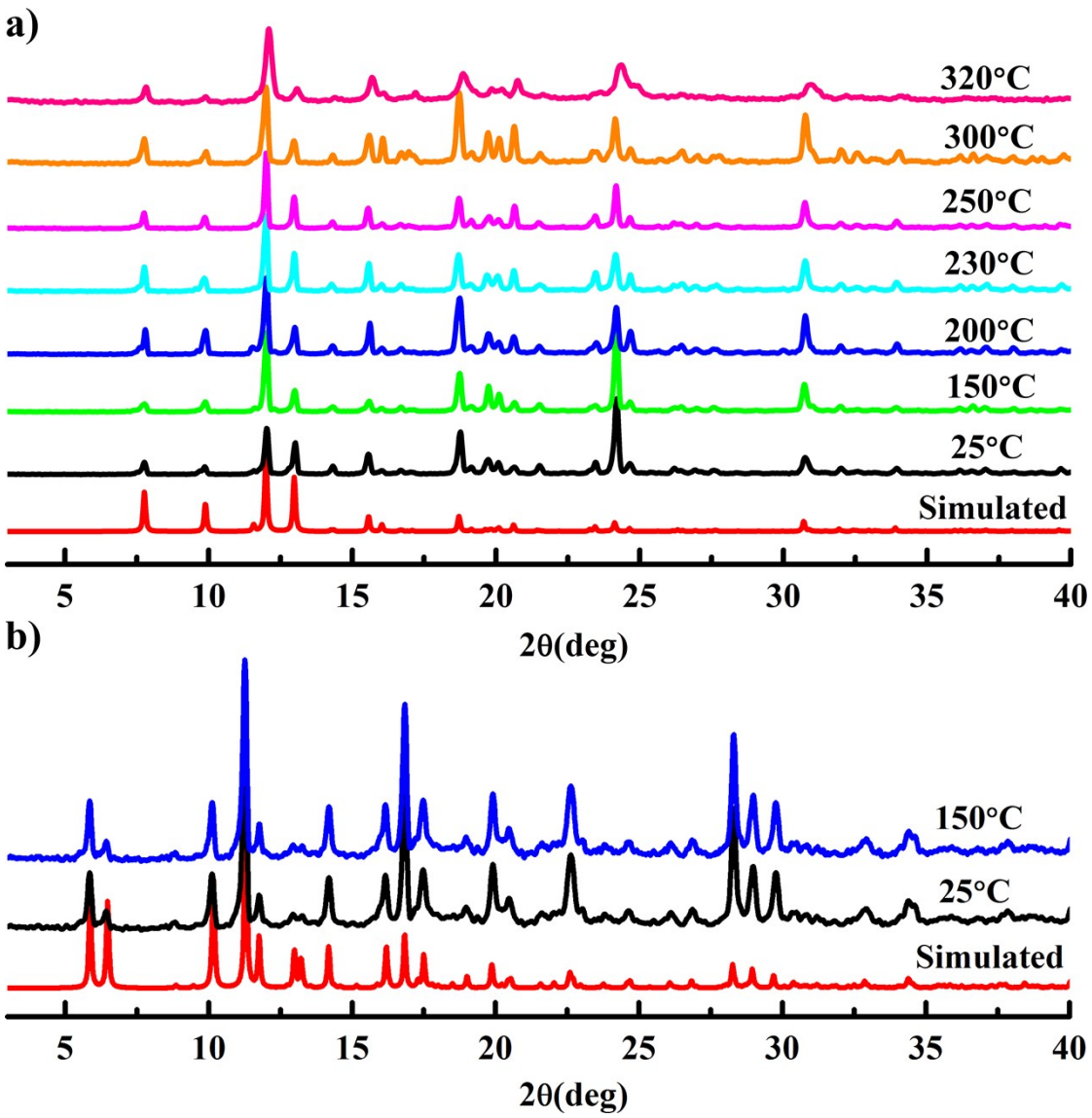

Figure S7. Power X-ray diffraction(PXRD) patterns for **1**(a) and **2**(b) at different temperature.

Experimental method:

Bulk of **1** and **2** were synthesized and the purities were examined by Powder X-ray diffraction (PXRD) (Figure S6a and S6b, Supporting Information). Then **1** and **2** were heating on Micrometrics ASAP 2020 volumetric gas sorption instrument at different temperature. The heating process were from 20°C to 150°C at the rate of 10°C/min, and constant about 15min, and then remove the sample immediately to measure the PXRD on a Rigaku Miniflex 600. Other PXRD at different temperature were measured in the same way.

Sorption Measurements.

Gas sorption experiments were carried out with a Micrometrics ASAP 2020 M volumetric gas sorption instrument. Before the measurement, the sample was soaked in acetone (CH_3COCH_3) for 3 days to remove DMF and H_2O, filtrated and dried at room temperature. Then the sample was loaded in the sample tube and dried under high vacuum (less than 10^{-5} Torr) at 100°C overnight to remove acetone and all residue solvents in the channels. 176.3 mg of the desolvated sample was used to the whole adsorption measurements. The BET (Brunauer-Emmet-Telle) was characterized by CO_2 isotherm measurement at 195 K in a dry ice-acetone bath. The gas sorption experiments of CO_2, CH_4 and N_2 were carried out at 273 K in an ice-water bath and 298 K in a temperature controlled circular bath, respectively.

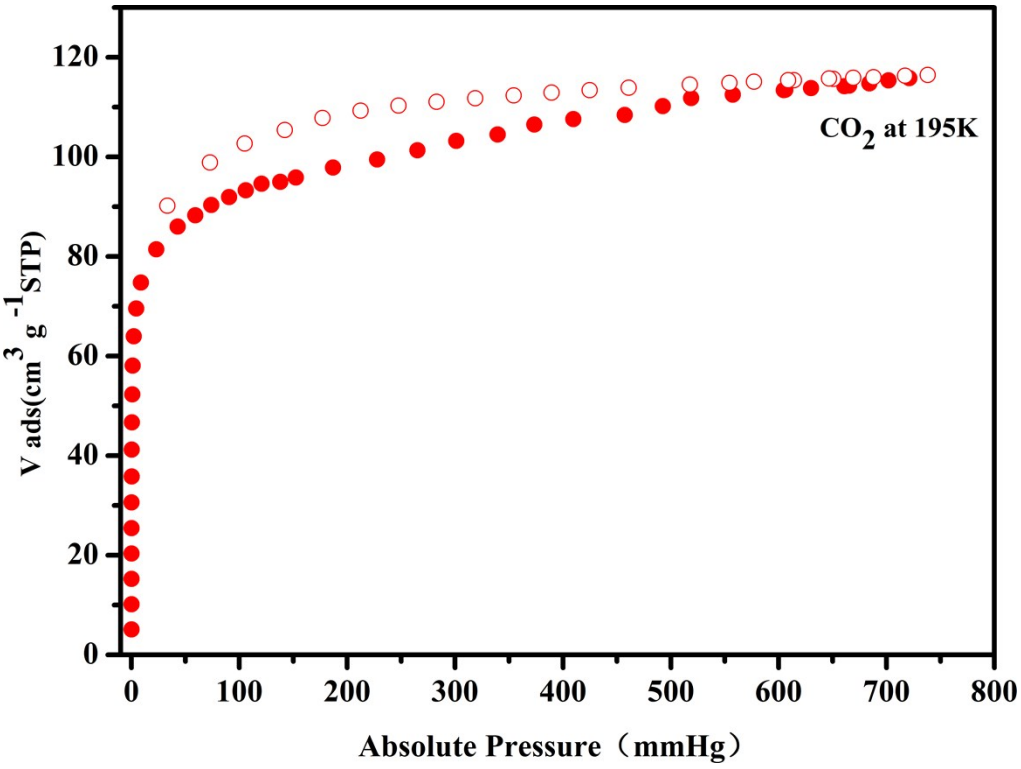

Figure S8. Gas sorption isotherms for **1a**. Adsorption and desorption data are shown as filled and open symbols, respectively.

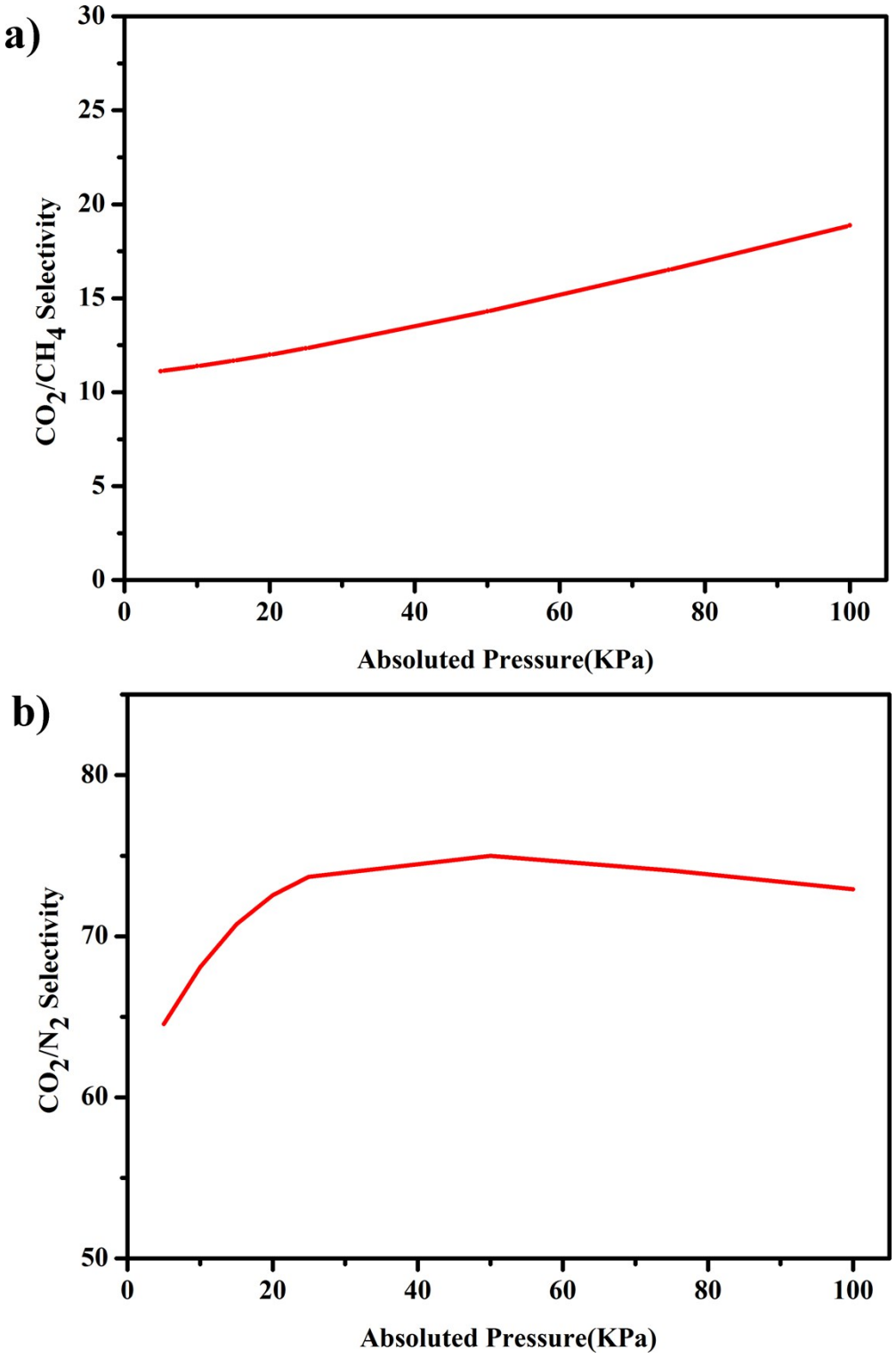

Figure S9. IAST predicted selectivity for **1a**: (a) CO_2 over CH_4 (50:50) at 298 K, and (b) CO_2 over N_2 (15:85) at 298 K.

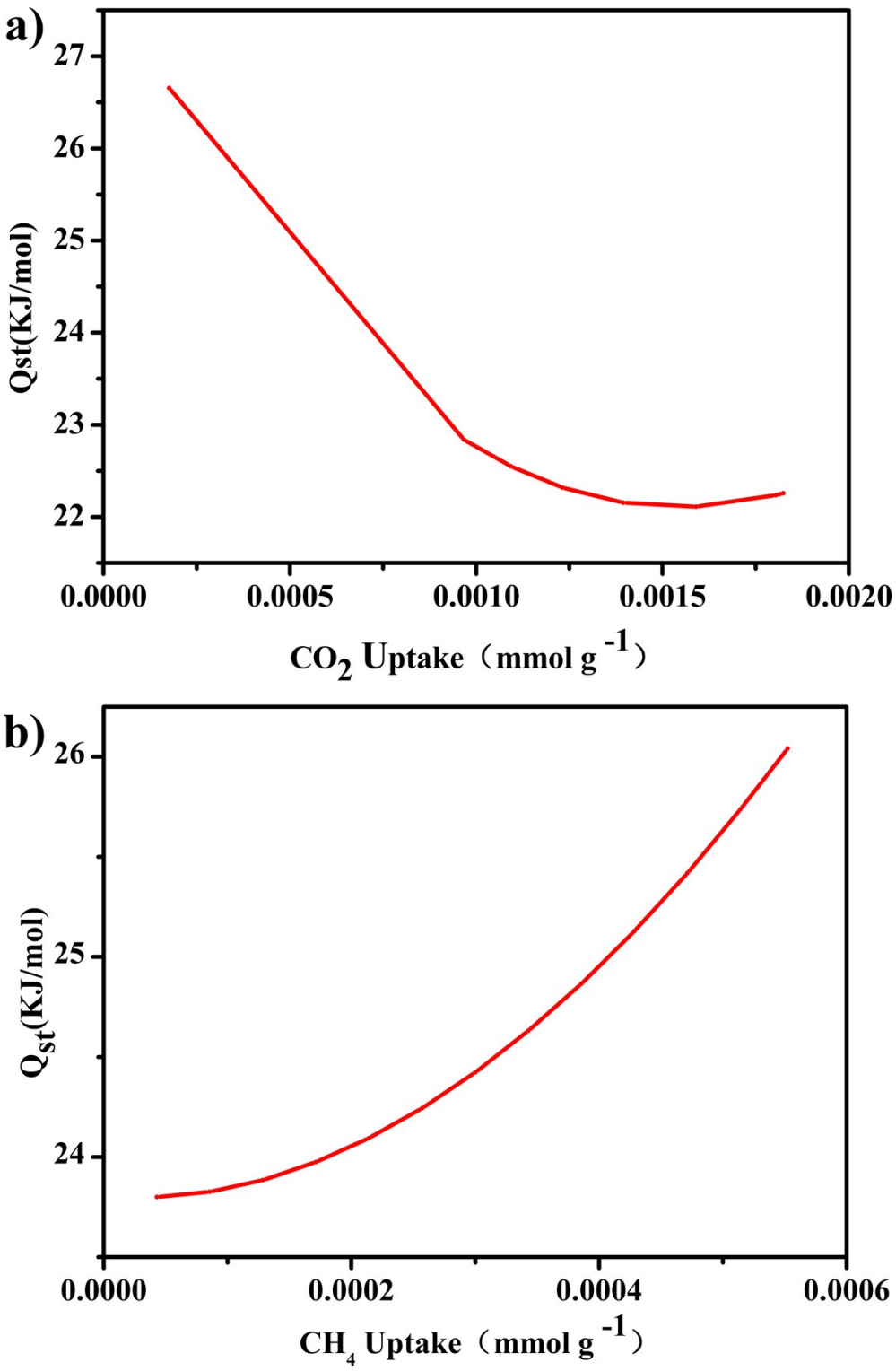

Figure S10. Isosteric heat of CO_2 (a) and CH_4 (b) adsorption for **1a**.