Supporting Information for

Unprecedented Li^+ Exchange in an Anionic Metal–Organic Framework: Significantly Enhanced Gas Uptake Capacity

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Section 1 Materials and Instrumentation

All reagents and solvents were commercially available and were used without further purification. Infrared spectra were obtained in KBr discs on a Nicolet Avatar 360 FTIR spectrometer in the 400−4000 cm^{-1} region. Elemental analyses of C, H, and N were performed with a Perkin Elmer 2400C Elemental Analyzer. Thermalgravimetric analyses (TGA) were carried out in nitrogen stream using a Netzsch TG209F3 equipment at a heating rate of 5 °C/min. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 ADVANCE X-ray powder diffractometer (Cu Kα, 1.5418 Å). Analyses for Li and Zn were carried out using an Optima 7300 DV inductively coupled plasma atomic emission spectrometer (ICP-AES). The sorption isotherms were measured with an automatic volumetric adsorption apparatus (Micrometrics ASAP 2020 M).

Section 2 Experimental Section

2.1 Synthesis of $[H_2N(CH_3)_2]_2[Zn_5(L)_3]\cdot 5.5DMF\cdot 3.5H_2O$ (1)

A mixture of $Zn(NO_3)_2\cdot 6H_2O$ (0.029 g,0.10 mmol), and H_4L (0.033 g, 0.10 mmol), dissolved in DMF 10 mL and placed in a Teflon-lined stainless steel vessel (25 mL), was heated at 130 °C for 72 h, and then cooled to room temperature at a rate of 3 °C min^{-1}. The resulting yellow block crystals of **1** were isolated by washing with DMF (5 mL×3) and dried in air (Yield: 52.2% based on H_4L). Anal. Calcd for $C_{68.5}H_{79.5}N_{7.5}O_{33}Zn_5$: C, 44.17; H, 4.30; N, 5.64. Found: C, 45.04; H, 3.91; N, 5.77. IR (cm^{-1}): 3445m, 3060w, 2931w, 2514w, 1793w, 1665s, 1624s, 1579s, 1412m, 1358s, 1310m, 1254w, 1176w, 1092m, 1023w, 907w, 829w, 778m, 724m, 662m.

2.2 Preparation of Li^+-exchanged framework (1-Li)

Crystals of as-synthesized **1** were immersed in a saturated methanol solution of $LiNO_3$ for ten days, and the solution of $LiNO_3$ was refreshed daily. Upon decanting the solution, the cation-exchanged sample was rinsed with methanol and soaked in methanol for three days to remove residual $LiNO_3$ on MOF surface. The solid was filtered off and dried in air. Anal. Calcd for **1-Li** (After activation): C, 45.90; H, 1.61; N, 0.00. Found: C, 43.91; H, 2.30; N, 0.06. The big difference between the calcd and the found ones may be due to a small amount of water absorbed in the activation samples. IR (cm^{-1}): 3420m, 2499w, 1624s, 1578s, 1414m, 1359s, 1308m, 1178w, 1084m, 1017w, 902w, 828w, 768m, 723m, 698m, 662m.

Section 3 Crystallography

Diffraction data were collected at 296(2) with a Bruker-AXS SMART CCD area detector diffractometer using ω rotation scans with a scan width of 0.3° and Mo Kα radiation (λ = 0.71073 Å). Absorption corrections were carried out utilizing SADABS routine. The structures were solved by direct methods and refined by full matrix least squares refinements based on F^2 with the SHELXTL program.[1] Non-H atoms were refined anisotropically with the hydrogen atoms added to their geometrically ideal positions and refined isotropically. The heavily disordered solvent molecules were trapped in the channels of **1** and **1-Li** could not be modeled properly. Thereby the SQUEEZE routine of PLATON[2] was applied to remove the contributions to the scattering from the guests. The final formulas of **1** and **1-Li** were determined by combining the single-crystal structures, elemental microanalyses and TGA data. Selected crystallographic data and structure refinement results are listed in Table S1.

References

1 Sheldrick, G. M. *SHELXL, version 6.12*; Bruker Analytical Instrumentation: Madison, WI, 2000.

2 Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7–13.

Table S1. Crystallographic Data and Structural Refinement for 1 and 1-Li

	1	**1-Li**
Formula	$C_{52}H_{34}N_2O_{24}Zn_5$	$C_{48}H_{18}LiO_{24}Zn_4$
M_r	1397.66	1247.12
T (K)	296(2)	296(2)
cryst syst	Monoclinic	Monoclinic
space group	C2/c	C2/c
a (Å)	12.3215(10)	12.260(6)
b (Å)	30.711(3)	30.207(15)
c (Å)	22.7224(18)	22.980(11)
α (deg)	90	90
β (deg)	94.229(2)	94.983(10)
γ (deg)	90	90
V (Å^3)	8574.7(12)	8478(7)
Z	4	4
D_{calc} (g cm^{-3})	1.083	0.977
F(000)	2808	2484
R_{int}	0.0681	0.0877
GOF on F^2	0.908	0.902
R1[a] [$I > 2\sigma(I)$]	0.0553	0.0562
wR2[b] (all data)	0.1527	0.1548

[a]$R1 = \sum|F_o| - |F_c|/\sum|Fo|$. [b]$wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

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

Zn(1)-O(8)#1	1.914(3)	Zn(2)-O(5)#3	1.911(3)
Zn(1)-O(10)	1.944(3)	Zn(2)-O(11)#4	1.941(3)
Zn(1)-O(4)#2	1.969(3)	Zn(2)-O(1)	1.946(3)
Zn(1)-O(2)	1.984(3)	Zn(2)-O(9)	1.990(3)
Zn(3)-O(3)#5	2.160(6)	Zn(3)-O(7)#6	2.254(4)
Zn(3)-O(3)	2.160(6)	Zn(3)-O(7)#7	2.254(4)
O(8)#1-Zn(1)-O(10)	122.84(16)	O(5)#3-Zn(2)-O(11)#4	114.34(16)
O(8)#1-Zn(1)-O(4)#2	120.62(16)	O(5)#3-Zn(2)-O(1)	125.57(16)
O(10)-Zn(1)-O(4)#2	110.48(17)	O(11)#4-Zn(2)-O(1)	106.50(15)
O(8)#1-Zn(1)-O(2)	100.55(18)	O(5)#3-Zn(2)-O(9)	99.11(15)
O(10)-Zn(1)-O(2)	101.52(16)	O(11)#4-Zn(2)-O(9)	95.31(14)
O(4)#2-Zn(1)-O(2)	92.06(16)	O(1)-Zn(2)-O(9)	111.57(14)
O(3)#5-Zn(3)-O(3)	135.5(5)	O(3)#5-Zn(3)-O(7)#6	91.38(18)
O(3)-Zn(3)-O(7)#6	96.96(16)	O(3)#5-Zn(3)-O(7)#7	96.96(16)
O(3)-Zn(3)-O(7)#7	91.38(18)	O(7)#6-Zn(3)-O(7)#7	157.9(4)

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

Table. S3 Selected bond lengths (Å) and bond angles (deg) for **1-Li**.

Zn(1)-O(8)#4	1.895(4)	Zn(2)-O(5)#6	1.902(4)
Zn(1)-O(10)	1.921(4)	Zn(2)-O(11)#7	1.938(3)
Zn(1)-O(4)#5	1.966(3)	Zn(2)-O(1)	1.973(4)
Zn(1)-O(2)	1.991(4)	Zn(2)-O(9)	1.986(3)
Li(1)-O(3)	1.933(7)	Li(1)-O(7)#2	2.005(8)
Li(1)-O(3)#1	1.933(7)	Li(1)-O(7)#3	2.005(8)
O(8)#4-Zn(1)-O(10)	119.33(18)	O(5)#6-Zn(2)-O(11)#7	115.65(18)
O(8)#4-Zn(1)-O(4)#5	115.05(16)	O(5)#6-Zn(2)-O(1)	121.04(18)
O(10)-Zn(1)-O(4)#5	112.44(15)	O(11)#7-Zn(2)-O(1)	108.46(16)
O(8)#4-Zn(1)-O(2)	104.63(17)	O(5)#6-Zn(2)-O(9)	101.13(16)
O(10)-Zn(1)-O(2)	108.29(16)	O(11)#7-Zn(2)-O(9)	95.03(15)
O(4)#5-Zn(1)-O(2)	93.03(16)	O(1)-Zn(2)-O(9)	112.13(15)
O(3)-Li(1)-O(3)#1	129.2(8)	O(3)-Li(1)-O(7)#2	100.10(17)
O(3)#1-Li(1)-O(7)#2	105.01(17)	O(3)-Li(1)-O(7)#3	105.01(17)
O(3)#1-Li(1)-O(7)#3	100.10(17)	O(7)#2-Li(1)-O(7)#3	119.1(7)

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

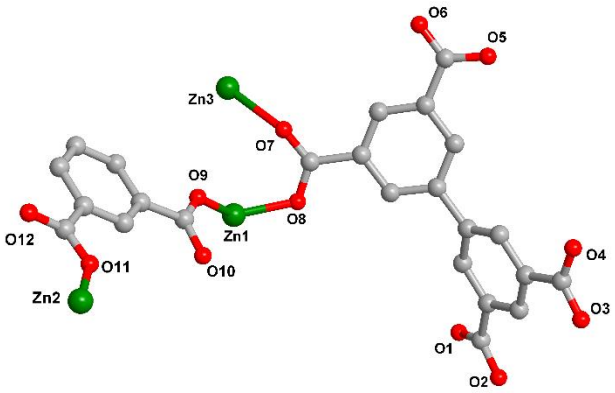
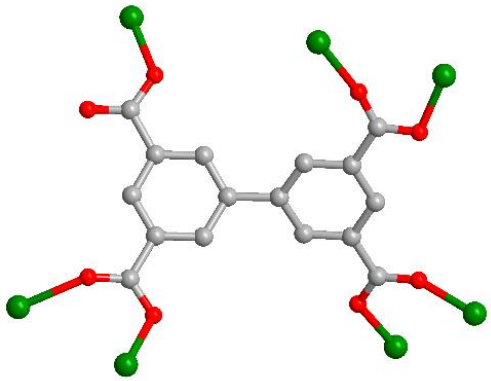
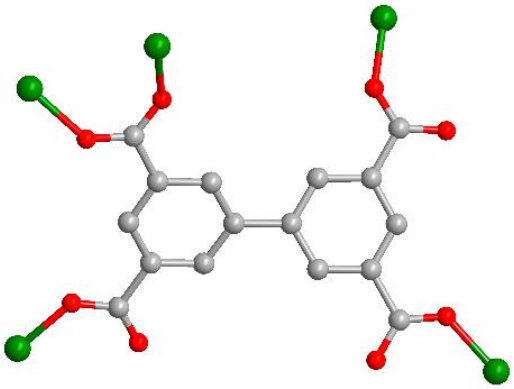


Figure S1. The coordination environment of Zn(II) in **1**.



(a)



(b)

Figure S2. Two kinds of bridging fashions of H_4L in **1**.

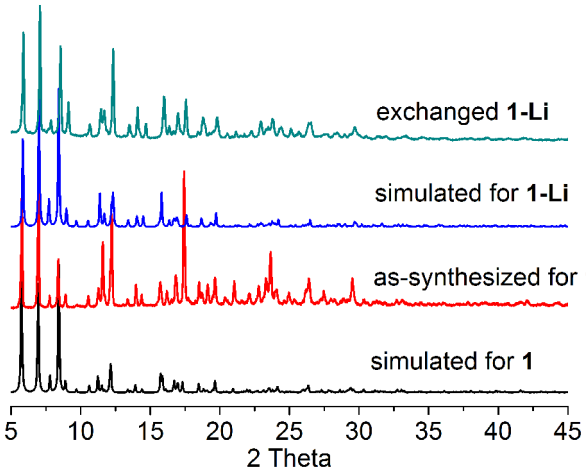


Figure S3. PXRD profiles of simulated and as-synthesized **1** and **1-Li**.

Section 4 Thermogravimetric analysis

Thermogravimetric (TG) analysis of **1** shows a significant weight loss of ~24.8 % in the range of 28-270 ˚C, which is attributed to the loss of guest DMF and H_2O molecules (calcd. 25.0%). Above 365 °C, a further heating induces decomposition of **1**. For **1-Li**, the first weight loss of about 12.9% within the temperature range 28-120 °C could be ascribed to the release of CH_3OH molecules (calcd. 13.0%). A weight loss of about 2.4% in the range 120-165 °C might correspond to the removal of H_2O molecules (calcd, 2.4%). After that, no further weight loss occurs before structural decomposition at 380 °C.

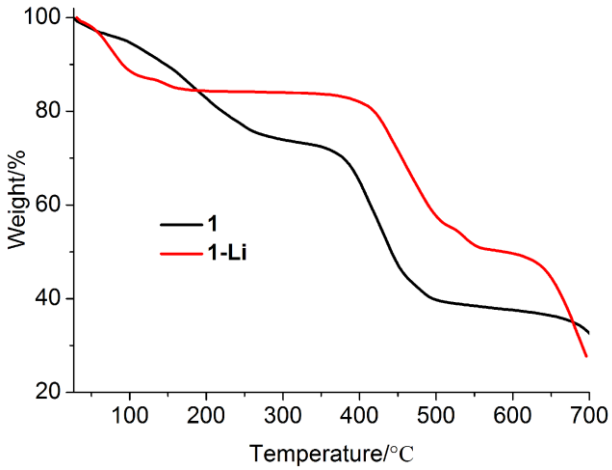


Figure S4. TGA plots for **1** and **1-Li.**

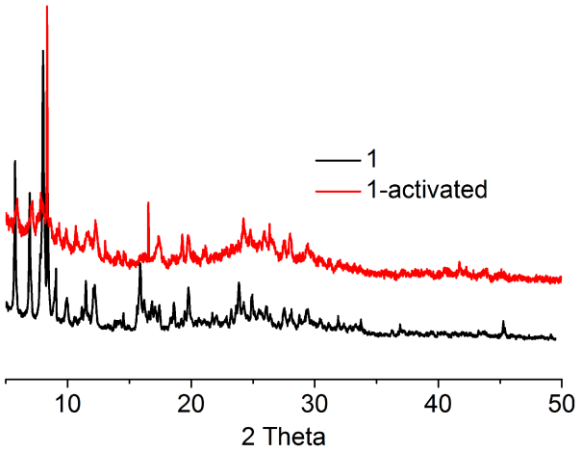


Figure S5. Experimental PXRD patterns for as-synthesized **1** and activated **1.**

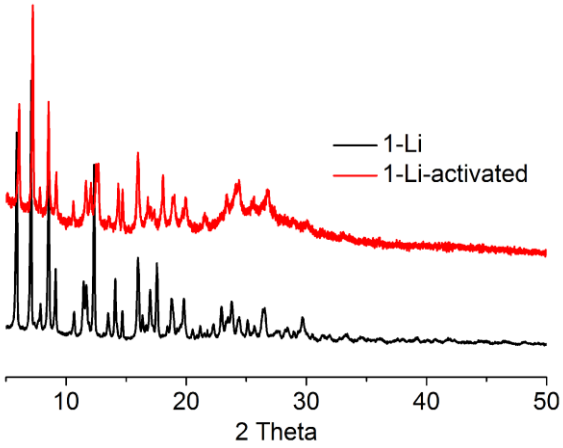
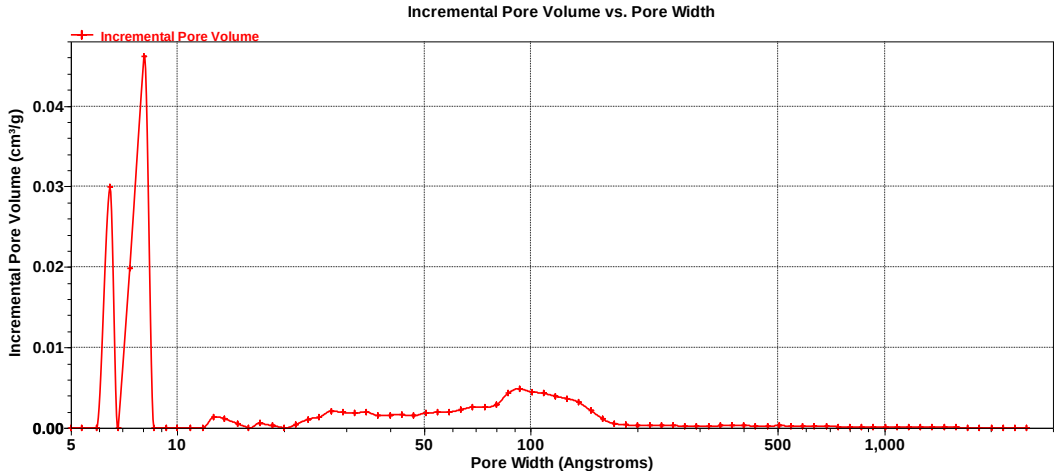
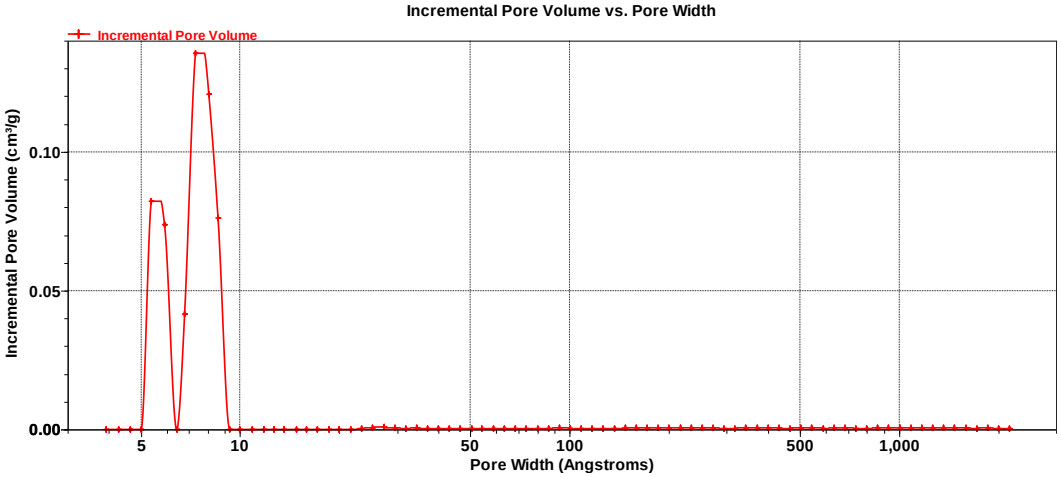


Figure S6. Experimental PXRD patterns for as-synthesized **1-Li** and activated **1-Li**.



(a)



(b)

Figure S7. Incremental pore volume as a function of pore width for **1** (a) and **1-Li** (b) calculated from the adsorption branch of 77 K N_2 using the Density Functional Model.

Section 5 IAST adsorption selectivity calculation:

The experimental isotherm data for pure CO_2 and CH_4 (measured at 298) 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, defined by

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

were calculated using the Ideal Adsorption Solution Theory (IAST) of Myers and Prausnitz.

Where x_i is the mole fraction of component i in the adsorbed phase and y_i is the mole fraction of component i in the bulk.

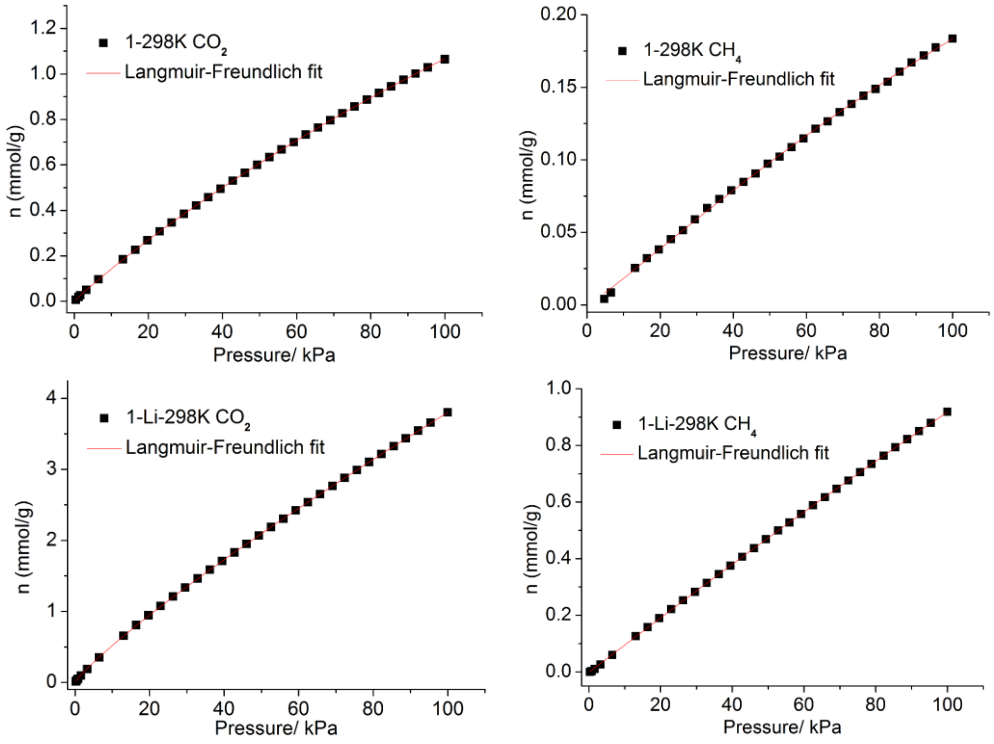
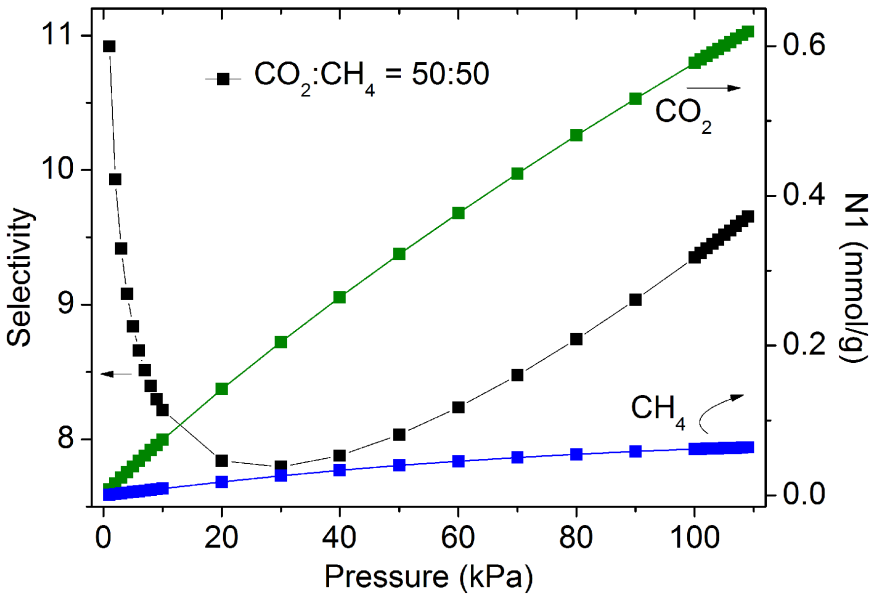
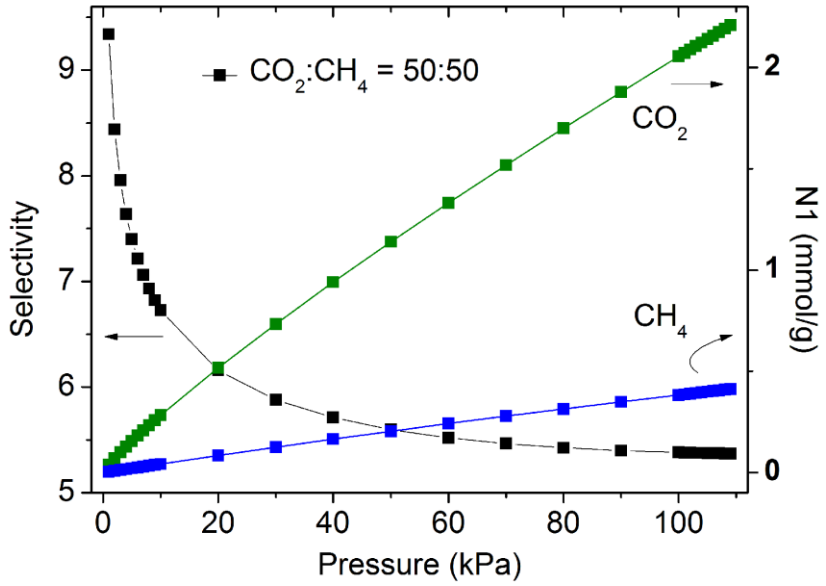


Figure S8. CO_2 adsorption isotherms of **1** with fitting by L-F model: a = 5.46092, b = 0.00294, c = 0.95865, Chi^2 = 9.03×10^{-7}, R^2 = 0.99999; CH_4 adsorption isotherms of **1** with fitting by L-F model: a = 0.70572, b = 0.00203, c = 1.11899, Chi^2 = 1.66×10^{-6}, R^2 = 0.99941; CO_2 adsorption isotherms of **1-Li** with fitting by L-F model: a = 173.36595, b = 3.99981×10^{-4}, c = 0.87426, Chi^2 = 3.20×10^{-5}, R^2 = 0.99998; CH_4 adsorption isotherms of **1-Li** with fitting by L-F model: a = 9.96716, b = 9.05345×10^{-4}, c = 1.0246, Chi^2 = 3.92×10^{-6}, R^2 = 0.99995.



(a)



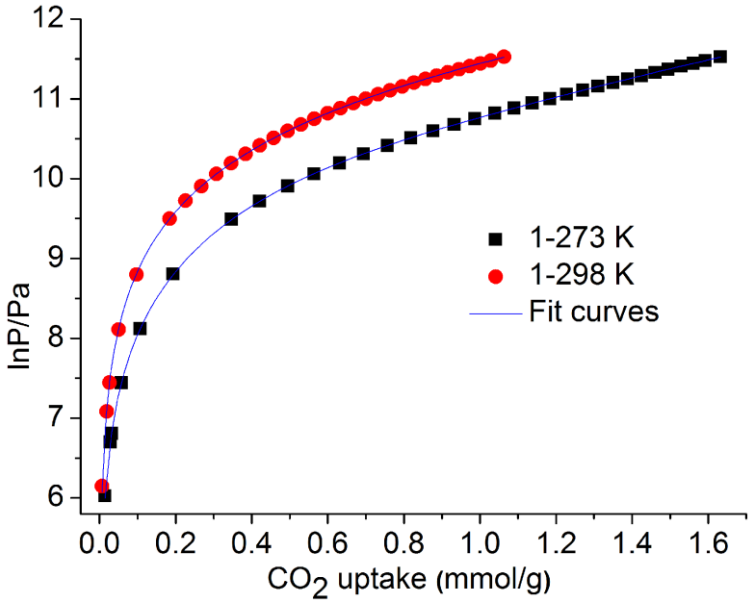
(b)

Figure S9. IAST adsorption selectivities of **1** (a) and **1-Li** (b) for equimolar mixtures of CO_2 and CH_4.

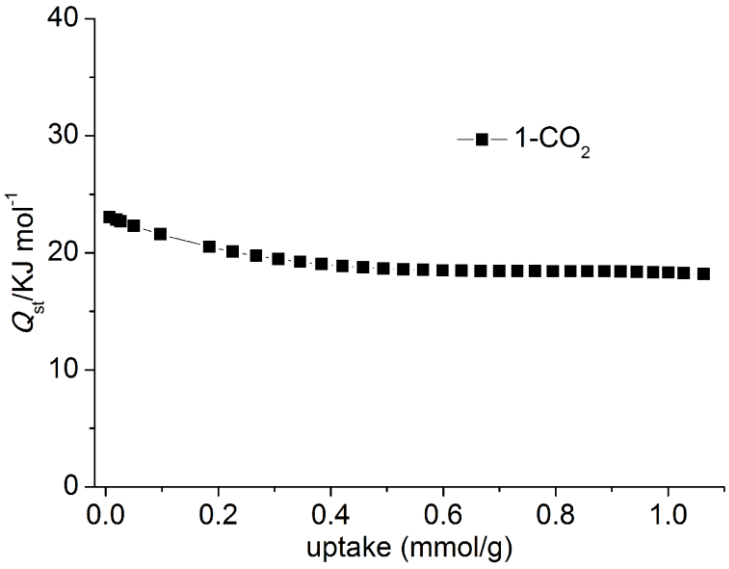
Section 6 Calculation of sorption heat for CO_2 uptake using Virial 2 model

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

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

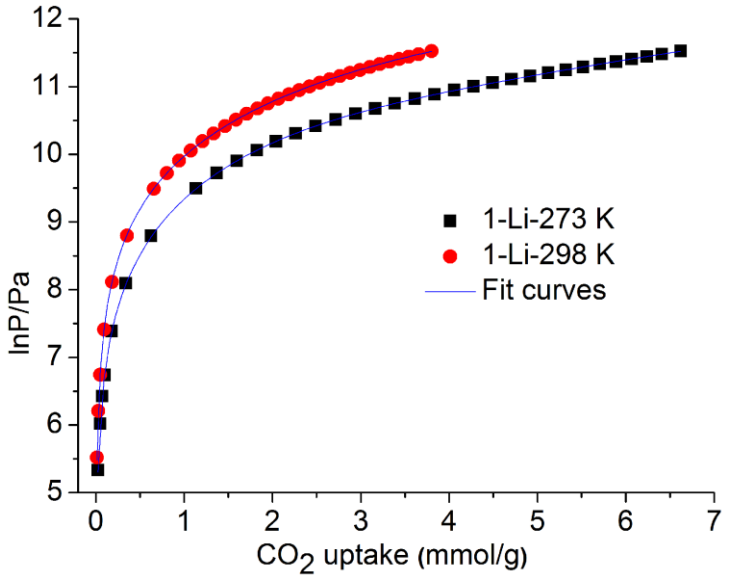


(a)

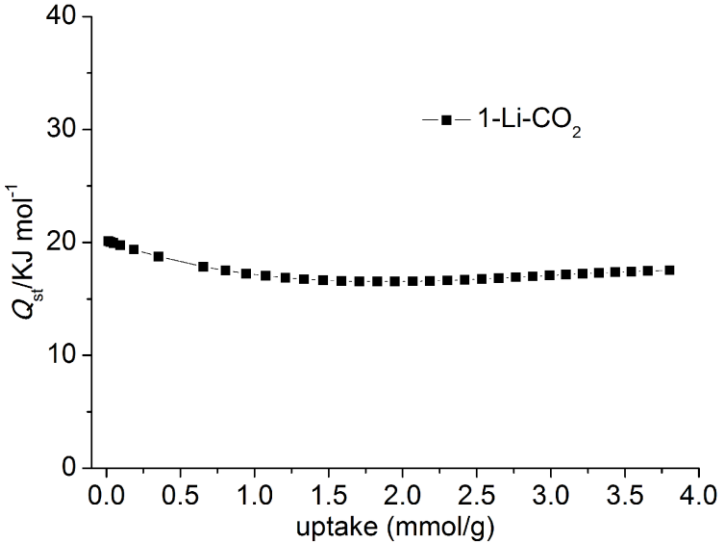


(b)

Figure S10. (a) CO_2 adsorption isotherms for **1** with fitting by Virial 2 model. Fitting results: a0 = -2785.16692, a1 = 2232.43384, a2 = -2971.99301, a3 = 1391.65324, a4 = -68.71331, b0 = 20.42979, b1 = -6.79223, b2 = 9.15472, b3 = -3.96077, Chi^2 = 1.71 × 10^{-4}, R^2 = 0.99992. (b) CO_2 adsorption heat calculated according to the virial equation.



(a)



(b)

Figure S11. (a) CO_2 adsorption isotherms for **1-Li** with fitting by Virial 2 model. Fitting results: a0 = -2425.96285, a1 = 559.00028, a2 = -223.08388, a3 = 26.84934, a4 = -0.28232, b0 = 17.91019, b1 = -1.61234, b2 = 0.67578, b3 = -0.07799, Chi^2 = 8.40×10^{-5}, R^2 = 0.99997. (b) CO_2 adsorption heat calculated according to the virial equation.