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Solvothermal reactions of an anthracene-based tetracarboxylic acid ligand, 5,5'-(anthracene-9,10-diyl)diisophthalic acid (H_4ADIP) with $Zn(NO_3)_2 \cdot 6H_2O$ afforded three novel metal–organic frameworks with unusual coordination geometries compared to the Cu analogue, PCN-14.

Microporous materials known as metal–organic frameworks (MOFs) or porous coordination polymers (PCPs) have attracted considerable attention, fundamentally but also industrially.^{1–6} Potential applications of such materials include gas storage,^{7–10} separation,¹¹ drug release,¹² catalysis^{13–15} and molecular recognition.¹⁶ MOFs can be best described as a hybrid material, consisting as the name suggests of metal and organic components that self-assemble using coordination bonding to give an infinite, uniform framework with periodic porosity. The self-assembly of the materials is an integral part of the process and varying the synthetic parameters such as metal precursor, organic ligands, solvent systems, concentration, pH, temperature and metal-to-ligand ratio can influence the self-assembly process. Here we describe a series of reaction conditions that yielded three zinc anthracene based carboxylate MOFs.

Zinc MOFs containing carboxylate ligands have two commonly preferred secondary building units (SBUs) that form, namely the dinuclear zinc paddlewheel unit $\{Zn_2(O_2CR)_4\}^{17}$ or the tetranuclear basic zinc acetate unit $\{Zn_4O(O_2CR)_6\}^{18,19}$ both of which are well represented in the literature.^{4,20,21} Although, there are few examples shown whereby the zinc metal ions have surprisingly adapted to constrained forms of traditional geometries.²² H_4ADIP (5,5'-(anthracene-9,10-diyl)diisophthalic acid)

A new family of zinc metal–organic framework polymorphs containing anthracene tetracarboxylates†

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is an attractive MOF ligand due to its hydrophobicity and potential to form highly coordinated structures, with large loadings of fused aromatic groups, that have previously shown to be attractive for natural gas storage.²³ Complexation with Zn^{II} in varying mixtures of DMF, H_2O and HBF_4 afforded $[Zn_3(ADIP)_{1.5}(DMF)_3(H_2O)_2] \cdot 3DMF$ (**Zn1**), $[Zn_2(ADIP)(DMF)_{0.67}(H_2O)_{0.33}] \cdot 6DMF$ (**Zn2**) and $[Zn_2(ADIP)(H_2O)_2] \cdot 1.5DMF$ (**Zn3**).

Notably, these three materials have the same empirical framework composition, $[Zn_2(ADIP)]$, with changes in synthetic conditions altering the topology and solvation. The three materials were obtained by varying pH, temperature and metal-to-ligand ratio (Fig. 1). Acidic reaction conditions were necessary to obtain crystalline products. From the four reaction conditions applied, three produced crystalline materials that could be isolated and structurally identified by single crystal X-ray diffraction. When a higher concentration of HBF_4 was used, a micro-crystalline powder was obtained which was identified by powder X-ray diffraction and thermal gravimetric analysis to be the purer polymorph compound of **Zn2** (**Bulk Zn2**) (see ESI†).

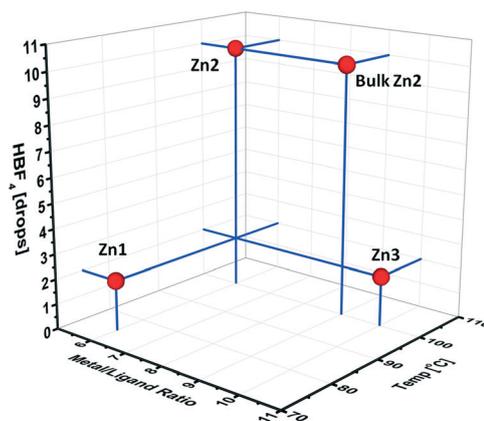


Fig. 1 Diagram exhibiting reaction conditions used to synthesise MOFs **Zn1–3**. Reaction conditions resulting in compounds: **Zn1**, **Zn2**, **Zn3** and **Bulk Zn2** (see ESI† S1 for all experimental details).

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† Electronic supplementary information (ESI) available: Detailed synthesis procedure, powder X-ray diffraction (PXRD) patterns, refinement details for X-ray crystal structures and TGA for compounds. CCDC 988120–988122 for **Zn1–3**. See DOI: 10.1039/c4ce00385c

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Crystallographic data and experimental details for structural analyses for **Zn1–3** are summarised in Table S1, and selected bond lengths and angles are listed in Table S2 in the ESI.† All of the structures contained significant void space and the data were treated using the SQUEEZE routine of PLATON (see ESI†).²⁴ The significant void space and very small (~20 μm) crystals give slightly high R factors, however connectivity and atom assignment is unambiguous.²⁵ The structure of **Zn1** was solved in the orthorhombic space group *Pmmn* and the asymmetric unit consists of three 1/2 occupancy Zn^{II} atoms on mirror planes, one 1/2 and one 1/4 ADIP ligand (the former bisected by a plane and the latter containing isophthalate groups coincidental with a mirror plane) and 1 and 1/2 coordinated DMF molecule (one of which lies on a mirror plane) as illustrated in Fig. 2a and b.

Metal atoms Zn(1) and Zn(2) are connected by three bridging carboxylate groups to form a {Zn₂(COO)₃} secondary building block unit with an interatomic Zn...Zn distance of 3.487 Å. Atom Zn(1) is coordinated to five oxygen atoms from three carbonyl groups of the ADIP ligands and two aqua ligands, displaying a distorted trigonal bipyramidal geometry. Atom Zn(2) has a distorted square pyramidal geometry with one carboxylate binding in a chelating fashion and the remaining sites occupied by oxygen atoms from bridging carboxylates. Atom Zn(3) is six-coordinate, with three DMF molecules and two carboxylate ligands, one monodentate and one chelating. Note, due to the position of the Zn(3) on a mirror plane there is a single crystallographically unique carboxylate that is disordered with both chelating and monodentate modes. Only one of these can be chelating at any given Zn position to give six coordinating atoms. Atom Zn(3) therefore acts topologically as a mononuclear, linear bridge between two ADIP ligands (Fig. 2a). Zn–O bond lengths in compound **Zn1** are in the range of 1.87–2.35 Å, consistent with literature values.²² Both of the crystallographically unique ADIP ligands bridge between six zinc atoms, with one bridging exclusively between {Zn₂(COO)₃} paddlewheels (two carboxylates forming part of the paddlewheel and two chelating to Zn(2)) and the

other ligand connecting the paddlewheel and atom Zn(3). With the chelating carboxylate group attached to the {Zn₂(COO)₃} paddlewheel, this is overall a four-connecting node.

Structure **Zn2** is a 3D network that was refined in the trigonal space group *R3c*. The asymmetric unit contains one unique Zn^{II} ion, one half of an ADIP ligand, one mixed DMF/H₂O ligand position (67:33 occupancy ratio) and one third of a lattice DMF molecule positioned across the 3-fold axis. This structure has the traditional {Zn₂(COO)₄} paddle wheel SBU with the zinc adopting a square pyramidal geometry with the coordinated solvent (DMF/H₂O) in the apical position. The interatomic Zn...Zn distance in the paddlewheel is 3.001 Å. This is shorter than in structure **Zn1**, 3.487 Å, likely due to the presence of an additional bridging carboxylate between the two metals. The ADIP ligand bridges between four paddlewheel SBUs. Depicted in Fig. 3a is the 3D net structure with lattice and coordinated solvent molecules removed for clarity. After removal of all the coordinated and interstitial solvent molecules, the vacant aperture size of structure **Zn2** is measured to be *ca.* 18.6 Å when calculated using centroids placed in the corners of the diisophthalic ring.

The single-crystal X-ray analysis of framework **Zn3** determined that it crystallizes in the trigonal *R3m* space group and the asymmetric unit is comprised of one of each; one half of a Zn^{II} ion, one 1/4 of an ADIP ligand and 1/2 a water molecule (with the Zn and water oxygen atom lying on a glide plane). As with compound **Zn2**, the structure contains the {Zn₂(COO)₄} paddlewheel SBU with the Zn^{II} ions having a square pyramidal geometry (Fig. 4b) as also seen in the copper and iron analogues PCN-14 and PCN-15 respectively.^{23,26} The 3D network has hexagonal channels parallel to the *c* axis (Fig. 4a) with the diameter of the channel window being up to 17.8 Å when calculated using centroids placed in the corners of the hexagon. These channels are larger compared to the iron analogue PCN-15 which has 13.6 Å channels (0 0 1 direction). Additionally **Zn3** has also found not to contain nanoscopic cages.²⁵ Compound **Zn3** exhibits a theoretical surface area of 2464 m² g⁻¹ (Fig. 4c) which exceeds the theoretical solvent accessible surface area of 1900 m² g⁻¹ in the copper analogue PCN-14.^{26,27}

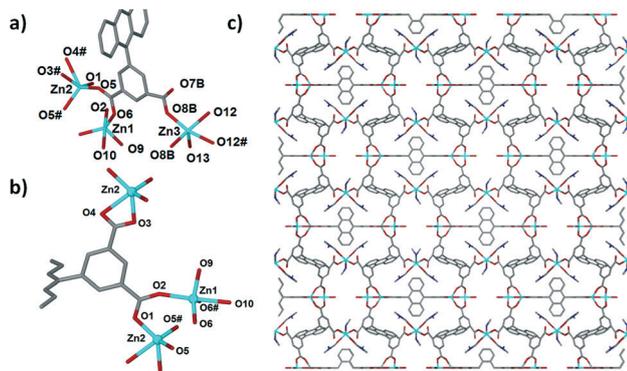


Fig. 2 a) The coordination environment of all three Zn^{II} ions in **Zn1** with hydrogen atoms and solvent molecules removed for clarity. b) The representation of chelating and bridging carboxyl groups in ligand ADIP with hydrogen atoms omitted for clarity. c) The 3D net structure of **Zn1**. # denotes symmetry generated atoms.

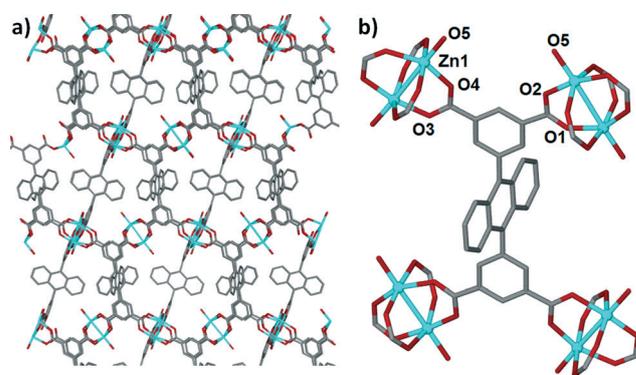


Fig. 3 a) The 3D net structure of **Zn2** looking along the *a* axis. b) Each ADIP ligand bridges between four zinc paddlewheel units (hydrogen atoms omitted for clarity).

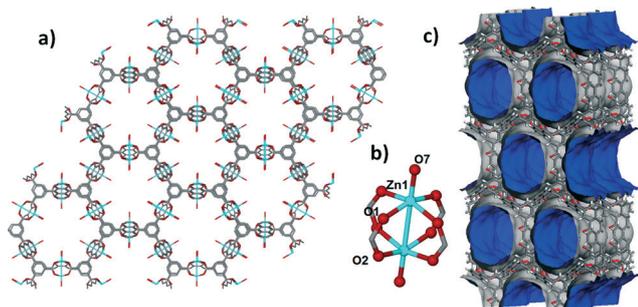


Fig. 4 a) The 3D net structure of **Zn3** looking along the *c* axis. b) The dinuclear zinc paddle-wheel motif. c) Theoretically calculated surface area of **Zn3**, with surface area highlighted in blue, region dominated by the organic ligand is coloured grey.

Sorption isotherms for compounds **Zn1** and **Bulk Zn2** were measured after samples were acetone-exchanged and degassed at 100 °C and 10^{-6} bar for 16 hours. Other compounds could not be isolated in sufficient quantities for adsorption measurements. The low pressure isotherms for N_2 , H_2 were measured at 77 K. The N_2 sorption isotherm (see ESI†) for compound **Bulk Zn2** shows a typical Type I sorption isotherm with an estimated Brunauer–Emmett–Teller (BET) surface of $307 \text{ m}^2 \text{ g}^{-1}$ and a pore volume of $0.2415 \text{ cm}^3 \text{ g}^{-1}$. The N_2 sorption isotherm of compound **Zn1** revealed that it adsorbed little to no N_2 and has negligible surface area ($2 \text{ m}^2 \text{ g}^{-1}$ with a pore volume of $0.0016 \text{ cm}^3 \text{ g}^{-1}$), indicating a solvated system. Both samples have much lower experimental surface areas than related tetracarboxylate MOFs by Schröder²⁸ or Zhou, although their theoretical surface areas are higher.^{23,26} The H_2 sorption isotherms collected at 77 K and 1.2 bar exhibit a storage capacity of 1.2 wt.% ($112 \text{ cm}^3 \text{ g}^{-1}$) for compound **Bulk Zn2** (see ESI†). The H_2 sorption isotherm of **Bulk Zn2** shows good reversibility and an absence of hysteresis. At low pressure, the H_2 adsorption appears far from saturation, indicating that the H_2 storage capacity is dominated by the affinity between the gas molecules and the framework. Thus, **Bulk Zn2** has a greater potential for H_2 adsorption at high pressures.

Conclusions

In summary, three materials were synthesised by changing the reaction conditions including metal-to-ligand ratio, temperature and pH, and structurally characterised by using X-ray crystallography to identify the zinc complexes. The subtle difference in synthesis conditions has resulted in a family of polymorph zinc ADIP structures consisting of 3D networks with Zn_2 paddle-wheel units, $\{Zn_2(COO)_3\}$ for **Zn1** and $\{Zn_2(COO)_4\}$ for **Zn2** and **Zn3**, connected by the tetra-topic ligand. All of the networks have the same empirical desolvated formula $[Zn_2(ADIP)]$, with variations occurring in the nature and amount of both coordinated solvents and solvents within the accessible pore spaces. The trigonal

structure of **Zn3** is particularly porous; with a predicted surface area of $2464 \text{ m}^2 \text{ g}^{-1}$, higher than anything previously seen for systems containing the ADIP ligand.

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