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Divergent topologies in luminescent and nitrobenzene-detecting zinc diphenate coordination

polymers with flexible dipyridylamide ligands

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#### Abstract

Hydrothermal reaction of zinc nitrate, diphenic acid (H<sub>2</sub>dip), and one of the dipyridylamide ligands *N*,*N*'-(hexane-1,6-diyl)diisonicotinamide (hdin), *N*,*N*'-(pentane-1,6diyl)diisonicotinamide (pedin), *N*,*N*'-(butane-1,6-diyl)diisonicotinamide (bdin), or *N*,*N*'-(ethane-1,6-diyl)diisonicotinamide (edin) resulted in coordination polymers whose dimensionalities depend on the aliphatic tether length within the coligand and the amount of base used in the synthesis. The five new phases were characterized by single crystal X-ray diffraction.  $\{[Zn(dip)(hdin)] \cdot 2.5H_2O\}_n$  (1) and  $\{[Zn(dip)(pedin)] \cdot 2.5H_2O\}_n$  (2) both possess undulating 2D coordination polymer layers with  $[Zn(dip)]_n$  chains spanned by looped dipyridylamine ligands into a 2,4-connected self-penetrated  $(6)(6^48.10)$  topology.  $[Zn(dipH)_2(bdin)]_n$  (3) manifests a 1-D zig-zag chain topology, while  $\{[Zn_3(dip)_3(bdin)_3] \cdot 13H_2O\}_n$  (4) and  $\{[Zn(dip)(edin)] \cdot 3H_2O]_n$ (5) manifest helical substructures linked into a rare two-fold interpenetrated  $6^48^2$  **nbo** topology. Thermal and luminescent properties were also probed; compounds 1–5 showed ability to detect nitrobenzene in ethanol suspension with the 3D derivatives 4 and 5 manifesting the best "turnoff" luminescence quenching behavior.

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#### **1. Introduction**

Coordination polymers containing divalent metal ions and aromatic dicarboxylate ligands have shown enticing properties in many industrially relevant applications [1], such as gas storage [2], small molecule separation [3], drug delivery [4], heterogeneous catalysis for organic transformations [5], and second harmonic generation for laser waveguides [6]. More recently coordination polymers based on closed-shell  $d^{10}$  metal ions have shown the capability to detect nitroaromatics for potential security applications, via luminescence quenching mechanisms [7]. A large variety of structural topologies are accessible within divalent metal coordination polymers depending on metal coordination geometry preferences, carboxylate-group binding modes, and the presence of dipodal dipyridyl-type coligands, in addition to empirical synthetic conditions [8]. Structural diversity is especially wide among divalent zinc coordination polymers [9]. The lack of crystal field stabilization in the  $d^{10}$  electronic configuration allows adjustment of coordination geometry in response to the conformational and steric requirements of the carboxylate and dipyridyl ligands.

The diphenate ligand (dip, biphenyl-2,2'-dicarboxylate, Scheme 1) has proven efficacious for the construction of coordination polymers with diverse topologies [10–15] because it can show flexible conformations about its central  $sp^2(C)-sp^2(C) \sigma$  bond in response to specific supramolecular conditions during self-assembly, which is not possible in more commonly employed monoaromatic ligands such as phthalate or isophthalate. In the class of zinc diphenate coordination polymers, diverse 1D, 2D, and 3D topologies have been observed depending on the nature of a dipyridyl-type coligand. For example,  $[Zn(dip)(bpy)]_n$  (bpy = 4,4'-bipyridine) manifests a rare 2-fold interpenetrated 3-D network with a uninodal 4-connected  $4^28^4$  topology,

built from linked helical  $[Zn(dip)]_n$  chains [12]. { $[Zn(dip)(4-bpmp)] \cdot 0.5H_2O\}_n$  (4-bpmp = bis(4pyridylmethyl)piperazine) also displays a 2-fold interpenetrated 3D network, but with a standard 6<sup>6</sup> diamondoid lattice [13]. { $[Zn_2(dip)_2(3-pna)_2] \cdot 3H_2O\}_n$  (3-pna = 3-pyridylnicotinamide) manifested a rare 4-connected 1D ribbon topology [14], while { $[Zn(dip)(dpa)] \cdot 3H_2O\}_n$  (dpa = 4,4'-dipyridylamine) shows a common (4,4) grid topology [15]. { $[Zn_4(dip)_4(H_2O)_2(4$ ppbp)\_2] \cdot 12H\_2O\_n (4-ppbp = propane-1,3-diylbis(piperidine-4,1-diyl))bis(pyridin-4ylmethanone) exhibited 2D 3,6-connected layers with (4<sup>3</sup>)<sub>2</sub>(4<sup>6</sup>6<sup>6</sup>8<sup>3</sup>) kgd topology featuring embedded R(8)A(2) classification 10-membered water clusters [14].

The conformationally flexible and hydrogen-bonding capable dipyridylamide ligands N,N'-(hexane-1,6-diyl)diisonicotinamide (hdin, Scheme 1), N,N'-(pentane-1,5-diyl)diisonicotinamide (pedin, Scheme 1), N,N'-(butane-1,4-diyl)diisonicotinamide (bdin, Scheme 1), and N,N'-(ethane-1,2-diyl)diisonicotinamide (edin, Scheme 1) have not been often employed in the construction of divalent metal coordination polymers despite their ease of synthesis [16]. A series of copper oxoanion and pseudohalide coordination polymers with bdin tethers were reported by Biradha's group [17]; 1D chain or 2D layer copper isophthalate coordination polymers containing bdin tethers have been prepared by Lin et al [18]. {[Cd(1,2-phenylenediacetate)(edin)(H<sub>2</sub>O)]·H<sub>2</sub>O}<sub>n</sub> (1) exhibited standard (4,4) grid layers stacked in an alternating *ABAB* pattern, while {[Cd(1,3-phenylenediacetate)(edin)(H<sub>2</sub>O)]·H<sub>2</sub>O}<sub>n</sub> manifested an uncommon 3D 4-fold interpenetrated  $6^{58}$  cds topology. Both of these cadmium phases showed "turn-off" luminescent sensing capability for nitrobenzene detection [19].

We therefore endeavored to synthesize a series of divalent zinc diphenate coordination polymers containing isonicotinamide-bearing dipyridylamide ligands with varying aliphatic tether length and with potential nitroaromatic detection capability. In this contribution we

present the single-crystal structures, discussion of topological features, luminescence properties, nitrobenzene detecting capabilities via "turn-off" luminescence quenching, and thermal degradation properties of five new zinc diphenate coordination polymers with varying dipyridylamide ligands: { $[Zn(dip)(hdin)] \cdot 2.5H_2O_n (1), {[Zn(dip)(pedin)] \cdot 2.5H_2O_n (2), [Zn(dipH)_2(bdin)]_n (3), {[Zn_3(dip)_3(bdin)_3] \cdot 13H_2O_n (4), and {[Zn(dip)(edin)] \cdot 3H_2O_n (5).$ 

#### 2. Experimental Section

#### 2.1 General Considerations

Zinc nitrate and diphenic acids were commercially obtained from Sigma Aldrich. *N*,*N*<sup>-</sup> (hexane-1,6-diyl)diisonicotinamide (hdin) was prepared by condensation of 1,6-hexanediamine and two molar equivalents of isonicotinoyl chloride hydrochloride in dry pyridine. The reaction mixture was quenched with water, and then the product was isolated via CH<sub>2</sub>Cl<sub>2</sub> extraction, drying with sodium sulfate, filtration, and removal of solvent *in vacuo* [16]. The pedin, bdin, and edin ligands were prepared similarly using 1,5-pentanediamine, 1,4-butanediamine, and 1,2-ethanediamine as the diamine starting materials, respectively. Water was deionized above 3M – cm in-house. IR spectra were recorded on powdered samples using a Perkin Elmer Spectrum One DRIFT instrument. Thermogravimetric analysis was performed on a TA Instruments Q-50 Thermogravimetric Analyzer with a heating rate of 10 °C/min up to 600 °C. Elemental Analysis was carried out using a Perkin Elmer 2400 Series II CHNS/O Analyzer. The luminescence spectra were obtained with a Hitachi F-4500 Fluorescence Spectrometer on solid crystalline samples anchored to quartz microscope slides with Rexon Corporation RX-22P ultraviolet-transparent epoxy adhesive.

2.2 Preparation of  $\{[Zn(dip)(hdin)] \cdot 2.5H_2O\}_n$  (1)

Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (110 mg, 0.37 mmol), diphenic acid (90 mg, 0.37 mmol), and hdin (121 mg, 0.37 mmol), and 0.75 mL of a 1.0 *M* NaOH solution were mixed with 10 mL of distilled H<sub>2</sub>O in a 23 mL Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 120 °C for 3 d, and then was cooled slowly to 25 °C. Brown crystals of **1** (177 mg, 70 % yield based on Zn) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal.* Calc. for  $C_{32}H_{35}N_4O_{8.5}Zn$  **1**: C, 56.76; H, 5.21; N, 8.28 % Found: C, 56.45; H, 5.04; N, 8.21 %. IR (cm<sup>-1</sup>): 3329 (w), 2922 (w), 2864 (w), 1667 (s), 1612 (s), 1582 (w), 1545 (s), 1475 (m), 1433(m), 1368 (s), 1302 (s), 1201 (w), 1179(w), 1160 (m), 1112 (w), 1061 (w), 1032 (w), 1004 (w), 853 (w), 830 (w), 813 (w), 782 (w), 756 (s), 697 (s), 664 (w), 648 (w).

2.3 Preparation of  $\{[Zn(dip)(pedin)] \cdot 2.5H_2O\}_n$  (2)

Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (110 mg, 0.37 mmol), diphenic acid (90 mg, 0.37 mmol), and pedin (115 mg, 0.37 mmol), and 0.75 mL of a 1.0 *M* NaOH solution were mixed with 10 mL of distilled H<sub>2</sub>O in a 23 mL Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at x °C for x d, and then was cooled slowly to 25 °C. Brown crystals of **2** (135 mg, 55 % yield based on Zn) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal.* Calc. for  $C_{31}H_{33}N_4O_{8.5}Zn$  **2** C, 56.15; H, 5.02; N, 8.45 % Found: C, 56.37; H, 4.68; N, 8.38 %. IR (cm<sup>-1</sup>): 3273 (w), 2932 (w), 1666 (s) 1612 (m), 1547 (s), 1475 (w), 1433 (w), 1371 (s), 1302 (m), 1233 (w), 1202 (w), 1112 (w), 1063 (w), 1026 (w), 1004 (w), 853 (m), 830 (w), 756 (s), 697 (s), 665 (w), 648 (w).

2.4 Preparation of  $[Zn(dipH)_2(bdin)]_n$  (3)

Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (110 mg, 0.37 mmol), diphenic acid (90 mg, 0.37 mmol), and bdin (110 mg, 0.37 mmol), and 0.75 mL of a 1.0 *M* NaOH solution were mixed with 10 mL of distilled H<sub>2</sub>O in a 23 mL Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 120 °C for 3 d, and then was cooled slowly to 25 °C. Brown crystals of **3** (148 mg, 47 % yield based on Zn) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal.* Calc. for C<sub>44</sub>H<sub>36</sub>N<sub>4</sub>O<sub>10</sub>Zn **3**: C, 62.45; H, 4.29; N, 6.62 % Found: C, 62.18; H, 4.64; N, 6.91 %. IR (cm<sup>-1</sup>): 3273 (w), 1667 (s), 1612 (s), 1582 (w), 1546 (s), 1475 (m), 1433 (m), 1369 (s), 1302 (m), 1201 (w), 1161 (w), 1032 (w), 1004 (w), 830 (w), 756 (s), 697 (s), 665 (w), 648 (w).

2.5 Preparation of  $\{[Zn_3(dip)_3(bdin)_3] \cdot 13H_2O\}_n$  (4)

Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (110 mg, 0.37 mmol), diphenic acid (90 mg, 0.37 mmol), and bdin (110 mg, 0.37 mmol), and 1.5 mL of a 1.0 *M* NaOH solution were mixed with 10 mL of distilled H<sub>2</sub>O in a 23 mL Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 120 °C for 3 d, and then was cooled slowly to 25 °C. Brown crystals of **4** (158 mg, 63 % yield based on Zn) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal.* Calc. for C<sub>90</sub>H<sub>78</sub>N<sub>12</sub>O<sub>18</sub>Zn<sub>3</sub> **4**: C, 59.66; H, 4.34; N, 9.28 % Found: C, 59.16; H, 4.62; N, 9.78 %. IR (cm<sup>-1</sup>): 3282 (w, br), 3056 (w), 2939 (w), 1649 (m), 1603 (w), 1584 (w), 1548 (s) 1497 (w), 1475 (w), 1439 (w), 1421 (w), 1376 (s), 1313 (w), 1150 (w), 1108 (w), 1066 (m), 1026 (w), 856 (m), 806 (w), 760 (s), 713 (w), 683 (m), 662 (w).

#### 2.6 Preparation of $\{[Zn(dip)(edin)] \cdot 3H_2O\}_n$ (5).

 $Zn(NO_3)_2 \cdot 6H_2O$  (110 mg, 0.37 mmol), diphenic acid (90 mg, 0.37 mmol), and edin (96 mg, 0.37 mmol), and 0.75 mL of a 1.0 *M* NaOH solution were mixed with 10 mL of distilled H<sub>2</sub>O in a 23

mL Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 120 °C for 3 d, and then was cooled slowly to 25 °C. Brown crystals of **5** (145 mg, 64 % yield based on Zn) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal*. Calc. for  $C_{28}H_{28}N_4O_9Zn$  **5**: C, 53.38; H, 4.48; N, 8.89 % Found: C, 52.50; H, 4.57; N, 8.64 %. IR (cm<sup>-1</sup>): 3274 (w), 2922(w), 1667 (s), 1612 (s), 1582 (w), 1546 (s), 1475 (w), 1439 (m), 1369 (s), 1301 (m), 1201 (w), 1179 (w), 1160 (w), 1112 (w), 1061 (w), 1032 (w), 1004 (w), 853 (m), 830 (w), 813 (w), 756 (s), 697 (s), 664 (m).

#### 2.7 Nitrobenzene detection studies

Suspensions of 5 mg finely ground samples of coordination polymers **1–5** were made in 5 mL ethanol in volumetric flasks, with immersion in an ultrasonic bath for 60 seconds to ensure an even dispersion. The fluorescence spectra of **1–5** in suspension were recorded with an excitation wavelength selected to optimize emission at 400 nm. Aliquots of a stock solution of nitrobenzene ( $1 \times 10^{-4} M$ ) in dimethyl sulfoxide were added sequentially to the ethanol suspensions of **1–5** in quartz cuvettes with sonication for 30 seconds after each addition. The emission spectra were then measured after each aliquot of analyte solution.

#### 3. X-ray Crystallography

Diffraction data for 1–5 were collected on a Bruker-AXS SMART-CCD X-ray diffractometer using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda$ = 0.71073 Å) at 173 K. The data for 1–5 were processed via SAINT [20], and corrected for both Lorentz and polarization effects and absorption effects using SADABS [21]. The crystal of **2** was non-merohedrally

twinned; diffraction data from both twin components were used in the refinement. The structures were solved using direct methods with ShelXT [22] and refined using ShelXL [22] within the OLEX2 crystallographic software suite [23]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined isotropically with a riding model. The diffuse electron density ascribed to unbound water molecules in 5 was modeled with a solvent mask subroutine embedded within the OLEX2 software suite [23]. Solutions and refinements for the crystal structure of 5 were attempted in several other monoclinic or rhombohedral space groups. However all were substantially poorer than the solution and refinement in the acentric space group R3c, with modeling as an inversion twin. Crystallographic disorder within the diphenate and dipyridylamide ligands in 4 and 5 were modeled with partial occupancies and separate parts. Weak crystal diffraction, full ligand disorder, and extensive diffuse solvent electron density for 4 and 5 resulted in higher than normal statistical factors, however atomic positions and thermal ellipsoids refined acceptably when restrained; the identification of the dimensionality and topology was unambiguous. Multiple crystals of 4 and 5 were selected and unit cell determinations were carried out. All had the same issues with weak diffraction at high angles. Crystallographic details for 1–5 are given in Table 1.

#### 4. Results and Discussion

4.1 Synthesis and Spectra

Crystalline samples of **1–5** were produced by the hydrothermal reaction of zinc nitrate, diphenic acid, and the requisite dipyridylamide ligand in the presence of aqueous base. The infrared spectra of **1–5** were consistent with their structural components as determined by single-crystal X-ray diffraction. Intense, broad asymmetric and symmetric C–O stretching bands within the carboxylate ligands were observed at 1545 and 1368 cm<sup>-1</sup> for **1**, 1546 and 1370 cm<sup>-1</sup> for **2**, at 1546 and 1370 cm<sup>-1</sup> for **3**, at 1548 and 1376 cm<sup>-1</sup> for **4**, and at 1547 and 1371 cm<sup>-1</sup> for **5**. Moderate intensity bands in the range of ~1600 cm<sup>-1</sup> to ~1300 cm<sup>-1</sup> are attributed to the stretching modes of the pyridyl rings of the dipyridylamide ligands and the aromatic rings within the phenyl and pyridyl moieties exist in the region between ~900 and ~650 cm<sup>-1</sup>. Broad, weak spectral bands in the vicinity of ~3000–3400 cm<sup>-1</sup> indicate the presence of unbound water molecules in the spectrum of **1–2** and **4–5**. The carbonyl stretching bands for the dipyridylamide ligands appeared at 1667 cm<sup>-1</sup> for **1**, 1667 cm<sup>-1</sup> for **2**, 1667 cm<sup>-1</sup> for **3**, 1649 cm<sup>-1</sup> for **4**, and 1666 cm<sup>-1</sup> for **5**.

#### 4.2 Structural description of $\{[Zn(dip)(hdin)] \cdot 2.5H_2O\}_n$ (1)

The asymmetric unit of compound **1** contains a divalent zinc atom, halves of two dip ligands whose ring junction C–C  $\sigma$  bonds rest on different crystallographic two-fold rotation axes (dip-A, dip-B), a complete hdin ligand, two water molecules of crystallization, and a third water molecule situated on another two-fold crystallographic rotation axis. A distorted square pyramidal {ZnN<sub>2</sub>O<sub>3</sub>} coordination environment is evident at zinc, with a trigonality factor  $\tau$  [25] of 0.07. The basal plane is occupied by a chelating carboxylate group from a dip-A ligand, a hdin pyridyl nitrogen donor atom, and a single carboxylate donor atom from a dip-B ligand. The

apical position is taken up by a pyridyl nitrogen donor atom from a second hdin ligand. A rendering of the coordination environment and complete ligand set is shown in thermal ellipsoid format in Fig. 1. Bond lengths and angles within the coordination environment are listed in Table 2.

Zinc atoms are bridged by bis(chelating) dip-A ligands and bis(monodentate) dip-B ligands to construct  $[Zn(dip)]_n$  coordination polymer chains (Fig. 2a) oriented along the *a* crystal direction. The Zn $\cdots$ Zn internuclear distances within the chain motifs measure 6.186(2) Å and 7.803(2) Å, through dip-A and dip-B respectively; the shorter distance is ascribed to the bis(chelating) binding mode of the dip-A ligands. Neighboring  $[Zn(dip)]_n$  chain motifs are connected into  $[Zn(dip)(hdin)]_n$  coordination polymer slabs by hdin ligands that curl above and below the chain motifs (Fig. 2b); the Zn…Zn through ligand distance measures 14.993(9) Å. The central NH-(CH<sub>2</sub>)<sub>6</sub>-NH tethers of the hdin ligands have an *anti-anti-anti-gauche* conformation (four-atom torsion angles = 174.9, 173.1, 179.3, 166.0,  $65.4^{\circ}$ ) that imparts the noticeable curling. Due to the curled hdin ligands that cross over and under the  $[Zn(dip)]_n$  chains within the coordination polymer slabs, the topology is not that of a simple 4-connected (4,4) grid like layer. Instead, the hbin ligands must be considered 2-connected looped linkers according to the nomenclature of Batten et al. [26]. As a result the underlying topology of the  $[Zn(dip)(hdin)]_n$ coordination polymer slabs in 1 can be reckoned as a rare looped 2,4-connected self-penetrated net with (6)(6<sup>4</sup>8.10) topology (Fig. 3a) as computed with TOPOS [27]. A close-up of the selfpenetrating Hopf linkages in the layers of **1** is shown in Fig. 3b.

Adjacent self-penetrated  $[Zn(dip)(hdin)]_n$  coordination polymer slabs stack in an *AAA* pattern along the *b* crystal axis (Fig. S1). Discrete D(5) classification [28] water molecule chains (Fig. S2) serve to anchor the neighboring layers together into the full crystal structure of **1**, via

hydrogen bonding mechanisms (Table S1) involving bound dip carboxylate oxygen atoms and hdin amine groups. According to a calculation performed with PLATON [29], the discrete water molecule chains in **1** occupy small inter-slab pockets comprising 10.4 % of the unit cell volume.

#### 4.3 Structural description of $\{[Zn(dip)(pedin)] \cdot 2.5H_2O\}_n$ (2)

The asymmetric unit of compound **2** contains a divalent zinc atom, halves of two dip ligands whose ring junction C–C  $\sigma$  bonds rest on different crystallographic two-fold rotation axes (dip-A, dip-B), a complete pedin ligand, two water molecules of crystallization, and a third water molecule situated on another two-fold crystallographic rotation axis. A distorted square pyramidal {ZnN<sub>2</sub>O<sub>3</sub>} coordination environment is evident at zinc, with a trigonality factor  $\tau$  of 0.16 revealing a greater distortion within the coordination sphere than seen in **1**. The basal plane is occupied by a chelating carboxylate group from a dip-A ligand, a pedin pyridyl nitrogen donor atom, and a single carboxylate donor atom from a dip-B ligand. The apical position is taken up by a pyridyl nitrogen donor atom from a second pedin ligand. The coordination environment and complete ligand set is shown in Fig. 4. Bond lengths and angles within the coordination environment are listed in Table 3.

As in **1**, the zinc atoms in **2** are bridged by bis(chelating) dip-A ligands and bis(monodentate) dip-B ligands to construct  $[Zn(dip)]_n$  coordination polymer chains (Fig. S3) oriented along the *a* crystal direction. The Zn···Zn internuclear distances within the  $[Zn(dip)]_n$ chain motifs measure 6.091(2) Å and 7.866(2) Å. Parallel  $[Zn(dip)]_n$  chains are connected into  $[Zn(dip)(pedin)]_n$  coordination polymer slabs (Fig. S4) in **2** by curled conformation pebin ligands, that span a Zn···Zn distance of 14.374(5) Å. The central NH–(CH<sub>2</sub>)<sub>5</sub>–NH tethers of the

pedin ligands have an *anti–anti–anti–gauche* conformation (four-atom torsion angles = 175.0, 173.3, 179.4, 65.4°) that imparts a noticeable curling similar to that seen in the hdin derivative **1**. The underlying network of **2** thus features the same  $(6)(6^48.10)$  topology 2,4-connected looped self-penetrated network seen in **1**. Additionally, similar D(5) classification water molecule chains are seen in **2** along with a similar *AAA* stacking pattern (Fig. S5) and interlamellar hydrogen bonding mechanisms (Table S1). The discrete water molecule chains in **2** occupy 9.4 % of the unit cell volume.

#### 4.4 Structural description of [Zn(dipH)<sub>2</sub>(bdin)]<sub>n</sub> (**3**)

The asymmetric unit of compound **3** contains a divalent zinc atom on a crystallographic two-fold rotation axis, a singly protonated dipH ligand, and half of a bdin ligand whose central C–C  $\sigma$  bond is situated over a crystallographic inversion center. Operation of the two-fold rotation axis generates a distorted {ZnN<sub>2</sub>O<sub>2</sub>} coordination tetrahedron (Fig. 5), where the oxygen donor atoms belong to deprotonated carboxylate groups of the dipH ligand and the nitrogen donor atoms belong to the pyridyl rings of the bdin ligands. Bond lengths and angles within the coordination environment are listed in Table 4.

The zinc atoms in **3** are bound by two dipH ligands to form  $[Zn(dipH)_2]$  coordination fragments that in turn are connected by *anti-anti-anti* conformation bdin ligands (four-atom torsion angles = 166.3, 180, 166.3°) into  $[Zn(dipH)_2(bdin)]_n$  zig-zag chains oriented along the *c* crystal direction (Fig. 6). The Zn···Zn through-ligand distance is 20.040(2) Å, substantially longer than the related distances seen in the hdin derivative **1** and pebin derivative **2**, ascribed to the lack of any *gauche* conformation induced curls in the dipyridylamide ligands of **3**. Neighboring chains interact along the *c* crystal direction (Fig. S6) via hydrogen bonding

donation from the bbin amine groups to the unligated oxygen atoms of the bound carboxylate groups of the dipH ligands.

#### .4 Structural description of $\{[Zn_3(dip)_3(bdin)_3] \cdot 13H_2O\}_n$ (4)

The asymmetric unit of compound **4** contains three divalent zinc atoms (one of which is disordered over two sets of positions), three dip ligands, and three bdin ligands with various amounts of crystallographic disorder. Diffuse electron density comprising an estimated thirteen water molecules of crystallization per asymmetric unit was modeled with a solvent mask technique. All the zinc atoms display a  $\{ZnN_2O_2\}$  distorted tetrahedral geometry, with single carboxylate oxygen donor atoms from two dip ligands and pyridyl nitrogen donor atoms from two bdin ligands taking up the four coordination sites (Fig. 7). Bond lengths and angles within the tetrahedral coordination environments are listed in Table 5.

Bis(monodentate) dip ligands connect the zinc atoms into  $\{[Zn_3(dip)_3]_n$  helical chains that are oriented along the *a* crystal direction (Fig. 8), connecting zinc atoms with Zn…Zn distances of 6.447(3), 6.331(2), and 6.375(3) Å. In turn these are connected into a 3D  $\{[Zn_3(dip)_3(bdin)_3]_n$ coordination polymer network (Fig. 9) by pillaring bdin ligands that span different Zn…Zn distances depending on their central butanediamine tether conformation. The Zn3…Zn1 connections, which measure 19.830(6) Å, are bridged by bdin ligands with an *anti-gauche-anti* conformation of their butanediamine central tethers (torsion angles = 147.0, 66.4, 173.8°). The Zn2…Zn1 connections, which span a slightly longer distance of 19.897(6) Å, are bridged by bdin ligands with a more splayed-open *anti-anti-anti* conformation of their butanediamine central tethers (torsion angles = 171.8, 163.6, 175.9°). The Zn2…Zn3 connections, which span a shorter distance of 18.592(7) Å, are bridged by bdin ligands with a curled *gauche-anti-gauche* conformation of their butanediamine central tethers (torsion angles = 86.8, 175.8, 53.0°). A

second 3D { $[Zn_3(dip)_3(bdin)_3]_n$  network fits within the voids left by the single network, resulting in a 2-fold interpenetrated 3D coordination polymer framework (Fig. 11) Analysis of the 4connected net of **4** with TOPOS software [27] indicates the presence of a rare 2-fold interpenetrated 6<sup>4</sup>8<sup>2</sup> **nbo** network topology (Fig. 11) [30–31]. The solvent-bearing incipient channels coursing down the *a* axis of the crystal of **4** occupy 20.1 % of the unit cell volume.

#### 4.6 Structural description of $\{[Zn(dip)(edin)] \cdot 3H_2O\}_n$ (5)

The asymmetric unit of compound 5 contains a fully occupied zinc atom at a general position, a dip ligand with disorder among eight of its carbon atom positions, an edin ligand with extensive disorder among its carbon atom positions along with both of its amide groups, and diffuse electron density accounting for three water molecules of crystallization. As in **4**, the zinc atom in **5** possesses a distorted  $\{ZnN_2O_2\}$  tetrahedral coordination geometry. A representation of the coordination environment with single dip and edin ligand disorder components is shown in Fig. 12. Pertinent bond lengths and angles are listed in Table 6.

Bis(monodentate) dip ligands connect zinc atoms into 3-fold  $[Zn(dip)]_n$  helices, with a Zn…Zn distance of 6.6413(6) Å, oriented along the *c* crystal direction. The pitch of the  $[Zn(dip)]_n$  helices is 19.378(3) Å, which corresponds to the *c* lattice parameter. In turn these are connected into a 3D { $[Zn(dip)(edin)] \cdot 3H_2O]_n$  2-fold interpenetrated coordination polymer net (Fig. 13). Analysis of the network with TOPOS, treating each zinc atom as a 4-connected node, reveals the same 2-fold interpenetrated  $6^48^2$  **nbo** network topology as seen in **4** (Fig. 11). The disordered water molecules of crystallization occupy incipient channels that comprise 7.4 % of the unit cell volume.

#### 4.7 Thermal Properties

Compound **1** underwent dehydration in two steps between ~70 and ~150 °C with a total mass loss of 7.0 % matching well with the calculated value of 6.7 % for elimination of 2.5 molar equivalents of water. Ligand ejection occurred above 280 °C. Compound **2** underwent dehydration between ~70 and ~105 °C with a mass loss of 6.0 % corresponding roughly to a calculated mass loss of 6.8 % for elimination of 2.5 molar equivalents of water. Ligand ejection occurred above 280 °C. Compound **3** showed a stable mass until ~275 °C whereupon ligand combustion occurred. Compound **4** underwent dehydration on long-term storage (~90 d). The dehydrated compound underwent decomposition above 280 °C. Compound **5** underwent dehydration between 25 °C and ~100 °C with an 8.2 % mass loss matching well with the predicted value of 8.6 % for elimination of three molar equivalents of water. The mass was stable until ~270 °C whereupon ligand combustion occurred. TGA traces for **1–5** are shown in Figs. S7–S11, respectively.

#### 4.8 Luminescence and Nitrobenzene detection studies

Powdered samples of compounds **1–5** were subjected to ultraviolet radiation to investigate the presence of any luminescent behavior. Excitation spectra were recorded by monitoring emission of a 5 mg sample of coordination polymer suspended in 5 mL 95% ethanol at 400 nm; the maximum excitation wavelengths (Table 7) were then used to irradiate the respective samples. Emissive behavior was observed in all cases, with maximum emission wavelengths as shown in Table 7. Emission profiles for **1–5** suspended in 95 % ethanol are depicted in Fig. S12. The emissive behavior is plausibly ascribed to  $n-\pi$  or  $\pi^*-\pi$  molecular orbital electronic transitions within the aromatic rings of the diphenate and dipyridylamide ligands. MLCT or LMCT

transitions are very unlikely due to the closed shell  $d^{10}$  configuration of the divalent zinc atoms [32].

Compounds 1–5 were assayed as potential nitrobenzene detecting sensors in ethanol. In all cases, emission quenching was observed as  $\mu$ L-sized aliquots of a 1 × 10<sup>-4</sup> *M* solution of nitrobenzene in DMSO were sequentially added to the coordination polymer ethanol suspensions. The quenching data for 1–5, for nitrobenzene absorption, were analyzed using the Stern-Volmer equation [33],  $I_0/I = K_{sv}[A] + 1$ , where  $I_0$  is the initial emission intensity in the absence of analyte, *I* is the emission intensity in the presence of analyte, [A] is the molarity of analyte, and  $K_{sv}$  is the Stern-Volmer quenching constant. A listing of Stern-Volmer constants ( $K_{SV}$ ) for 1–5 is given in Table 8. Electron transfer from the aromatic molecular orbital excited states in the coordination polymer to the  $\pi^*$  molecular orbitals of the electron-withdrawing nitrobenzene analyte is the likely mechanism for the emission quenching in all derivatives 1–5 [6]. Stern-Volmer plots for 1–5 (Figs. S13–S17) revealed that the 3D derivatives 4 and 5 manifested the best "turn-off" sensor behavior for nitrobenzene detection out of the compounds in this study, potentially due to their more accessible incipient channels allowing greater approach of the analyte to the coordination polymer framework.

#### 5. Conclusions

Zinc diphenate coordination polymers containing long-spanning dipyridylamide ligands adopt diverse dimensionalities and topologies depending on dipyridylamide tether length and level of diphenate deprotonation. With the longer six-carbon and five-carbon tethers in the hdin and pedin ligands, respectively, rare looped self-penetrated layer topologies were observed in the resulting coordination polymers. Using the shorter two-carbon and four-carbon tethering in the

edin and bdin ligands afforded rare two-fold interpenetrated nbo lattices built from pillaring of zinc diphenate helical subunits. Employing a smaller amount of aqueous base during a synthetic trial resulted in a 1D zig-zag chain variant in the zinc diphenate bdin system. All five coordination polymers investigated in this study underwent blue-violet visible light transmission when irradiated with ultraviolet light. The 1D channel-bearing, two-fold interpenetrated **nbo** topologies in the zinc diphenate edin and bdin materials showed optimum absorption of nitrobenzene as revealed by turn-off luminescence quenching behavior.

#### **Supplementary Material**

Additional molecular graphics and thermogravimetric analysis plots. Crystallographic data (excluding structure factors) for **1–5** have been deposited with the Cambridge Crystallographic Data Centre with Nos. 1825730–1825734, respectively. Copies of the data can be obtained free of charge via the Internet at <a href="https://summary.ccdc.cam.ac.uk/structure-summary-forms">https://summary.ccdc.cam.ac.uk/structure-summary-forms</a>.

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Data	1	2	3
Empirical Formula	$\Gamma$	$\Gamma$	$C_{44}H_{24}N_4O_{10}Zn$
Empirical Formula Weight	677.01	662.98	846 14
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group			
Space group	12.72((2))	P2/N	C2/C
a (A)	13.736(2)	13.5976(14)	20.322(3)
<i>b</i> (A)	11.995(2)	11.9522(12)	7.8700(12)
<i>c</i> (A)	20.387(3)	19.382(2)	24.296(4)
α (°)	90	90	90
β (°)	109.334(2)	107.428(1)	95.731(2)
γ (°)	90	90	90
$V(\text{\AA}^3)$	3169.6(9)	3005.4(5)	3866.2(10)
Z	4	4	4
$D (\text{g cm}^{-3})$	1.419	1.465	1.454
$\mu (mm^{-1})$	0.833	0.877	0.703
Min./max. transmission	0.835	0.800	0.910
hkl ranges	$-16 \bullet h \bullet 16,$	$-15 \bullet h \bullet 16,$	$-24 \bullet h \bullet 24,$
	$-14 \bullet k \bullet 14,$	$-14 \bullet k \bullet 14,$	$-9 \bullet k \bullet 9,$
	$-24 \cdot l \cdot 24$	$0 \bullet l \bullet 23$	$-29 \bullet l \bullet 29,$
Total reflections	49186	46064	15029
Unique reflections	5874	17593	3540
R(int)	0.1491	0.0738	0.0333
Parameters	420	409	268
$R_1$ (all data)	0.1233	0.0876	0.0431
$R_1(I > 2(I))$	0.0576	0.0541	0.0351
$wR_2$ (all data)	0.1557	0.1378	0.0911
$wR_2(I > 2 (I))$	0.1240	0.1203	0.0853
Max/min residual $(e^{-7} \text{ Å}^3)$	0.694/-0.539	0.887/-0.370	0.355/0.288
G.O.F.	1.018	1.055	1.040

### Table 1. Crystal and Structure Refinement Data for 1–5.

Data	4	5
Empirical Formula	$C_{90}H_{78}N_{12}O_{18}Zn_3$	$C_{28}H_{28}N_4O_9Zn$
Formula Weight	2045.88	629.94
Crystal system	Monoclinic	Trigonal
Space group	$P2_1/n$	R3c
<i>a</i> (Å)	18.9567(19)	27.819(4)
<i>b</i> (Å)	31.463(3)	27.819(4)
<i>c</i> (Å)	20.809(2)	19.378(3)
α (°)	90	90
β (°)	126.3420(10)	90
γ (°)	90	120
$V(\text{\AA}^3)$	9997.3(17)	12988(4)
Ζ	4	18
$D (\mathrm{g \ cm}^{-3})$	1.359	1.450
$\mu (mm^{-1})$	0.780	0.897
Min./max. transmission	0.6432	0.9086
hkl ranges	$-22 \bullet h \bullet 22,$	$-33 \bullet h \bullet 32,$
	$-37 \cdot k \cdot 37,$	$-33 \bullet k \bullet 33,$
Total unfloations	-23 • l • 23	-23 • 1 • 23
	148703	5202
	18387	5292
R(int)	0.2955	0.0721
Parameters	1084	221
$R_1$ (all data)	0.2217	0.1468
$R_{1}(I > 2(I))$	0.0929	0.1199
$wR_2$ (all data)	0.3022	0.3594
$wR_2(I > 2 (I))$	0.2259	0.3262
$\frac{\text{Max/min residual}}{(e^{-7} \text{ Å}^3)}$	1.698/-0.908	1.978/-0.835
G.O.F.	0.959	1.310

#### Table 1. Crystal and Structure Refinement Data for 1–5.

Zn1–O1	1.976(3)	$O1-Zn1-N4^{#1}$	94.36(13)
Zn1–O3	2.213(3)	O4–Zn1–O3	60.27(12)
Zn1–O4	2.100(3)	O4–Zn1–N4 <sup>#1</sup>	91.82(14)
Zn1–N1	2.050(4)	N1–Zn1–O3	113.88(14)
Zn1–N4 <sup>#1</sup>	2.112(4)	N1–Zn1–O4	98.64(15)
O1–Zn1–O3	94.01(12)	N1–Zn1–N4 <sup>#1</sup>	97.47(14)
01–Zn1–O4	143.97(14)	$N4^{#1}$ –Zn1–O3	139.80(14)
O1–Zn1–N1	115.61(14)		

Table 2. Selected Bond Distance (Å) and Angle (°) Data for 1.

Symmetry transformation: #1 x - 1/2, -y + 1, z + 1/2.

Table 3. Selected Bond Distance (Å) and Angle (°) Data for 2. 5

Zn1–O1	2.110(3)	O3–Zn1–N1	116.69(14)
Zn1–O2	2.167(3)	O3–Zn1–N4 <sup>#1</sup>	93.84(13)
Zn1–O3	1.983(3)	N1–Zn1–O1	97.11(14)
Zn1–N1	2.057(4)	N1–Zn1–O2	116.79(14)
$Zn1-N4^{#1}$	2.088(4)	N1–Zn1–N4 <sup>#1</sup>	101.15(14)
O1–Zn1–O2	60.58(12)	$N4^{#1}$ –Zn1–O1	91.59(14)
O3–Zn1–O1	143.88(13)	$N4^{#1}$ –Zn1–O2	134.21(14)
O3–Zn1–O2	91.22(12)		

Symmetry transformation: #1 x - 3/2, -y + 1, z - 1/2.

Table 4. Selected Bond Distance (Å) and Angle (°) Data for **3**.

$Zn1-O5^{#1}$	2.0285(17)	$O5^{\#1}$ –Zn1–N2 <sup>#1</sup>	94.02(7)
Zn1–O5	2.0285(17)	O5–Zn1–N2	94.01(7)
$Zn1-N2^{#1}$	2.1043(17)	$O5^{\#1}$ –Zn1–N2	128.39(7)
Zn1–N2	2.1043(17)	$O5-Zn1-N2^{\#1}$	128.39(7)
$O5^{\#1}$ –Zn1–O5	121.88(10)	$N2^{\#1}$ –Zn1–N2	89.32(9)

Symmetry transformation: #1 - x + 3/2, y + 1/2, -z + 3/2

SCRIF

Zn1–O1	1.933(5)	$O12^{\#1}$ –Zn1–N5	118.9(3)
Zn1–O12 <sup>#1</sup>	1.981(6)	$O12^{\#1}$ -Zn1-N12 <sup>#2</sup>	97.7(3)
Zn1–N5	2.041(7)	N5–Zn1–N12 <sup>#2</sup>	89.7(3)
Zn1-N12 <sup>#2</sup>	2.060(8)	O4–Zn2–O5	124.7(2)
Zn2–O4	1.925(6)	O4–Zn2–N1	114.6(3)
Zn205	1.961(5)	O4–Zn2–N9	101.3(3)
Zn2–N1	2.062(7)	O5–Zn2–N1	97.5(3)
Zn2–N9	2.041(7)	O5–Zn2–N9	117.5(3)
Zn3–O8	1.938(7)	N9-Zn2-N1	98.7(3)
Zn309	2.034(9)	08–Zn3–O9	132.7(4)
Zn3–N4 <sup>#3</sup>	1.942(9)	08–Zn3–N4 <sup>#3</sup>	104.7(3)
Zn3–N8 <sup>#4</sup>	2.102(8)	08–Zn3–N8 <sup>#4</sup>	105.9(3)
$O1-Zn1-O12^{\#1}$	126.2(3)	O9–Zn3–N8 <sup>#4</sup>	91.1(4)
01–Zn1–N5	105.1(3)	$N4^{\#3}$ -Zn3-O9	114.2(4)
O1–Zn1–N12 <sup>#2</sup>	112.6(3)	$N4^{#3}$ -Zn3-N8 <sup>#4</sup>	102.8(3)

Table 5. Selected Bond Distance (Å) and Angle (°) Data for 4.

Symmetry transformations: #1 x - 1, y, z; #2 -x + 3/2, y + 1/2, -z + 3/2; #3 x, y, z - 1; #4 -x + 1/2, y - 1/2, -z + 1/2.

Table 6. Selected Bond Distance (Å) and Angle (°) Data for 5.

Zn1–O1	1.945(12)	O1–Zn1–N1	112.6(7)
$Zn1-O4^{#1}$	1.973(12)	O1-Zn1-N4 <sup>#2</sup>	100.0(7)
Zn1–N1	2.006(16)	$O4^{\#1}$ –Zn1–N1	99.8(6)
$Zn1-N4^{#2}$	2.059(17)	$O4^{\#1}$ –Zn1–N4 <sup>#2</sup>	112.0(7)
$O1-Zn1-O4^{\#1}$	128.0(4)	N1–Zn1–N4 <sup>#2</sup>	102.0(5)

Symmetry transformations: #1 - y + 4/3, -x + 2/3, z + 1/6; #2 - x + y + 1/3, y + 5/3, z + 1/6.

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Compound	Excitation $\lambda_{(max)}$	Emission $\lambda_{(max)}$
	(nm)	(nm)
1	350	432
2	320	431
3	350	417
4	295	435
5	290	354

Table 7. Excitation and Emission Spectral Data for 1–5.

5	290	354	
Table 8. Ste	rn-Vollmer consta	nts for <b>1–5</b> for ab	sorption of nitrobenzene.
Compound	Stern-Vollmer co	onstants (1/M)	
1	1.0 ×	10 <sup>6</sup>	6
2	$2.0 \times 1$	$10^{6}$	
3	5.4 × 1	10 <sup>5</sup>	
4	8.0×1	$10^{6}$	
5	$1.0 \times 1$	$10^{7}$	

Scheme 1. The ligands used in this study.





Figure 1. Coordination environment and complete ligand sets in **1**. Thermal ellipsoids are depicted at 50% probability. Symmetry codes are as in Table 2.

Figure 2. a)  $[Zn(dip)]_n$  coordination polymer chain in **1**. b) Face view of the  $[Zn(dip)(hdin)]_n$  coordination polymer slab in **1** with  $[Zn(dip)]_n$  coordination polymer chain drawn in red in the online version of this article. c) Side view of the  $[Zn(dip)(hdin)]_n$  coordination polymer slab in **1**.





Figure 3. a) Looped 2,4-connected self-penetrated net with  $(6)(6^48.10)$  topology in **1**. The dip ligands are shown as red rods in the online version of this article. b) A close-up of a self-penetrating Hopf linkage of six-membered circuits in the slab motif in **1**.





Figure 4. Coordination environment and complete ligand sets in **2**. Thermal ellipsoids are depicted at 50% probability. Symmetry codes are as in Table 3.



Figure 5. Coordination environment and complete ligand sets in **3**. Thermal ellipsoids are depicted at 50% probability. Symmetry codes are as in Table 4.

Figure 6.  $[Zn(dipH)_2(bdin)]_n$  zig-zag chain in **3**.



Figure 7. Coordination environments and complete ligand sets in **4**. Only one disordered component of each ligand is shown. Thermal ellipsoids are depicted at 50% probability. Symmetry codes are as in Table 5.





Figure 8.  $[Zn_3(dip)_3]_n$  helical chain in **4**.

Figure 9. Single  $[Zn_3(dip)_3(bdin)_3]_n$  3D net in 4. The  $[Zn_3(dip)_3]_n$  helical chains are shown in red.



Figure 10. Interpenetration of  $[Zn_3(dip)_3(bdin)_3]_n$  3D nets in **4** showing incipient channels coincident with the *a* crystal axis.





Figure 11. Schematic representation of the 2-fold interpenetrated  $6^4 8^2$  **nbo** topology in **4** and **5**.

Figure 12. Coordination environment and complete ligand sets in **5**. Thermal ellipsoids are depicted at 50% probability. Only one of each disordered ligand component is shown. Symmetry codes are as in Table 6.



Figure 12. Two-fold interpenetrated system of 3D  $[Zn(dip)(edin)]_n$  coordination polymer nets in **5**, showing incipient 1D tubules parallel to the *c* crystal direction.





 $\{[Zn(diphenate)(edin)]\cdot 3H_2O\}_n$  (edin = N,N'-(ethane-1,6-diyl)diisonicotinamide, pictured) manifests helical substructures linked into a rare two-fold interpenetrated  $6^48^2$  **nbo** topology. This material showed ability to detect nitrobenzene in ethanol suspension by "turn-off" luminescence quenching behavior.