Supplementary Information

Extending the family of Zn-based MOFs: Synthetic approaches to chiral framework structures and MOFs with large pores and channels

Nianyong Zhu, Gerard Tobin and Wolfgang Schmitt*

A	Syntheses of MOFs
В	TGA Analyses
С	Crystallographic Data
D	Surface Area Measurements

A. Syntheses of MOFs:

TCM-1: 0.147 g BTEB (0.288 mmol) were added to a solution of 20 mL DMF containing 0.28 g $Zn(NO_3).6H_2O$ (0.94 mmol). The mixture was stirred and sonicated for 10 minutes, transferred into a 50 mL sealed glass vial and heated for 3 days at 85°C. After cooling to room temperature needle-shaped crystals of **[TCM-1].solv** were separated, washed with DMF and kept in DMF for storage. Yield *ca*. 75%. Elemental Analysis (%) for $[Zn_3(C_{33}H_{15}O_6)_2(DMF)_2].DMF.3H_2O$: Calc. C 60.69, H 3.87, N 2.83; Found C 60.47, H 3.38, N 2.51.

TCM-2: analogous synthetic procedure as for **[1].solv** using 0.126 g Zn(NO₃).6H₂O (0.42 mmol) and 0.033 g BTEB (0.065 mmol). Pale yellowish block crystals were obtained. Yield *ca*. 33%. Elemental Analysis (%) for (Me_2NH_2) [Zn₅(OH)₂(C₃₃H₁₅O₆)₃(DMF)₂].6DMF.9H₂O: Calc. C56.10, H4.86, N4.71; Found C 55.63, H 4.31, N 5.00.

B. TGA Measurements:

TGA was recorded on a Perkin-Elmer under N₂-gas flow (20ml.min⁻¹).

[TCM-1].sov was prepared as described, separated and dried at room temperature in an open beaker for ca. 12 hrs. The crystals were then stored in a closed tube. The TGA measurement of such crystals (5.7 mg) was carried out under N_2 gas flow (20 ml.min⁻¹) between 30°C and 700°C (heating rate: 3°C per minute).





[TCM-2].sov was prepared as described, separated and dried at room temperature in an open beaker for ca. 12 hrs. The crystals (3.6 mg) were then stored in a closed tube. The TGA measurement of such crystals was carried out under N_2 gas flow (20 ml.min⁻¹) between 30°C and 700°C (heating rate: 3°C per minute). Prior to the measurement the sample was held for 5 minutes at 30°C (around 4% weight loss).

Electronic Supplementary Material (ESI) for Chemical Communications This journal is C The Royal Society of Chemistry 2012



Fig. S2. TGA of **[TCM-2].sov** recorded from 30°C to 700°C at a heating rate of 3°C per minute.

C. Crystallographic data.

Single crystals of **[TCM-1].solv** and **[TCM-2].solv** were protected with Krytox lubricant and mounted on a glass fiber. Data were collected on a Bruker APEX CCD diffractometer (Platform with full threecircle goniometer). The diffractometer was equipped with a 4K CCD detector. The single crystals were cooled to 250(1) K for **[TCM-1].solv** and 120 K for **[TCM-2].solv** using an Oxford Cryostream low-temperature device. Intensity measurements were performed using graphite monochromated Mo-K α radiation from a sealed ceramic diffraction tube. Generator settings were 50 KV/40 mA. The programme SMART was used for the preliminary determination of the unit cell constants. The intensities of the reflections of a hemisphere were collected by a combination of 4 exposure sets (frames). Each set had a different ϕ angle and each exposure covered a range of 0.3° in ω . A total of 1315 frames were collected with an exposure time of 60.0 seconds per frame. The overall data collection time was 24 h for each crystal. Data integration and global cell refinement was performed with the program SAINTPLUS. Intensity data were corrected for Lorentz and polarization effects, scale variation, for decay and absorption: a multi-scan absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (SADABS), and reduced to Fo². The program suite SHELXTL was used for space group determination (XPREP).

[TCM-1].sov crystallizes in a tetragonal unit cell, **[TCM-2].sov** in a monoclinic cell. Reduced cell calculations did not indicate any higher metric lattice symmetry. The structures were solved by Direct Methods and extension of the models were accomplished by the difference Fourier map. The positional and anisotropic displacement parameters for the non-hydrogen atoms were refined. Hydrogen atoms were constrained to idealized geometries and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent displacement parameter of their carrier atoms. Both structures contain huge solvent accessible void volumes in which solvent molecules could not reliably be located. And R-indexes were close to 10%. The Platon-Squeeze routine was used to calculate the void volumes and re-generate reflections files by excluding the diffraction contributions of these un-located solvent molecules. The final results were based on the new reflections files (results listed in Table S1). The absolute structure of **[TCM-1].sov** was determined by Flack's absolute structure parameter refinement (x = 0.08(2)). Crystal data and numerical details for the data collection and refinement are given in Table S1. Final fractional atomic coordinates, equivalent displacement parameters and anisotropic displacement parameters for the non-hydrogen atoms are given in the cif files.

Table S1. Crystallographic data for [TCM-1].solv and [TCM-2].solv.

	[TCM-1].solv	[TCM-2].solv
Crystal data		
Moiety Formula	$C_{72}H_{44}N_2O_{14}Zn_3$	$C_{105}H_{59}N_2O_{22}Zn_5$
Formula Weight, g.mol ⁻¹	1357.20	2027.39
Crystal system	Tetragonal	Monoclinic
Space group, no.	<i>P</i> 4 ₃ 2 2 (#95)	C 2/c
a, Å	20.269(2)	25.136(2)
<i>b,</i> Å	20.269(2)	37.055(2)
<i>c,</i> Å	39.645(4)	20.259(1)
β , deg	90	124.71(2)
V, Å ³	16287(3)	15510(4)
reflections	77843	36437
Formula_Z	4	4
Space Group_Z	8	8
ρ calc, mg.cm ⁻³	0.553	0.868
F(000), electrons	2768	4116
μ (Mo Kα), mm ⁻¹	0.465	0.807
Color, habit	Colorless,	Yellow,
	square prism	block
Approx. crystal dimension, mm	0.30 x 0.20 x 0.20	0.50 x 0.40 x 0.25
Data collection		
Radiation type; λ, Å	0.71073	0.71073
Temperature, K	250	120
heta range; min. max., deg		
Index ranges	-24 ≤ h ≤ 22	-29 ≤ h ≤ 30
	-24 ≤ k ≤ 24	-40 ≤ k ≤ 45
	-48 ≤ l ≤ 40	-24 ≤ l ≤ 21
Min Max. absorption transmission factor	0.754/1.000	0.5889/1.0000
X-ray exposure time per frame (second)	60	60
Total data	77843	36437
Unique data	15488	14739
Data with criterion: $(F_o \ge 4.0 \sigma (F_o))$	6650	9682
$R_{int} = \sum \left[\left F_o^2 - F_o^2 (\text{mean}) \right \right] / \sum \left[F_o^2 \right]$	0.1204	0.0353
$R_{sig} = \Sigma \sigma(F_o^2) / \Sigma[F_o^2]$	0.1128	0.0501
<u>Refinement</u>		
Number of reflections	15488	14739
Number of refined parameters	391	597
Number of restraints	7	0
Final R- index without Platon-squeeze	R(<i>F</i>) = 0.1057	R(<i>F</i>)=0.1009
$wR(F^2) = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$		
$R(F) = \Sigma \left(\left \left F_{o} \right - \left F_{c} \right \right \right) / \Sigma \left F_{o} \right $		
For $F_o > 4.0 \ \sigma \ (F_o)$		

Final R-indexes with Platon-squeeze	R(F) = 0.0431,	R(F) = 0.0472,
$wR(F^2) = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$	$wR(F^2) = 0.0678$	$wR(F^2) = 0.1303$
$R(F) = \Sigma \left(\left \left F_{o} \right - \left F_{c} \right \right \right) / \Sigma \left F_{o} \right $		
For $F_o > 4.0 \sigma (F_o)$		
Weighting scheme: a, b	0.0224, 0.0000	0.0939, 0.0000
$w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where P =		
$[\max(F_o^2, 0) + 2F_c^2] / 3$		
Flack parameter x	0.082(9)	
GooF = S = $[\Sigma [w(F_o^2 - F_c^2)^2] / (n-p)]^{\frac{1}{2}}$	0.762	0.914
<i>n</i> = number of reflections		
<i>p</i> = number of parameters refined		
Residual electron density in final	0.390 and -0.154	1.312 and -0.563
Difference Fourier map, e/A ³		
Max. (shift/ σ) final cycle	0.001	0.001
Average (shift/σ) final cycle	0.001	0.001
Total Potential Solvent Accessible Void Vol (Å ³)	11111	7677
per unit cell		
Electron Count/cell to be included in D_{calc} , F_{000}	4081	1660
& MW		

Crystallographic data, CCDC 810330 ([TCM-1].solv) and 843699 ([TCM-2].solv), can be obtained free

of charge from the Cambridge Crystallographic Data Centre via

www.ccdc.cam.ac.uk/data_request/cif.

D. Surface Area Measurements of TCM-2 using N₂; H₂ absorption measurements

Crystals of **[TCM-2].solv** were prepared according to the described method. The DMF solvent was removed from the reaction flask using a syringe. Afterwards the crystals were 2x washed with acetone and then soaked in acetone for 3 days. During this period the acetone was exchanged 3x. Afterwards the crystals were soaked in dichloromethane for 3 days. During this period the acetone was exchanged 3x.

For surface area analyses wet crystals were transferred into a quarz cell (0.0294 g). Outgassing was performed on the Quantachrome Autoabsorb IQ at 30°C for one hour. Then the quarz cell was moved to the measurement station. Pure helium, nitrogen and hydrogen gases were used for the measurement.

Fig. S3. N₂-sorption of **TCM-2** measured at 77 K.

Fig. S4. H₂-sorption of **TCM-2** measured at 77K (P₀ set at 1 atm).

Fig. S5 BET graph of **TCM-2**.

Fig. S6 Langmuir surface area calculation of TCM-2.