Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary material

Novel zinc(II) metal-organic framework with diamond-like structure: synthesis, study of thermal robustness and gas adsorption properties

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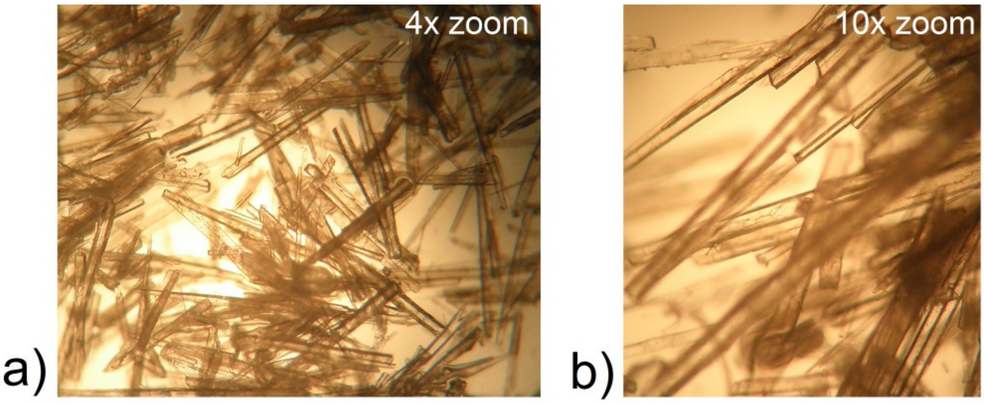

Fig. S1 Optical microscopy images of crystals of compound **1** stored in Formblin® oil: a) 4 x zoom, b) 10 x zoom.

Table S1 Crystal data and structure refinement summary for complex $\{[Zn_2(\mu_4\text{-}MTB)(\kappa^4\text{-}CYC)_2]\cdot 2DMF\cdot 7H_2O\}_n$.

Formula	$\{[Zn_2(\mu_4\text{-}MTB)(\kappa^4\text{-}CYC)_2]\cdot 2DMF\cdot 7H_2O\}_n$	Monochromator	graphite
Empirical formula	$Zn_2C_{55}H_{92}N_{10}O_{17}$	Θ range (°)	3.121-26.49
Formula weight	1296	Reflections measured	12 383
		Independent reflections	3792
Crystal parameters		Reflections observed$^{\#}$	1733
Crystal shape	needle	Linear abs. coeff. (mm^{-1})	0.720
Crystal colour	colourless	*F(000)*	1376
Crystal size (mm)	0.5 x 0.1 x 0.1	Reflections for cell measure.	23353 with $3.223 < \theta < 26.24$
Crystal system	tetragonal	h	-21 to 21
Space group (number)	*P4/n* (85)	k	-21 to 14
Unit cell dimensions		l	-10 to 15
a (Å)	17.1627 (10)		
c (Å)	12.407 (2)	*Refinement*	
V_c (Å^3)	3654.6 (7)	Refinement method	full matrix least-squares on F^2
Molecules per cell, Z	2	Parameters	153
D_x ($g.cm^{-3}$)	1.178	Goodness-of-fit on F^2	0.947
		$R_{int.}$	0.114
Meas. of intensity data		R_1 (observed/all)	0.0639 / 0.1310
Instrument	Xcalibur2	wR_2 (observed/all)*	0.1647 / 0.2013
Temperature (°C)	-100 (2)	Max. and min. height in final diff. synthesis (e.Å^{-3})	0.413 and -0.554
Radiation λ (Å)	0.71073		

$^{\#}$ $[I > 2\sigma(I)]$, * $w = 1/[\sigma^2(F_o^2) + (0.1463P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$.

Table S2 Selected bond distances (Å) and angles (°) in the crystal structure of $\{[\mathrm{Zn_2}(\mu_4\text{-MTB})(\kappa^4\text{-CYC})_2]\cdot\mathrm{2DMF\cdot 7H_2O}\}_n$.

Bond distances			
Zn–N1^{i}	2.125 (4)	C2–C3	1.486 (8)
Zn–N1	2.125 (4)	C4–C5^{i}	1.516 (8)
Zn–N2^{i}	2.089 (4)	C6–C7	1.564 (7)
Zn–N2	2.089 (4)	C7–C8	1.361 (6)
Zn–O1^{i}	2.195 (3)	C7–C12	1.379 (6)
Zn–O1	2.195 (3)	C8–C9	1.390 (6)
O1–C6	1.223 (5)	C9–C10	1.392 (6)
O2–C6	1.207 (6)	C10–C11	1.389 (6)
N1–C1	1.452 (7)	C11–C12	1.406 (6)
N1–C5	1.488 (7)	C10–C13	1.552 (4)
N2–C3	1.470 (6)	C10^{ii}–C13	1.552 (4)
N2–C4	1.442 (7)	C10^{iii}–C13	1.552 (4)
C1–C2	1.542 (9)	C10^{iv}–C13	1.552 (4)
Bond angles			
N1–Zn–N2	94.51 (18)	O1–C6–C7	114.9 (4)
N1–Zn–N2^{i}	85.49 (18)	O2–C6–C7	116.2 (5)
N1^{i}–Zn–N2	85.49 (18)	C1–N1–C5	115.2 (4)
N1^{i}–Zn–N2^{i}	94.50 (18)	C4–N2–C3	115.3 (4)
N2–Zn–N2^{i}	180.0	C1–C2–C3	117.8 (5)
N1–Zn–O1	88.24 (15)	C6–C7–C8	119.7 (4)
N1^{i}–Zn–O1	91.76 (15)	C6–C7–C12	121.4 (4)
N1^{i}–Zn–O1^{i}	88.24 (15)	C7–C8–C9	120.8 (4)
N1–Zn–O1^{i}	91.76 (15)	C7–C12–C11	121.2 (4)
N2–Zn–O1	93.06 (14)	C8–C7–C12	118.9 (4)
N2^{i}–Zn–O1	86.94 (14)	N2–C4–C5^{i}	110.5 (4)
N2^{i}–Zn–O1^{i}	93.06 (14)	C8–C9–C10	121.4 (4)
N2–Zn–O1^{i}	86.94 (14)	C9–C10–C11	117.8 (4)
O1^{i}–Zn–O1	180.0 (2)	C9–C10–C13	119.0 (3)
Zn–O1–O6	131.0 (3)	C10–C11–C12	119.8 (4)
Zn–N1–C1	114.9 (4)	C10–C13–C10^{ii}	110.97 (15)
Zn–N1–C5	103.4 (3)	C10–C13–C10^{iii}	110.97 (15)
Zn–N2–C4	105.8 (3)	C10^{ii}–C13–C10^{iii}	106.5 (3)
Zn–N2–C3	115.2 (3)	C10–C13–C10^{iv}	106.5 (3)
N1–C1–C2	110.9 (5)	C10^{ii}–C13–C10^{iv}	110.97 (15)
N1–C5–C4^{i}	110.3 (4)	C10^{iii}–C13–C10^{iv}	110.97 (15)
N2–C3–C2	113.2 (5)	C11–C10–C13	123.1 (3)

Symmetry codes: (i) −x, −y, −z; (ii) x+1/2, −y, −z+1; (iii) −x, y−1/2, −z+1; (iv) −x−1/2,

−y+1/2, z.

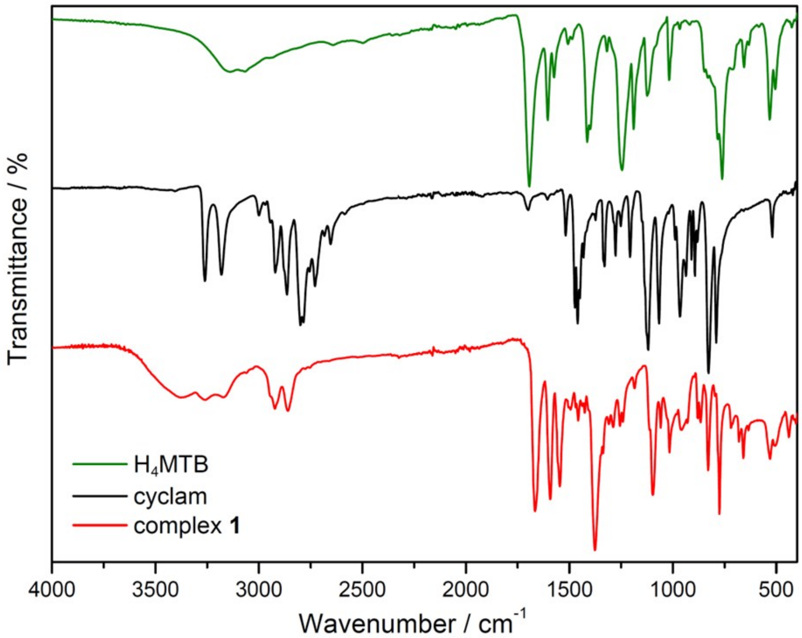

Fig. S2 FT-IR spectra of free ligands methanetetrabenoic acid (green line), cyclam (black line) and complex **1** (red line).

FT-IR spectrum of compound **1** measured at room temperature (Fig. S2) exhibits a broad absorption band centred at 3374 cm^{-1} corresponding to stretching vibration of clathrated water molecules ($\upsilon(OH)_{water}$). The presence of cyclam molecules in compound **1** is evident from two medium intensive bands located at 3258 and 3167 cm^{-1} corresponding to antisymmetric and symmetric stretching vibrations of N-H groups. Similarly, the stretching vibrations of CH_2 groups, $\upsilon_{as}(CH)_{aliph}$ and $\upsilon_{s}(CH)_{aliph}$ are present at 2923 and 2860 cm^{-1}, respectively. Very weak absorption bands observed in the range of 3080-3030 cm^{-1} are assigned to C-H aromatic stretching vibrations of MTB^{4-} molecules. FT-IR spectrum exhibits very strong and sharp band at 1666 cm^{-1} corresponding to stretching vibration of $\nu(C=O)$, which can be attributed to DMF molecules. The evident presence of MTB^{4-} ligand in compound **1** is reflected by the carboxylate vibrations, which dominate the IR spectra. The lack of strong absorption band at 1694 cm^{-1} (corresponding to $\upsilon(C=O)$ vibration of carboxylic group of the free H_4MTB, see Table S2 and Fig. S2) indicates that all carboxyl groups of

H_4MTB molecule were completely deprotonated during the synthesis.

The band of antisymmetric carboxylate stretch, υ_{as}(COO$^-$), was found at 1546 cm^{-1}, the band of symmetric υ_s(COO$^-$) stretch was found at 1376 cm^{-1} and the band of deformation δ(COO$^-$) was observed at 775 cm^{-1}, respectively. The frequencies of carboxylate stretching vibrations and the magnitude of their separation, $\Delta = \upsilon_{as}$(COO$^-$) - υ_s(COO$^-$), are often used as a spectroscopic criterion to determine the coordination mode of carboxylate group. Consequently, the calculated value of separation between the antisymmetric and symmetric COO$^-$ stretches was 170 cm^{-1}. The separation value is in a good agreement with coordination mode of the carboxylate group found in compound **1** (monodentate).

Table S3 Assignment of IR spectral data of complex **1**, methanetetrabenzoic acid (H_4MTB) and cyclam (CYC) (band positions are in cm^{-1}).

	compound 1	methanetetrabenzoic	cyclam (CYC)
υ(OH)$_{water}$	3374 (m, br)	-	-
υ(NH)	3258 (m), 3169 (m)	-	3261 (m), 3181
υ(CH)$_{ar}$	3077 (vw), 3061 (vw),	3064 (w)	-
υ_s(CH)$_{aliph}$	2923 (m)	-	2921 (m)
υ_{as}(CH)$_{aliph}$	2860 (m)	-	2864 (m)
υ(C=O)	1666 (s)	1694 (vs)	-
υ(C=C)$_{ar}$	1592 (s), 1502 (w)	1604 (s), 1574 (m), 1507 (w)	-
υ_{as}(COO$^-$)	1546 (s)	-	-
δ(C-O) + δ(OH)	-	1414(s), 1246(vs)	
υ_s(COO$^-$)	1376 (vs)	-	-
δ(CCH)$_{ar}$	1185 (w), 1097 (s), 1016 (m)	1189 (s), 1124 (m), 1017 (w)	-
γ(CCH)$_{ar}$	-	761 (s), 784 (vs)	-

$\delta(COO^-)$	775 (s)	-	-

(band intensity: vs – very strong, s – strong, m – medium, w – weak, vw – very weak, type of vibration: ar – aromatic, aliph – aliphatic, s – symmetric, as – antisymmetric).

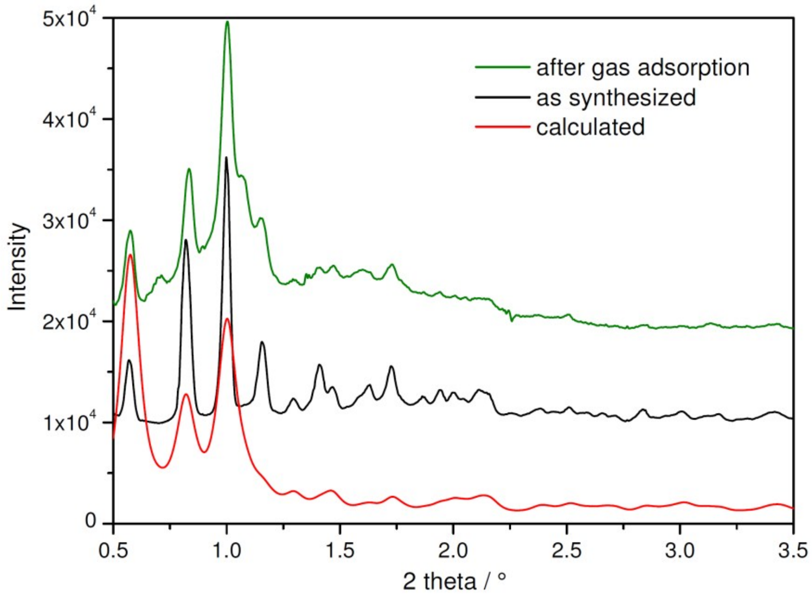

Fig. S3 HE-PXRD patterns of **1** a) calculated from the single crystal X-ray data (red line), b) as synthesized sample (black line) and c) after adsorption measurements (green line) (sample **1´**).

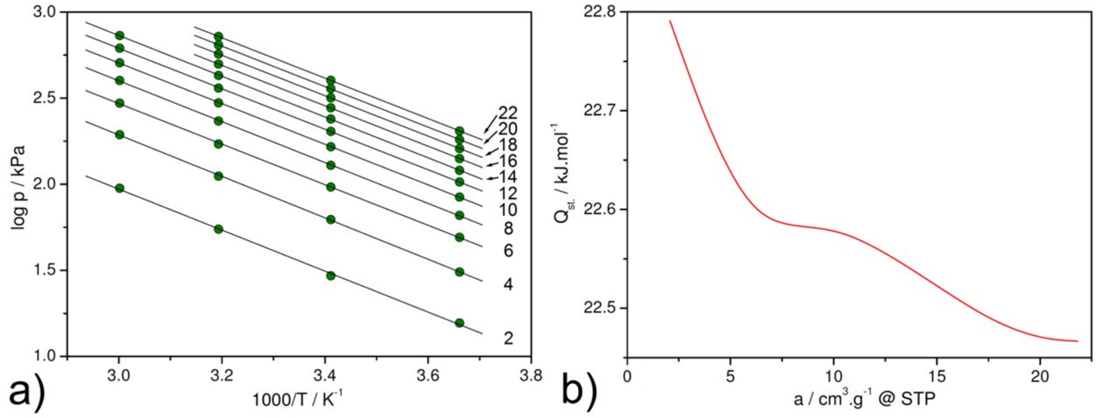

Fig. S4 a) Adsorption isosteres of CO_2. Points were calculated by numerical interpolation/extrapolation of adsorption isotherms, lines represent linear fit. All the isosteres are marked with corresponding amount adsorbed in $cm^3.g^{-1}$ at STP. b) Isosteric heats of adsorption of carbon dioxide on $\{[Zn_2(\mu_4\text{-MTB})(\kappa^4\text{-CYC})_2]\}_n$.

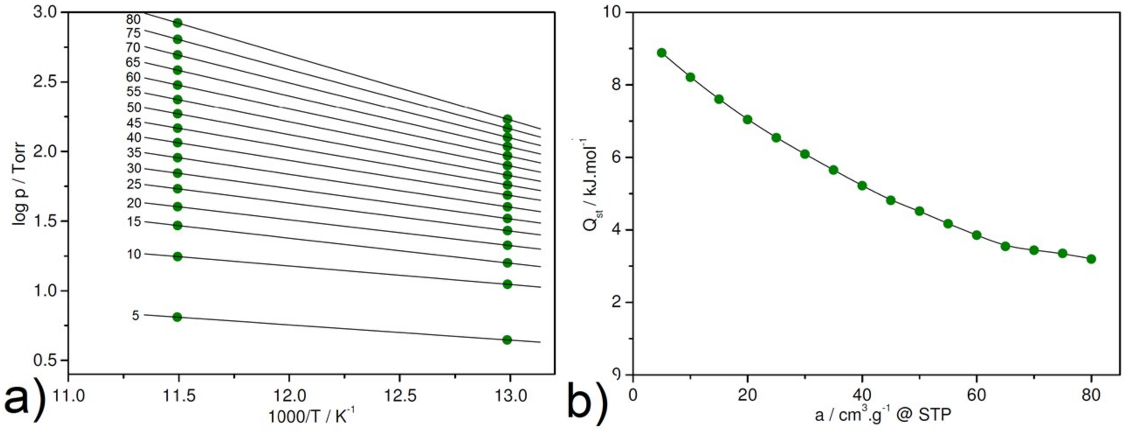

Fig. S5 a) Adsorption isosteres of hydrogen. All the isotheres are marked with corresponding amount adsorbed in cm^3.g^{-1} at STP c) Coverage dependence of the isosteric heat of adsorption for hydrogen in **1´** calculated from the interpolation/extrapolation of the corresponding isotherms.