Supporting information for:

A new family of zinc metal-organic framework polymorphs containing anthracene tetracarboxylates**

Kristina Konstas,[a] Kim F. Taupitz,[a] David R. Turner, [b] Danielle F. Kennedy* and Matthew R. Hill*

Supporting Information

Table of Contents

Section 1   *Synthetic Procedure* **S1**

Section 2   *General Characterisation Information*   **S2**

Section 3   *Data Analysis*   **S3**

Section 1   *Synthetic Procedure* **S1**

Synthesis of anthracene-9,10-diboronic acid

This reaction was performed using a modified procedure from Kim *et. al.*[1] To a pre-dried and evacuated Schlenk flask, 9,10-dibromoanthracene (30.00 g, 89.28 mmol, 1.0 eq) was added and the material was evacuated and backfilled with argon (cycle x 3). Under an argon atmosphere, dry THF (1 L) was added and the solution was cooled to -78 °C. To this, *n*-BuLi (1.6 M, 180 mL, 288 mmol, 3.2 eq) was added and stirred at -78 °C for 2.5 h . Triethyl borate (44.4 mL, 259 mmol, 2.9 eq) was added and the reaction stirred for an additional 2 h at -78 °C until it warmed up to room temperature and stirred overnight. After the reaction finished, it was acidified with diluted HCl solution, extracted with Et_2O (50 mL, x 3), the combined organic phases were washed with water (50 mL, x 4) and dried over $MgSO_4$. After removing the solvent, the residue was re-dissolved in acetone (60 mL) and added to dichloromethane (50 mL) to give a precipitate which was filtered, washed and dried *in vacuo* to give a white powder (8.082 g, 30.38 mmol, 34%). The compound was stored in the freezer until further use.

^{1}H-NMR (400 MHz, DMSO-d_6, δ): 8.66 (s, 4 H, B(OH)$_2$), 7.93 (q, 4 H, H-1), 7.42 (q, 4 H, H-2). **EI$^+$-MS**: 266.1.

Synthesis of dimethyl-5-bromo-isophthalate

5-Bromoisophthalic acid (25.85 g, 105.9 mmol, 1.0 eq) was dissolved in methanol (400 mL) and concentrated H_2SO_4 (15 mL) was added. The reaction was stirred overnight under reflux conditions. After removing the solvent, the precipitate was redissolved in ethyl acetate (250 mL) and the organic phase was washed with water (50 mL, x 5), dried over $MgSO_4$, evaporated and dried *in vacuo* to give a white coloured compound (27.21 g, 100.0 mmol, 94%).

^{1}H-NMR (400 MHz, CDCl$_3$, δ): 8.58 (t, 1 H, H-2), 8.33 (d, 2 H, H-4, H-6), 3.93 (s, 6 H, OMe).

Synthesis of 5,5'-(9,10-Anthracenediyl)bis(1,3-benzenedimethoxy-carbonyl)

This reaction was performed using a modified procedure from Ma *et. al.*[2] A pre-dried and evacuated Schlenk flask was charged with anthracene-9,10-diboronic acid (0.5008 g, 1.883 mmol, 1.00 eq), dimethyl-5-bromo-isophthalate (1.707 g, 6.253 mmol, 3.3 eq) and Pd(PPh$_3$)$_4$ (25.0 mg, 0.0216 mmol, 0.01 eq) which were pumped under vacuum for 2.5 h. Then, degassed THF (70 mL) and degassed 2 M Na$_2$CO$_3$ (20 mL) were added and heated to reflux under argon atmosphere for 43 h. Water (100 mL) and dichloromethane (150 mL) were added to the reaction mixture and the phases were separated. The water phase was extracted with DCM (4 x 75 mL) and the combined organic phase dried over $MgSO_4$, filtered and the solvent was removed *in vacuo*. The brown crude product was purified by recrystallisation from acetone to give a yellow solid (0.5587 g, 1.048 mmol, 56%).

^{1}H-NMR (400 MHz, CDCl$_3$, δ): 8.92 (s, 2 H, H-2), 8.37 (s, 4 H, H-4), 7.56 (m, 4 H, H-1'), 7.37 (m, 4 H, H-2'). **EI$^+$-MS**: 562.1.

[1] S.-K. Kim, B. Yang, Y. Ma, J.-H. Lee and J.-W. Park, *J. Mater. Chem.*, **2008**, 18, 3376.
[2] S. Ma, D. Sun, J. Simmons, C. Collier, D. Yuan and H.-C. Zhou, *J. Am. Chem. Soc*, **2008**, 130, 1012.

Synthesis of 5,5'-(9,10-anthracenediyl)di-isophthalic acid (H$_4$adip)

This reaction was performed using a modified protocol of Ma *et. al.*[2] 5,5'-(9,10-anthracenediyl)bis(1,3-benzenedimethoxycarbonyl) (800 mg, 1.423 mmol, 1 eq) was suspended in THF (65 mL) and KOH aqueous solution 2 M, 15 mL) was added. The mixture was stirred overnight at room temperature. THF was evaporated and dilute HCl (2 M) was added to the remaining aqueous solution until it became acidic. The precipitate was filtered off and washed several times with water and CHCl$_3$ to give a yellow solid (0.6728 g, 1.3296 mmol, 93%).

^{1}H-NMR (400 MHz, DMSO, δ): 13.45 (s, 4 H, COOH), 8.70 (m, 2 H, H-2), 8.13 (m, 4 H, H-4), 7.54 (m, 4 H, H-1'), 7.47 (m, 4 H, H-2'). **EI$^+$-MS**: 506.1.

General procedure for the synthesis of ZnADIP

ZnADIP crystals were synthesized by *in situ.* ligand transformation in a solvothermal approach. A mixture of Zn(NO$_3$)$_2$.6H$_2$O and 5,5'-(9,10-Anthracenediyl)di-isophthalic acid (H$_4$ADIP) in DMF were sealed in a pyrex tube and dissolved by sonication. Fluoroboric acid was added and the tubes were heated for two days according to the prescribed temperature. The resulting crystals were washed with DMF before further analysis. See table 1 for details.

Table 1: Reaction conditions and reactant weights

Sample	m (Zn(NO$_3$)$_2$.6H$_2$O) [mg]	DMF [mL]	m (H$_4$ADIP) [mg]	Ratio	HBF$_4$	Temp °C
1	18.8	1.5	5.3	1/6	2 drops	75
2	19.4	1.5	5.3	1/6	10 drops	100
3	28	1.5	5.1	1/9	10 drops	100
4	28.6	1.5	5	1/10	2 drops	100

Section 2   *General Characterisation Information*   **S2**

S2.1   General NMR Experimental

Approximately 10 mg of the organic compound were dissolved in 0.5 ml deuterated solvent. Spectra were recorded using a Bruker Av400 operating with a 9.4 T magnet and 400.13 MHz 1H frequency. It is equipped with a 5 mm 1H-, 19F-, 13C-, 31P- QNP probe with z-gradient and a 60-holder sample changer. It is running with Bruker BioSpin's ICON-NMR software. Spectra were analysed using MestReNova Lite Version 5.2.5.

S2.2   Mass Spectroscopy

Positive and negative ion electro-spray mass spectra were acquired with a VG Platform mass spectrometer using a cone voltage of 50V and the source was maintained at 80 °C. The used solvent was methanol with a flow rate of 0.04 mL/min.

S2.3   Low Pressure Gas Sorption

Gas adsorption isotherms for pressures in the range of 0-1.2 bar were measured by a volumetric method using a Micromeritics ASAP 2420 instrument. Freshly prepared sample was transferred to a pre-dried and weighed analysis tube which was stoppered with a Transeal cap. The sample was evacuated and activated at 200 °C under dynamic vacuum at 10^{-6} Torr for 24h. Accurate sample masses were calculated using degassed samples. Gas adsorption measurements were performed using ultra-high purity Ar, He, H_2, CO_2 and CH_4 gas.

S2.4   Single-Crystal X-Ray Crystallography

Data for **Zn1** and **Zn3** were collected using the MX1 beamline at the Australian Synchrotron, operating at 17.4 KeV (λ = 0.7107 Å). Data collections were controlled using the Blu Ice software,[3] with indexing and data reduction conducted using the XDS package.[4] Data for **Zn2** was collected using an Oxford Xcalibur diffractometer equipped with Cu-Kα radiation (λ = 1.5418 Å). Data collection and reduction was conducted using the CrysAlisPro software.[5]

---

[3] T. M. McPhillips, S. E. McPhillips, H. J. Chiu, A. E. Cohen, A. M. Deacon, P. J. Ellis, E. Garman, A. Gonzalez, N. K. Sauter, R. P. Phizackerley, S. M. Soltis, P. Kuhn, *J. Synchrotron Radiat.*, 2002, **9**, 401 –406.

[4] W. Kabsch, *J. Appl. Crystallogr.*, 1993, **26**, 795 –800.

S2.5   Powder X-ray Crystallography

A Bruker D8 Advance X-ray Diffractometer operating under CuKα radiation (40kV, 40mA) equipped with a LynxEye silicon strip detector was employed to obtain the XRD patterns. The samples were scanned over the 2θ range 1° to 30° with a step size of 0.02° 2θ and a count time of 0.8 seconds per step. 52 sensor strips of the LynxEye detector gave equivalent count times of 41.6 seconds per step. Analyses were performed on the collected XRD data using the Bruker XRD search match program EVA™.

S2.6   Thermal Gravimetric Analysis

A pre-weighed sample of crystals were analysed on a PerkinElmer Pyris 1 Thermal Gravimetric Analyser within a temperature range from 25 °C to 800 °C and a heating ramp of 10 °C per minute after a 10 minute nitrogen gas flow at 25 °C.

---

[5] CrysAlisPro, Oxford Diffraction Ltd., Version 1.171.34.36.

Section 3   *Data Analysis*   **S3**

S3.1   Adsorption Data Analysis

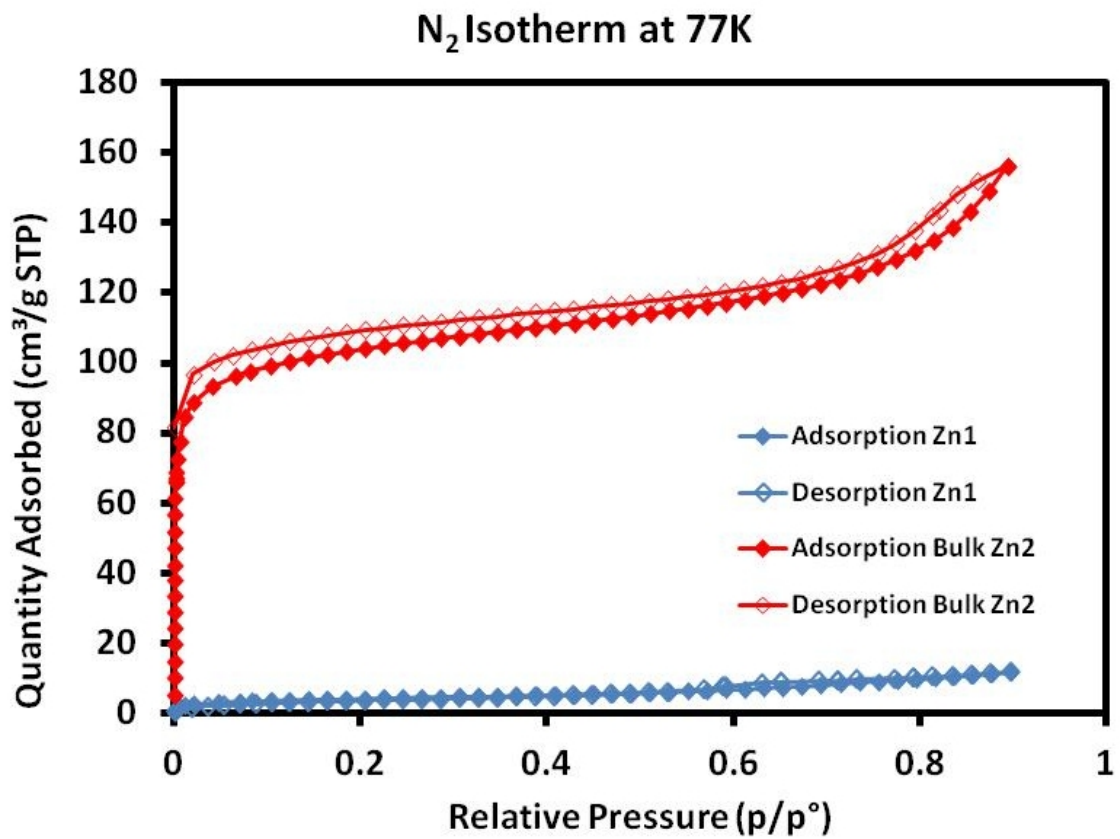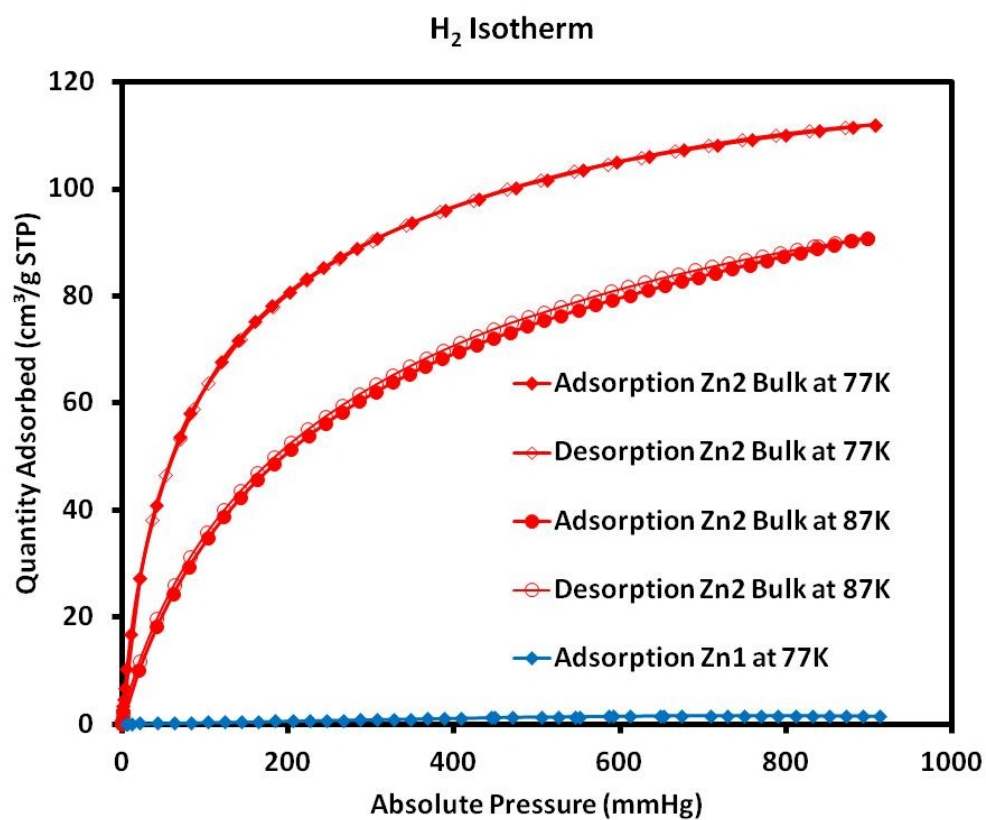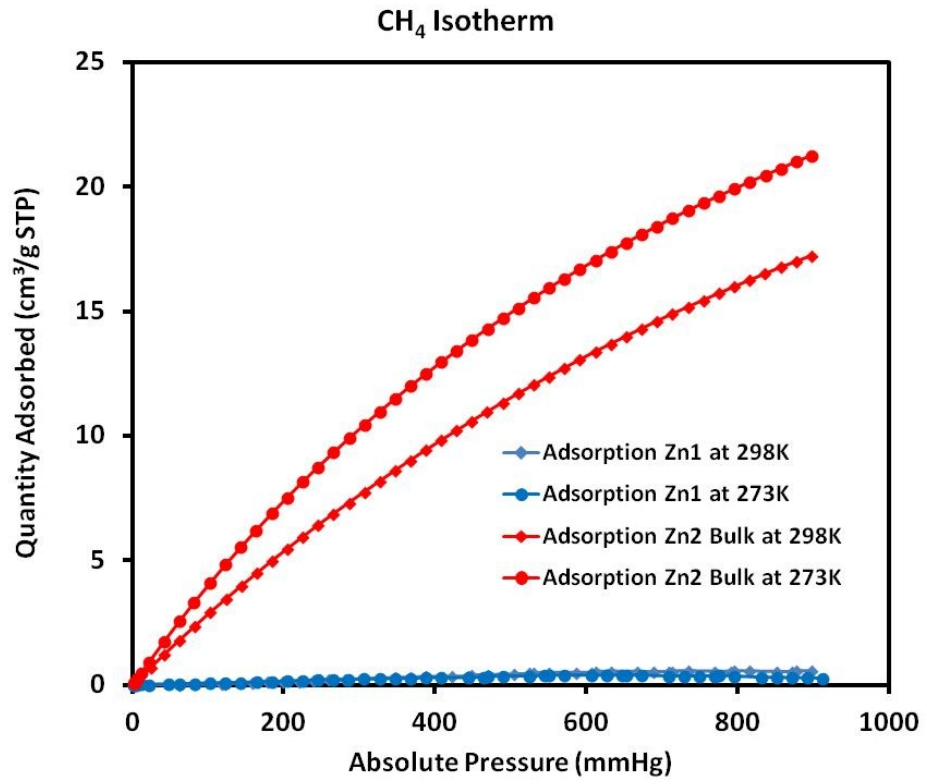*Nitrogen Adsorption Isotherm*

N₂ Isotherm at 77K

Figure SI-1: Experimental N$_2$ adsorption (solid diamonds) and desorption (empty diamonds) isotherm of Zn1 and Bulk Zn2 at 77 K and 1 .

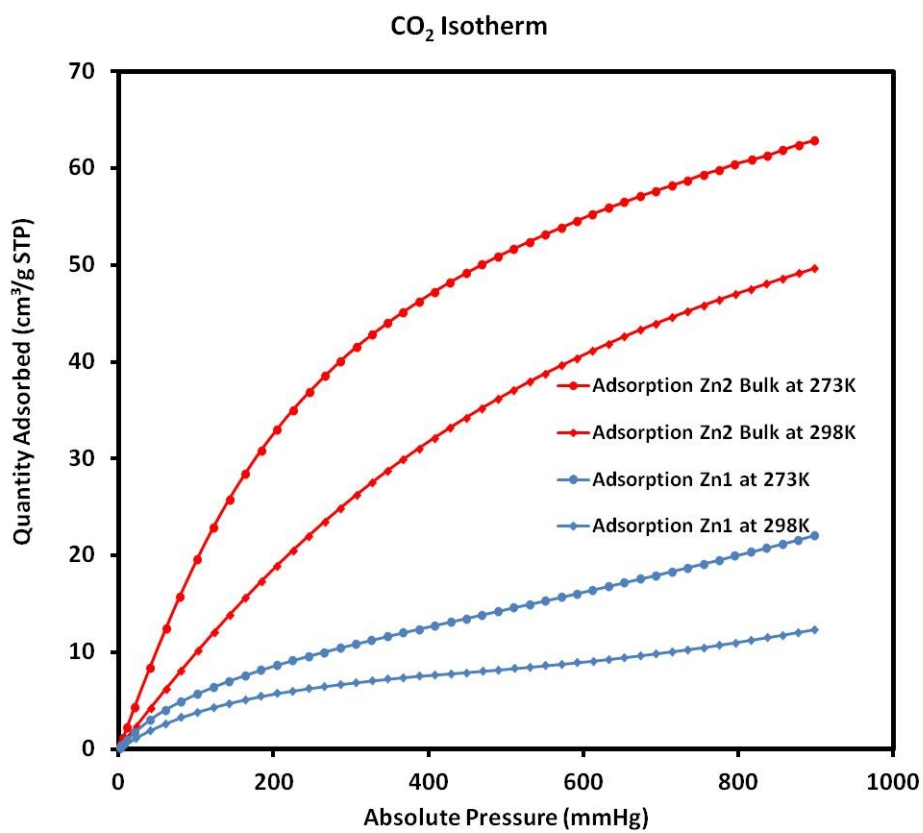*Hydrogen Adsorption Isotherm*

H₂ Isotherm

Methane Adsorption Isotherm

CH$_4$ Isotherm

- Adsorption Zn1 at 298K
- Adsorption Zn1 at 273K
- Adsorption Zn2 Bulk at 298K
- Adsorption Zn2 Bulk at 273K

Y-axis: Quantity Adsorbed (cm³/g STP)

X-axis: Absolute Pressure (mmHg)

9

Carbon Dioxide Adsorption Isotherm

CO$_2$ Isotherm

S3.2   X-ray Analysis

Single Crystal X-ray Diffraction Analysis

All structures were solved by direct methods using SHELXS-97 and refined against F^2 using SHELXL-2013.[6]   The program X-Seed was used as a graphical interface.[7]   All non-hydrogen atoms were refined using an anisotropic model, except for instances of disordered solvent (see supporting information for full details). Hydrogen atoms attached to carbon were placed in idealised X-ray positions and refined using a riding model.

Data have been deposited with the Cambridge Crystallographic Data Centre and are available from www.ccdc.cam.ac.uk/deposit.

Structure **Zn1** [Zn$_3$(ADIP)$_{1.5}$(DMF)$_3$(H$_2$O)$_2$]·3DMF

Data was treated using the SQUEEZE routine of PLATON[8] due to the presence of significant void space containing residual electron density that could not be modelled. A total void space of 2436 Å^3 in the unit cell containing a total of 474 e$^-$ (the full SQUEEZE output is available in the CIF file). Solvent assignment was made on the basis of calculated electron count and theromogravimetric analysis. Structure **Zn1** has 3 DMF solvent molecules included per formula unit.   The squeeze shows more solvent than in the TGA measurement which may be due to some solvent lost prior to the experiment.

Hydrogen atoms of the aqua ligands could not be located from the Fourier difference map and are therefore not included in the model, but have been included in the given formula unit. The DMF ligands were refined using distance and angle restraints using isotropic models due to the presence of disorder in these sites that could not be accurately modelled, complicated by the mirror plane passing through the metal and one of the DMF ligands. The DMF that resides across the mirror plane shows some disorder, although this could not be fully resolved - one of the methyl groups is modelled as 50:50 on either side of the mirror with the other lying on the mirror.   A residual peak of 1.5 e- lies close to the Zn3 site (that attached to the DMF ligands) which could not be sensibly assigned due to a steric clash with other ligands around this site and it is possible that there is additional, unresolvable disorder around this location.

The O7/C20/O8 carboxylate group is disordered between a chelating and monodentate coordination mode. This disorder was modelled with a restraint imposing co-planarity of the atoms in the 'B' component and no further restraints. The relative occupancy of the two components was refined freely to *ca.* 2:1 (chelating:monodentate). Disorder further along the molecule (i.e. the ring to which the carboxylate is bonded) could not be modelled.

[6] G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 2008, **64**, 112 –122.

[7] L. J. Barbour, *J. Supramol. Chem.*, 2001, **1**, 189 –191.

[8] A .L. Spek, *Acta Cryst*. 2009, D65, 148-155.

Large anisotropic parameters are associated with some of the atoms that lie on the mirror planes, suggesting some disorder of these ligands that could not be modelled with the average site of these atoms imposed by crystallographic symmetry.

Structure **Zn2** [Zn$_2$(ADIP)(DMF)$_{0.67}$(H$_2$O)$_{0.33}$]·6DMF

Data was treated using the SQUEEZE routine of PLATON due to the presence of significant void space containing residual electron density that could not be modelled. A single void space of 10319 Å^3 was located in the unit cell containing a total of 4422 e$^-$. Solvent assignment was made on the basis of calculated electron count and theromogravimetric analysis. Structure **Zn2** has 6 DMF solvent molecules included per formula unit. The squeeze shows more solvent than in the TGA measurement which may be due to some solvent lost prior to the experiment.

Modelling of coordinated and uncoordinated solvent was complicated by the high symmetry of the structure. Each zinc paddlewheel has two, symmetry-related terminal solvent sites that appear to be 2/3 H$_2$O and 1/3 DMF. The 1/3 DMF is disorder over two positions which were located from the Fourier difference map and refined using distance and angle restraints using an isotropic model (note, the full occupancy oxygen site was modelled anisotropically). The methyl groups of the DMF ligands were refined with their U$_{iso}$ values riding on that of the nitrogen to which they are attached due to their low site occupancy. The DMF ligands are required to be 1/3 occupancy due to their orientation around a 3-fold axis meaning that only one can be present at any given time with the remaining two sites around the axis being occupied by aqua ligands. A non-coordinated DMF site was located in a small pore. Although full occupancy, its location on a 3-fold axis means that it is present 2/3 of the time for each zinc paddlewheel. It appears that one C-N bond lies along the 3-fold axis with the remaining methyl group coinciding with the position of a carbonyl carbon atom from another orientation of the disorder. Given the overlap of these positions and the high symmetry, the atoms were assigned at the correct occupancies but hydrogen atoms could not be attached to the model.

Hydrogen atoms of the coordinated and uncoordinated solvent could not be located from the Fourier difference map and are therefore not included in the model, but have been included in the given formula unit.

Structure **Zn3** [Zn$_2$(ADIP)(H$_2$O)$_2$] ·1.5DMF

Data was treated using the SQUEEZE routine of PLATON due to the presence of significant void space containing residual electron density that could not be modelled. The calculations found three identical voids of 1700 Å^3 in the unit cell containing 607 e$^-$ each. Solvent assignment was made on the basis of calculated electron count and theromogravimetric analysis. Structure **Zn3** has 1.5 DMF solvent molecules included per formula unit. The squeeze shows more solvent than in the TGA measurement which may be due to some solvent lost prior to the experiment.

Hydrogen atoms of the aqua ligands could not be located from the Fourier difference map and are therefore not included in the model, but have been included in the given formula unit.
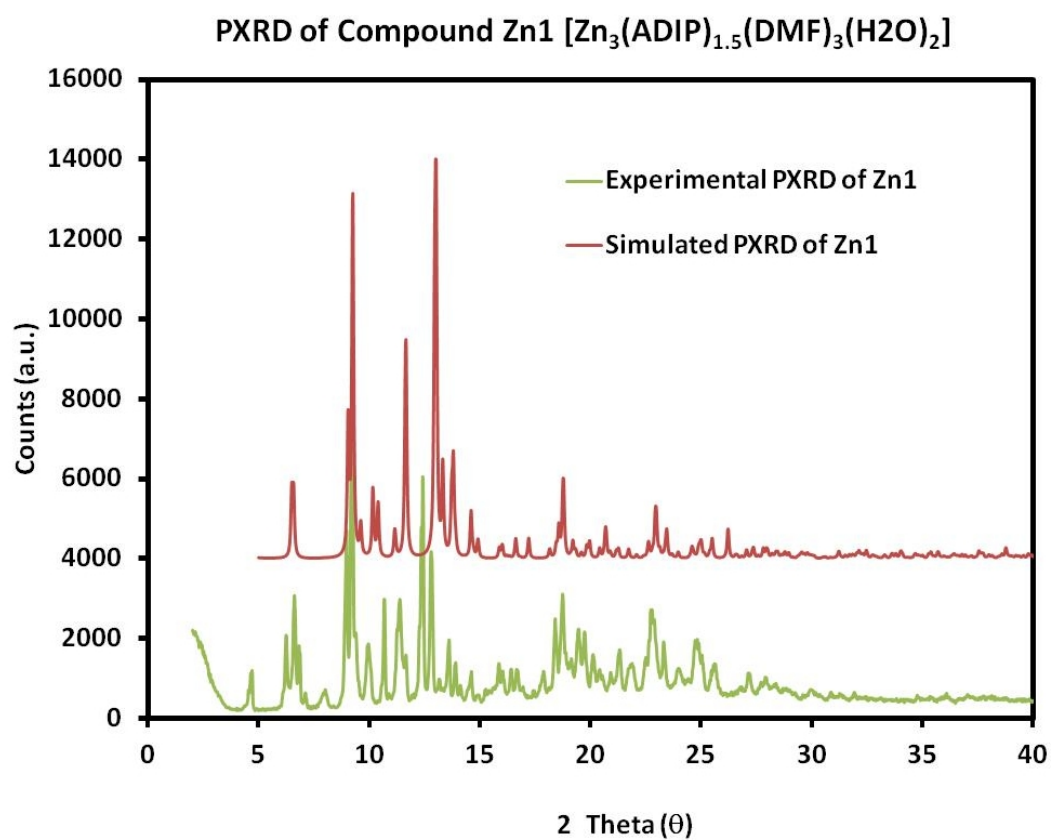
Crystallography Data
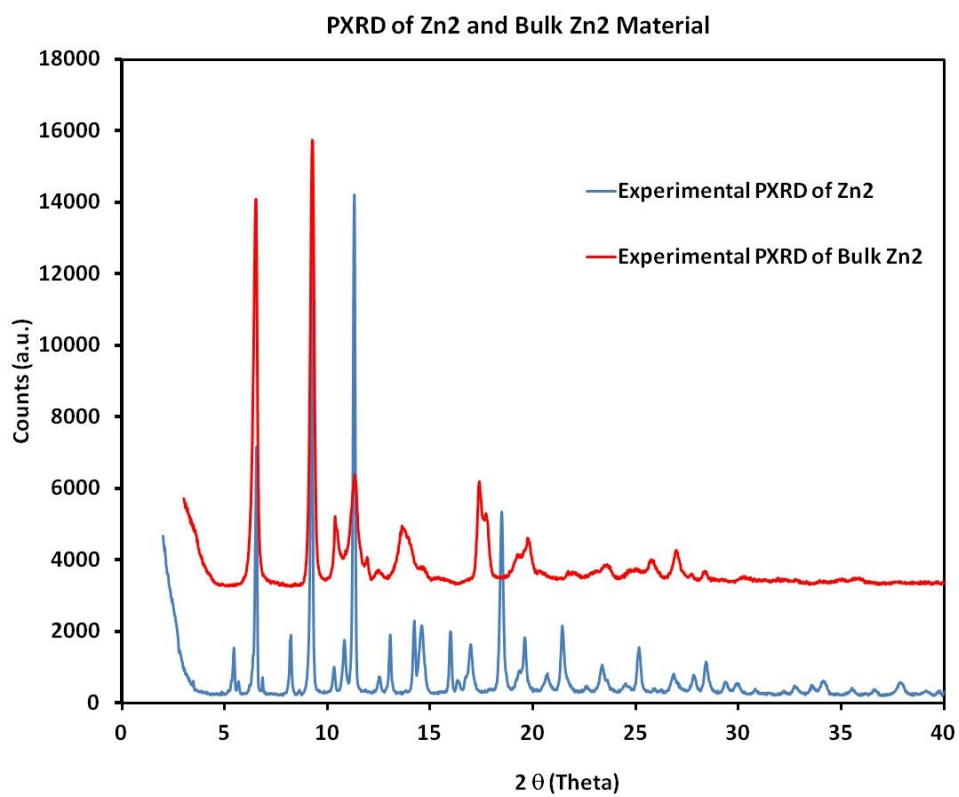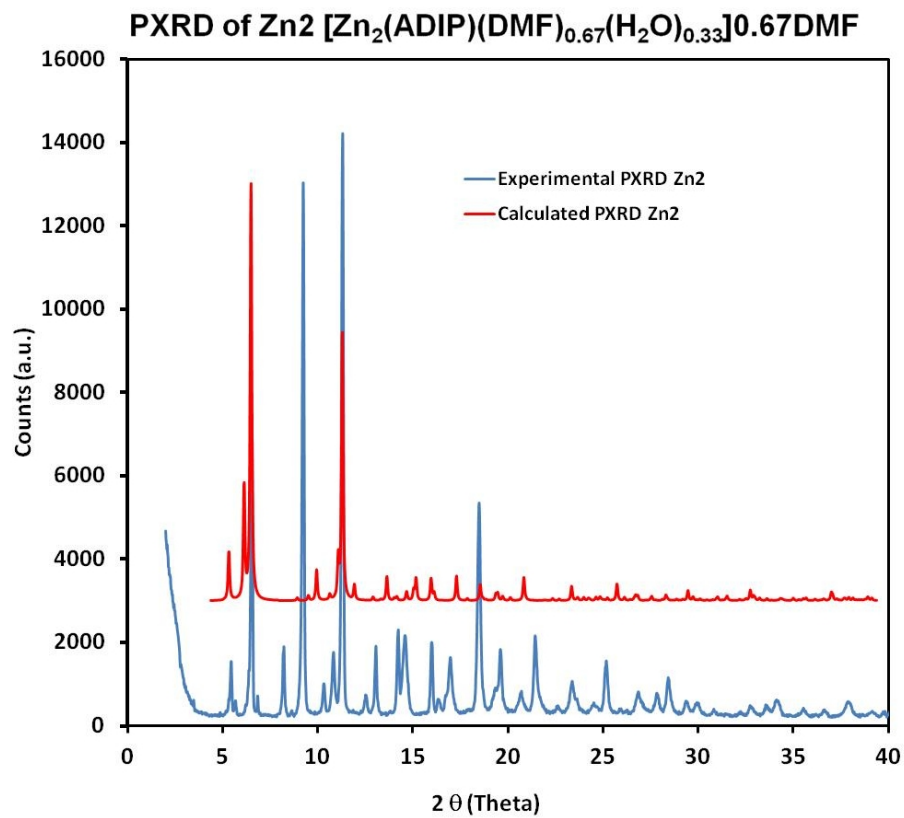
Table 1 Crystal data for **Zn1-3**

Compound	**Zn1**	**Zn2**	**Zn3**
Formula	$[Zn_3(ADIP)_{1.5}(DMF)_3(H_2O)_2] \cdot 3DMF$	$[Zn_2(ADIP)(DMF)_{0.67}(H_2O)_{0.33}] \cdot 6DMF$	$[Zn_2(ADIP)(H_2O)_2] \cdot 1.5DMF$
Empirical formula	$C_{63}H_{67}N_6O_{20}Zn_3$	$C_{53}H_{68}N_{7.33}O_{16.67}Zn_2$	$C_{34.50}H_{28.50}N_{1.50}O_{11.50}Zn_2$
Formula weight	1424.33	1193.20	778.83
T(K)	100(2)	123(2)	100(2)
Crystal system	Orthorhombic	Trigonal	Trigonal
Space group	P*mmn*	R-*3c*	R-*3m*
a/Å	26.846(5)	18.5127(3)	27.063(9)
b/Å	27.178(5)	18.5127(3)	27.063(9)
cÅ	9.766(2)	78.4908(18)	16.107(3)
α/°	90	90	90
β/°	90	90	90
γ/°	90	120	120
V/Å^3	7125(2)	23296(9)	10216(7)
Z	4	18	9
F(000)	2948	11244	3582
D_{calcd}(g/cm^3)	1.328	1.531	1.139
Reflections collected	146327	28882	71870
Unique reflections	11559	4615	3753
Final *GooF*	1.204	1.028	1.177
R(int.)	0.0982	0.1067	0.0906
R_1	0.1213	0.0922	0.0690
wR_2	0.3507	0.2160	0.1920

13

Table 2 Selected bond lengths (Å) and angles (°) for **Zn1-3**

Compound **Zn1**					
Zn1–O2	2.075(8)	Zn1–O6	1.870(6)	Zn1–O9	1.90(1)
Zn1–O10	2.17(1)	Zn2–O1	1.962(7)	Zn2–O5	1.940(6)
Zn2–O3	1.989(9)	Zn2–O4	2.35(2)	Zn3–O8B	2.10(2)
Zn3–O12	2.17(1)	Zn3–O13	1.99(1)	Zn1–Zn2	3.487
O2–Zn1–O6	100.1(3)	O2–Zn1–O9	93.7(4)	O2–Zn1–O10	177.3(5)
O6–Zn1–O9	114.8(4)	O6–Zn1–O10	81.1(5)	O6–Zn1–O6(i)	124.6(3)
O9–Zn1–O10	83.6(6)	O1–Zn2–O5	107.5(3)	O1–Zn2–O3	139.4(4)
O1–Zn2–O4	85.3(4)	O5–Zn2–O5(ii)	116.1(2)	O5–Zn2–O3	93.2(4)
O5–Zn2–O4	117.3(4)	O8B–Zn3–O12	91.2(5)	O8B–Zn3–O13	102.2(6)
O8B–Zn3–O12(iii)	165.3(5)	O13–Zn3–O12	89.1(5)		

Symmetry codes: (i) x,1/2-y, z (ii) x, ½ -y, z; (iii) 3/2-x, y, z

Compound **Zn2**					
Zn1–O4	2.050(4)	Zn1–O5	1.978(4)	Zn1–O1(i)	2.041(6)
Zn1–O3(ii)	2.010(4)	Zn1–O2(iii)	2.017(3)	Zn1–Zn1(iv)	3.003
O4–Zn1–O1	148.7(2)	O4–Zn1–O3	86.7(2)	O4–Zn1–O2	88.0(2)
O5–Zn1–O1	104.1(2)	O5–Zn1–O3	97.1(2)	O5–Zn1–O2	94.8(2)
O1–Zn1–O3	89.8(2)	O1–Zn1–O2	89.0(2)	O4–Zn1–O5	107.3(2)

Symmetry codes: (i) 1-x,1x+-y, ½-z (ii) x-y, -y, ½-z; (iii) 1-x+y, 1-xz; (iv) x, y, z

Compound **Zn3**					
Zn1–O1	2.021(2)	Zn1–O7	1.970(4)	Zn1–O2(i)	2.014(5)
Zn1–O1(ii)	2.021(5)	Zn1–Zn1(iii)	3.033	O1–Zn1–O7	101.1(2)
O1–Zn1–O2	84.8(2)	O1–Zn1–O2(i)	157.6(1)	O1–Zn1–O1(ii)	90.7(1)
O7–Zn1–O2	101.3(2)	O7–Zn1–O1	101.1(2)	O2–Zn1–O2(i)	91.1(2)

Symmetry codes: (i) 1/3-x, 2/3-y, 2/3-z (ii) –x+y, y, z (iii) x, y, z

Powder X-ray Diffraction Analysis

PXRD of Compound Zn1 [Zn$_3$(ADIP)$_{1.5}$(DMF)$_3$(H2O)$_2$]

PXRD of Zn2 [Zn$_2$(ADIP)(DMF)$_{0.67}$(H$_2$O)$_{0.33}$]0.67DMF

PXRD of Zn2 and Bulk Zn2 Material

PXRD of Zn3 [Zn$_2$(ADIP)(H$_2$O)$_2$]
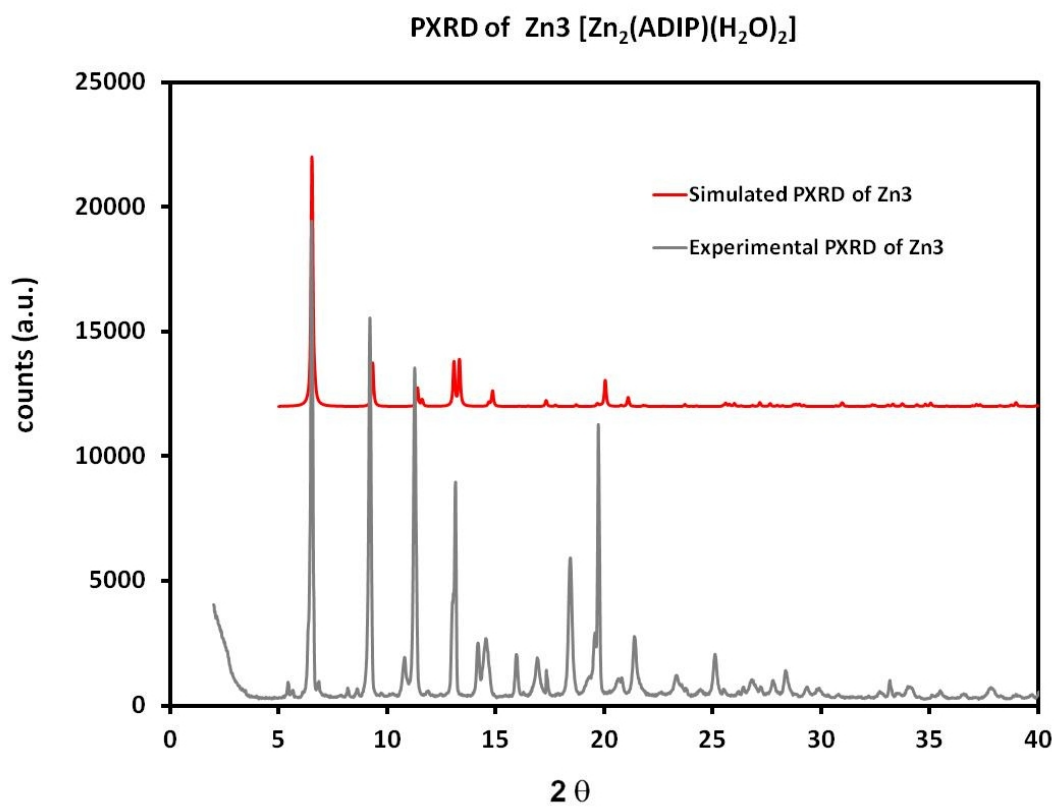
S3.3   Thermal Gravimetric Analysis

TGA of Compounds Zn1-3 and Bulk Zn2 Material

Legend:
- Zn1
- Zn2
- Zn2 Bulk
- Zn3

X-axis: Temperature °C
Y-axis: Weight % Loss