Electronic Supporting Information (ESI)

for

Two microporous Co^{II}-MOFs with dual active sites for highly selective adsorption of CO_2/CH_4 and CO_2/N_2

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S1. Experimental Section

Materials and methods.

All chemicals were commercially purchased and used as received.

Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 II analyzer (Perkin-Elmer, USA). The powder X-ray diffraction (PXRD) was obtained on a D/MAX-rA (Rigaku) diffractometer with Cu K_α radiation (λ = 1.542 Å) with a scan rate of 4° min^{-1}. The tube voltage and current are 36 kV and 20 mA, respectively. FT-IR spectra were recorded on a FT6700 spectrometer (USA) using KBr disc method in the range of 400–4000 cm^{-1}. Simulation of the PXRD spectra were carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program available free of charge *via* the Internet at http://www.iucr.org.

Syntheses of LCU-105 and LCU-106:

$\{[H_2N(CH_3)_2]_2[Co(BPTC)]\cdot 4DMAC\cdot 5H_2O\}_n$ (LCU-105):

A mixture of $Co(NO_3)_3\cdot 6H_2O$ (87.31 mg, 0.3 mmol) and H_4BPTC (99 mg, 0.3 mmol) in DMAC (6 mL) was sealed in a Teflon-lined stainless steel vessel (23 mL), which was heated at 120 °C for 4 days and then cooled to room temperature at a rate of 10 °C·h^{-1}. Block-like purple crystals of **LCU-105** were collected. Yield: 30% based on Co. Elemental analysis (%) for activated sample **LCU-105a**, $C_{20}H_{22}O_8N_2Co$ (M = 477.33): *Calcd.*: C, 50.32; H, 4.65; N, 5.87; *Found*: C, 50.41; H, 4.56; N, 5.81;. IR (KBr disk, cm^{-1}) see **Fig. S6** in ESI.

$\{[H_2N(CH_3)_2]_2[Co_{0.5}Na(BPTC)]\cdot DMF\}_n$ (LCU-106):

A mixture of $Co(NO_3)_3\cdot 6H_2O$ (87.31 mg, 0.3 mmol), H_4BPTC (99 mg, 0.3 mmol) and NaOH (20 mg, 0.5 mmol) in DMF (6 mL) was sealed in a Teflon-lined stainless steel vessel (23 mL), which was heated at 120 °C for 4 days and then cooled to room temperature at a rate of 10 °C·h^{-1}. Block-like purple crystals of **LCU-106** were collected. Yield: 26% based on Co. Elemental analysis (%) for activated sample **LCU-106a**, $C_{40}H_{44}O_{16}N_4Na_2Co$ (M = 941.71): *Calcd.*: C, 51.02; H, 4.71; N, 5.95; *Found*: C, 51.13; H, 4.66; N, 5.87. IR (KBr disk, cm^{-1}) see **Fig. S7** in ESI.

X-ray Crystallography.

The crystallographic data of **LCU-105** and **LCU-106** were collected on a Rigaku SCX-mini diffractometer and Bruker SMART at 100(2) K with Mo-Kα radiation (λ = 0.71073 Å), respectively. The crystal data were solved by direct methods and refined by a full-matrix least-square method on F^2 using the *SHELXL-97* crystallographic software package.[S1] Co and Na atoms in **LCU-105** and **LCU-106** were found from *E*-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. The hydrogen atoms of organic ligands were added theoretically, riding on the concerned atoms and refined with fixed thermal factors. During the refinement of the two compounds, the command "omit -3 50" was used to omit some disagreeable reflections. The command "dfix" was used to fix bonds of solvent and $[NH_2(CH_3)_2]^+$ cations. For **LCU-105**, the commands "sadi" and "flat" were used to solve the alert of "Large Hirshfeld Difference...". The atoms C17, C18, C19, C20, C22, C24, N1, N2, N3 and O2w were restrained using thermal restraints (isor and simu) to sovle ADP or NDP alerts and make the displacement parameters more reasonable. In order to subtract the contribution from the disordered solvent molecules, the SQUEEZE command was applied, which gave a new HKL file. The number of located electrons, 174 in two voids per unit cell, is included in the formula, formula weight, calculated density, and F(000). These residual electron density were assigned to three DMAC and three water for **LCU-105**. So SQUEEZE removed three DMAC and three water per unit cell. And the tentative formula for this compound is presented as in the text. For **LCU-106**, the commands "sadi" and "flat" were used to solve the alert of "Large Hirshfeld Difference...". The atoms N3, O9, C20, C22 and C23 were restrained using thermal restraints (isor and simu) to solve ADP or NDP alerts and make the displacement parameters more reasonable. The H atoms of the coordinated water molecules in **LCU-105** cannot be added in the calculated positions, and they were directly included in the final molecular formula. Due to the limited crystal quality, the more solvents, and the relatively high "restraints" in the both compounds, which all result the higher *R* value. Further details of crystal data and structure refinement for **LCU-105** and **LCU-106** were summarized as follows in Table S1. Selected bond lengths of them were given in Table S2 and Table S3. Full crystallographic data for **LCU-105** and **LCU-106** have been deposited with the CCDC (1918594 for **LCU-105**, and 1918595 for **LCU-106**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.[S3]

References

S1 (a) G. M. Sheldrick, *SHELXL97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997; (b) G. M. Sheldrick, *SHELXS97, Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997.

S2 A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, Untrecht University, 2003.

S3 The checkcif program available at: http://journals.iucr.org/services/cif/checkcif.html.

Crystal data for LCU-105 and LCU-106

Table S1. Crystal Data and Structure Refinement Parameters for Compounds LCU-105 and LCU-106.

Compounds	**LCU-105**	**LCU-106**
Formula	$C_{36}H_{68}O_{17}N_6Co$	$C_{48}H_{62}O_{18}N_8Na_2Co$
F_w	915.89	1143.96
λ/Å	0.71073	0.71073
T/K	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2/c$	$C2/c$
a [Å]	19.601(4)	17.6254(16)
b [Å]	9.3797(19)	19.9755(15)
c [Å]	18.630(4)	15.3066(11)
α[°]	90	90
β [°]	95.69(3)	104.504(8)
γ[°]	90	90
V (Å ^{3})	3408.3(12)	5217.3(7)
Z	4	4
D_c/Mg·m^{-3}	1.113	1.520
F(000)	1144	2492
Reflections collected/unique	26897/5995	16997/5028
R_{int}	0.2573	0.0540
Data/Restraints/Parameters	5995/116/352	5028/93/332

R_1/wR_2 [$I>2\sigma(I)$] [a]	0.0.1492/0.3669	0.1128/0.3335
R_1/wR_2 [(all data)] [a]	0.2352/0.4167	0.1261/0.3526
GOF on F^2	1.130	1.105

[a] $R_1 = \Sigma(||F_0| - |F_C||)/\Sigma|F_0|$ $wR_2 = [\Sigma w(|F_0|^2 - |F_C|^2)^2/(\Sigma w|F_0|^2)^2]^{1/2}$.

Sorption measurements.

Gas adsorption/desorption measurements were carried out using a Micrometrics ASAP 2020M volumetric gas adsorption instrument. UHP-grade gases were used in measurements. Before the measurement, the samples of **LCU-105** and **LCU-106** were soaked in anhydrous methanol (CH_3OH) for 3 days to remove DMAC and DMF solvent molecules in the channels, and then filtrated, and activation of the methanol-exchanged **LCU-105** and **LCU-106** at 120 °C under high vacuum (less than 10^{-5} Torr) overnight led to the formation of activated sample **LCU-105a** and **LCU-106a**. About 110 mg (for **LCU-105**) and 100 mg (for **LCU-106**) of the desolvated samples were used for the entire adsorption/desorption measurements. The Ar adsorption/desorption isotherm measurements were proceeded at 77 K in a liquid nitrogen bath. The CO_2, CH_4 and N_2 adsorption/desorption isotherm measurements were carried out at 273 K in an ice-water bath, respectively.

S2. Figures in Supporting Information

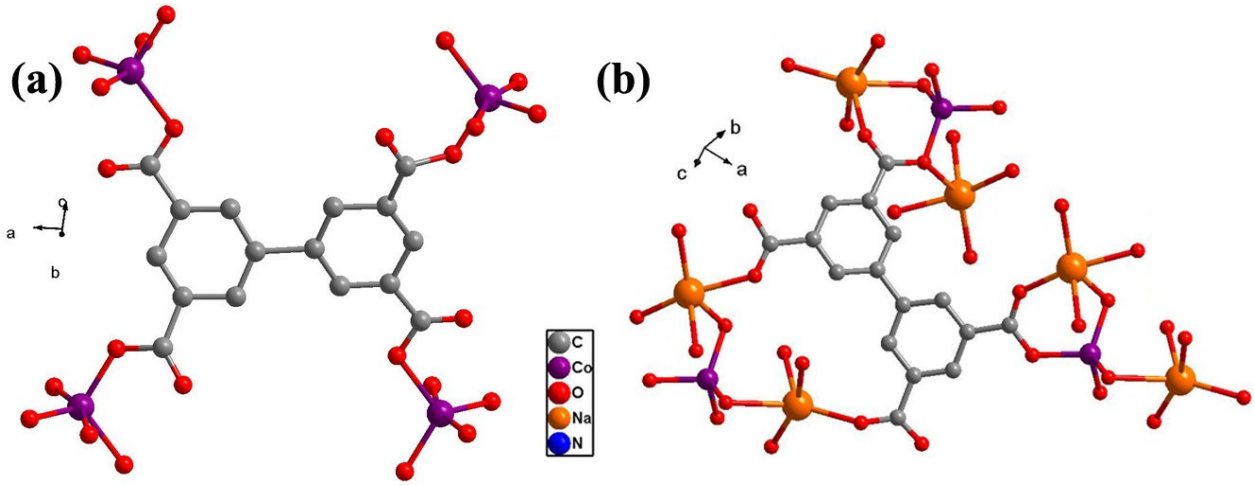

Fig. S1 The coordination mode of the ligands in (a) **LCU-105** and (b) **LCU-106**.

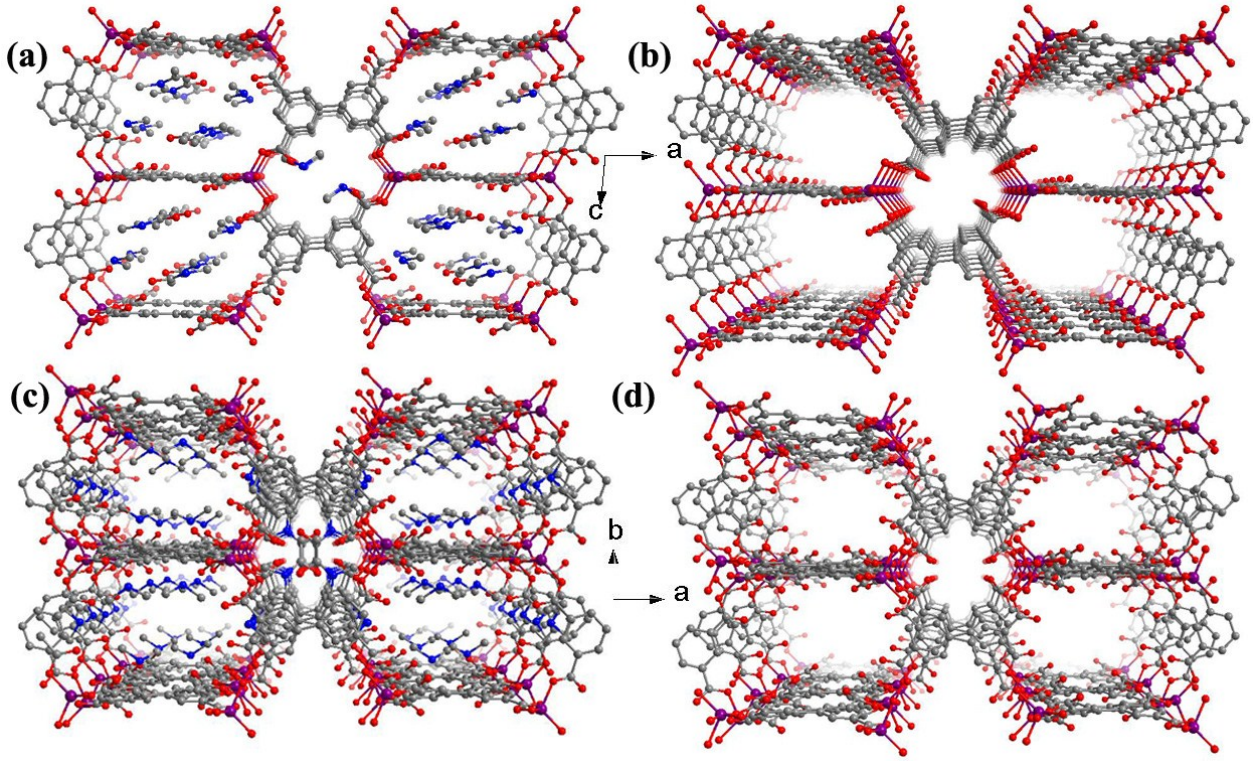

Fig. S2 The 3D structure of **LCU-105** in different directions.

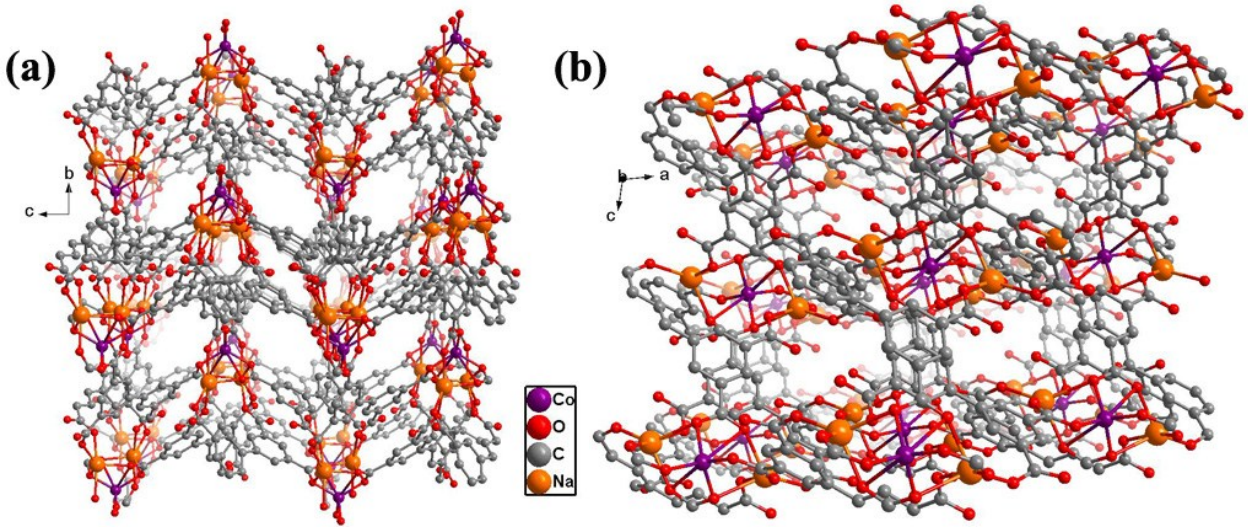

Fig. S3 The 3D structure of **LCU-106** in different directions.

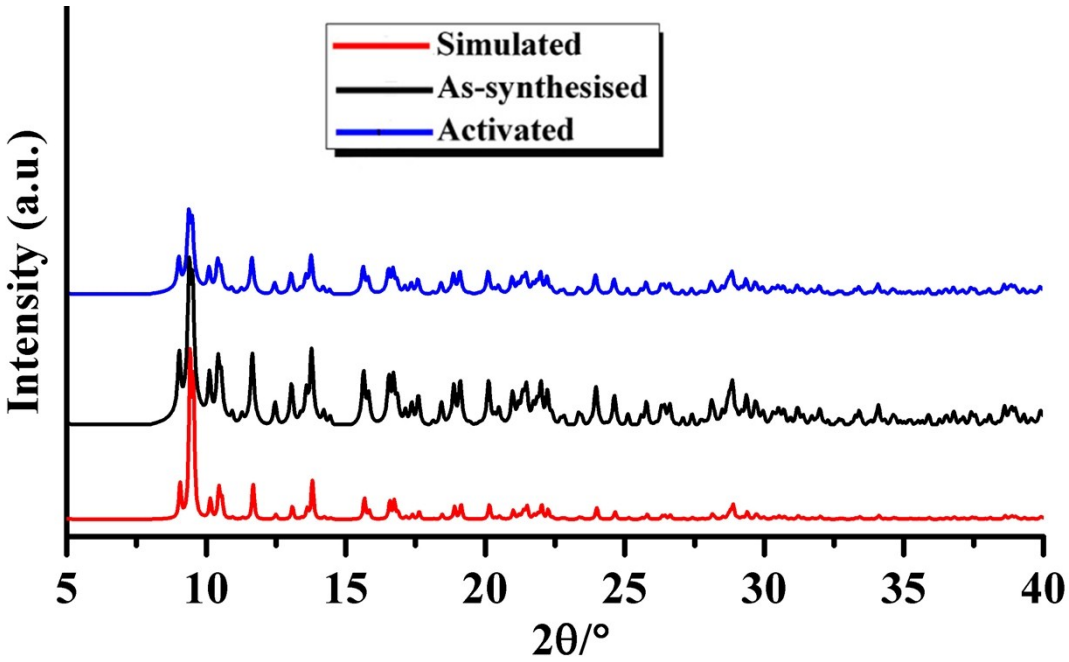

Fig. S4 PXRD patterns of **LCU-105** and **LCU-105a**.

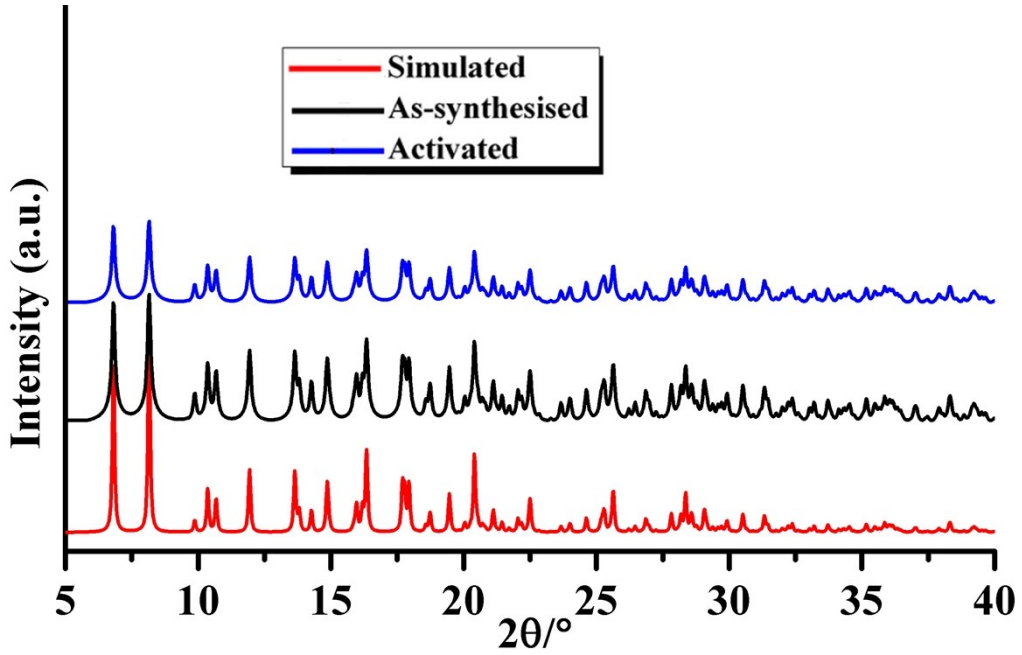

Fig. S5 PXRD patterns of **LCU-106** and **LCU-106a**.

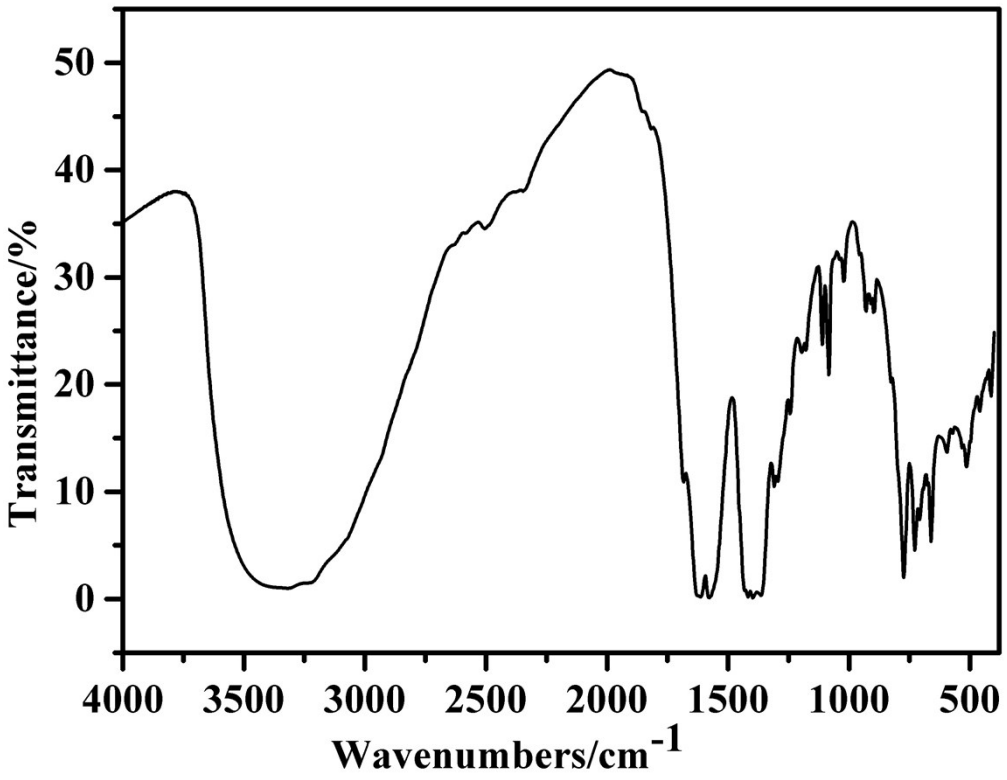

Fig. S6 IR spectra of compound **LCU-105**.

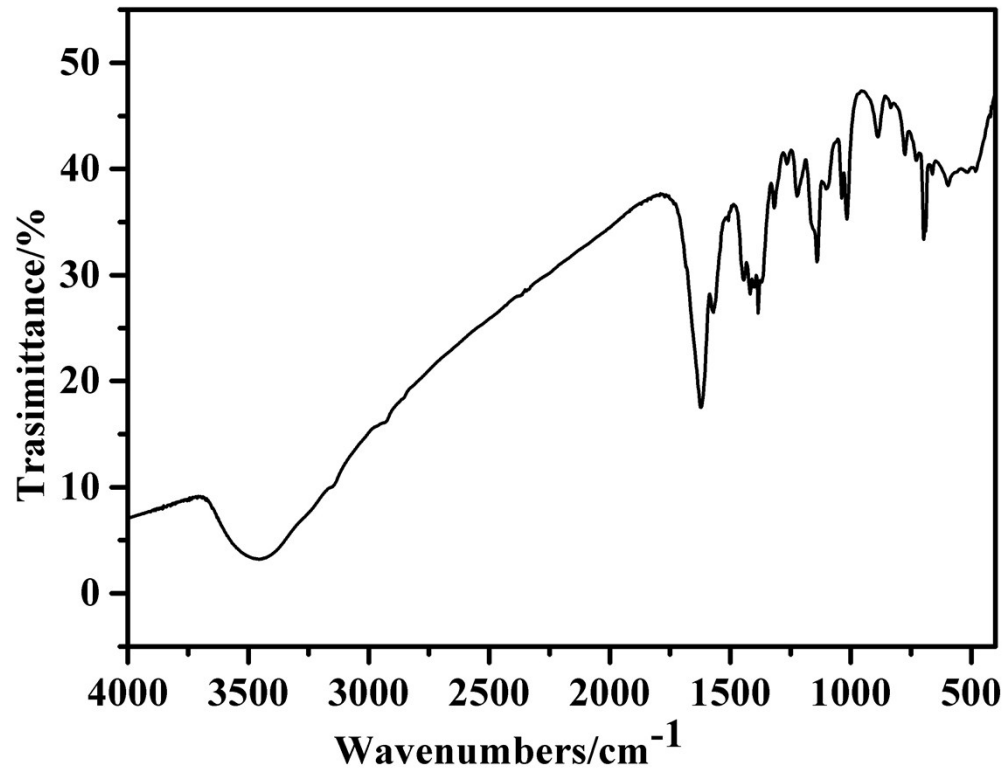

Fig. S7 IR spectra of compound **LCU-106**.

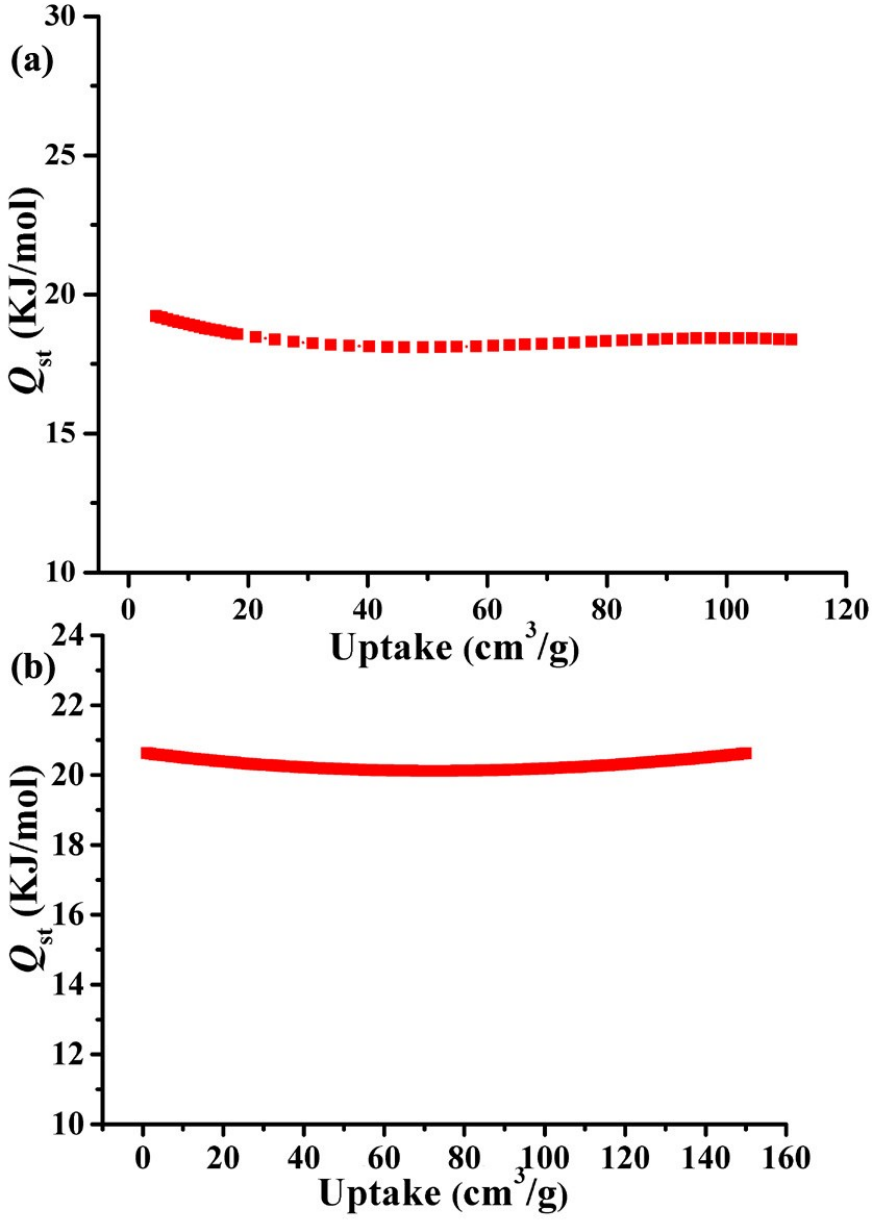

Fig. S8 CO_2 adsorption enthalpy of **LCU-105a** and **LCU-106a** calculated from the CO_2 adsorption isotherms at 273 K and 298 K.

S3. IAST adsorption selectivity calculation:[S4-S5]

IAST (ideal adsorption solution theory) 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 SA/B in a binary mixture of components A and B is defined as (xA/yA) / (xB/yB), where xi and yi are the mole fractions of component i (i = A, B) in the adsorbed and bulk phases, respectively.

S4 F. Daniels, R. A. Alberty, J. W. Williams, C. D. Cornwell, P. Bender and J. E. Harriman, *Experimental Physical Chemistry, 6th Ed, McGraw-Hill Book Co. Inc.*, New York, **1962**.

S5 M. Dincă and J. R. Long, *J. Am. Chem. Soc.,* 2005, **127**, 9376−9377.

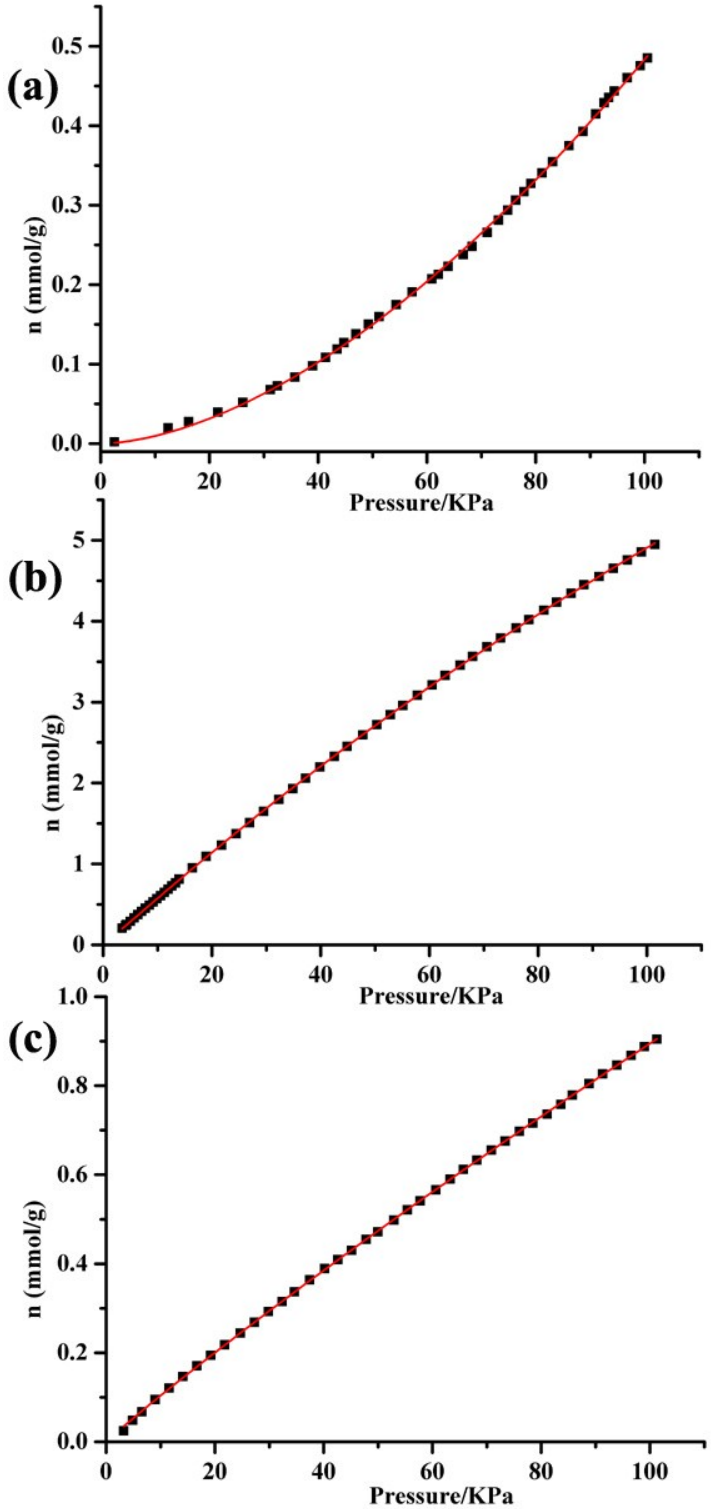

Fig. S9 N_2, CO_2 and CH_4 adsorption isotherms of **LCU-105a** with fitting by Langmuir-Freundlic Fit model at 273 K.

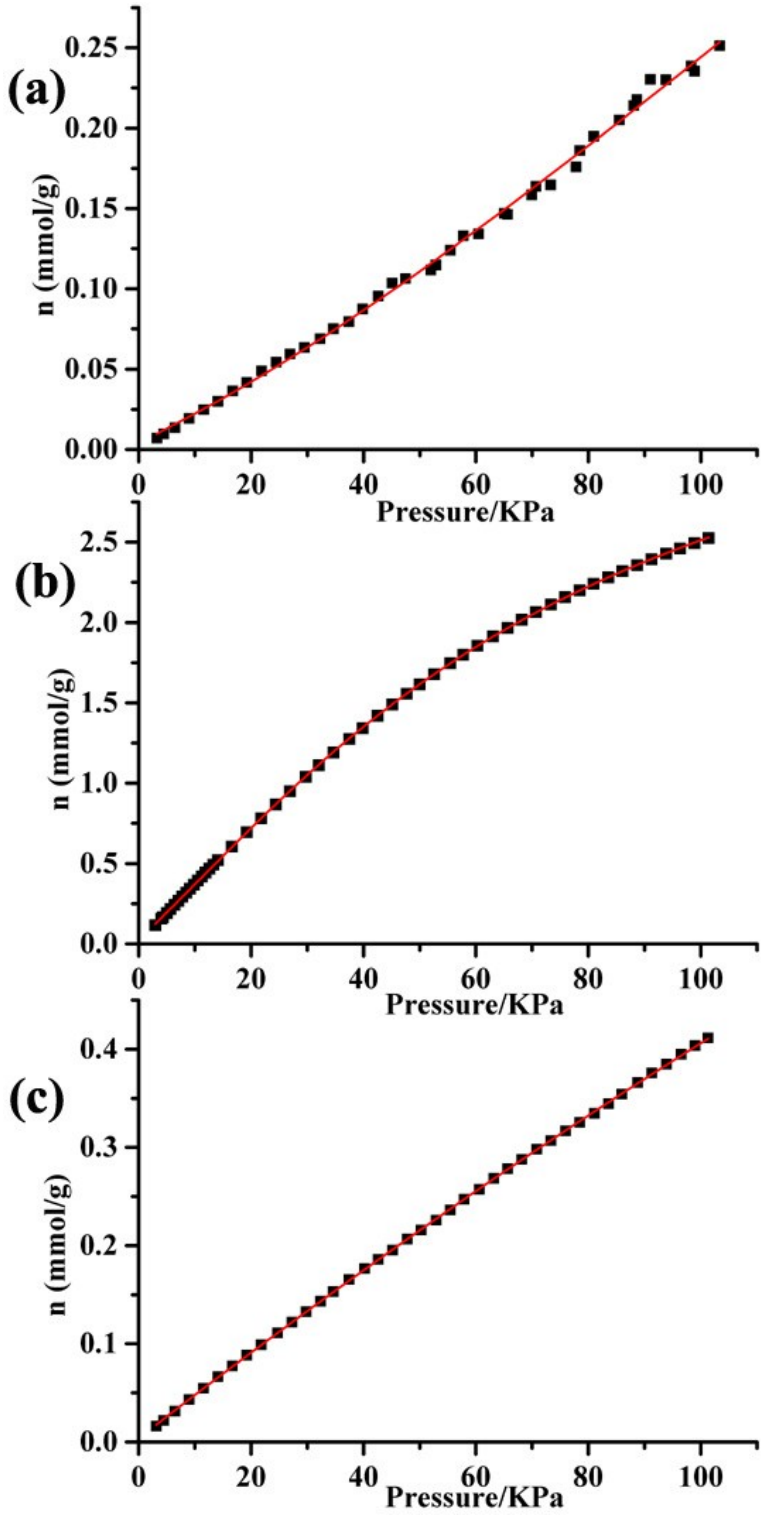

Fig. S10 N_2, CO_2 and CH_4 adsorption isotherms of **LCU-106a** with fitting by Langmuir-Freundlic Fit model at 273 K.

S4 The computational simulation studies of gases adsorption

To further investigate interactions between CO_2 molecules and the **LCU- 105** and **LCU-10**6, grand canonical Monte Carlo (GCMC) simulations were carried out using the Sorption module of Materials Studio 5.0 package.[S6] The Locate and Metropolis methods[S7] were used to predict the possible binding sites of CO_2 molecules onto the frameworks. The unit cell frameworks of **LCU-105** and **LCU-106** were constructed from experimental crystal X-ray diffraction data. The loading number of CO_2 adsorbed onto each unit cell of the two kinds of frameworks was choose as 10 based on our experimental data. During the simulation, the CO_2 and dimethylamine molecules including the frameworks were considered as rigid, and periodic boundary conditions were applied in all three directions. The interaction energy between CO_2 and frameworks were calculated by the Coulomb and Lennard-Jones 6-12 (LJ) potentials. A cutoff radius of 12.5 Å for the LJ potentials was used throughout the simulation. All parameters including the partial charges were assigned by the COMPASS force field[S8] embedded in the Sorption module.

S6 *Accelrys*, *Materials Studio Getting Started, release 5.0; Accelrys Software*, Inc.: San Diego, CA, 2009.

S7 N. Metropolis and S. Ulam, *J. Am. Stat.l Assoc.*, 2012, **44**, 335−341.

S8 H. Sun, *J. Phys. Chem. B*, 1998, **102**, 7338−7364.

S5. The selected bond lengths [Å] and angles [º] of compounds LCU-105 and LCU-106.

Table S2 The selected bond lengths [Å] and angles [º] of compound **LCU-105**.

O(7)-Co(2)#1	1.923(8)	Co(2)-O(1)	1.909(10)
Co(2)-O(5)	1.920(9)	Co(2)-O(7)#2	1.923(8)
Co(2)-O(4)#3	1.951(9)	O(4)-Co(2)#4	1.951(9)
O(1)-Co(2)-O(5)	98.1(4)	O(1)-Co(2)-O(7)#2	111.5(4)
O(5)-Co(2)-O(7)#2	112.9(4)	O(1)-Co(2)-O(4)#3	111.3(4)
O(5)-Co(2)-O(4)#3	109.3(4)	O(7)#2-Co(2)-O(4)#3	112.9(4)
Symmetry transformations used to generate equivalent atoms: #1: x, y+1, z; #2: x, y-1, z; #3: x, -y, z+1/2; #4: x, -y, z-1/2.			

Table S3 The selected bond lengths [Å] and angles [º] of compound **LCU-106**.

Co(1)-O(7)#1	1.971(4)	Co(1)-O(7)#2	1.971(4)
Co(1)-O(1)	1.978(4)	Co(1)-O(1)#3	1.978(4)
O(7)-Co(1)#1	1.971(4)		
O(7)#1-Co(1)-O(7)#2	95.4(2)	O(7)#1-Co(1)-O(1)	107.44(15)
O(7)#2-Co(1)-O(1)	112.27(16)	O(7)#1-Co(1)-O(1)#3	112.27(16)
O(7)#2-Co(1)-O(1)#3	107.44(15)	O(1)-Co(1)-O(1)#3	119.4(2)
Symmetry transformations used to generate equivalent atoms:#1: -x+3/2, -y+1/2, -z; #2: x-1/2, -y+1/2, z-1/2; #3: -x+1, y, -z-1/2.			