Electronic Supplementary Information (ESI)

ROD-8, a rod MOF with pyrene-cored tetracarboxylate linker: framework disorder, derived nets and selective gas adsorption

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Experimental Details

Materials and instruments.

All reagents and solvents were purchased from commercial sources and used without further purification. The ligand 1,3,6,8-tetrakis(*p*-benzoic acid)pyrene (short for H_4TBAPy) was synthesized according to the literature method.[S1] FT-IR spectra were measured using a Nicolet Avatar 360 FT-IR spectrophotometer. Thermogravimetric analysis (TGA) was carried out in a nitrogen stream using Q50 TGA (TA) thermal analysis equipment with a heating rate of 10 °C min^{-1}. Powder X-ray diffraction patterns (PXRD) of the bulk samples were measured on a Bruker D8 Advance diffractometer (Cu Kα, λ = 1.5418 Å) under room temperature. Low-pressure (up to 1 bar) gas adsorption isotherms (N_2, CO_2, CH_4) were measured on the Micrometrics ASAP 2020 Surface Area and Porosity Analyzer. In one typical run, about 150 mg methanol exchanged samples were activated at 180 °C for 15 hours by using the "outgas" function of the surface area analyzer before measurements.

Synthesis of $[Cd_2(TBAPy)(H_2O)_2]$·DMF·0.5dioxane (ROD-8).

A mixture of $Cd(NO_3)_2·4H_2O$ (6.94 mg, 0.0225 mmol), H_4TBAPy (5.12 mg, 0.0075 mmol), and DMF/Dioxane/H_2O mixed solvent (2.0 mL, 2:1:1, v/v) were sealed in a Pyrex glass tube and heated in an oven at 120 °C for 72 hours. After cooling to room temperature at a rate of 5 °C/h, the yellow block-like crystals were obtained by filtration and washing with DMF for 3 times (2.0 ml each time, yield: 3.0 mg).

[S1] K. C. Stylianou, R. Heck, S. Y. Chong, J. Bacsa, J. T. A. Jones, Y. Z. Khimyak, D. Bradshaw and M. J. Rosseinsky, *J. Am. Chem. Soc.*, 2010, **132**, 4119.

Crystal Structure Description

Crystal structure determination.

A suitable crystal of the complex was mounted with glue at the end of a glass fiber. Data collection was performed on an Agilent Technologies Gemini A System (Cu Kα, λ = 1.54178 Å) at room temperature (293 K). The data were processed using the software *CrysAlisPro.1*. The structure was solved by direct methods and refined by full-matrix least-squares refinements based on F^2. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The hydrogen atoms were generated geometrically. The crystallographic calculations were performed using the *SHELXL-97* programs.[S2] The dioxane molecules in the channels of **ROD-8** are highly disordered, which are squeezed by using the program SQUEEZE/PLATON.[S3] The void volume (excluding guest solvent molecules) in the crystal cell was calculated using the program *PLATON*.[S3] Crystal data and structure refinement are summarized in Table S1.

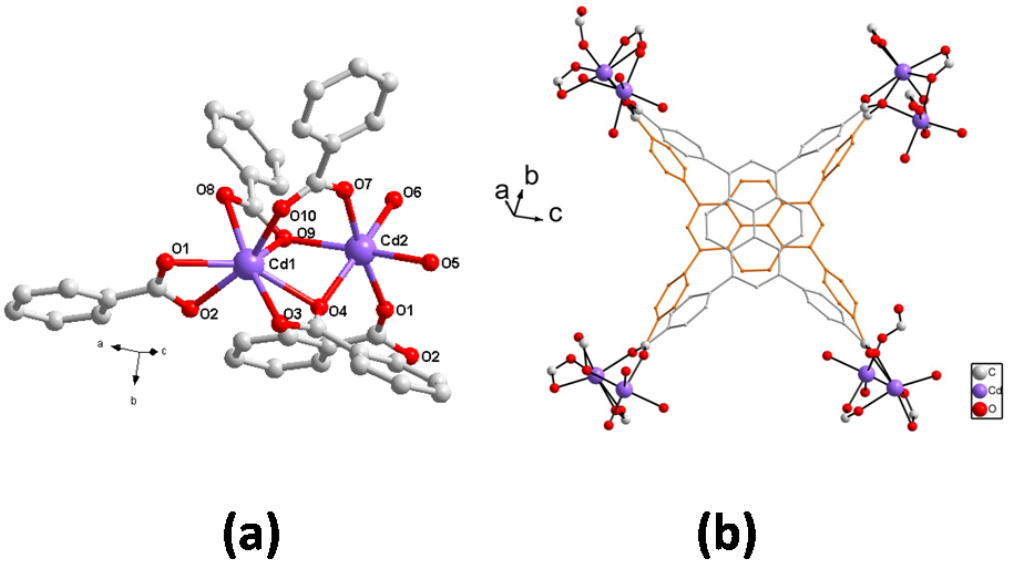
[S2] G. M. Sheldrick, *Acta Crystallogr. A*, 2007, **64**, 112.
[S3] A. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.

Table S1. Crystal data and structure refinements for ROD-8

	ROD-8
Formula	C_{49} H_{37} Cd_2 N O_{12}
Mr.	1012.54
Crystal system	Monoclinic
Space group	$P2_1/c$
Temp. (K)	293.3
a (Å)	7.1510(1)
b (Å)	24.8988(4)
c (Å)	28.6097(4)
α (°)	90
β (°)	93.406(1)
γ (°)	90
V (Å^3)	5085.00(13)
Z	4
D_c (g·cm^{-3})	1.323
no. of reflns	14688
no. of unique	8079
unique refl.(R_{int})	0.0481
GOF on F^2	1.060
$R_1[I \geq 2\sigma(I)]^a$	0.0523
$wR_2[I \geq 2\sigma(I)]^b$	0.1249
R_1[all data]	0.0887
wR_2[all data]	0.1429

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

CCDC No.: 984649



(a) (b)

Fig. S1 Coordination environments of the metal (Cd1 and Cd2) (a) and ligand (b) in ROD-8.

Topological Analysis

Topological information[S4] for lrk:

Point Symbol:[S5] $(3.14^2)(3.8.9)_2(4^2.6.8^2.10)_2$

TD10: 621

Systre file (.cgd) is given below:

```
CRYSTAL
   NAME "lrk; ROD-8"
   GROUP Cccm
   CELL 7.87476 1.91261 6.89075 90.0000 90.0000 90.0000
   NODE 3 3    0.55596 0.37573 0.50000
   NODE 7 4    0.26863 0.00014 0.17747
   NODE 1 3    0.15318 0.33617 0.07247
   EDGE    0.15318 0.33617 0.07247      0.05596 0.12427 -0.00000
   EDGE    0.55596 0.37573 0.50000      0.44404 0.62427 0.50000
   EDGE    0.26863 0.00014 0.17747      0.26863 -0.00014 0.32253
   EDGE    0.26863 0.00014 0.17747      0.23137 -0.50014 0.17747
   EDGE    0.26863 0.00014 0.17747      0.34682 0.16383 0.07247
   EDGE    0.26863 0.00014 0.17747      0.23137 0.49986 0.17747
   EDGE    0.15318 0.33617 0.07247      0.15318 0.33617 -0.07247
# EDGE_CENTER    0.10457 0.23022 0.03624
# EDGE_CENTER    0.50000 0.50000 0.50000
# EDGE_CENTER    0.26863 -0.00000 0.25000
# EDGE_CENTER    0.25000 -0.25000 0.17747
# EDGE_CENTER    0.30773 0.08198 0.12497
# EDGE_CENTER    0.25000 0.25000 0.17747
# EDGE_CENTER    0.15318 0.33617 0.00000
END
```

[S4] (a) O. Delgado-Friedrichs and M. O'Keeffe, *Acta Crystal. A*, 2003, **59**, 351. *Systre* is available at http://www.gavrog.org/. (b) M. O'Keeffe, M. A. Peskov, S. J. Ramsden and O. M. Yaghi, *Acc. Chem. Res.*, 2008, **41**, 1782. *RCSR* (Reticular Chemistry Structure Resource) is available at http://rcsr.anu.edu.au/.

[S5] V. A. Blatov, M. O'Keeffe and D. M. Proserpio, *CrystEngComm*, 2010, **12**, 44.

Topological information for lrl:

Point Symbol: $(3.10.11)_2(3.12^2)(4^2.6.10^2.12)_2$

TD10: 713.6

Systre file (.cgd) is given below:

```
CRYSTAL
   NAME "lrl; ROD-8"
   GROUP Cccm
   CELL 1.72063 5.46508 9.16178 90.0000 90.0000 90.0000
   NODE 5 3    0.32149 0.07219 0.35090
   NODE 1 4    0.00000 0.20336 0.30457
   NODE 7 3    0.00000 0.50000 0.05457
   EDGE    0.00000 0.50000 0.05457      0.17851 0.57219 0.14910
   EDGE    0.00000 0.20336 0.30457      -0.50000 0.29664 0.30457
   EDGE    0.00000 0.20336 0.30457      -0.00000 0.20336 0.19543
   EDGE    0.00000 0.50000 0.05457      0.00000 0.50000 -0.05457
   EDGE    0.00000 0.20336 0.30457      0.32149 0.07219 0.35090
   EDGE    0.32149 0.07219 0.35090      0.67851 -0.07219 0.35090
   EDGE    0.00000 0.20336 0.30457      0.50000 0.29664 0.30457
# EDGE_CENTER    0.08925 0.53610 0.10184
# EDGE_CENTER    -0.25000 0.25000 0.30457
# EDGE_CENTER    0.00000 0.20336 0.25000
# EDGE_CENTER    0.00000 0.50000 0.00000
# EDGE_CENTER    0.16075 0.13778 0.32774
# EDGE_CENTER    0.50000 0.00000 0.35090
# EDGE_CENTER    0.25000 0.25000 0.30457
END
```

Topological information for lrj:

Point Symbol: (4.8.10)(4^2.6.8^2.10)

TD10: 830

Systre file (.cgd) is given below:

```
----------------------------------------
CRYSTAL
   NAME "lrj; basic net of lrk and lrl"
   GROUP Cccm
   CELL 5.23705 1.68608 6.17560 90.0000 90.0000 90.0000
   NODE 2 3    0.07317 0.19051 0.41904
   NODE 1 4    0.30135 0.00000 0.16904
   EDGE    0.30135 0.00000 0.16904      0.19865 -0.50000 0.16904
   EDGE    0.07317 0.19051 0.41904      -0.07317 -0.19051 0.41904
   EDGE    0.30135 0.00000 0.16904      0.30135 -0.00000 0.33096
   EDGE    0.07317 0.19051 0.41904      0.07317 0.19051 0.58096
   EDGE    0.30135 0.00000 0.16904      0.42683 -0.30949 0.08096
   EDGE    0.30135 0.00000 0.16904      0.19865 0.50000 0.16904
# EDGE_CENTER    0.25000 -0.25000 0.16904
# EDGE_CENTER    0.00000 -0.00000 0.41904
# EDGE_CENTER    0.30135 -0.00000 0.25000
# EDGE_CENTER    0.07317 0.19051 0.50000
# EDGE_CENTER    0.36409 -0.15474 0.12500
# EDGE_CENTER    0.25000 0.25000 0.16904
END
----------------------------------------
```

Additional Characterization

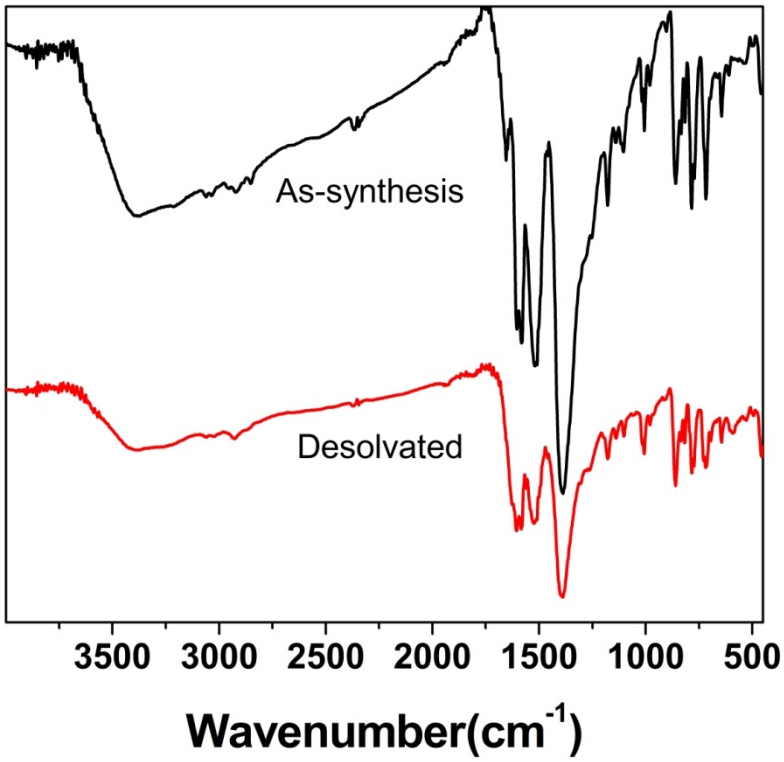


Fig. S2 IR spectra of the as-synthesis ROD-8 (black) and activated sample (red) by heating under vacuum at 180 °C (before heating, ROD-8 was immersed in MeOH for a week).

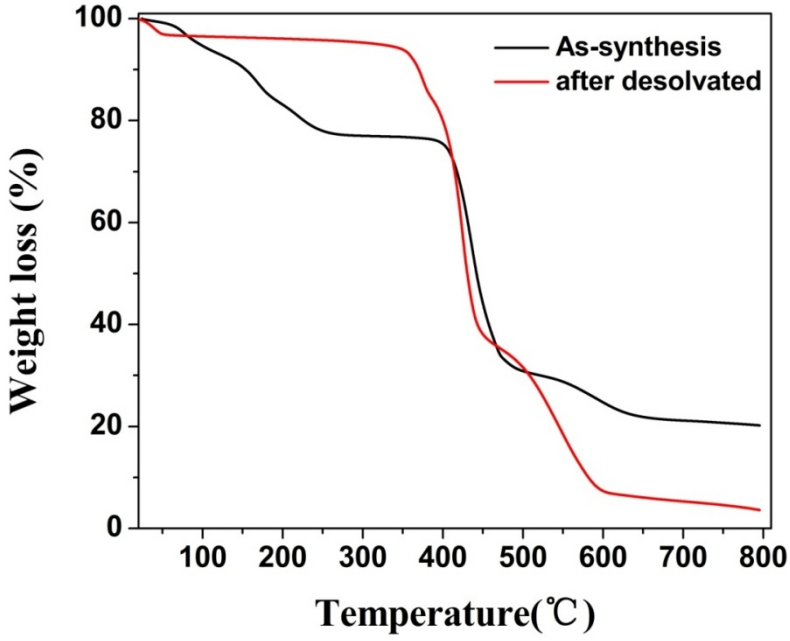


Fig. S3 TGA plots of the as-synthesis ROD-8 (black) and activated sample (red) by heating

under vacuum at 180 °C.

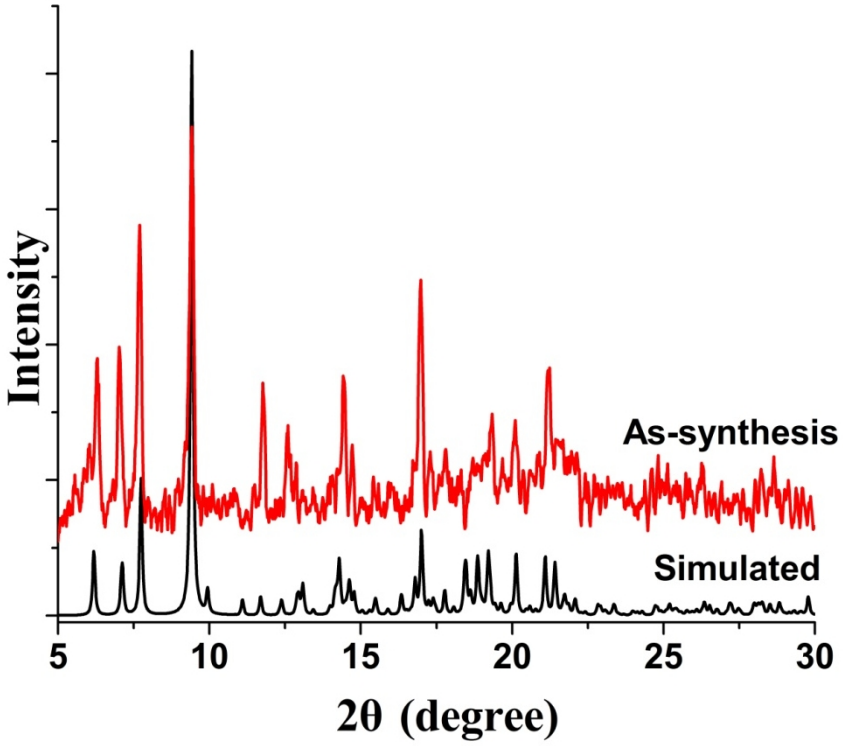


Fig. S4 PXRD patterns of the as-synthesis (red) and simulated ROD-8 (black).

Gas Adsorption Measurements and Analysis

Calculation of isosteric heat of adsorption

The isosteric heat of adsorption (Q_{st}) for the CO_2 adsorption of ROD-8 is calculated via the Clausius–Clapeyron equation expatiated below. The adsorption isotherms used for the calculations are the ones measured at 273 K, 298 K and 303 K given in Fig. 2b in the main text. The results are given in Fig. 3a in the main text.

The isosteric heat of adsorption (Q_{st}) can be calculated via the Clausius–Clapeyron equation:

$$Q_{st} = -R\left[\frac{\partial \ln p}{\partial(1/T)}\right]_N \quad (E1)$$

where p is the pressure, T is the temperature, N is the amount adsorbed, R is the universal gas constant. Integrating equation (E1) gives:

$$(\ln p)_N = -\left(\frac{Q_{st}}{R}\right)\left(\frac{1}{T}\right) + C \quad (E2)$$

where C is a constant. Here an isotherm is first fitted to a high-order polynomial equation to obtain an expression for N as a function of p. Then the values of p at a given N for each T can be interpolated from the fitted equation. At each given N, the isostere plot of $(\ln p)_N$ as a function of $(1/T)$, which is obtained from linear regression, matches with the form of equation (E2), and therefore the Q_{st} values can be computed from the slopes of the isostere plot.

Fitting of adsorption isotherms.

Before further calculation and analysis of the adsorption and separation properties, the adsorption isotherms must be fitted properly to adsorption models of physical meanings. Here the measured experimental data on pure component isotherms for CO_2, N_2 and CH_4 at 273K and 298K are fitted using dual-site Langmuir (DSL) model:

DSL: $$q = \frac{q_{sat,A} b_A p}{1 + b_A p} + \frac{q_{sat,B} b_B p}{1 + b_B p} \quad (E3)$$

where q is the adsorption quantity, q_{sat} is the saturate adsorption quantity, b is the coefficients the subscripts A and B indicate the parameters for the adsorption sites A and B, respectively.

The fitting results are given in Fig. S5-S6 and Table S2-S4.

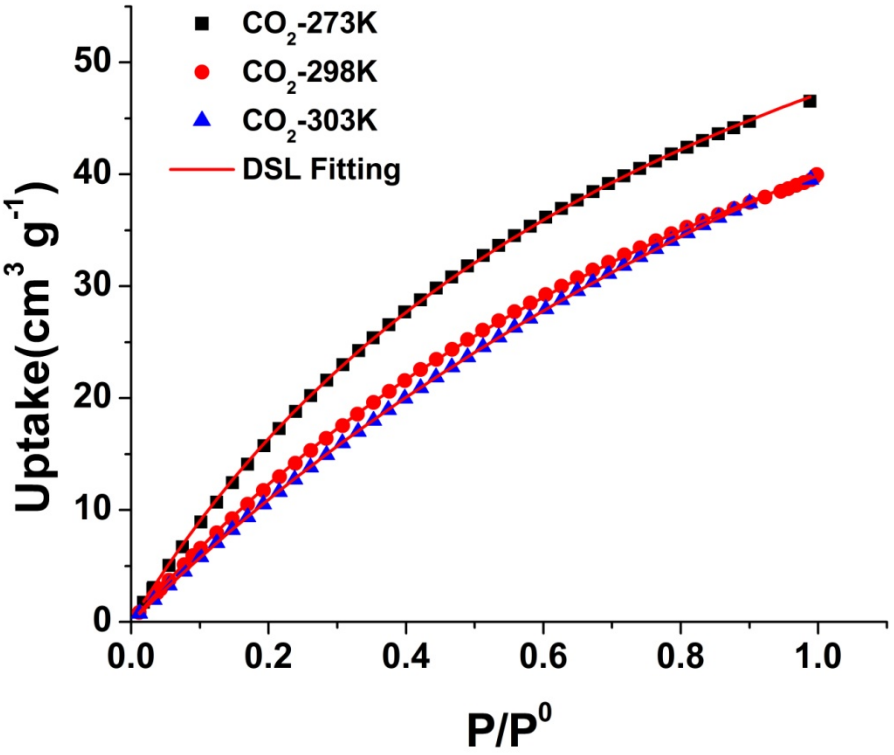


Fig. S5 DSL models fitting for the CO_2 adsorption isotherms of ROD-8. Dots are experimental data; lines are fitting curves.

Table S2 Dual site Langmuir fitting parameters for CO_2 adsorption for ROD-8

	273 K	298 K	303 K
$q_{sat,A}$	44.52988	45.48613	60.74641
b_A	1.12654	0.78095	0.49447
$q_{sat,B}$	44.52988	45.48613	60.74641
b_B	1.12654	0.78095	0.49447
R^2	0.99988	0.99993	0.99996

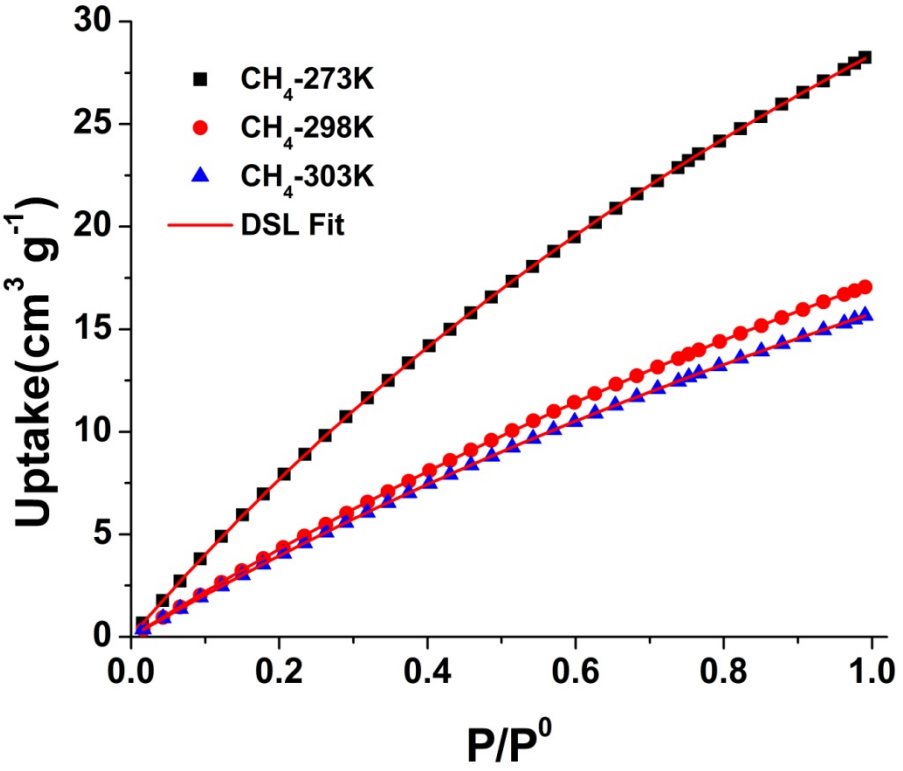


Fig. S6 DSL models fitting for the CO_2 adsorption isotherms of ROD-8. Dots are experimental data; lines are fitting curves.

Table S3 Dual site Langmuir fitting parameters for CH_4 adsorption for ROD-8

	273 K	298 K	303 K
$q_{sat,A}$	43.52768	35.33205	31.08915
b_A	0.48373	0.32192	0.33951
$q_{sat,B}$	43.52768	35.33205	31.08915
b_B	0.48373	0.32192	0.33951
R^2	0.99999	0.99999	0.99999

For ROD-8, the adsorption isotherms for N_2 at 273K and 298K can also be fitted to the DSL model, fitting parameters are shown in Table. S4.

Table S4 Dual site Langmuir fitting parameters for N_2 adsorption for ROD-8

	273K	298K
$q_{sat,A}$	6.48906	5.6747
b_A	0.40749	0.35044
$q_{sat,B}$	6.48906	5.6747
b_B	0.40749	0.35044
R^2	0.9997	0.99879

Calculation of CO_2/N_2, CO_2/CH_4 and CH_4/N_2 adsorption selectivity.

The Ideal Adsorbed Solution Theory (IAST)[S6] is used to estimate the composition of the adsorbed phase from pure component isotherm data and predict the selectivity of the binary mixture CO_2/N_2, CO_2/CH_4 and CH_4/N_2. For the IAST, the following equation is proposed:

$$\int_0^{p_a} \frac{q_a}{p} dp = \int_0^{p_b} \frac{q_b}{p} dp \quad (E4)$$

where p_a and p_b are the pressure of component a and b at the same spreading pressure and the same temperature as that of the mixture respectively. And for the ideal binary gas mixture, according to the Raoult's law, there are the following two equations:

$$y\, p_t = x\, p_a \quad (E5)$$

$$(1-y)\, p_t = (1-x)\, p_b \quad (E6)$$

where p_t is the total gas pressure, y and x are the molar fraction of a in bulk phase and molar fraction of a in the adsorbed phase respectively. Combining equations (E3), (E4), (E5) and (E6), the molar fraction of a in the adsorbed phase can be obtained from the following equation:

$$\int_0^{\frac{yp_t}{x}} \frac{q_a}{p} dp = \int_0^{\frac{(1-y)p_t}{1-x}} \frac{q_b}{p} dp \quad (E7)$$

Before using equation (E7), the adsorption isotherms of the pure components must be fitted properly by the Langmuir adsorption models or others. Then one can get the Langmuir fitting parameters of adsorption equilibrium of pure a and pure b. Given the total pressure p_t and the molar fraction of a in bulk phase y, there is only one unknown variable quantity x (absorbed phase) in equation (E7), which can be solved by *MATLAB* software.

After calculating the molar faction of a in adsorbed phase x, one can calculate the adsorption selectivity, which is defined as:

$$S = \frac{x_a / y_a}{x_b / y_b} \quad (E8)$$

where x_a, y_b are the molar fraction of a in the adsorbed phase and molar fraction of a in bulk

[S6] K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae and J. R. Long, *Chem. Rev.*, 2012, **112**, 724.

phase respectively, x_b, y_b are the molar fraction of b in the adsorbed phase and molar fraction of j in bulk phase respectively. The results are given in Fig. 3 (298 K) in the main text and Fig. S7 (273 K).

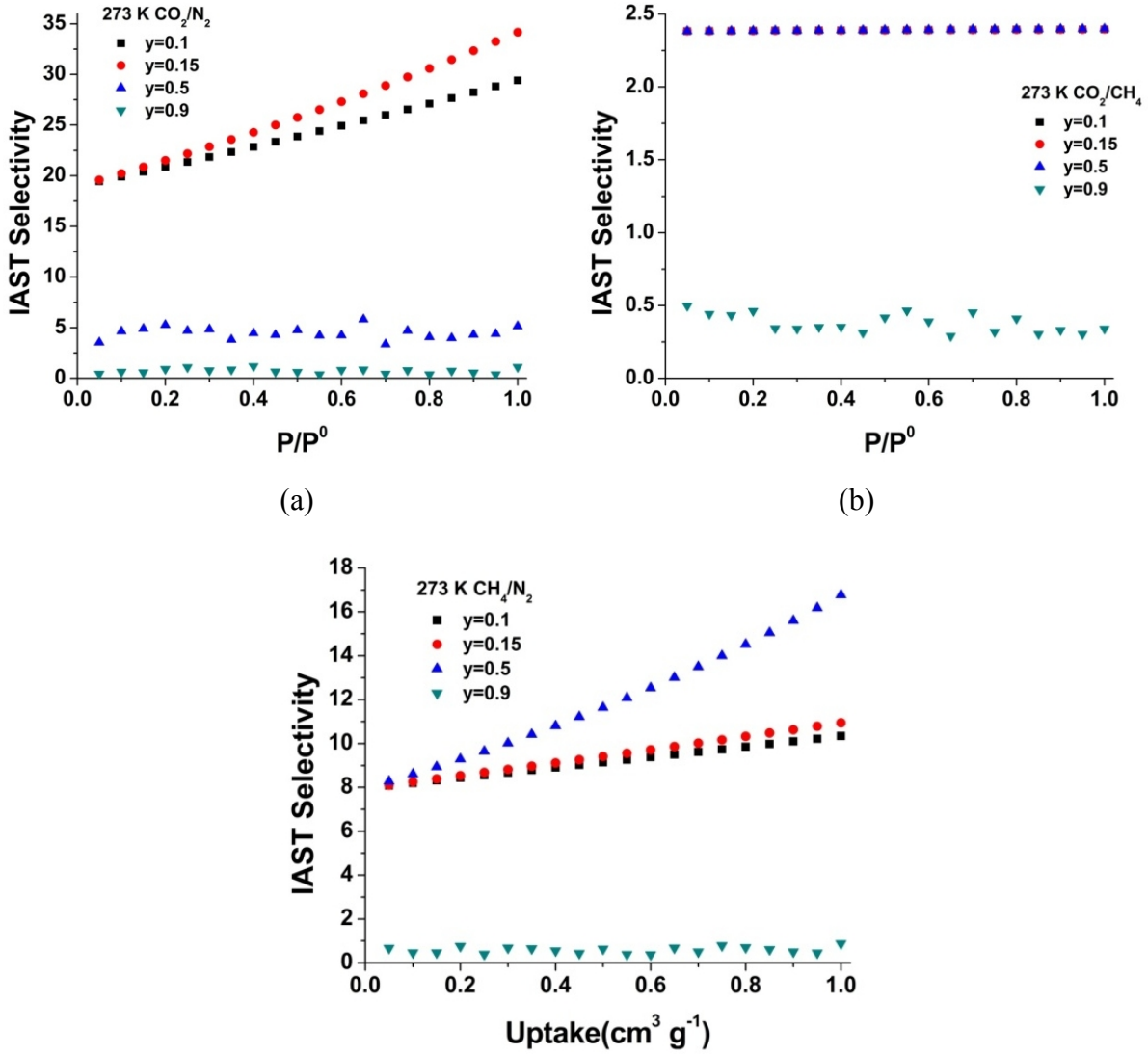


Fig. S7 The predicted IAST selectivity (dots) of (a) CO_2/N_2, (b) CO_2/CH_4 and (c) CH_4/N_2 at 273 K for ROD-8a. In all calculations, the DSL model is used. y denotes the molar fraction of the former (i.e. CO_2 in (a) and (b) and CH_4 in (c)) in the bulk phase.