Electronic Supplementary Information (ESI)

A highly stable MOF with rod SBU and tetracarboxylate linker: unusual topology and CO₂ adsorption behaviour at ambient condition

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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 H₄TBAPy) 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. ¹H NMR spectrum was recorded on Brucker Biospin Avance (400 MHz) equipment. Powder X-ray diffraction patterns (PXRD) of the bulk samples were measured on a Bruker D8 Advance diffractometer (Cu K α , λ = 1.5418 Å) under room temperature. Low-pressure (up to 1 bar) gas adsorption isotherms (N₂, CO₂, CO) were measured on the Micrometrics ASAP 2020 Surface Area and Porosity Analyzer. In one typical run, about 150 mg as-synthesis samples were activated at 180 °C for 15 hours by using the "outgas" function of the surface area analyzer before measurements.

Synthesis of [Mn₂(TBAPy)(H₂O)₂]·DMF·H₂O (ROD-6).

A mixture of 50 % aqueous $Mn(NO_3)_2$ (8.06 mg, 0.0225 mmol) or $MnCl_2 \cdot 4H_2O$ (4.45 mg, 0.0225 mmol), H₄TBAPy (5.12 mg, 0.0075 mmol), and DMF/H₂O mixed solvent (2.0 mL, 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 orange block-like crystals were obtained by filtration and washing with DMF for 3 times (2.0 ml each time, yield: 6.0 mg).

Synthesis of [In₂(TBAPy)(OH)₂] · guests (ROD-7).

The samples of ROD-7 were synthesized according the literature¹ with slight modification. A mixture of $In(NO_3)_3 \cdot 9H_2O$ (24 mg 0.06 mmol) and H₄TBAPy (20,

^{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.

0.03 mmol), and DMF/dioxane/H₂O mixed solvent (8.0 mL, 2:1:1, v/v) with 20 μ L concentrated hydrochloric acid were sealed in a 15mL vial. And the vial was heated in an oven at 85 °C for 12 hours. After cooling to room temperature at rates 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: 24.0 mg).

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 K α , $\lambda = 1.54178$ 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 F². 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 void volume (excluding guest solvent molecules) in the crystal cell was calculated using the program *PLATON*.^{S3} Crystal data and structure refinements are summarized in Table S1. Selected bond lengths and angles are given in Table S2.

^{S2} G. M. Sheldrick, Acta Crystallographica. A, 2007, 64, 112.

^{S3} A. Spek, J. Appl. Crystallogr., 2003, **36**, 7.

	ROD-6
Formula	C ₄₇ H ₃₅ Mn ₂ NO ₁₂
Mr.	915.64
Crystal system	Monoclinic
Space group	$P2_{1}/c$
Temp. (K)	293.3
<i>a</i> (Å)	6.9970(2)
<i>b</i> (Å)	25.4831(9)
<i>c</i> (Å)	28.2642(8)
α (°)	90
β (°)	92.712(2)
γ (°)	90
$V(\text{\AA}^3)$	5034.0(3)
Ζ	4
$D_{\rm c}({\rm g\cdot cm}^{-3})$	1.208
no. of reflns	24252
no. of unique	8870
unique refl.(R_{int})	0.0508
GOF on F ²	1.170
$R_1[I \ge 2\sigma(I)]^a$	0.1056
$wR_2[I \ge 2\sigma(I)]^b$	0.3062
R_{1} [all data]	0.1418
wR_2 [all data]	0.3306

Table S1. Crystal data and structure refinements for ROD-6

 ${}^{a} R_{I} = \Sigma(||F_{0}| - |F_{c}||) / \Sigma |F_{0}|; {}^{b} w R_{2} = [\Sigma w (F_{0}^{2} - F_{c}^{2})^{2} / \Sigma w (F_{0}^{2})^{2}]^{1/2}$

Table S2. Selected bond lengths (Å) and angles (°) for ROD-6

ROD-6

Mn(2)-O(10)#1	2.123(4)	O(10)#1-Mn(2)-O(4)#2	159.18(19)	O(10)#1-Mn(2)-O(6)#3	99.57(18)
Mn(2)-O(4)#2	2.148(5)	O(10)#1-Mn(2)-O(7)	93.36(18)	O(4)#2-Mn(2)-O(6)#3	95.24(19)
Mn(2)-O(7)	2.201(4)	O(4)#2-Mn(2)-O(7)	104.91(17)	O(7)-Mn(2)-O(6)#3	73.35(16)
Mn(2)-O(5)#3	2.305(6)	O(10)#1-Mn(2)-O(5)#3	85.5(2)	O(3)#2-Mn(2)-O(6)#3	129.86(15)
Mn(2)-O(3)#2	2.381(4)	O(4)#2-Mn(2)-O(5)#3	91.3(2)	O(8)-Mn(2)-O(6)#3	130.02(17)
Mn(2)-O(8)	2.390(5)	O(7)-Mn(2)-O(5)#3	126.68(19)	O(2)-Mn(1)-O(1)	92.0(2)
Mn(2)-O(6)#3	2.425(5)	O(10)#1-Mn(2)-O(3)#2	102.03(17)	O(9)#4-Mn(1)-O(6)#5	85.3(2)
Mn(1)-O(2)	2.144(5)	O(7)-Mn(2)-O(3)#2	148.07(17)	O(9)#4-Mn(1)-O(7)#6	93.72(19)
Mn(1)-O(1)	2.150(5)	O(5)#3-Mn(2)-O(3)#2	82.75(19)	O(6)#5-Mn(1)-O(7)#6	78.38(16)
Mn(1)-O(9)#4	2.170(5)	O(10)#1-Mn(2)-O(8)	86.22(19)	O(6)#5-Mn(1)-O(3)	100.05(17)
Mn(1)-O(6)#5	2.185(5)	O(4)#2-Mn(2)-O(8)	95.4(2)	O(7)#6-Mn(1)-O(3)	90.54(17)
Mn(1)-O(7)#6	2.196(4)	O(5)#3-Mn(2)-O(8)	171.2(2)	O(3)#2-Mn(2)-O(8)	96.21(16)
Mn(1)-O(3)	2.207(4)				

(symmetry operations: #1: x-1,-y+2,-z+2; #2: x-2,-y+3/2,z+1/2; #3: -x,y+1/2,-z+5/2; #4: -x,y-1/2,-z+3/2; #5: -x+1,-y+1,-z+2; #6: x+1,-y+3/2,z-1/2).



Fig. S1 The coordination environments of the metal (Mn1 and Mn2) (a) and ligand (b) in ROD-6.

The asymmetric unit of ROD-6 contains two Mn^{II} ions, one deprotonated TBAPy ligands and two coordinated H₂O. Mn1 shows a distorted octahedral configuration, fulfilled by four carboxylate-O from four TBAPy and the other two coordinated oxygen atoms from H₂O, while Mn2 is coordinated with seven carboxylate-O from four TBAPy ligands and adopts a distorted pentagonal bipyramidal geometry (Fig. S1a). Each pyrene-core ligand is eight-coordinate to eight Mn atoms (Fig. S1b). The two crystallographically independent Mn ions are mono- or triply bridged by caroxylates to generate an infinite rod-shape second building unit (rod SBU, Fig. S2a) for ROD-6. ROD-7 has a slightly different rod SBU (Fig. S2b). Note that for ROD-6 there are coordinated H₂O molecules, while in ROD-7 these are replaced by charged hydroxyl groups to balance the extra valency of In^{III}. The rod SBUs in ROD-6 are further linked through the TBAPy ligands to form a three-dimensional MOF (see Fig. 1b in the main text). If viewed along a axis, there exist two type distorted square channels. The dimensions for the larger channel are 13.975×8.795 Å² and for the smaller one are 12.942×9.152 Å². The channels are filled with free DMF and water molecules. The solvent-accessible volume is 40.2 % calculated by PLATON.



Fig. S2 The rod SBUs in ROD-6 (a) and ROD-7 (b). Color codes: Mn magenta; In pink; O red; C black; H white. Note the different of the coordinated H_2O and -OH.

Topological Analysis

Method and Software.

The deconstruction method of the rod SBUs in ROD-6 and ROD-7 follows the proposed principles outlined recently.^{S4} The tetratopic organic linkers in ROD-6 and ROD-7 are simplified as linked triangles (by counting the two branch points in the tetracarboxylate linker as the vertices of the underlying nets), following a recent review on this topic.^{S5} The branch points in the linker are converted to triangles (their vertex figure) rather than just single 3-c nodes, because for rod SBUs the points of extension are taken as nodes of the net rather than, as for finite SBUs, taking the centers of the clusters as nodes.

As shown in Fig. S3 and S4, the underlying nets of ROD-6 and ROD-7 are **lrk** and **frz**, respectively. The identification of the nets and computation of their ideal symmetry are performed through the program *Systre*.^{S6} These two nets are both new to RCSR.^{S7} **lrk** and **frz** are derived from the basic nets of **lrj** and **fry** nets (also shown in Fig. S3 and S4). They are closely related. **fry** is known to RCSR, while **lrj** is also new. The topological information of the new nets are given below, and the .cgd file for specifying the new nets are shown below and also attached as an electronic file accompanying this ESI.

It is worth noting that for each of the basic nets **lrj** and **fry**, there are at least two possibilities for the derived nets, by splitting the squares (blue in Fig. S3 and S4) in different directions (along **a** direction or perpendicular to **a** direction; **b** is the direction of the rod axis; see Section 3.6 in a recent review^{S5} for similar treatment of NU-1000). In the observed MOFs with nets **lrk** (ROD-6) and **frz** (ROD-7) the splitting vector is normal to **a**. The derived nets with the vector parallel to **a** have RCSR symbols **lrl** and **frx** respectively.

^{S4} M. O'Keeffe and O. M. Yaghi, Chem. Rev., 2012, 112, 675.

^{S5} M. Li, D. Li, M. O'Keeffe and O. M. Yaghi, Chem. Rev., DOI: 10.1021/cr400392k.

^{S6} O. Delgado-Friedrichs and M. O'Keeffe, *Acta Crystallogr. A*, 2003, **59**, 351. *Systre* is available at <u>http://www.gavrog.org/</u>

^{S7} M. O'Keeffe, M. A. Peskov, S. J. Ramsden and O. M. Yaghi, *Acc. Chem. Res.*, 2008, **41**, 1782. RCSR is available at <u>http://rcsr.anu.edu.au/</u>

ROD-6 (Mn MOF)

ROD-6 (Mn MOF)



Fig. S3 Deconstruction of ROD-6 (upper) and the underlying net **lrk** derived from **lrj** (lower). Note **lrk** and **lrj** are new nets for RCSR.

Topological information for lrk:

Point Symbol:^{S8} (3.14²)(3.8.9)₂(4².6.8².10)₂

TD10: 621

Systre file (.cgd) is given below:

CRYSTAL

NAME "lrk; ROD-6" **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**

^{S8} V. A. Blatov, M. O'Keeffe and D. M. Proserpio, *CrystEngComm*, 2010, **12**, 44.

Topological information for lrj:

Point Symbol: (4.8.10)(4².6.8².10)

TD10: 830

Systre file (.cgd) is given below:

CRYSTAL NAME "lrj; basic net of lrk" **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 -----

S12

ROD-7 (In MOF)



ROD-7 (In MOF)



Fig. S4 Deconstruction of ROD-7 (upper) and the underlying net **frz** derived from **fry** (lower). Note **frz** is a new net for RCSR; **fry** is known.

Topological information for frz:

Point Symbol: (3.12²)(3.8.9)₂(4².6.8².10)₂

TD10: 565

Systre file (.cgd) is given below:

CRYSTAL

```
NAME "frz; ROD-7"
  GROUP Cmmm
  CELL 8.47313 1.95254 3.53229 90.0000 90.0000 90.0000
  NODE 3 4 0.26299 0.00000 0.35849
  NODE 2 3 0.44095 0.00000 0.00000
  NODE 1 3 0.33877 0.00000 0.14142
  EDGE 0.33877 0.00000 0.14142
                                 0.26299 0.00000 0.35849
  EDGE 0.33877 0.00000 0.14142
                                 0.33877 0.00000 -0.14142
  EDGE 0.26299 0.00000 0.35849
                                 0.26299 0.00000 0.64151
  EDGE 0.44095 0.00000 0.00000
                                 0.33877 0.00000 0.14142
  EDGE 0.26299 0.00000 0.35849
                                 0.23701 0.50000 0.35849
  EDGE 0.44095 0.00000 0.00000
                                 0.55905 0.00000 -0.00000
# EDGE CENTER 0.30088 0.00000 0.24995
# EDGE CENTER 0.33877 0.00000 -0.00000
# EDGE CENTER 0.26299 0.00000 0.50000
# EDGE CENTER 0.38986 0.00000 0.07071
# EDGE CENTER 0.25000 0.25000 0.35849
# EDGE CENTER 0.50000 0.00000 -0.00000
END
```

Topological information for fry can be found in RCSR:

http://rcsr.anu.edu.au/nets/fry

Additional Characterization



Fig. S5 IR spectra of the as-synthesis ROD-6 (black) and activated sample (red) by heating under vacuum at 180 °C.



Fig. S6 TGA plots of the as-synthesis ROD-6 (black) and activated sample (red) by heating under vacuum at 180 °C. The weight loss of 15 wt% to 215 °C corresponds to the evacuation of one free DMF, one free water and two coordinated water (ca. 13.88 wt% in total). The

activated framework is stable from 215 to 485 °C.



Fig. S7 (a) PXRD patterns of the as-synthesis (magenta) and simulated ROD-6 (black), and those after heating and stirring under 80 °C for 24 hours in distilled water (red), hydrochloric acid solution of pH = 3 (blue), and sodium hydroxide solution of pH = 10 (teal); (b) PXRD patterns of the as-synthesis (red) and simulated ROD-6 (black), and those after immersing under room temperature for 12 hours in distilled water (blue), hydrochloric acid solution of

pH = 2 (teal), and sodium hydroxide solution of pH = 11 (magenta).



(b)

Fig. S8 (a) PXRD patterns of the as-synthesis (red) and simulated ROD-7 (black). (b) Varied

temperature PXRD from room temperature to 650 $^{\circ}\text{C}.$

Gas Adsorption Measurements and Analysis



Fig. S9 (a) N_2 adsorption and desorption isotherms at 77 K and CO_2 adsorption and desorption isotherms at 195 K for ROD-6. (b) N_2 adsorption and desorption isotherms at 77 K for ROD-6 after immersing under distilled water for 12 h.

The permanent porosity of the activated sample of ROD-6 is confirmed by N₂ sorption isotherm at 77 K (Fig. S9). The isotherm shows a type-I curve, with the amounts increasing sharply at the beginning and then reaching a plateau of 148 cm³ (STP) g⁻¹ at 1.0 atm. The BET and Langmuir surface areas are 345 and 535 m² g⁻¹, respectively, which are calculated using the adsorption data in the relative pressure range of $p/p^0 = 0.06-0.3$. The total pore volume of ROD-6 is 0.166 cm³ g⁻¹ obtained by a single point at relative pressure of 0.094. At 195 K, ROD-6 shows a type-I CO₂ adsorption isotherm, and without hysteresis (Fig. S9). The CO₂ uptake is 150 cm³ (STP) g⁻¹ at 1.0 bar, corresponding to 29.46 wt%, which is almost the same quantity of N₂ at 77 K. The CO₂ uptake amount is lower than the theoretical saturated value (186.4 cm³ (STP) g⁻¹, 36.61 wt%) calculated from the crystal density, free void and liquid CO₂ density (1.1 g cm⁻³). The adsorption amount of ROD-6 after treating with water for 12 h is 153 cm³ (STP) g⁻¹ at 1.0 atm (Fig. S9b), and its BET and Langmuir surface areas are 449 and 683 m² g⁻¹, respectively.



Fig. S10 N₂ adsorption and desorption isotherms at 77 K and CO₂ adsorption and desorption isotherms at 195 K for ROD-7.

The N₂ sorption isotherm at 77 K of ROD-7 reported by the literature^{S1} can be reproduced (Fig. S9). The CO₂ adsorption and desorption isotherms are measured in this work (Fig. S9). Interestingly, the adsorption isotherm shows a plateau below the pressure $p/p^0 = 0.2$, and then the uptake increases again and reach saturation at $p/p^0 = 0.4$. The desorption isotherm shows a pronounced hysteresis. These striking features of the CO₂ sorption isotherms resemble those of MIL-53 (Al, Cr),^{S9} which are also based on a similar zigzagladder SBU. MIL-53 (Al, Cr) is known to exhibit a "breathing" effect of the host framework due to the interaction between the exposed hydroxyl group and the quadrupole moment of the adsorbed CO₂ molecules.^{S9} This is also the case for ROD-7, but not for ROD-6 (hydroxyl replaced by water). Note that the CO₂ adsorption isotherms for MIL-53 indicating the breathing effect are measured at room temperature (304 K) and high pressure (up to 30 bar), while those for ROD-7 at 195 K and low pressure (up to 1 bar). The room temperature CO₂ adsorption does not exhibit such effect (shown below).



Fig. S11 N₂, CO₂ and CO adsorption and desorption isotherms at 273K, 298K and 303K for ROD-6. CO₂ uptake 39.36 cm³ (STP) g⁻¹ (7.73 wt %) at 1.0 bar at 298 K; 59.23 cm³ (STP) g⁻¹

^{S9} G. Férey, C. Serre, T. Devic, G. Maurin, H. Jobic, P. L. Llewellyn, G. D. Weireld, A. Vimont, M. Daturi and J.-S. Chang, *Chem. Soc. Rev.*, 2011, **40**, 550.

at 273 K; 36.82 cm³ (STP) g⁻¹ at 303 K.



Fig. S12 N_2 , CO₂ and CO adsorption and desorption isotherms at 273K, 298K and 303K for ROD-7. CO₂ uptake 34.09 cm³ (STP) g⁻¹ (6.7 wt %) at 1.0 bar at 298 K.



Fig. S13 Comparison of the CO₂ adsorption isotherms for ROD-6 (Mn-3D) and ROD-7 (In-3D) at 273 K (a), 298 K (b) and 303 K (c).

At 298 K for example, the CO₂ uptake at 1.0 bar for ROD-7 (34.09 cm³ (STP) g⁻¹, 6.7 wt %) is lower than that of ROD-6 (39.36 cm³ (STP) g⁻¹, 7.73 wt %). In contrast, at lower pressures ($p/p^0 < 0.35$), the CO₂ uptake of ROD-7 is higher than that of ROD-6. The situations at 273 K and 303 K are similar to that in 298 K. For ROD-7, if one μ_2 -OH group (the interacting site) combines a CO₂ molecule, the calculated saturation uptake for ROD-7 is 47.66 cm³ (STP) g⁻¹, higher than the maximum uptake (34.09 cm³ (STP) g⁻¹) of ROD-7 at 1.0 bar at 298 K. For ROD-6, there is no such interacting site (low heat of adsorption), but the uptake at 298 K is higher, indicating a different adsorption process may occur.

Calculation of Isosteric Heat of Gas Adsorption (Q_{st}).

The isosteric heat of adsorption (Q_{st}) for the CO₂ adsorption of ROD-6 and ROD-7 are calculated via the two methods (A. direct method; B. virial method) expatiated below. The adsorption isotherms used for the calculations are the ones measured at 273 K, 298 K and 303 K given above (Fig. S11 and S12). The results are given in Fig. 2b in the main text.

A. direct method

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. B. virial method

At first, the adsorption data are fitted using the virial-type equation:

$$lnp = lnN + \left(\frac{1}{T}\right)\sum_{i=0}^{m} a_i N^i + \sum_j^n b_j N^j \quad (E3)$$

Here p is the pressure expressed in Torr, N is the amount adsorbed in mmol/g, T is the temperature in K, a_i and b_i are virial coefficients, and m, n represent the number of coefficients required to adequately describe the isotherms. Then the Clausius–Clapeyron equation (E1) was employed to calculate the enthalpies of CO₂ adsorption. Combining equations (E1) and (E3), the isosteric heat of adsorption can be calculated using the following equation:

$$Q_{st} = -R \sum_{i=0}^{m} a_i N^i \quad (E4)$$

The fitting parameters of the virial model are given in Fig. S14, and the adsorption enthalpies (Q_{st}) expressed as a function of uptake are shown in Fig. S15.





(b)

S25

Fig. S14 Virial fitting of the CO_2 adsorption isotherms for ROD-6 (a) and ROD-7 (b). Dots are experimental data; lines are fitting curves; fitting parameters given within figures.



Fig. S15 Calculated adsorption enthalpies of CO_2 (Q_{st}) of ROD-6 (Mn-3D, red line) and ROD-7 (In-3D, black line) via the virial method.

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 CO₂, N₂ and CO at 273K, 298K are fitted using single-site Langmuir (SSL) or dual-site Langmuir (DSL) models:

SSL:
$$q = \frac{q_{sat}bp}{1+bp} \quad (E5)$$
$$q = \frac{q_{sat,A}b_Ap}{1+b_Ap} + \frac{q_{sat,B}b_Bp}{1+b_Bp} \quad (E6)$$

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

The adsorption isotherms of ROD-6 and ROD-7 are each fitted to the SSL and DSL models respectively. The fitting results and parameters are given in Fig. S16 and S17, and Table S3–S6. It is shown that the SSL model can better fit to ROD-6, while the DSL model is better for ROD-7.



Fig. S16 The SSL (a) and DSL (b) models fitting for the CO₂ adsorption isotherms of ROD-6.

Table 55 Single site Langinum fitting parameters for CO ₂ adsorption for KOD-0						
	273K	298K	303K			
$q_{ m sat}$	110.68529	118.24368	128.04075			
b	1.20046	0.49175	0.39804			
\mathbb{R}^2	0.99971	0.99999	0.99997			
Table S4 Du	al site Langmuir fitting	g parameters for CO ₂ a	dsorption for ROD-6			
	273K	298K	303K			
$q_{\mathrm{sat,A}}$	61.13114	59.14242	127.96721			
b_{A}	1.20052	0.49179	0.39839			
$q_{ m sat,B}$	49.55384	59.10126	-0.00282			
$b_{ m B}$	1.20041	0.49172	-69.68963			
R ²	0.99969	0.99999	0.99997			

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Note: No pronounced difference between SSL and DSL, but $q_{sat,B}$ for 303 K is abnormal.



Fig. S17 The SSL (a) and DSL (b) models fitting for the CO₂ adsorption isotherms of ROD-7.

Table 55 Single site Langinum fitting parameters for CO ₂ adsorption for ROD-7						
	273K	298K	303K			
$q_{ m sat}$	73.4821	67.76816	62.40913			
b	1.88698	0.9938	0.92796			
R ²	0.99825	0.99978	0.99992			
Table S6 Du	al site Langmuir fitting	g parameters for CO ₂ a	dsorption for ROD-7			
	273K	298K	303K			
$q_{\mathrm{sat,A}}$	82.09178	69.87046	7.75152			
b_{A}	0.52915	0.61874	2.56376			
$q_{ m sat,B}$	24.82517	9.50422	61.38268			
$b_{ m B}$	5.21739	3.19927	0.66719			
R ²	1	0.99996	0.99998			

 Table S5 Single site Langmuir fitting parameters for CO₂ adsorption for ROD-7

Note: Fitting to DSL is better than to SSL.

For ROD-6, the adsorption isotherms for N_2 and CO at 273K and 298K can also be fitted to the SSL model, shown in Fig. S18.



Fig. S18 The SSL fitting for CO_2 , N_2 and CO adsorption isotherms of ROD-6 at 273K and 298K. Dots are experimental data; lines are fitting curves; fitting parameters given within figures.

Calculation of CO₂/N₂ and CO₂/CO Adsorption Selectivity.

The Ideal Adsorbed Solution Theory $(IAST)^{S10}$ 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 and CO_2/CO . For the IAST, the following equation is proposed:

$$\int_{0}^{p_a} \frac{q_a}{p} dp = \int_{0}^{p_b} \frac{q_b}{p} dp \quad (E7)$$

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:

$$y p_t = x p_a$$
 (E8)
(1 - y) $p_t = (1 - x) p_b$ (E9)

^{S10} 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.

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 (E5) [or (E6)], (E7), (E8) and (E9), the molar fraction of a in the adsorbed phase can be obtained from the following equation:

$$\int_{0}^{\frac{yp_{t}}{x}} \frac{q_{a}}{p} dp = \int_{0}^{\frac{(1-y)p_{t}}{x}} \frac{q_{b}}{p} dp \quad (E10)$$

Before using equation (E10), 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 (E10), 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:

$$S = \frac{\frac{x_a}{y_a}}{\frac{x_b}{y_b}} \quad (E11)$$

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

Here the SSL model is used for the adsorption isotherms of ROD-6, while DSL for ROD-7. The predicted IAST selectivity as a function of uptake capacity is given in Fig. S19–22. Fig. S20 gives a plot of the CO_2/N_2 selectivity of ROD-6 as a function of the varying percentage of CO_2 in the gas mixture (298 K) for comparison.



Fig. S19 The predicted IAST selectivity (dots) of CO_2/N_2 at 273 K and 298 K for ROD-6. SSL model is used. y1 denotes the molar fraction of CO_2 in the bulk phase. The lines are linear fitting to the dots for clarity.



Fig. S20 The predicted IAST selectivity (dots) of CO_2/N_2 at 298 K for ROD-6, showing the selectivity as a function of varying percentage of CO_2 in the gas mixture of the bulk phase (total pressure 1 bar). The line just connects the dots. Increasing trend is observed.



Fig. S21 The predicted IAST selectivity (dots) of CO_2/CO at 273 K and 298 K for ROD-6. SSL model is used. y1 denotes the molar fraction of CO_2 in the bulk phase. The lines are linear fitting to the dots for clarity. The selectivity is lower than that of CO_2/N_2 .



Fig. S22 The predicted IAST selectivity (dots) of CO_2/N_2 at 273 K and 298 K for ROD-7. DSL model is used. The fractional numbers denote the molar fraction of CO_2 in the bulk phase. The lines are linear fitting to the dots for clarity.

Comparison of Adsorption Performance with Important MOFs.

		BET Surface	CO ₂ Uptake		Referenc
Chemical Formula	Common Name	Area (m²/g)	(wt %)	Category	e
Mg ₂ (dobdc)	Mg-MOF-74	1800	26.7	А	S11
Cu ₃ (BTC) ₂	HKUST-1	1400	18.4	В	S12
$H_3[(Cu_4Cl)_3(BTTri)_8(mmen)_{12}]$	mmen-CuBTTri	870	15.4	А	S13
Al(OH)(BDC)	MIL-53(Al)	1300	10.6	С	S14
Zn ₄ O(BDC) ₃	MOF-5	2304	8.5	В	S15
V ^{IV} O(BDC)	MIL-47	600	8.1	С	S16
Zr ₆ (TBAPy) ₂ (OH) ₁₆	NU-1000	2320	7.92	D	S17
Mn ₂ (TBAPy)(H ₂ O) ₂	ROD-6	345	7.73	C, D	this work
In ₂ (TBAPy)(OH) ₂	ROD-7	1189	6.7	C, D	this work
Zn(meIm) ₂	ZIF-8	1135	4.3	В	S16
Zn ₄ O(BTB) ₂	MOF-177	5400	3.6	В	S11

Table S7. CO₂ adsorption performance of selected important MOFs^{S10} at ambient conditions (1 atm, 298 K), compared with those in this work.

Note: A: MOFs with exposed metal sites and high uptake; B: important and commercialized MOFs; C: MOFs with rod SBUs; D: MOFs based on TBAPy ligand (same as this work).

Although the CO_2 uptake of ROD-6 at ambient condition is not as high as those best ones, one should note that the BET surface of ROD-6 is very low. Given that ROD-6 does not have strongly interacting sites, evidenced by its low adsorption enthalpy, the CO_2 uptake behavior may be different from common one, especially when compared with ROD-7 and NU-1000 based on the same ligand. Also the high thermal stability of ROD-6 approaching

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those of Zr MOFs is a merit of this material.