

Blue photoluminescent zinc coordination polymers with supertetranuclear cores†

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Two photoluminescent two- and three-dimensional coordination polymers consisting of Zn_4O [or $Zn_4(OH)_2$] cores, dicarboxylate (isophthalate or fumarate) and 4,4'-bipyridine ligands as building blocks have been hydrothermally synthesized and structurally characterized.

The construction of supramolecular architectures are currently of great interest owing to their intriguing network topologies and potential functions as new classes of materials.¹ Polynuclear d^{10} metal (Cu^I , Ag^I , Au^I , Zn^{II} or Cd^{II}) complexes have been found to exhibit intriguing structural and photoluminescent properties.^{2–5} We have been pursuing synthetic strategies for non-interpenetrating open frameworks with variable cavities or channels using simple units as building blocks.⁶ We now extend to work towards extended networks based on metal clusters as building blocks, and report here the preparation and crystal structures of two novel coordination polymers constructed by zinc cluster cores, 4,4'-bipyridine (4,4'-bpy) and dicarboxylate ligands, namely $[Zn_4O(ip)_3(4,4'-bpy)]$ (ip = isophthalate) **1** and $[Zn_4(OH)_2(fa)_3(4,4'-bpy)_2]$ (fa = fumarate) **2**.

The hydrothermal reactions of zinc salts with the dicarboxylates and 4,4'-bpy in molar ratio 1 : 1 : 1 at 180 °C (7 days) and 140 °C (60 h) led to the formation of colourless **1** and **2**, respectively. Elemental analysis confirmed the formulae of **1** and **2**.[‡] Thermogravimetric analysis (TGA) performed on the polycrystalline samples indicate that they are thermally stable up to 380 °C, in accord with the fact that hydrothermal products are usually stable.

X-Ray single-crystal analysis§ has revealed that **1** contains two-dimensional polymeric grids with supertetranuclear Zn_4O cores as building units, in which each zinc atom is coordinated by the central μ_4 -oxo atom, two oxygen atoms from two μ -carboxylate, and a monodentate carboxylate or 4,4'-bpy groups to furnish tetrahedral coordination, as shown in Fig. 1. The average Zn–O length (1.971 Å) is somewhat longer than that (av. 1.939 Å) found in $[Zn_4O(O_2CPh)_6]$.⁵ The ip ligands in **1** act in both bisbidentate and bismonodentate modes, though the Zn(2)–O(4) distance of 2.547(2) Å suggests a non-negligible interaction, or semi-chelate coordination mode for the bismonodentate tp ligand.⁷ The different coordination environments around two crystallographically independent zinc atoms may be attributed to the different Zn–O(oxo) distances, the Zn(2)–O(5) bond (1.993 Å) is much longer than that (1.931 Å) of Zn(1)–O(5).

The most striking feature of **1** is the connection of Zn_4O cores via organic ligands to form infinite two-dimensional networks with two different types of cavities (8.7×8.7 and 8.7×10.4 Å), as shown in Fig. 2. The Zn_4O cores are bridged by bismonodentate and bisbidentate ip ligands into infinite one-dimensional ladder-like $[Zn_4O(ip)_3]$ chains, and adjacent ladders are interlinked through μ -4,4'-bpy spacers, resulting in a

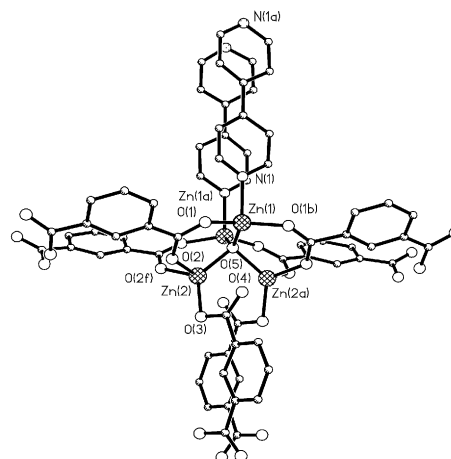


Fig. 1 The coordination environments of zinc atoms in **1**. Selected bond distances (Å) and angles (°): Zn(1)–O(1) 1.970(2), Zn(1)–O(5) 1.931(1), Zn(2)–O(2) 1.989(2), Zn(2)–O(3) 1.969(3), Zn(2)–O(5) 1.993(2), Zn(1)–N(1) 2.076(3); O(1)–Zn(1)–N(1) 96.4(1), O(1)–Zn(1)–O(5) 113.1(1), O(5)–Zn(1)–N(1) 117.0(1), O(2)–Zn(2)–O(3) 94.0(1), O(2)–Zn(2)–O(5) 108.3(1), O(3)–Zn(2)–O(5) 128.8(1).

novel two-dimensional grid. It is noteworthy that the topology of **1** can be simplified to (4,4) if we connect only the core (O5) of the supertetrahedra.

Complex **2** is made up of an infinite interpenetrating three-dimensional framework with $Zn_4(\mu_3-OH)_2$ cores and organic bridges. Unlike **1**, the tetranuclear core in **2** is unprecedented in zinc coordination chemistry, and similar to the butterfly-like tetranuclear manganese complexes.⁸ Atom Zn(1) is in a distorted octahedral geometry, coordinated by two μ_3 -OH groups, one 4,4'-bpy group, and three oxygen atoms from one chelate and one monodentate carboxylate groups (Fig. 3). The Zn–O(hydroxo) distances are compatible to those documented

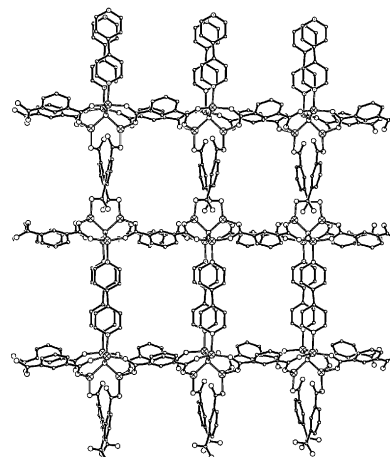


Fig. 2 Perspective view of the two-dimensional framework of **1**.

† Electronic supplementary information (ESI) available: X-ray powder diffraction data for complexes **1** and **2**. See <http://www.rsc.org/suppdata/cc/b0/b005753n/>

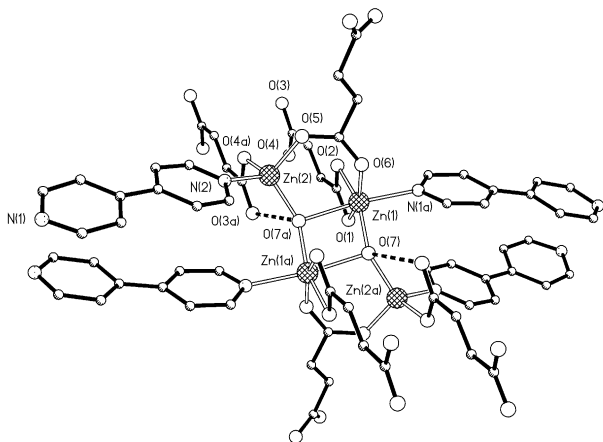


Fig. 3 The coordination environments of zinc atoms in **2**. Selected bond distances (Å) and angles (°): Zn(1)–O(1) 2.367(4), Zn(1)–O(2) 2.089(4), Zn(1)–O(6) 2.054(4), Zn(1)–O(7) 2.015(3), Zn(1)–N(1a) 2.192(4), Zn(2)–O(4a) 1.973(4), Zn(2)–O(5) 1.955(3), Zn(2)–O(7a) 1.950(3), Zn(2)–N(2) 2.054(4), O(7a)···O(3a) 2.755(5); O(1)–Zn(1)–O(2) 58.8(1), O(6)–Zn(1)–O(7) 95.0(1), O(7)–Zn(1)–N(1a) 95.5(1), O(4a)–Zn(2)–O(7a) 109.4(1), O(5)–Zn(2)–O(7a) 110.9(1), O(7a)–Zn(2)–N(2) 116.8(2), O(4a)–Zn(2)–N(2) 105.0(1), O(5)–Zn(2)–N(2) 100.0(2).

in the literature.⁹ The μ_3 -OH group is also hydrogen-bonded to the monodentate carboxylate [O(7a)···O(3a) 2.755(5) Å]. Zn(2) atom is tetrahedrally coordinated by μ_3 -OH, one 4,4'-bpy group and two oxygen atoms from two fa ligands. The $Zn_4(OH)_2$ cores are interlinked by the carboxylate groups of six fa ligands in both bisbidentate and chelate-monodentate fashions, resulting in infinite two-dimensional $[Zn_4(OH)_2(fa)_3]$ sheets [Fig. 4(a)], which are pillared by the 4,4'-bpy ligands to generate an infinite three-dimensional prismatic-like framework [Fig. 4(b)]. The actual crystal structure has two such 3D frameworks that interpenetrate each other. The topology of **2** can be related to the simple cubic α -Po two-fold interpenetrated lattice.

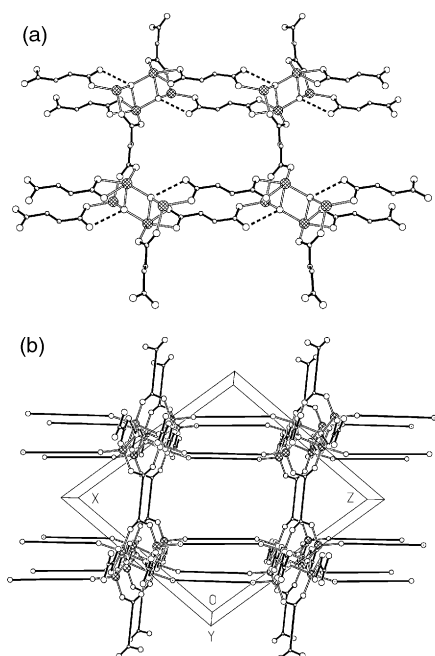


Fig. 4 Perspective views of the two-dimensional framework of $[Zn_4(OH)_2(fa)_3]$ (a) and the building unit of three-dimensional framework (b) of **2**. For clarity, both the 4,4'-bpy ligands and the ethylene groups of fa ligands in (b) are shown as solid lines.

It is noteworthy that **1** and **2** are the first examples of coordination polymers constructed by oxo or hydroxo metal clusters with mixed bridging organic ligands, though the first three-dimensional framework constructed by Zn_4O cores and dicarboxylates has recently been documented in $[Zn_4O(BDC)_3](DMF)_8(C_6H_5Cl)$ (BDC = 1,4-benzenedicarboxylate).¹⁰

In the solid state **1** and **2** exhibit intense photoluminescence upon photoexcitation at 320 and 398 nm, respectively. The emissions of **1** ($\lambda_{max} = 432$ nm) and **2** ($\lambda_{max} = 453$ nm) may be assigned as ligand-to-metal charge transfer (LMCT).¹¹ They may be good candidates for blue-light emitting diode devices, since these condensed materials are highly thermally stable and insoluble in common polar and non-polar solvents.

In conclusion, we have synthesised two stable polynuclear zinc polymers under hydrothermal conditions, providing a new synthetic route for metal coordination polymers with promising photoelectronic properties.

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Notes and references

‡ Anal. Calc. for $C_{34}H_{20}N_2O_{13}Zn_4$ **1**: C, 44.10; H, 2.18; N, 3.02. Found: C, 43.85; H, 2.07; N, 2.90%. Calc. for $C_{32}H_{24}N_4O_{14}Zn_4$ **2**: C, 40.45; H, 2.55; N, 5.90. Found: C, 40.30; H, 2.45; N, 5.72%.

§ Crystal data for **1**: $C_{34}H_{20}N_2O_{13}Zn_4$, $M_r = 926.00$, tetragonal, space group $P4_2/mmm$ (no. 136), $a = 17.346(2)$, $c = 10.428(2)$ Å, $V = 3137.6(8)$ Å³, $Z = 4$, $D_c = 1.960$ g cm⁻³, μ (Mo-K α) = 3.099 cm⁻¹. **2**: $C_{32}H_{24}N_4O_{14}Zn_4$, $M_r = 950.03$, monoclinic, space group $P2/n$ (no. 13), $a = 17.096(7)$, $b = 11.183(6)$, $c = 18.607(12)$ Å, $\beta = 103.52(1)^\circ$, $V = 3459(3)$ Å³, $Z = 4$, $D_c = 1.824$ g cm⁻³, μ (Mo-K α) = 2.817 cm⁻¹. Data collections ($2\theta \leq 30^\circ$ for **1**, $2\theta \leq 27^\circ$ for **2**) were performed at 293 K on Bruker CCD and Siemens R3m diffractometers (Mo-K α , $\lambda = 0.71073$ Å) for **1** and **2**, respectively. The structures were solved with direct methods (SHELXS-97)¹² and refined by full-matrix least squares (SHELXL-97),¹³ giving for **1** a final R_1 value of 0.0294 for 164 parameters and 1845 unique reflections with $I \geq 2\sigma(I)$ and wR_2 of 0.0859 for all 2295 reflections, and for **2** a final R_1 value of 0.0431 for 487 parameters and 5414 unique reflections with $I \geq 2\sigma(I)$ and wR_2 of 0.1119 for all 6801 reflections.

CCDC 182/1775. See <http://www.rsc.org/suppdata/cc/b0/b005753n/> for crystallographic files in .cif format.

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