Electronic Supplementary Information (ESI) for

# A metal-organic framework with rod secondary building unit based on the Boerdijk-Coxeter helix

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#### **Experimental Section**

**General**: Reagents and solvents employed were commercially available and used as received. Infrared (IR) spectra were obtained in KBr disks on a Nicolet Avatar 360 FTIR spectrometer in the range of 4000-400 cm<sup>-1</sup>; abbreviations used for the IR bands are w = weak, m = medium, b = broad, vs = very strong.<sup>1</sup>H-NMR spectroscopy was performed on a Bruker DPX 400 spectrometer using the TMS as internal standard. All  $\delta$  values are given in ppm. Thermogravimetric (TGA) measurements were performed on a TA Instruments Q50 Thermogravimetric Analyzer under nitrogen flow of (40 mL·min<sup>-1</sup>) at a typical heating rate of 10°C·min<sup>-1</sup>. Powder X-ray diffraction (PXRD) patterns of the bulk samples were measured on a Bruker D8 Advance diffractometer (Cu  $K\alpha$ ,  $\lambda = 1.5418$  Å) under room temperature. Low-pressure (up to 1 bar) gas adsorption isotherms were measured on the Micrometrics ASAP 2020 Surface Area and Porosity Analyzer. The as-synthesis samples of ROD-1 were thermally activated before measurements.

Synthesis of ligand:



Synthesis of methyl 4-(2-acetyl-3-oxobutyl)benzoate. Acetylacetone (1 ml, 10 mmol) was added to a stirred solution prepared from potassium tert-butoxide (1.12 g, 10 mmol) and tert-butanol (70 mL). After 15 minutes, methyl4-(bromomethyl)benzoate (2.29 g,10 mmol) was added during a 15-min period. The reaction mixture was stirred and heated at reflux temperature of 75 °C for 20 h, cooled to temperature and poured into H<sub>2</sub>O (50 ml) and extracted with  $CH_2Cl_2$  (20 mL × 5). The organic phase was concentrated under reduced pressure to give a yellow oily residue of methyl 4-(2-acetyl-3-oxobutyl)-benzoate.

Synthesis of methyl 4-((3,5-dimethyl-1*H*-pyrazol-4-yl)methyl)benzoate. The oily residue of methyl 4-(2-acetyl-3-oxobutyl)benzoate was added in ethanol (50 mL) and treated with an excess of hydrazine (80%, 2 mL). The solution was stirred and heated at

reflux temperature of 70°C for 15 h, cooled to temperature and poured into H<sub>2</sub>O (200 ml). The white solid was filtered off and dried to give 1.52 g of 4-((3,5-dimethyl-1*H*-parazol)methyl)benzoate. Yield: 62.3%. IR (KBr pellet, cm<sup>-1</sup>): 3180(w), 3138(w), 3086(w), 2956(w), 2926(w), 1719(vs), 1612(m), 1431(m), 1414(m), 1275(vs), 1183(m), 1107(vs), 1017(w), 833(w), 734(w), 477(w). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  7.93 (d, *J* = 8.2 Hz, 2H, CHph), 7.17 (d, *J* = 8.1Hz, 2H, CHph), 3.89(s, 3H, CH<sub>3</sub>), 3.79(s, 2H, CH<sub>2</sub>), 2.14(s, 6H, CH<sub>3</sub>).

Synthesis of (3,5-dimethyl-1*H*-pyrazol-4-yl)-methylene)benzoic acid (H<sub>2</sub>L). 4-((3,5-dimethyl-1*H*-parazol)methyl)benzoate (1.52 g, 6.23 mmol) and NaOH (0.50 g, 12.46 mmol) were added in a solution of methanol (25 ml) and H<sub>2</sub>O (25 ml), the mixture was stirred at room temperature for 10 h, and then HCl was added until pH =6. After three-fourths of the solvent was distilled, the solid residue was filtered and dried to give 0.76 g of H<sub>2</sub>L. Yield: 50%. IR (KBr pellet, cm<sup>-1</sup>):3284(vs),2917(m), 2438(b), 1933(b),1677(vs),1607(m), 1434(m), 1409(vs), 1291(vs), 1177(m),1067(w), 778(w), 741(vs),704(w),510(m).

#### Synthesis of ROD-1:

 $H_2L$  (4.58 mg, 0.02 mmol) and Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (8.48 mg, 0.027 mmol) were loaded into a heavy-wall glass tube, and then a solution of methanol (2.5 mL) was added. The tube was then flame-sealed and heated at 140°C in a programmable oven for 48 h, followed by slow cooling (5 °C/h) to room temperature. Colorless crystals were collected and air-dried (Yield: 72% based on the ligand). IR (KBr pellet, cm<sup>-1</sup>): 3421(b), 2920(w), 2360(w), 2342(w), 1610(m), 1588(m), 1523(vs), 1398(vs), 1212(m), 1114(w), 1018(w), 859(w), 814(w), 774(w), 743(w), 635(w), 422(w).

#### **Crystal Data Section**

**Crystallography:** Selected suitable crystals of the ROD-1before or after gas adsorption *were mounted with glue at the end of a glass fiber, respectively. Data collection was* performed on an Oxford Diffraction Gemini E (Enhanced Cu X-Ray source, Ka,  $\lambda$ = 1.54056 Å) equipped with a graphite monochromator and ATLAS CCD detector (CrysAlis CCD, Oxford Diffraction Ltd) at room temperature (293K) or 100 K. Using Olex2,<sup>1</sup> the structure was solved with the ShelXS<sup>2</sup>structure solution program using direct methods and refined with the ShelXL<sup>3</sup>(version 2014/7) refinement package using least squares minimisation. All non-hydrogen atoms were refined with an arefined with isotropic thermal parameters, and all hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on those of the parent atoms. Crystal data and structure refinement parameters are summarized in Table S1. Selected bond lengths and angles are given in Table S2.

<sup>&</sup>lt;sup>1</sup> O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howardand H. Puschmann, J. Appl. Cryst., 2009, 42, 339.

<sup>&</sup>lt;sup>2</sup> G. M. Sheldrick, Acta Crystrallogr. A, 2008, 64, 112.

<sup>&</sup>lt;sup>3</sup> G.M. Sheldrick, Acta Crystrallogr. C,2015, 71, 3.

	ROD-1-293K	ROD-1-100K	ROD-1-CO <sub>2</sub> -100K	ROD-1-N <sub>2</sub> -100K
CCDC No.	1483585	1483586	1483587	1483588
Formula	$C_{13}H_{12}CdN_2O_2$	$C_{13}H_{12}CdN_2O_2$	$C_{13}H_{12}CdN_2O_2$	$C_{13}H_{12}CdN_2O_2$
Formula weight	340.65	340.65	340.65	340.65
Crystal system	tetragonal	tetragonal	tetragonal	tetragonal
Space group	$I4_1/a$	$I4_1/a$	I4 <sub>1</sub> /a	$I4_1/a$
<i>a</i> (Å)	24.5830(4)	24.0666(7)	24.6108(3)	24.0290(5)
<i>b</i> (Å)	24.5830(4)	24.0666(7)	24.6108(3)	24.0290(5)
c (Å)	10.8704(3)	10.5856(11)	10.76785(17)	10.5501(3)
$V(Å^3)$	6569.2(3)	6131.2(7)	6522.00(17)	6091.5(3)
Z	16	16	16	16
<i>T</i> (K)	293(2)	100(2)	100(2)	100(2)
$D_{\text{calcd}} \left( \mathbf{g} \cdot \mathbf{cm}^{-3} \right)$	1.378	1.476	1.388	1.486
Ref. collected	5853	4737	6213	6144
Ref. unique	3144	2336	3172	2973
R <sub>int</sub>	0.0361	0.0398	0.0201	0.0226
GOF	1.134	1.074	1.045	1.076
$R_1 [I > 2\sigma(I)]^a$	0.0428	0.0566	0.0236	0.0281
$wR_2 [I > 2\sigma(I)]^b$	0.1297	0.1276	0.0556	0.0723
$R_1$ [all data] <sup>a</sup>	0.0647	0.0852	0.0289	0.0348
$wR_2$ [all data] <sup>b</sup>	0.1480	0.1426	0.0584	0.0763

**Table S1.** Crystal Data and Structure Refinement Parameters for the ROD-1-293K, ROD-1-100K, ROD-1-CO2-100K and ROD-1-N2-100K.

 ${}^{a}R_{1} = \sum(||F_{o}| - |F_{c}||) / \sum |F_{o}|; {}^{b}wR_{2} = [\sum w(F_{o}^{2} - F_{c}^{2})^{2} / \sum w(F_{o}^{2})^{2}]^{1/2}$ 

	ROD-1-293K						
Cd(1)-N(1)#5	2.165(5)	N(1)#5-Cd(1)-N(2)#4	127.3(2)				
Cd(1)-N(2)#4	2.182(5)	N(1)#5-Cd(1)-O(1)	102.60(19)				
Cd(1)-O(1)	2.349(5)	N(2)#4-Cd(1)-O(1)	89.05(19)				
Cd(1)-O(1)#2	2.524(5)	O(1)-Cd(1)-O(2)#2	78.14(16)				
Cd(1)-O(2)#2	2.400(4)	N(1)#5-Cd(1)-O(2)#3	89.29(18)				
Cd(1)-O(2)#3	2.415(5)	N(2)#4-Cd(1)-O(2)#3	98.54(18)				
Cd(1)-Cd(1)#1	3.3872(3)	O(2)#2-Cd(1)-O(2)#3	80.91(10)				
Symmetry codes	: #1 -1/4+Y,3/4-X,-1/4+Z; #	#2 -3/4-Y,1/4+X,1/4+Z; #3 1	/2-X,1-Y,1/2+Z;				
#4 3/4-Y,-1/4+2	X,-1/4-Z; #5 1-X,1-Y,-Z; #6	6 1/2-X,1-Y,-1/2+Z; #7 1/4+	Y,3/4-X,-1/4-Z				
	ROD-	1-100K					
Cd(1)-N(1)#2	2.180(7)	N(1)#2-Cd(1)-N(2)	129.0(3)				
Cd(1)-N(2)	2.185(8)	N(1)#2-Cd(1)-O(1)#4	141.7(3)				
Cd(1)-O(2)#4	2.584(6)	N(2)-Cd(1)-O(1)#4	89.3(2)				
Cd(1)-O(2)#5	2.346(6)	O(1)#4-Cd(1)-O(2)#4	53.1(2)				
Cd(1)-O(1)#3	2.381(7)	N(1)#2-Cd(1)-O(2)#4	88.6(3)				
Cd(1)-O(1)#4	2.359(6)	N(2)-Cd(1)-O(2)#5	92.7(3)				
Cd(1)-Cd(1)#1	3.3869(6)	O(2)#5-Cd(1)-O(2)#4	80.45(13)				
Symmetry codes:	Symmetry codes:#1 -1/4+Y,3/4-X,-1/4+Z; #2 3/4-Y,1/4+X,1/4+Z; #3 1/4+Y,3/4-X,-1/4-Z;						
#4 +X,1/2+Y,	-Z; #5 1/4-Y,1/4+X,1/4-Z;	#6 +X,-1/2+Y,-Z; #7 -1/4+Y	,1/4-X,1/4-Z;				
	#8 3/4-Y,-1	/4+X,-1/4-Z					
	ROD-1-CO <sub>2</sub> -100K						
Cd(1)-N(1)#3	2.183(2)	N(2)#5-Cd(1)-N(1)#3	126.84(8)				
Cd(1)-N(2)#4	2.170(2)	N(1)#3-Cd(1)-O(1)#1	91.66(7)				
Cd(1)-O(1)	2.3930(17)	N(2)#5-Cd(1)-O(1)#1	141.28(7)				
Cd(1)-O(1)#2	2.4103(17)	O(1)#1-Cd(1)-O(2)#1	53.69(6)				
Cd(1)-O(2)#5	2.3357(17)	N(1)#3-Cd(1)-O(2)#4	88.52(7)				
Cd(1)#1-O(2)	2.4978(17)	N(2)#5-Cd(1)-O(2)#1	87.61(7)				
Cd(1)-Cd(1)#2	3.38206(13)	O(2)#4-Cd(1)-O(2)#1	87.35(4)				

Table S2. Selected Bond Lengths (Å) and Bond Angles (°).

Symmetry codes: #1 3/4-Y,1/4+X,1/4+Z,-1/4+Z; #2 -1/4+Y,3/4-X,-1/4+Z; #3 -1/4+Y,5/4-X,1/4-Z; #4 -1/2+X,+Y,1/2-Z; #5 1/2-X,1-Y,-1/2+Z; #6 5/4-Y,1/4+X,1/4-Z; #7 1/2+X,+Y,1/2-Z; #8 1/2-X,1-Y,1/2+Z

ROD-1-N <sub>2</sub> -100K					
Cd(1)-N(1)#3	2.162(3)	N(1)#3-Cd(1)-N(2)#4	128.96(11)		
Cd(1)-N(2)#4	2.185(3)	N(1)#3-Cd(1)-O(1)#2	142.09(10)		
Cd(1)-O(1)	2.371(2)	N(2)#4-Cd(1)-O(1)#2	88.92(9)		
Cd(1)-O(1)#2	2.349(2)	O(1)#2-Cd(1)-O(2)#2	53.06(8)		
Cd(1)-O(2)#5	2.346(2)	N(1)#3-Cd(1)-O(2)#5	95.39(10)		
Cd(1)-O(2)#2	2.594(2)	N(2)#4-Cd(1)-O(2)#5	92.79(9)		
Cd(1)-Cd(1)#1	3.3848(2)	O(2)#5-Cd(1)-O(1)#2	79.19(8)		
Symmetry codes:#1 3/4-Y,1/4+X,1/4+Z; #2 -1/4+Y,3/4-X,-1/4+Z; #3 -1/2+X,+Y,1/2-Z;					
#4 -1/4+Y,5/4-X,1/4-Z; #5 1/2-X,1-Y,-1/2+Z; #6 1/2+X,+Y,1/2-Z; #7 5/4-Y,1/4+X,1/4-Z;					
#8 1/2-X,1-Y,1/2+Z					



 $(c) \qquad (d)$ 

Fig. S1. Structure of ROD-1. (a) ORTEP drawing (50% probability) of the asymmetric unit.
(b) Coordination mode of the linker. (c) Coordination environment of Cd<sup>II</sup> ions in the rod.
(d) Crystal packing diagram. Color codes: Cd: green, N: blue, O: red, C: grey, H omitted.

The asymmetric unit of ROD-1 contains one Cd<sup>II</sup> ion and one ligand. Two adjacent cadmium atoms are bound by one pyrazolyl group and two carboxyl groups. The ligand coordinates to Cd<sup>II</sup> ions through two different coordination modes: one coordinates to two different Cd<sup>II</sup> ions by two nitrogens of pyrazolyl group, the other coordinates to three Cd<sup>II</sup> ions by carboxyl group. The Cd–N bond lengths for ROD-1-293K are 2.165(5) Å, 2.182(5) Å and the Cd–O bond lengths are in the range of 2.349(5)–2.524(5) Å. The bond angles around each Cd<sup>II</sup> ion range from 78.14(16) to 157.91(16)°. The adjacent Cd<sup>II</sup> ions are linked together to construct a Cd<sup>II</sup>-pyrazolate-carboxylate 1D building block running along the *c* axis, with a Cd…Cd separation of 3.3872(3) Å. Each 1D building block was connected with adjacent for rods through the heteroditopic ligands to form a 3D framework.

#### **Topological Information Section**

**Topological Analysis:** The identification and symmetry calculation of the underlying net were performed by using the program *Systre*.<sup>4</sup> The point symbol and vertex symbol<sup>5</sup> were computed by using *TOPOS*.<sup>6</sup> The three-letter symbol **wuy** is assigned in the database *RCSR*.<sup>7</sup>

*Systre* file of **wuy** net:

**CRYSTAL** NAME wuy GROUP I41/amd:2 CELL 3.98423 3.98423 2.48063 90.0000 90.0000 90.0000 NODE 1 7 0.12667 0.04547 0.19131 EDGE 0.12667 0.04547 0.19131 0.37333 0.04547 0.30869 EDGE 0.12667 0.04547 0.19131 0.12667 -0.04547 -0.19131 EDGE 0.12667 0.04547 0.19131 0.29547 0.12333 -0.05869 EDGE 0.12667 0.04547 0.19131 0.20453 0.12333 0.55869 EDGE 0.12667 0.04547 0.19131 -0.12667 0.04547 0.19131 EDGE 0.12667 0.04547 0.19131 0.29547 -0.12333 0.05869 # EDGE CENTER 0.25000 0.04547 0.25000 # EDGE CENTER 0.12667 0.00000 0.00000 # EDGE CENTER 0.21107 0.08440 0.06631 # EDGE CENTER 0.16560 0.08440 0.37500 # EDGE CENTER -0.00000 0.04547 0.19131 # EDGE CENTER 0.21107 -0.03893 0.12500 END

*TOPOS* report for **wuy** net:

Topology for C1

Ato	om (	C1 links by l	bridge ligan	ds and has			
Co	mmo	on vertex wi	ith			R(A-A)	
С	1	0.2045	-0.1233	0.4413	(0-10)	0.966A	1
С	1	0.2955	0.1233	-0.0587	(00-1)	0.966A	1

<sup>4</sup>O. Delgado-Friedrichs and M. O'Keeffe, Acta Crystrallogr. A,2003, 59, 351.

<sup>5</sup>V. A. Blatov, M. O'Keeffe and D. M. Proserpio, CrystEngComm, 2010, 12, 44.

<sup>6</sup>V. A. Blatov, A. P. Shevchenkoand D. M. Proserpio, Cryst. GrowthDes., 2014, 14, 3576.

<sup>7</sup>M. O'Keeffe, M. A. Peskov, S. J. Ramsden and O. M. Yaghi, Acc. Chem. Res., 2008, 41, 1782.

С	1	0.2955	-0.1233	0.0587	(0-10)	1.006A	1
С	1	-0.1267	0.0455	0.1913	(000)	1.009A	1
С	1	0.2045	0.1233	0.5587	(000)	1.011A	1
С	1	0.1267	-0.0455	-0.1913	(000)	1.016A	1
С	1	0.3733	0.0455	0.3087	(0-10)	1.025A	1

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Structural group analysis

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Structural group No 1

Structure consists of 3D framework with C

Coordination sequences

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C1: 1 2 3 4 5 6 7 8 9 10 Num 7 17 43 74 116 167 230 299 379 467 Cum 8 25 68 142 258 425 655 954 1333 1800

TD10=1800

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Vertex symbols for selected sublattice

\_\_\_\_\_

C1 Point symbol: {3^9.4^6.5^3.6^3}

Extended point symbol: [3.3.3.3.3.3.3.3.3.4.4.6(2).6(3).5.5.4.4(2).4(2).4(2).5(3).6(2)] Vertex symbol: [3.3.3.3.3.3.3.3.3.4.6(2).6(2).8(3).8(3).\*.\*.\*.\*.\*] All rings (up to 16): [3.3.3.3.3.3.3.4.6(2).(6(2),8(3)).(6(2),8(3)).8(3).8(3).\*.\*.\*.\*.\*] ATTENTION! Some rings \* are bigger than 16, so likely no rings are contained in that angle

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Point symbol for net: {3^9.4^6.5^3.6^3} 7-c net; uninodal net

## **Physical Measurement Section**



Fig. S2. Simulated and measured powder X-ray diffraction (PXRD) patterns for ROD-1.



Fig. S3. Temperature-varied PXRD patterns for ROD-1.



Fig. S4. TGA plots of ROD-1 at the temperature range of 30-800°C.



Fig. S5. Temperature-varied CO<sub>2</sub> adsorption/desorption isotherms of ROD-1 used for calculating adsorption/desorption isosteric enthalpy ( $Q_{st}$ ) and change of entropy ( $\Delta S$ ).

**Calculations:** The differential enthalpies  $(\Delta H_n)$  and entropies of adsorption  $(\Delta S_n)$  were calculated as a function of amount adsorbed (*n*) from the isotherms measured over a range of temperatures using the van't Hoff isochore, which is given by the following equation:

$$ln^{\underline{III}}(p)_n = \frac{\Delta H_n}{RT} - \frac{\Delta S_n}{R}$$

A plot of  $\ln(p)$  versus 1/T at constant amount adsorbed allows  $\Delta H_n$  and  $\Delta S_n$  and also the

isosteric enthalpy of adsorption/desorption ( $Q_{st}$ ) to be determined.

### **Computational Section**



**Fig.S6**. (a) Calculated density distribution diagram of  $CO_2$  in ROD-1(193 K and 1 bar) from GCMC simulation (red dots represent the statistical positions of  $CO_2$ ). (b) The snapshot of  $CO_2$  adsorption sites for the lowest-energy frame, highlighting the  $CO_2$ - $CO_2$  interaction marked with interaction distances in the blue box.

**Computational details:** Grand canonical Monte Carlo (GCMC) simulations were performed to evaluate the distribution of  $CO_2$  in a 1×1×3 cell of ROD-1, set at 193.0 K and

1.0 bar in Sorption Module of Materials Studio.<sup>8</sup>Spherical Lennard-Jones (LJ) 12-6 potentials were used to discribe van der waals interaction among CO<sub>2</sub> and ROD-1 based on universal force field (UFF),<sup>9</sup> and the atomic charges of ROD-1 and CO<sub>2</sub> calculated by charge equilibration method<sup>10</sup> were used to describe electrostatic interaction. In this work, a total of  $2 \times 10^7$  steps were used; the first 50% of these moves were used for equilibration, and the remaining  $10^7$  steps were used for calculating the ensemble averages.

<sup>&</sup>lt;sup>8</sup> D.Farrusseng, C. Daniel, C. Gaudillère, U. Ravon, Y. Schuurman, C. Mirodatos, D. Dubbeldam, H. Frost and R. Q. Snurr, *Langmuir*, 2009, **25**, 7383.

<sup>9</sup> A. K. Rappé, C. J. Casewit, K. S. Colwell, W. A. Goddard III and W. M. Skiff, J. Am. Chem. Soc., 1992, 114, 10024.

<sup>&</sup>lt;sup>10</sup> A. K. Rappé and W. A. Goddard III, J. Phys. Chem., 1991, **95**, 3358.