Supporting Information

Targeted Structure Modulation of "Pillar-Layered" Metal-Organic Frameworks for CO_2 Capture

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Table S1. Selected Bond Lengths (Å) and Angles (°) for Complexes 1-2[a].

Compound 1			
N(1)-Zn(1)	2.011(3)	Zn(1)-O(6)#4	1.967(3)
N(3)-Zn(2)#2	2.089(4)	O(1W)-Zn(2)	2.146(3)
O(1)-Zn(1)	1.932(3)	Zn(2)-O(7)#6	2.138(3)
O(3)-Zn(1)#3	1.954(3)	Zn(2)-O(8)#6	2.196(3)
O(4)-Zn(2)	2.029(3)	Zn(2)-C(16)#6	2.489(4)
O(1)-Zn(1)-O(3)#5	111.68(12)	O(7)#6-Zn(2)-O(5)	87.27(11)
O(1)-Zn(1)-O(6)#4	95.62(12)	O(4)-Zn(2)-O(1W)	86.28(11)
O(3)#5-Zn(1)-O(6)#4	102.77(12)	N(3)#2-Zn(2)-O(1W)	86.20(13)
O(1)-Zn(1)-N(1)	117.17(14)	O(7)#6-Zn(2)-O(1W)	93.38(12)
O(3)#5-Zn(1)-N(1)	114.44(13)	O(5)-Zn(2)-O(1W)	172.85(11)
O(6)#4-Zn(1)-N(1)	112.67(13)	N(3)#2-Zn(2)-O(5)	89.89(12)
O(4)-Zn(2)-N(3)#2	104.62(13)	O(7)#6-Zn(2)-O(5)	87.27(11)
O(4)-Zn(2)-O(7)#6	103.32(11)	O(4)-Zn(2)-O(1W)	86.28(11)
N(3)#2-Zn(2)-O(7)#6	151.97(13)	N(3)#2-Zn(2)-O(1W)	86.20(13)
O(4)-Zn(2)-O(5)	100.51(11)	O(7)#6-Zn(2)-O(1W)	93.38(12)
N(3)#2-Zn(2)-O(5)	89.89(12)	O(5)-Zn(2)-O(1W)	172.85(11)
Compound 2			
C(8)-Zn(2)#1	2.488(2)	O(1W)-Zn(2)	2.1267(19)
N(1)-Zn(1)	2.002(2)	Zn(1)-O(7)#5	1.9337(17)
O(1)-Zn(2)	2.1816(16)	Zn(2)-N(2)#6	2.085(2)
O(2)-Zn(1)#3	1.9605(17)	Zn(2)-O(3)#3	2.1517(17)
O(7)#5-Zn(1)-O(6)	113.37(7)	O(5)-Zn(2)-O(1)	97.84(6)
O(7)#5-Zn(1)-O(2)#1	96.03(7)	N(2)#6-Zn(2)-O(1)	87.96(7)
O(6)-Zn(1)-O(2)#1	101.42(7)	O(1W)-Zn(2)-O(1)	174.26(7)
O(7)#5-Zn(1)-N(1)	116.64(8)	O(3)#3-Zn(2)-O(1)	84.63(6)
O(6)-Zn(1)-N(1)	114.70(7)	O(5)-Zn(2)-O(4)#3	100.01(6)
O(2)#1-Zn(1)-N(1)	111.90(7)	N(2)#6-Zn(2)-O(4)#3	151.59(7)
O(5)-Zn(2)-N(2)#6	108.36(7)	O(1W)-Zn(2)-O(4)#3	93.71(7)
O(5)-Zn(2)-O(1W)	87.76(7)	O(3)#3-Zn(2)-O(4)#3	60.79(6)
N(2)#6-Zn(2)-O(1W)	89.11(8)	O(1)-Zn(2)-O(4)#3	86.54(6)
O(5)-Zn(2)-O(3)#3	160.58(6)	O(5)-Zn(2)-C(8)#3	130.77(7)

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

Table S2. The elapsed time for the the sorption of same amount of N_2 at 77 K.

	Quantity Adsorbed ($cm^{-3}g^{-1}$ STP)	Elapsed Time (h:min)
Complex 1	5.0518	01:47
	10.1034	02:56
Complex 2	5.5949	09:05
	9.8225	14:48

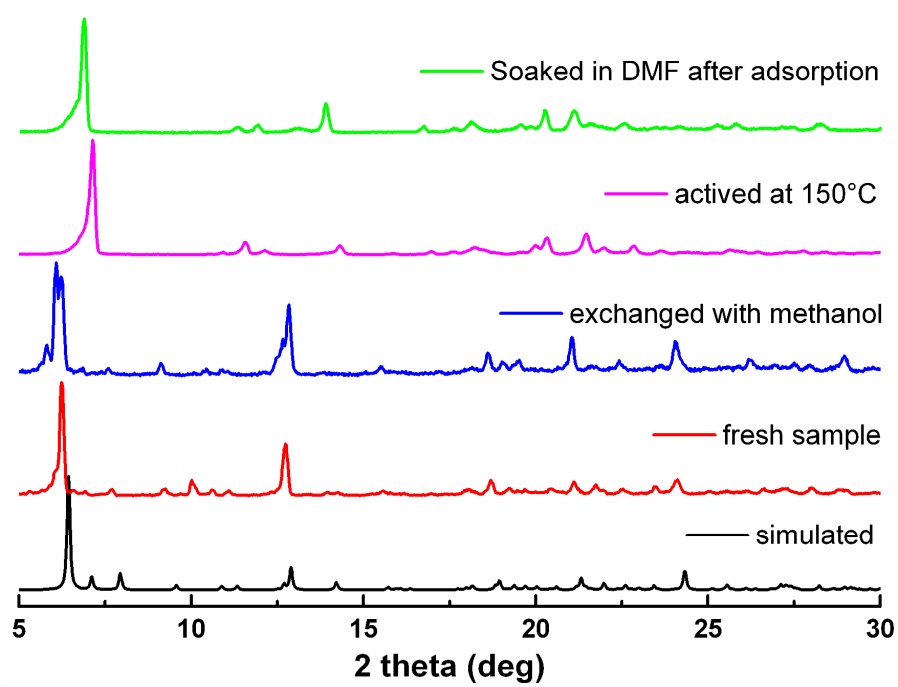


Figure S1. PXRD patterns of complex **1.**

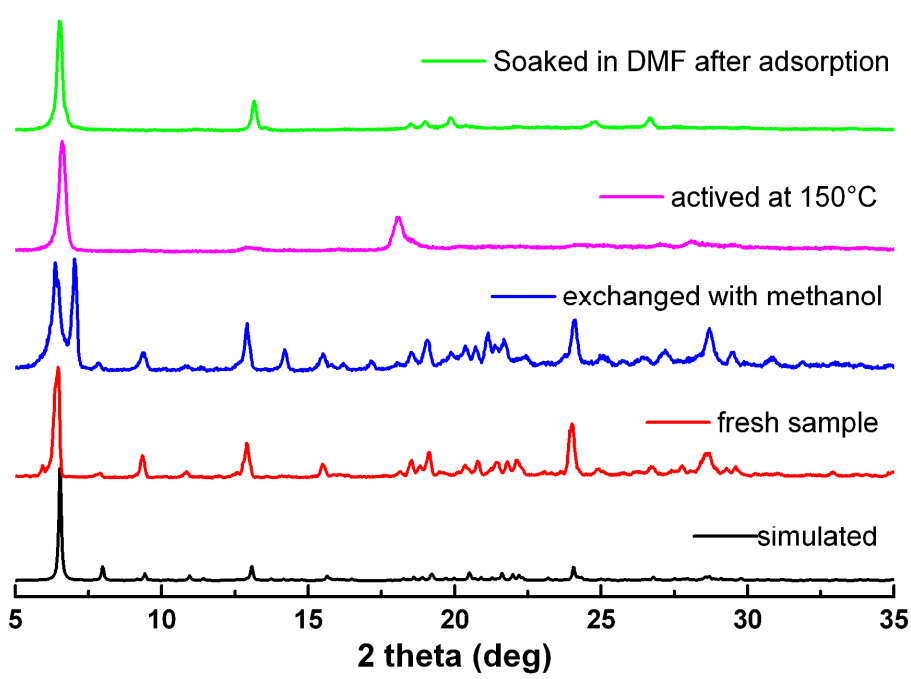


Figure S2. PXRD patterns of complex **2**.

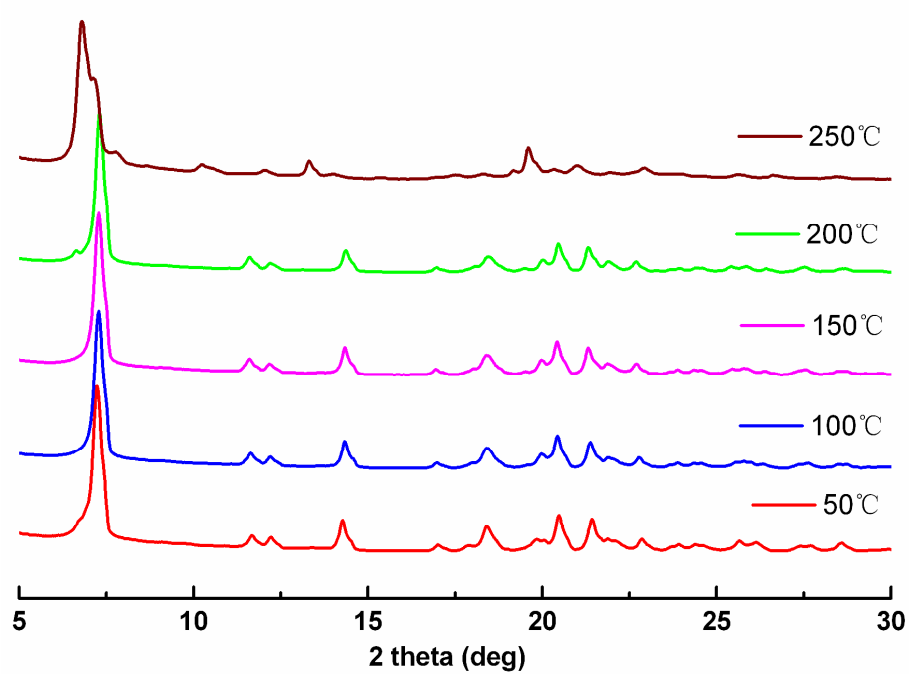


Figure S3. the temperature-dependent PXRD patterns of complex **1**.

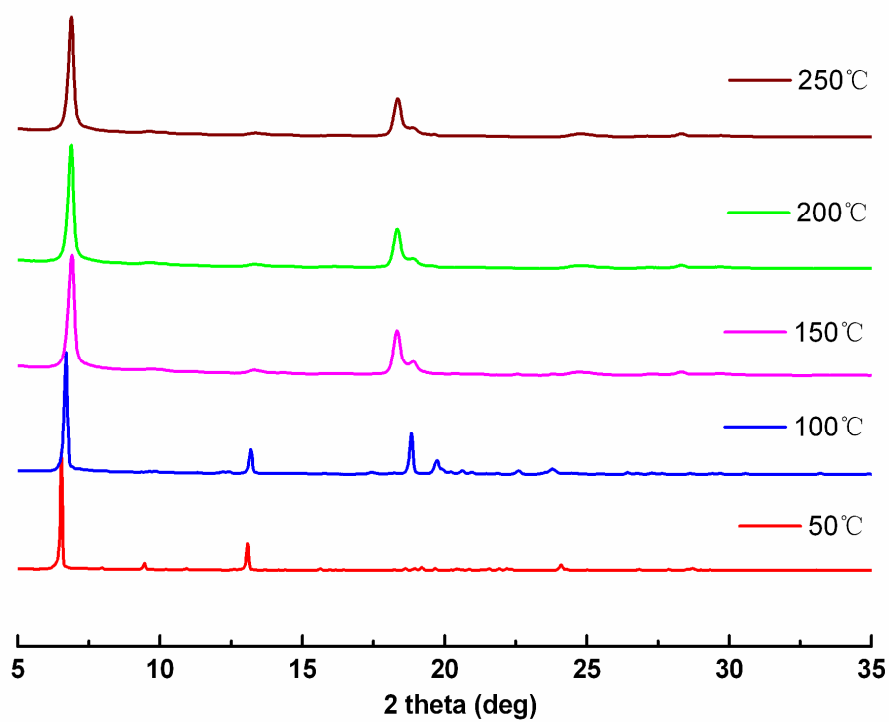


Figure S4. the temperature-dependent PXRD patterns of complex **2**.

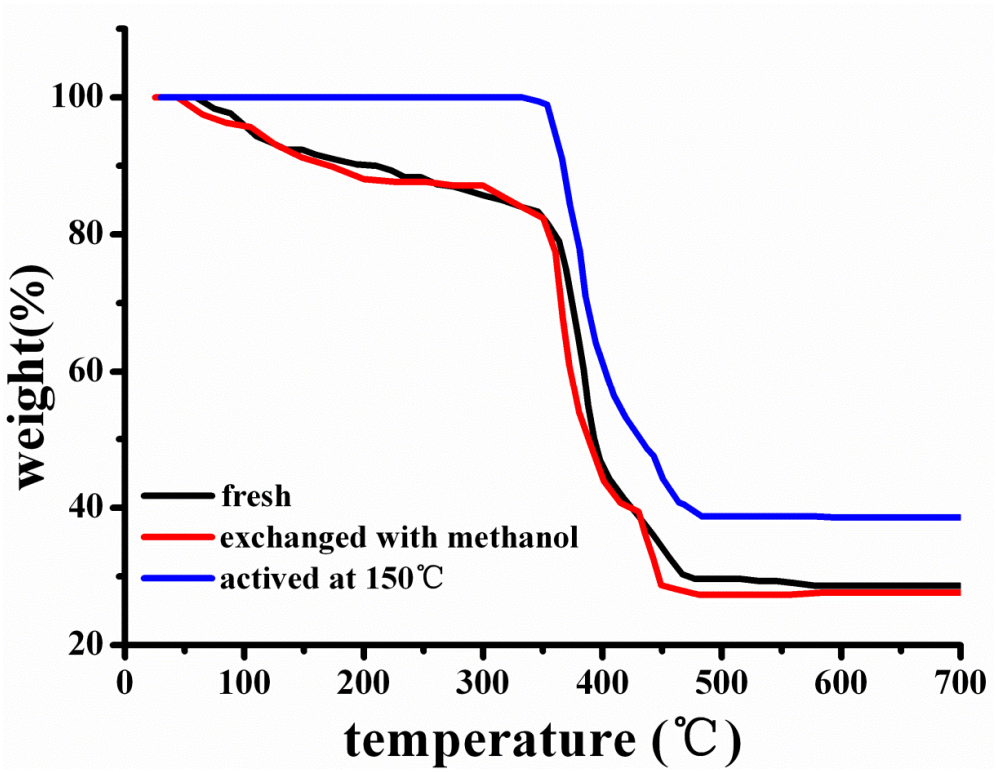


Figure S5. The TGA diagram for complex **1**.

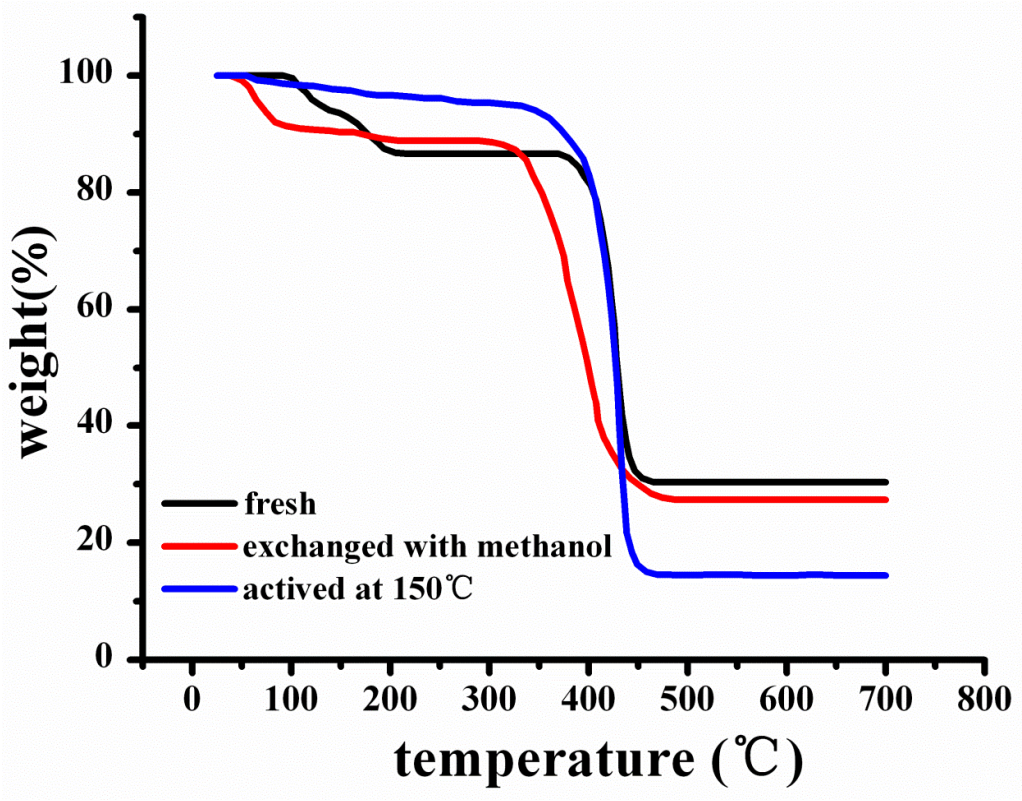


Figure S6. The TGA diagram for complex **2**.

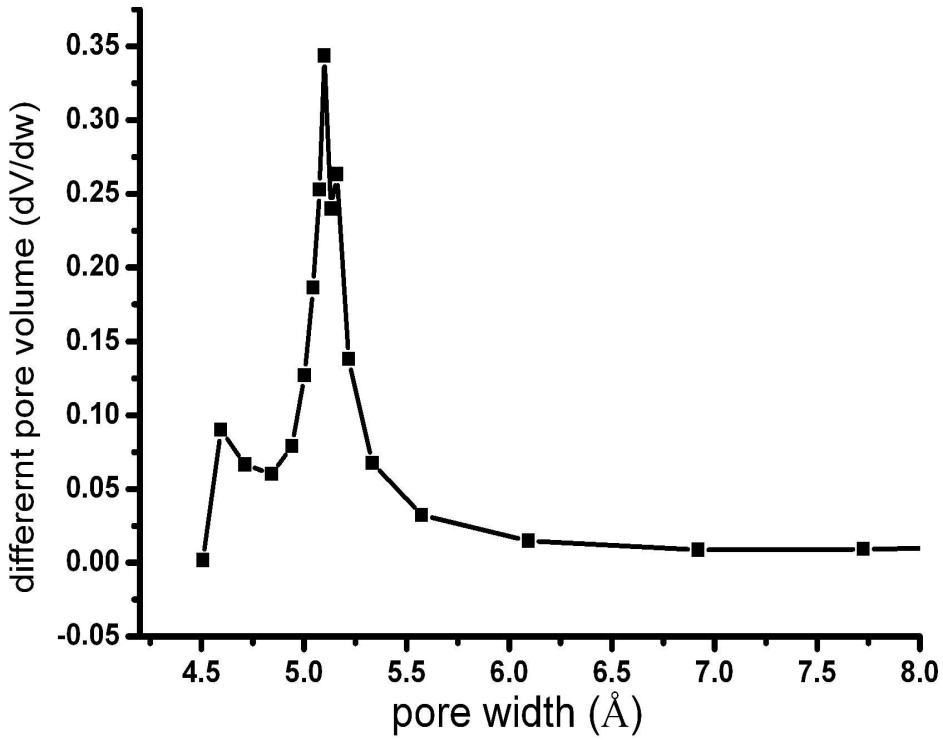


Figure S7. The pore distribution plot of complex **1**.

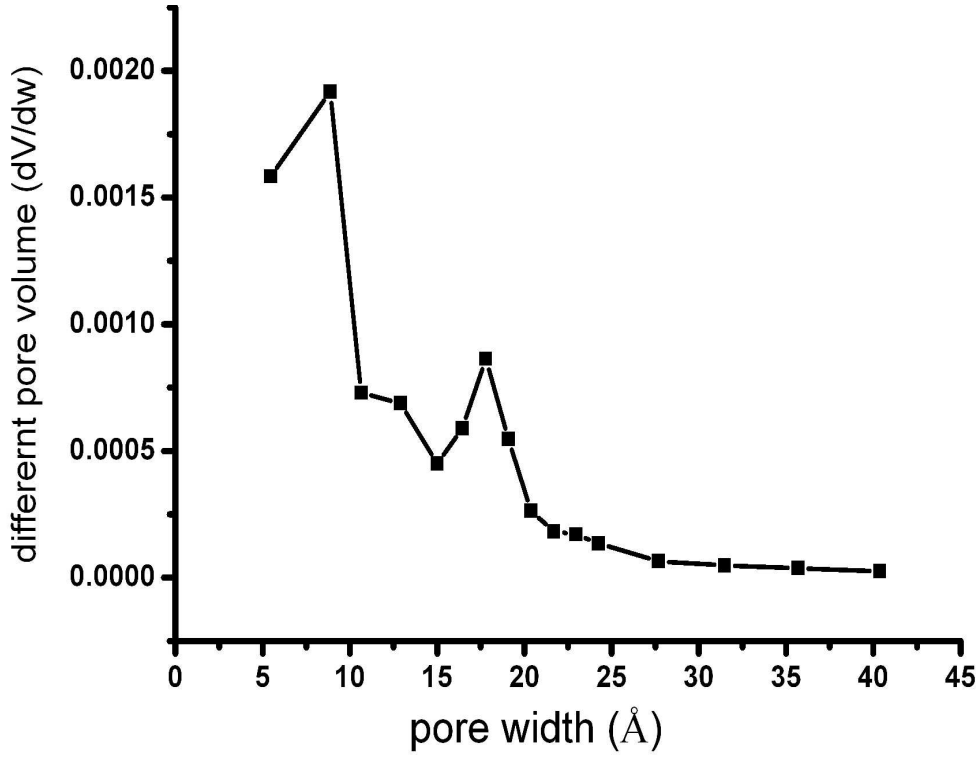


Figure S8. The pore distribution plot of complex **2**.

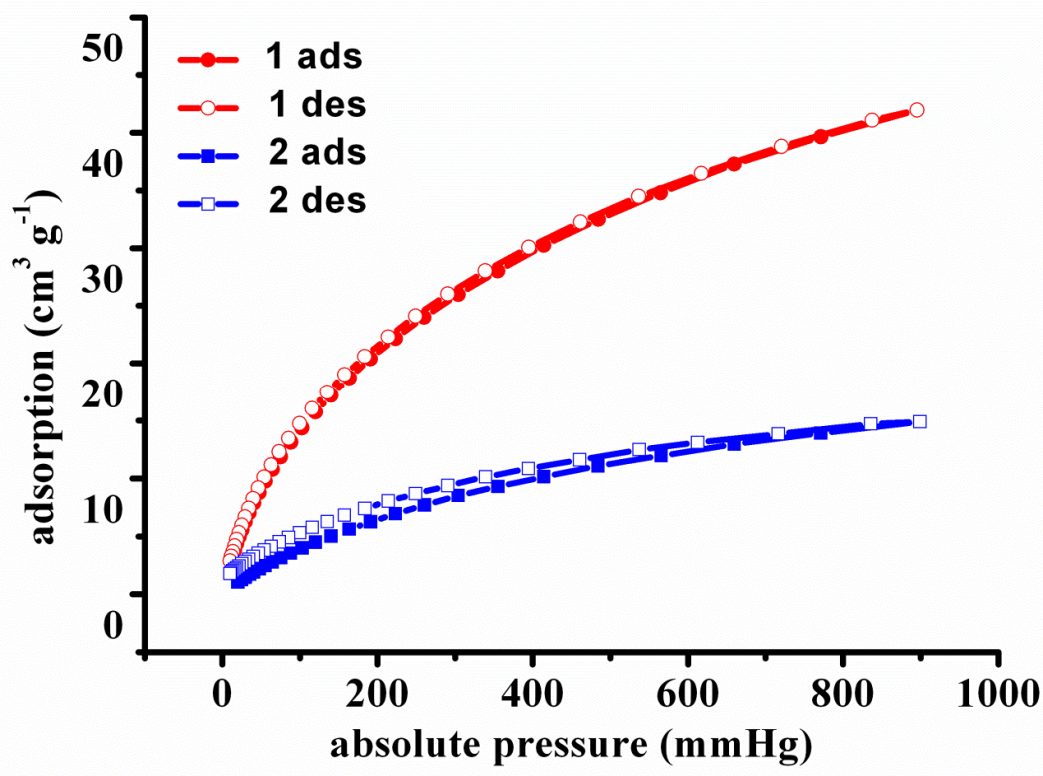


Figure S9. The CO_2 adsorption capacities of complexes **1-2** at 298 K.

Analysis of Gas Sorption Isotherms:

All the methods employed here for dealing with the sorption data are according to the reference 1. The gas adsorption isotherms were fitted using the Langmuir-Freundlich equation. The surface area of compound **1** and **2** were determined by fitting the N_2 isotherm to the BET equation. The enthalpy of gas adsorption onto the framework was calculated using a modified version of the Clausius-Clapeyron equation:

$$\ln\left(\frac{P_1}{P_2}\right) = \Delta H_{ads} \times \frac{T_2 - T_1}{RT_1T_2} \qquad \textbf{(I)}$$

Where P_i=pressure for isotherm i
T_i=temperature for isorherm i

R=8.315J/(K•mol)

Equation (**I**) can be used as a function of the quantity of adsorbed gases to calculate the adsorption enthalpy. The pressures as a function of the amount of gases adsorbed were determined by using Langmuir-Freundlich fit for the adsorption isotherms.

$$\frac{Q}{Q_m} = \frac{B \times P^{(1/t)}}{1 + B \times P^{(1/t)}} \qquad \textbf{(II)}$$

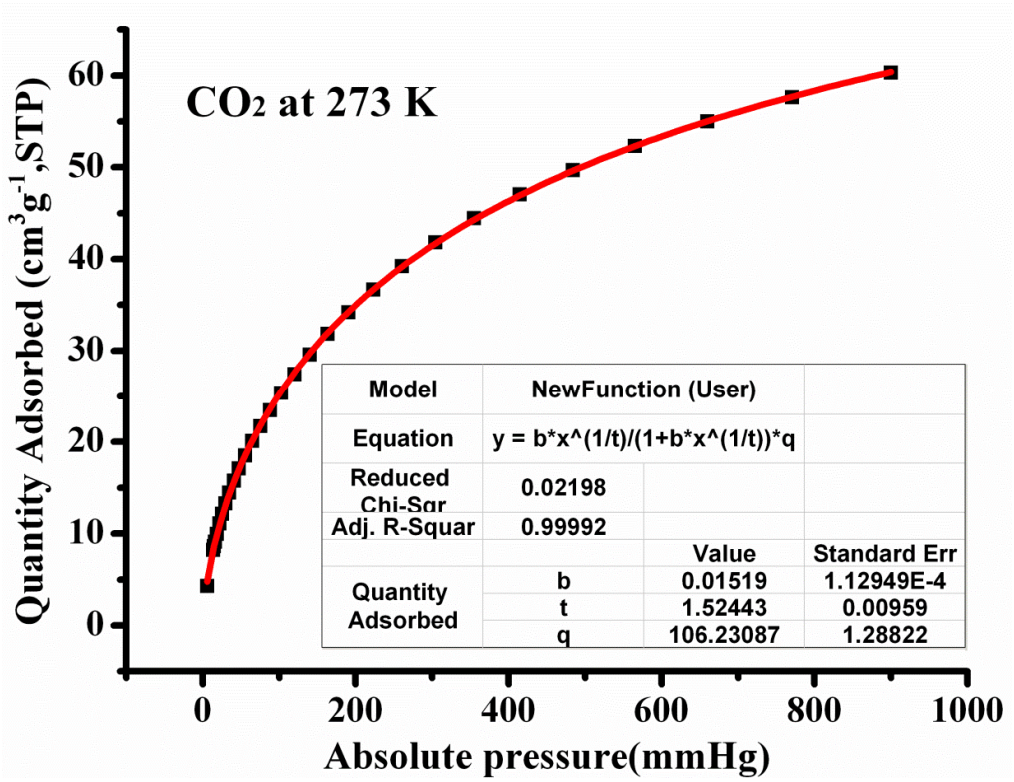
Where $\boldsymbol{Q}$ = moles adsorbed
$\mathbf{Q}_{\boldsymbol{m}}$= moles adsorbed at saturation
$\boldsymbol{P}$=pressure
$\boldsymbol{B}$ and t are constants

Rearranging (**II**) to obtain:

$$P = \left(\frac{Q/Q_m}{B - B \times Q/Q_m}\right)^t$$

Replacing $\boldsymbol{P}$ in equation (**I**), therefore, the $\boldsymbol{\Delta H_{ads}}$ can be calculated from the following formula

$$\Delta H_{ads} = \frac{R \times T_1 \times T_2}{T_2 - T_1} \times \ln \frac{\left(\dfrac{Q/Q_{m1}}{B_1 - B_1 \times Q/Q_{m1}}\right)}{\left(\dfrac{Q/Q_{m2}}{B_2 - B_2 \times Q/Q_{m2}}\right)}$$



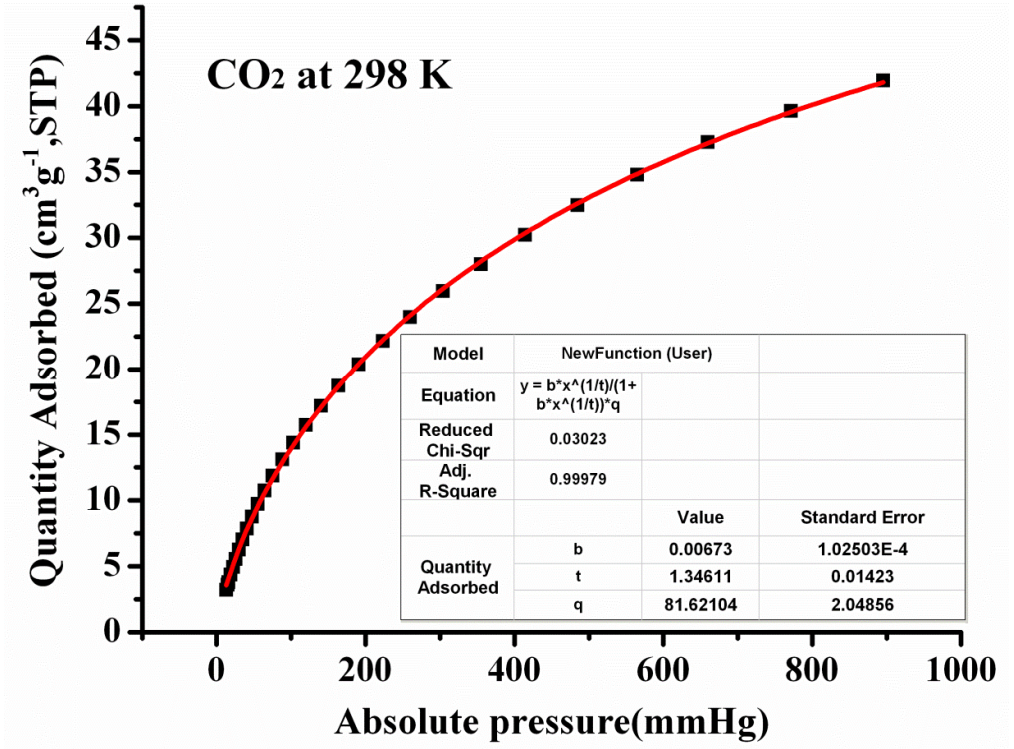
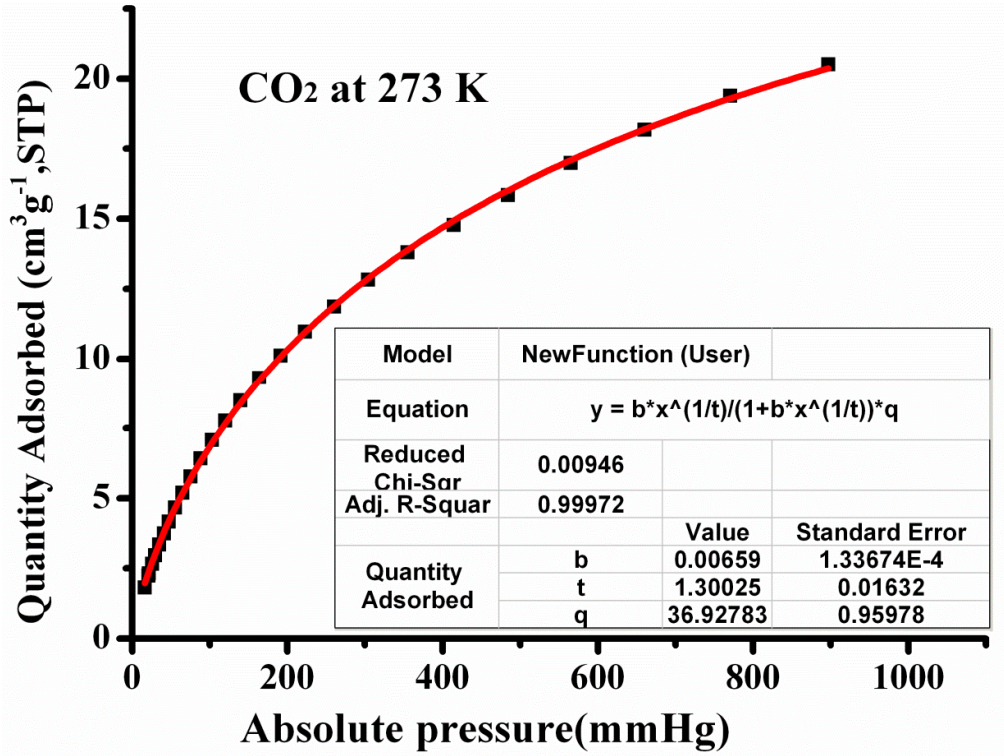


Figure S10. Fitting CO_2 adsorption isotherms (up 273 K and down 298 K) of **1** using the Langmuir-Freundlich equation.



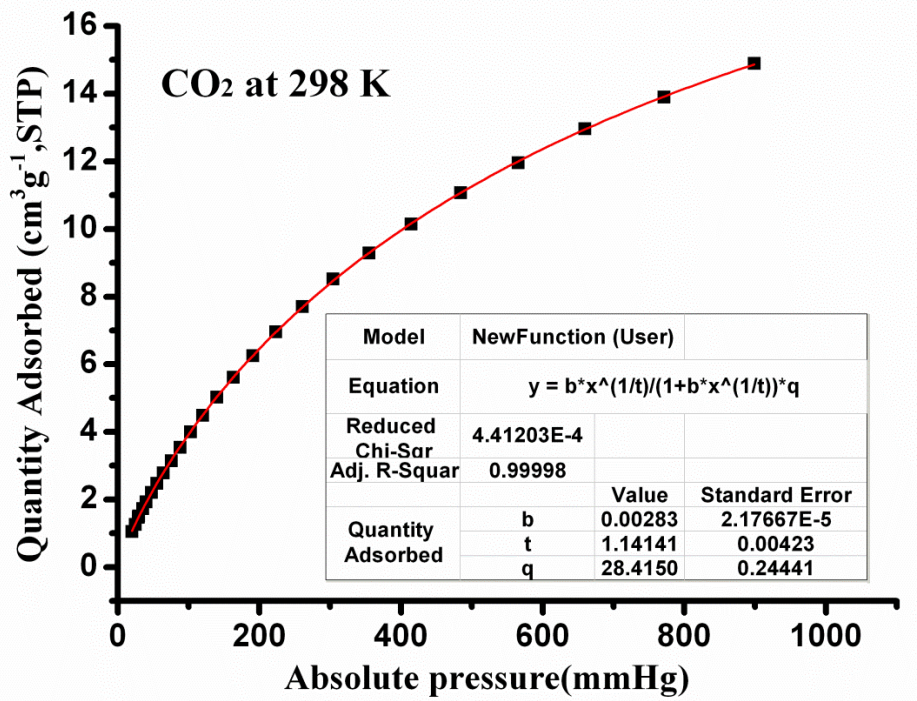


Figure S11. Fitting CO_2 adsorption isotherms (up 273 K and down 298 K) of **2** using the Langmuir-Freundlich equation.

Prediction of the Gases Adsorption Selectivity by IAST

IAST (ideal adsorption solution theory)[2-3] was used to predict binary mixture adsorption from the experimental pure-gas isotherms. In order to perform the integrations required by IAST, the single component isotherms should be fitted by a proper model. In practice, several methods to do this are available. We found for this set of data that the dual-site Langmuir-Freundlich equation was successful in fitting the data.

$$q = \frac{q_{m,1} b_1 p^{1/n_1}}{1 + b_1 p^{1/n_1}} + \frac{q_{m,2} b_2 p^{1/n_2}}{1 + b_2 p^{1/n_2}}$$

Here, P is the pressure of the bulk gas at equilibrium with the adsorbed phase (kPa), q is the adsorbed amount per mass of adsorbent (mmol/g), $q_{m,1}$ and $q_{m,2}$ are the saturation capacities of sites 1 and 2 (mmol/g), b_1 and b_2 are the affinity coefficients of sites 1 and 2 (1/kPa), and n_1 and n_2 represent the deviations from an ideal homogeneous surface. The fitted parameters were then used to predict multicomponent adsorption with IAST.

The selectivity $S_{A/B}$ in a binary mixture of components A and B is defined as $(x_A/y_A) / (x_B/y_B)$, where x_i and y_i are the mole fractions of component i (i = A , B) in the adsorbed and bulk phases, respectively.

References:

1. Dinca, M.; Long, J. R. *J. Am. Chem. Soc.* **2005**, *127*, 9376.
2. (a) Bae, Y. S.; Mulfort, K. L.; Frost, H.; Ryan, P.; Punnathanam, S.; Broadbelt, L.; Hupp, J. T. and Snurr, R. Q. *Langmuir* **2008**, *24*, 8592; (b) Mu, B.; Li, F. and Walton, K. S. *Chem. Commun.* **2009**, 2493.
3. Myers, A. L. and Prausnitz, J. M. *AIChE J.* **1965**, *11*, 121.