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Divergent topologies in luminescent zinc and cadmium substituted isophthalate coordination polymers constructed from long-spanning dipyridylamide ligand precursors

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#### Abstract

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Hydrothermal reaction of zinc or cadmium nitrate, a 5-position substituted isophthalic acid, and the long-spanning dipyridylamide ligand N,N'-(hexane-1,6-diyl)dinicotinamide (hdn) resulted in coordination polymers whose dimensionalities depend on the nature of the ring substituent and the metal coordination environment. The six new phases were characterized by single crystal Xray diffraction. { $[Zn_2(hip)_2(H_2O)_2(hdn)] \cdot 2H_2O$ }<sub>n</sub> (1, hip = 5-hydroxyisophthalate) shows a 1D ladder topology with  $[Zn(hip)(H_2O)]_n$  uprights spanned by disordered hdn rungs.  $\{[Zn_2(nip)_2(hdn)_2] \cdot 2H_2O\}_n$  (2, nip = 5-nitroisophthalate) displays a 1D ribbon motif with  $[Zn(nip)]_n$  chains pillared by looped pairs of hdn ligands.  $[Zn_3(tbip)_2(nic)_2]_n$  (3, tbip = 5-tertbutylisophthalate, nic = nicotinate) shows trimeric  $[Zn_3(OCO)_2]$  clusters connected into a 3D 8connected  $4^{24}6^4$  bcu net by thip and *in situ* generated nic ligands.  $\{ [Cd_2(ip)_2(H_2O)_4(hdn)] \cdot 2H_2O \}_n$  (4, ip = isophthalate) and  $\{ [Cd_2(tbip)_2(H_2O)_4(hdn)] \cdot H_2O \}_n$  (5) both show a ladder topology similar to that in 1.  ${[Cd(mip)(hdn)] \cdot H_2O]_n}$  (6, mip = 5methylisophthalate) manifests a 2D (4,4) grid topology based on linked dimeric  $[Cd_2(OCO)_2]$ units. Luminescent properties were probed; compounds 4 and 6 showed good ability to detect nitrobenzene in ethanol suspension.

#### **1. Introduction**

Academic and industrial research into the synthesis and property characterization of divalent metal coordination polymers has continued largely unabated over the past ten years. This genre of materials can exhibit remarkable multifunctional properties in diverse applications such as gas storage [1], selective separations [2], pharmaceutical delivery [3], and industrially relevant heterogeneous catalysis [4]. The undeniable aesthetic appeal of their molecular-level structures and topologies also spurs continued study [5], with exploratory synthesis playing an inordinately large role in the uncovering of new entangled or interpenetrated topologies because of the difficulty of strictly a priori structure design [6]. Many coordination polymer solids are self-assembled under hydrothermal or solvothermal conditions from divalent metal salts and simple aromatic dicarboxylate ligands such as isophthalate (ip, Scheme 1) [7] or terephthalate (tp) [8]. Inclusion of dipyridyl-type coligands such as the rigid-rod linker 4,4'-bipyridine (bpy) can influence the structural topology and resulting functional properties. For instance, the apohost of  $\{[Zn_2(tp)_2(bpy)] \cdot H_2O \cdot DMF\}_n$  can separate mixtures of light weight gaseous alkanes [9]. Some cadmium and zinc aromatic dicarboxylate coordination polymers have recently shown utility as detectors for nitroaromatic contaminants, via luminescence quenching mechanisms [10-12].

It has been possible to alter the dimensionalities and topologies of isophthalate-based coordination polymers by employing dicarboxylate ligands with sterically bulkier substituents on their aromatic rings. Yang and co-workers identified a trend of lower coordination polymer dimensionality when 5-position substituted isophthalate derivatives such as 5-*tert*-butylisophalate (tbip, Scheme 1) or 5-hydroxyisophthalate (hip, Scheme 1) were employed

during self-assembly in the presence of pyridine capping ligands [13]. In a series of zinc isophthalate coordination polymers with the longer-spanning coligand bis(4-

pyridylmethyl)piperazine (bpmp), substituent-dependent structural trends were less clear.  $[Zn(ip)(bpmp)]_n$  and  $\{[Zn(hip)(bpmp)]\cdot H_2O\}_n$  both showed a system of five-fold interpenetrated  $6^6$  diamondoid nets [14–15]. Even the very bulky *tert*-butyl group in tbip afforded a 3D topology in  $[Zn_2(tbip)_2(bpmp)]_n$ , although with a shift to a dimer-based two-fold interpenetrated  $4^{12}6^3$  **pcu** topology.  $\{[Zn(meoip)(bpmp)]\cdot 8H_2O\}_n$  adopted an undulating (4,4) single-grid 2-D topology, in concert with the dimensionality reducing trend identified by Yang. The methyl group in 5methylisophthalate (mip, Scheme 1) can also induce significant structural changes.  $\{[Cd_2(ip)_2(H_2O)_2(bpfp)]\cdot 7H_2O\}_n$  and  $\{[Cd(mip)(H_2O)(bpfp)]\cdot 3H_2O\}_n$  both display a (4,4) grid topology, but the former exhibits simple stacked layers while the latter exhibits  $2D + 2D \rightarrow 3D$ 

mutual inclined interpenetration [16].

The long-spanning and conformationally flexible dipyridylamide coligand *N*,*N*<sup>'</sup>-(hexane-1,6-diyl)dinicotinamide (hdn, Scheme 2) has infrequently been employed in coordination polymer chemistry to date, although Wang and co-workers have reported some examples in recent years [17–19]. Wang's group prepared the divalent coordination polymer  $\{[Cu(ip)(hdn)]\cdot H_2O\}_n$ , which manifested a 3,5 connected 3,5L2 layered topology, and underwent reversible electrochemical reduction to Cu<sup>1</sup> when admixed with carbon paste [17]. There are no current reports of 5-position substituted isophthalate zinc- or cadmium-based coordination polymers containing hdn, although a few years ago Wang's group reported some copper [18] and cobalt [19] derivatives containing these ligands. We therefore endeavored to synthesize a series of divalent zinc and cadmium coordination polymers containing 5-substituted isophthalate ligands and hdn.

In this contribution we present the single-crystal structures, divergent topological features, luminescence properties, nitrobenzene detecting capabilities, and thermal degradation of six new zinc and cadmium coordination polymers with hdn and substituted isophthalate ligands:  $\{[Zn_2(hip)_2(H_2O)_2(hdn)] \cdot 2H_2O\}_n$  (1),  $\{[Zn_2(nip)_2(hdn)_2] \cdot 2H_2O\}_n$  (2),  $[Zn_3(tbip)_2(nic)_2]_n$ (3, nic = nicotinate),  $\{[Cd_2(ip)_2(H_2O)_4(hdn)] \cdot 2H_2O\}_n$  (4),  $\{[Cd_2(tbip)_2(H_2O)_4(hdn)] \cdot H_2O\}_n$  (5), NSC and  $\{[Cd(mip)(hdn)] \cdot H_2O\}_n$  (6).

#### 2. Experimental Section

#### 2.1 General Considerations

Metal nitrates and the dicarboxylic acids were commercially obtained from Sigma Aldrich. N,N'-(hexane-1,6-diyl)dinicotinamide (hdn) was prepared by condensation of 1,6hexanediamine and two molar equivalents of nicotinoyl chloride hydrochloride in dry pyridine. The reaction mixture was guenched with water, and then the product was isolated via CH<sub>2</sub>Cl<sub>2</sub> extraction and removal of solvent *in vacuo* [20]. Water was deionized above  $3M\Omega$ -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 ultraviolettransparent epoxy adhesive.

#### 2.2 Preparation of $\{[Zn_2(hip)_2(H_2O)_2(hdn)] \cdot 2H_2O\}_n$ (1)

Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (83 mg, 0.28 mmol), 5-hydroxyisophthalic acid (51 mg, 0.28 mmol), and hdn (91 mg, 0.28 mmol), and 0.55 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 4 d, and then was cooled slowly to 25 °C. Straw-colored crystals of **1** (82 mg, 66 % yield based on Zn) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal*. Calc. for C<sub>34</sub>H<sub>38</sub>N<sub>4</sub>O<sub>16</sub>Zn<sub>2</sub> **1**: C, 45.91; H, 4.31; N, 6.30 % Found: C, 45.56; H, 4.51; N, 6.04 %. IR (cm<sup>-1</sup>): 3712 (w), 3315 (w), 2936 (w), 2860 (w), 2073 (w), 1633 (m), 1608 (w), 1544 (s), 1485 (w), 1459 (w), 1435 (w), 1366 (s), 1319 (w), 1294 (w), 1270 (m), 1210 (m), 1167 (w), 1117 (w), 1102 (w), 1062 (w), 1035 (w), 1025 (w), 978 (w), 935 (w), 890 (w), 825 (w), 814 (w), 776 (m), 739 (m), 655 (m).

#### 2.3 Preparation of $\{[Zn_2(nip)_2(hdn)_2] \cdot 2H_2O\}_n$ (2)

 $Zn(NO_3)_2 \cdot 6H_2O$  (83 mg, 0.28 mmol), 5-nitroisophthalic acid (59 mg, 0.28 mmol), and hdn (91 mg, 0.28 mmol), and 0.55 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 5 d, and then was cooled slowly to 25 °C. Colorless crystals of **2** (109 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>52</sub>H<sub>54</sub>N<sub>10</sub>O<sub>16</sub>Zn<sub>2</sub> **2**: C, 51.80; H, 4.51; N, 11.62 % Found: C,

51.41; H, 4.26; N, 11.10 %. IR (cm<sup>-1</sup>): 3377 (w, br), 2923 (w), 1634 (m), 1627 (m), 1577 (w), 1542 (m), 1474 (w), 1384 (m), 1344 (s), 1294 (m), 1090 (w), 1083 (w), 934 (w), 836 (m), 765 (m), 734 (s), 702 (s), 652 (m), 615 (m).

#### 2.4 Preparation of $[Zn_3(tbip)_2(nic)_2]_n$ (3)

Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (83 mg, 0.28 mmol), 5-*tert*-butylisophthalic acid (62 mg, 0.28 mmol), and hdn (91 mg, 0.28 mmol), and 0.55 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 4 d, and then was cooled slowly to 25 °C. Colorless crystals of **3** (15 mg, 18 % yield based on Zn) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal*. Calc. for  $C_{36}H_{32}N_2O_{12}Zn_3$  **3**: C, 49.09; H, 3.66; N, 3.18 % Found: C, 48.79; H, 3.78; N, 3.28 %. IR (cm<sup>-1</sup>): 2967 (w), 2563 (w), 1994 (w), 1683 (w), 1603 (w), 1550 (s), 1445 (w), 1409 (w), 1366 (s), 1318 (w), 1277 (w), 1112 (w), 1071 (w), 1013 (w), 947 (w), 912 (w), 855 (w), 781 (w), 759 (w), 727 (w), 694 (w), 687 (w), 662 (w).

2.5 Preparation of  $\{ [Cd_2(ip)_2(H_2O)_4(hdn)] \cdot 2H_2O \}_n (4)$ 

Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (86 mg, 0.28 mmol), isophthalic acid (47 mg, 0.28 mmol), and hdn (91 mg, 0.28 mmol), and 0.55 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 4 d, and then was cooled slowly to 25 °C. Colorless crystals of **4** (20 mg, 14 % yield based on Cd) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal.* Calc. for  $C_{34}H_{42}Cd_2N_4O_{16}$  **4**: C, 41.35; H, 4.29; N, 5.67 % Found: C, 41.41; H, 4.01; N, 5.39 %. IR (cm<sup>-1</sup>): 3008 (w), 2923 (s), 2854 (m), 2149 (w), 2047 (w), 1743 (s), 1656 (m), 1602 (w), 1549 (s), 1464 (m), 1378 (s), 1228 (m), 1160 (s), 1097 (m), 912 (w), 853 (w), 832 (w), 722 (m), 682 (m), 662 (m).

#### 2.6 Preparation of $\{ [Cd_2(tbip)_2(H_2O)_4(hdn)] \cdot H_2O \}_n$ (5)

Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (86 mg, 0.28 mmol), 5-*tert*-butylisophthalic acid (62 mg, 0.28 mmol), and hdn (91 mg, 0.28 mmol), and 0.55 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 4 d, and then was cooled slowly to 25 °C. Colorless crystals of **5** (121 mg, 80 % yield based on Cd) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal*. Calc. for C<sub>42</sub>H<sub>56</sub>Cd<sub>2</sub>N<sub>4</sub>O<sub>15</sub> **5**: C, 46.63; H, 5.22; N, 5.18 % Found: C, 46.82; H, 5.10; N, 5.42 %. IR (cm<sup>-1</sup>): 3277 (w), 2926 (w), 1668 (m), 1644 (m), 1601 (m), 1547 (s), 1475 (m), 1416 (m), 1365 (s), 1310 (m), 1244 (w), 1200 (w), 1115 (w), 1033 (w), 833 (w), 776 (m), 729 (s), 699 (s), 667 (w).

#### 2.7 Preparation of $\{ [Cd(mip)(hdn)] \cdot H_2O \}_n$ (6)

Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (86 mg, 0.28 mmol), 5-methylisophthalic acid (50 mg, 0.28 mmol), and hdn (91 mg, 0.28 mmol), and 0.55 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 4 d, and then was cooled slowly to 25 °C. Colorless crystals of **6** (76 mg, 43 % yield based on Cd) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal*. Calc. for  $C_{27}H_{30}CdN_4O_7$  **6** C, 51.07; H, 4.76; N, 8.82 % Found: C, 50.92; H, 4.39; N, 8.68 %. IR (cm<sup>-1</sup>): 3260 (w), 2927 (w), 2863 (w), 1667 (m), 1641 (m), 1601 (m), 1475 (m), 1546 (s), 1416 (m), 1364 (m), 1306 (m), 1244 (m), 1196 (m), 1115 (m), 1048 (m), 1033 (m), 947 (w), 928 (w), 835 (w), 774 (m), 728 (s), 699 (s).

#### 2.8 Nitrobenzene detection studies

Suspensions of 5 mg finely ground samples of coordination polymers **4** and **6** 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 **4** and **6** in suspension were recorded with an excitation wavelength of 270 nm. Aliquots of a stock solution of nitrobenzene  $(1 \times 10^{-4} M)$  in dimethyl sulfoxide were added sequentially to the ethanol suspensions of **4** and **6** in quartz cuvettes with sonication for 30 seconds after each addition. The emission spectra were then measured after each aliquot of analyte solution.

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#### 3. X-ray Crystallography

Diffraction data for 1–6 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 were processed via SAINT [21], and corrected for both Lorentz and polarization effects and absorption effects using SADABS [22]. The structures were solved using direct methods with SHELXTL [23] within the OLEX2 crystallographic software suite [24]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined isotropically with a riding model. Crystallographic disorder within the hdn ligands in some cases and the *tert*-butyl groups in **5** was successfully modeled with partial occupancies and separate parts. Crystallographic details for 1–6 are given in Table 1.

#### 4. Results and Discussion

4.1 Synthesis and Spectra

Crystalline samples of **1–6** were produced by the hydrothermal reaction of zinc or cadmium nitrate, the requisite dicarboxylic acid, and hdn in the presence of aqueous base. The infrared spectra of **1–6** 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 1544 and 1366 cm<sup>-1</sup> for **1**, 1542 and 1384 cm<sup>-1</sup> for **2**, at 1550 and 1366 cm<sup>-1</sup> for **3**, at 1549 and 1378 cm<sup>-1</sup> for **4**, at 1547 and 1365 cm<sup>-1</sup> for **5**, and at 1545 and 1364 cm<sup>-1</sup> for **6**. 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 hdn ligands [25]. Features corresponding to C–H bending and ring puckering within the 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 bound and unbound water molecules in the spectrum of **1–2** and **4–6**. The carbonyl stretching bands for the hdn ligands appeared at 1633 cm<sup>-1</sup> for **1**, 1634 cm<sup>-1</sup> for **2**, 1656 cm<sup>-1</sup> for **4**, 1668 cm<sup>-1</sup> for **5**, and 1667 cm<sup>-1</sup> for **6**.

#### 4.2 Structural description of $\{[Zn_2(hip)_2(H_2O)_2(hdn)] \cdot 2H_2O\}_n$ (1)

The asymmetric unit of compound **1** contains a divalent zinc atom, a fully deprotonated hip ligand, an aqua ligand, a water molecule of crystallization, and an hdn ligand best refined with each atom at half-occupancy indicating full ligand disorder across a crystallographic inversion center. The zinc atom displays a distorted  $\{ZnO_3N\}$  tetrahedral coordination environment (Fig. 1) with the nitrogen atom donor being supplied by the pyridyl ring of the disordered hdn ligand. Two of the oxygen donors belong to different hip ligands, with the aqua

ligand filling the remaining coordination site. Bond lengths and angles within the coordination tetrahedron are listed in Table 2.

 $[Zn(H_2O)]^{2+}$  coordination fragments are linked into neutral  $[Zn(hip)(H_2O)]_n$  coordination polymer chains that are oriented along the *a* crystal direction by bis(monodentate) hip ligands (Fig. 2a); the Zn···Zn through-ligand distance of 10.093(1) Å matches the *a* lattice parameter. Pairs of these chain motifs are pillared into  $[Zn_2(hip)_2(H_2O)_2(hdn)]_n$  1D coordination polymer ladders by disordered hdn ligands that serve as the rungs (Fig. 2b). The Zn...Zn internuclear distance spanned by the hdn ligands measures 16.49(2) Å. Both disordered hdn conformations show an anti-anti-anti disposition of their central aliphatic chains with four-C atom torsion angles of 175.5, 177.9, and 178.7°. Close  $\pi$ - $\pi$  stacking of the aromatic rings of the hip ligands (ring centroid-ring centroid = 3.479(3) Å) serves to aggregate neighboring  $[Zn_2(hip)_2(H_2O)_2(hdn)]_n$  1D ladder motifs into supramolecular layers coincident with the ac crystal planes (Fig. 3). In turn the supramolecular layers are aggregated into the full crystal structure of **1** in an AAA stacking pattern along the b crystal direction (Fig. S1) by hydrogen bonding donation between the bound water molecules and unligated hip carboxylate oxygen atoms (Table S1). Unligated water molecules are held in the interlamellar regions by accepting hydrogen bonding from the hydroxyl substituents of the hip ligands, and donating hydrogen bonding to the amide carbonyl groups of the hdn ligands.

#### 4.3 Structural description of $\{[Zn_2(nip)_2(hdn)_2] \cdot 2H_2O\}_n$ (2)

The asymmetric unit of compound **2** contains a divalent zinc atom, a fully deprotonated nip ligand, an hdn ligand, and a water molecule of crystallization. A distorted  $\{ZnN_2O_2\}$  coordination tetrahedron is observed at zinc (Fig. 4a), with pyridyl nitrogen donor atoms from

two hdn ligands and single carboxylate oxygen atom donors from two nip ligands. Bond lengths and angles within the coordination tetrahedron are listed in Table 3.

Similar to the chain structural motif seen in 1, the zinc atoms are connected into 1D  $[Zn(nip)]_n$  coordination polymer chains by bis(monodentate) nip ligands that span  $Zn \cdots Zn$ internuclear distances of 9.580(3) Å (Fig. 4b). These are linked into [Zn<sub>2</sub>(nip)<sub>2</sub>(hdn)<sub>2</sub>]<sub>n</sub> ribbons by pairs of hdn ligands that connect Zn atoms at a distance of 16.78(3) Å (Fig. 4c). The hdn ligands have a splayed-open anti-anti conformation about their central hexamethylene units with torsion angles of 166.7, 178.1, and 169.9°. The 1D ladder and ribbon topologies of 1 and 2 stand in contrast with the undulating 2D (4,4) grid structure of the previously reported unsubstituted zinc isophthalate phase  $\{[Zn(ip)(hdn)] \cdot 1.5H_2O\}_n$  [16], corroborating a trend of 5position substituents resulting in a decrease in coordination polymer dimensionality. When viewed down the *b* crystal direction, incipient small channels within the ribbon motif can be seen (Fig. 5d); these contain comprise 3.7 % of the unit cell volume, as calculated by PLATON [26], and contain isolated water molecules of crystallization that engage in hydrogen bonding donation to hdn carbonyl groups as well as unligated nip carboxylate oxygen atoms (Table S1). Adjacent ribbon motifs aggregate into supramolecular layers by two different intermolecular interactions. Hydrogen bonding donation between hdn N-H groups and unligated nip nitro group oxygen atoms provides the main impetus for aggregation, while close  $\pi - \pi$  stacking between aromatic rings of neighboring nip ligands (centroid-to-centroid distance = 3.472(8) Å) imparts an ancillary structure directing effect. These supramolecular layers further interact by hydrogen bonding between hdn N–H groups and hdn carbonyl oxygen atoms, stacking in a direct AAA pattern along the *a* crystal direction (Fig. S2).

#### 4.4 Structural description of $[Zn_3(tbip)_2(nic)_2]_n$ (3)

The asymmetric unit of compound **3** contains a divalent zinc atom (Zn1) on a crystallographic inversion center, a divalent zinc atom (Zn2) on a general position, a fully deprotonated tbip ligand, and a nicotinate (nic) ligand that was generated *in situ* from amide hydrolysis of the hdn starting material. A symmetry-enforced { $ZnO_6$ } coordination octahedron is observed at Zn1, with single carboxylate oxygen donor atoms from two nic ligands in the nominal axial positions. Its nominal equatorial positions are taken up by single carboxylate oxygen atom donors from four different tbip ligands. On the other hand, Zn2 displays a { $ZnNO_3$ } distorted tetrahedral coordination environment, with the single nitrogen donor atom part of a nic ligand, a single carboxylate oxygen atom from another nic ligand, and carboxylate oxygen atom donors from two different tbip ligands (Fig. 5a). Pertinent bond lengths and angles for **3** are listed in Table 4.

Bridging carboxylate groups from four different tbip ligands and two different nic ligands construct trinuclear { $Zn_3(OCO)_6$ } linear cluster units (Fig. 5b), that have  $Zn1\cdots Zn2$  distances of 3.532(1) Å. These are linked by the full span of four tbip ligands to construct [ $Zn_3(tbip)_2$ ]<sub>n</sub> coordination polymer layers arranged parallel to the (1 0 1) crystal planes (Fig. 6a), here each trinuclear cluster acts as a 4-connected node in a (4,4) grid topology. The { $Zn_3(OCO)_6$ } clusters are also connected by four nic ligands to construct [ $Zn_3(nic)_2$ ]<sub>n</sub> coordination polymer layers oriented parallel to the (1 0 1) crystal planes (Fig. 6b), orthogonally situated to the [ $Zn_3(tbip)_2$ ]<sub>n</sub> layer motifs. Both sets of layer patterns intersect to afford a 3D [ $Zn_3(tbip)_2(nic)_2$ ]<sub>n</sub> coordination polymer network (Fig. 7); if the { $Zn_3(OCO)_6$ } clusters are considered 8-connected nodes, a 4<sup>24</sup>6<sup>4</sup> **bcu** body-centered cubic topology can be invoked (Fig. 8), as calculated by TOPOS [27]. The

lack of any incipient void space in the 3D network of **3** prevents the occlusion of any cocrystallized species.

#### 4.5 Structural description of $\{ [Cd_2(ip)_2(H_2O)_4(hdn)] \cdot 2H_2O \}_n$ (4)

The asymmetric unit of compound **4** contains a divalent cadmium atom, a fully deprotonated, unsubstituted ip ligand, two aqua ligands, a water molecule of crystallization, and half of an hdn ligand. The cadmium atom exhibits a distorted  $\{CdO_6N\}$  pentagonal bipyramidal coordination environment (Fig. 9a) with bound water molecules in the axial positions. The equatorial plane consists of chelating carboxylate groups from two ip ligands and a pyridyl nitrogen donor atom from an hdn ligand. Bond lengths and angles within the coordination environment are given in Table 5.

 $[Cd(H_2O)_2]^{2+}$  cationic coordination fragments are conjoined into neutral  $[Cd(ip)(H_2O)_2]_n$ coordination polymer chain motifs that are oriented parallel to the *a* crystal direction by bis(chelating) ip ligands with a Cd···Cd through-ligand distance of 10.258(1) Å. Pairs of parallel  $[Cd(ip)(H_2O)_2]_n$  motifs are pillared into  $[Cd_2(ip)_2(H_2O)_4(hdn)]_n$  1D coordination polymer ladders (Fig. 9b) by *anti-anti-anti* conformation hdn ligands (torsion angles = 177.6, 180, 177.6°) that span a Cd···Cd distance of 20.221(8) Å. Neighboring  $[Cd_2(ip)_2(H_2O)_4(hdn)]_n$  ladders stack along the *b* crystal direction (Fig. S3) via hydrogen bonding donation from bound water molecules to ip carboxylate oxygen atoms, and stack along *c* by means of hydrogen bonding donation from bound water molecules to the co-crystallized water molecules, and on to hdn carbonyl groups (Table S1). The co-crystallized water molecules in **4** occupy small incipient pockets comprising 2.0 % of the unit cell volume.

4.6 Structural description of  $\{ [Cd_2(tbip)_2(H_2O)_4(hdn)] \cdot H_2O \}_n$  (5)

The asymmetric unit of compound **5** contains a divalent cadmium atom, a fully deprotonated tbip ligand, two aqua ligands, a water molecule of crystallization best refined at half-occupancy, and an hdn ligand with full ligand disorder across a crystallographic inversion center. The cadmium atom manifests a distorted  $\{CdO_6N\}$  pentagonal bipyramidal coordination environment (Fig. 10a) with bound water molecules in the axial positions. In the equatorial plane of the pentagonal bipyramid lies a single pyridyl nitrogen donor atom from an hdn ligand, and chelating carboxylate groups from two tbip ligands. Bond lengths and angles within the coordination environment are listed in Table 6.

 $[Cd(H_2O)_2]^{2+}$  coordination fragments are connected into neutral  $[Cd(tbip)(H_2O)_2]_n$ coordination polymer chains that are oriented along the *a* crystal direction by bis(chelating) tbip ligands (Fig. 10b) with the Cd···Cd through-ligand distance of 10.146(1) Å delineating the *b* lattice parameter. Pairs of parallel  $[Cd(tbip)(H_2O)_2]_n$  chain patterns are linked into  $[Cd_2(tbip)_2(H_2O)_4(hdn)]_n$  1D coordination polymer ladders by disordered hdn ligands (Fig. 10c) that connect cadmium atoms at a Cd···Cd distance of 20.54(2) Å. As in **1**, both disordered hdn ligand conformations show an *anti-anti-anti* disposition of their central aliphatic chains with four-C atom torsion angles of 173.1, 178.1, and 172.8°. Individual  $[Cd_2(tbip)_2(H_2O)_4(hdn)]_n$ ladders aggregate into the supramolecular structure of **5** (Fig. S4) via hydrogen bonding donation from bound water molecules to hdn carbonyl groups (Table S1). Disordered water molecules of crystallization are located in small regions between the chain motifs, anchored in place by hydrogen bonding patterns involving the bound water molecules. These occupy 3.7 % of the unit cell volume.

#### 4.7 Structural description of $\{ [Cd(mip)(hdn)] \cdot H_2O \}_n$ (6)

The asymmetric unit of compound **6** contains a divalent cadmium atom, a fully deprotonated mip ligand, an hdn ligand, and a water molecule of crystallization. A distorted  $\{CdN_2O_4\}$  octahedral coordination environment is observed at cadmium (Fig. 11), with trans pyridyl nitrogen donor atoms from two hdn ligands. A chelating carboxylate group from an mip ligand, and cis-disposed single carboxylate oxygen atoms from two other mip ligands complete the coordination sphere. Pertinent bond lengths and angles are listed in Table 7.

All mip ligands in **6** adopt an exotridentate bridging mode, with a chelating carboxylate group binding to one cadmium atom, with the other carboxylate group bridging two cadmium atoms in a *syn-anti* fashion. The bridging carboxylate groups form  $[Cd_2(mip)_2]$  units (Fig. 11b) with embedded  $\{Cd_2(OCO)_2\}$  clusters; the Cd···Cd through-space distance across the cluster pattern is 3.890(5) Å. The full span of the mip ligands connect the cluster units into  $[Cd_2(mip)_2]_n$  coordination polymer chains that are arranged parallel to the *b* crystal direction. These in turn are pillared into  $[Cd(mip)(hdn)]_n$  coordination polymer layers (Fig. 12) by pairs of hdn ligands with an *anti-anti* conformation of their hexamethylene central moieties (torsion angles = 165.6, 173.6, 172.2°); the through-ligand Cd···Cd distance is 19.12(2) Å. Isolated water molecules of crystallization occupy small pockets within the layer motif, anchored to the coordination polymer framework by hydrogen bonding acceptance from hdn N–H groups, and hydrogen bonding donation to mip carboxylate oxygen atoms (Table S1). As each  $\{Cd_2(OCO)_2\}$  cluster can be defined as a 4-connected node, the topology of the  $[Cd(mip)(hdn)]_n$  layer motif becomes that of a decorated (4,4) grid. Adjacent  $[Cd(mip)(hdn)]_n$  layers stack in *AAA* pattern along the *a* 

crystal direction (Fig. S5) via hydrogen bonding donation from hdn N–H groups in one layer, to hdn carbonyl groups in a neighboring layer (Table S1).

#### 4.5 Thermal Properties

Compound 1 underwent dehydration in two stages, with a 7.0% mass loss between 140 and 170 °C and a subsequent 2.4% mass loss between 170 and 320 °C. The total 9.4 % mass loss corresponds roughly to the 8.1 % calculated value for four molar equivalents of water. Ligand combustion occurred above 320 °C. Compound 2 underwent dehydration between 25 and 120 °C, with a 2.5 % mass loss corresponding to the calculated value of 2.9 % for elimination of two molar equivalents of water. A subsequent 8.5 % mass loss between 120 and 300 °C corresponded roughly to a putative elimination of two molar equivalents of NO<sub>2</sub> from loss of the nitro functional groups from the nip ligands. Ligand combustion occurred above 300 °C. Compound 3 showed a 4.0% mass loss between 25 and 215 °C, indicative of partial decarboxylation. Loss of one molar equivalent of CO<sub>2</sub> would have resulted in a mass loss of 5.2 %. Combustion of the organic components occurred above 215 °C. Compound 4 underwent elimination of all its bound and unbound water molecules between 25 and 85 °C with the observed mass loss of 11.0 % exactly matching the predicted value. Ejection of the organic components occurred above 325 °C. Compound 5 underwent dehydration in two stages between 35 and 230 °C with a total mass loss of 10.3 % corresponding roughly to the calculated value of 8.3 % for elimination of five molar equivalents of water. Ligand combustion occurred above 230 °C. Compound 6 underwent dehydration between 25 and 110 °C, with the observed value of 4.0 % slightly higher than the predicted value of 2.8 % for one molar equivalent of water. This complex may have absorbed

some atmospheric water vapor on long-term storage. Ejection of the organic ligands occurred above 290 °C. The TGA traces for **1–6** are shown in Figs. S6–S11, respectively.

#### 4.6 Luminescent Properties

Ground samples of compounds **1–6** were subjected to ultraviolet radiation to investigate the presence of any luminescent behavior. Excitation spectra were recorded by monitoring emission at 400 nm; the maximum excitation wavelengths (Table 8) were then used to irradiate the respective samples. Emissive behavior was observed in all cases, with maximum emission wavelengths as shown in Table 8. Compounds **2** and **3** only showed very weak emission, while compound 6 manifested a strong emission of blue light. The emission of moderate intensity violet light was observed for compounds **1**, **4**, and **5**. Emission profiles for **1–6** are depicted in Fig. 13. The emissive behavior is ascribed to  $n-\pi$  or  $\pi^*-\pi$  molecular orbital electronic transitions within the aromatic rings of the dicarboxylate ligands (**1–6**) and the dipyridylamide ligands (**1–2**, **4–6**) after ultraviolet excitation [28]. MLCT or LMCT transitions are very unlikely due to the closed shell  $d^{10}$  configuration of the divalent zinc or cadmium atoms.

#### 4.7 Nitrobenzene detection

Compounds **4** and **6** were assayed as potential nitrobenzene detectors in ethanol suspension (insufficient luminescence of **1**, **2**, **3**, and **5** in ethanol suspension precluded further study). In both cases, emission quenching was observed as  $\mu$ L-sized aliquots of a  $1 \times 10^{-4} M$  solution of nitrobenzene in DMSO were sequentially added to the coordination polymer ethanol suspension (Figs. 14 and 15). 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 **4** and **6**. As seen in

the plots of intensity percent remaining vs  $\mu$ L nitrobenzene solution added (Fig. S12), compound **6** undergoes a greater extent luminescence quenching than compound **4** for the same amount of analyte. It is thus plausible that the nitrobenzene analyte is more easily absorbed in the interlamellar regions of the stacked layered coordination polymer **6**, than between the stacked ladder motifs in **4**.

#### 5. Conclusions

Substituted and unsubstituted isophthalate ligands and the long spanning flexible dipyridylamide ligand *N*,*N*'-(hexane-1,6-diyl)dinicotinamide (hdn) afforded a series of 1D ladder and 2D layered zinc and cadmium coordination polymers. Synergistic effects on the part of the divalent metal coordination environments, the nature of the 5-position isophthalate substituent, and the conformational flexibility of the hdn ligands, act during self-assembly to induce the observed dimensionality and topology. A 3D body centered cubic topology phase was formed by *in situ* hydrolysis of the hdn precursor to afford nicotinate ligands. While all of the six coordination polymers in this series underwent ultraviolet or visible light emission upon excitation with ultraviolet light, two showed potential as detectors for small quantities of nitrobenzene in ethanol suspension. The layered phase **6** exhibited stronger luminescence quenching behavior in the presence of nitrobenzene than did the ladder polymer phase **4**, due to enhanced analyte absorption within the interlamellar regions.

#### **Supplementary Material**

Additional molecular graphics and thermogravimetric analysis plots. Crystallographic data (excluding structure factors) for **1–6** have been deposited with the Cambridge Crystallographic

Data Centre with Nos. 1514939, 1523516, 1514040, 1523517, 1514041, and 1514042,

respectively. Copies of the data can be obtained free of charge via the Internet at

<https://summary.ccdc.cam.ac.uk/structure-summary-form>.

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Data	1	2	3
Empirical Formula	$C_{34}H_{38}N_4O_{16}Zn_2$	$C_{52}H_{54}N_{10}O_{16}Zn_2$	$C_{36}H_{32}N_2O_{12}Zn_3$
Formula Weight	889.42	1237.78	880.74
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\overline{1}$	PĪ	$P2_1/n$
<i>a</i> (Å)	10.0927(12)	9.073(3)	11.1979(13)
b (Å)	10.4387(13)	9.580(3)	12.7884(15)
<i>c</i> (Å)	10.5492(14)	16.323(5)	13.0353(15)
α (°)	102.288(2)	73.288(3)	90
β (°)	98.709(2)	76.785(4)	106.3520(10)
γ (°)	118.794(3)	80.860(4)	90
$V(\text{\AA}^3)$	908.9(2)	1316.2(7)	1791.2(4)
Ζ	1	1	2
$D (\mathrm{g} \mathrm{cm}^{-3})$	1.625	1.562	1.633
$\mu (mm^{-1})$	1.401	0.998	2.059
Min./max. transmission	0.8630	0.7705	0.9092
<i>hkl</i> ranges	$-12 \le h \le 12,$ $-12 \le k \le 12,$ $-12 \le l \le 12$	$-10 \le h \le 10,$ $-11 \le k \le 11,$ $-19 \le l \le 19$	$-13 \le h \le 13,$ $-15 \le k \le 9,$ $-15 \le l \le 15,$
Total reflections	15525	17539	9695
Unique reflections	3344	4828	3295
R(int)	0.0250	0.1224	0.0418
Parameters	300	373	244
$R_1$ (all data)	0.0407	0.1379	0.0533
$R_1 (I > 2\mathbf{q}(I))$	0.0389	0.0682	0.0403
$wR_2$ (all data)	0.1068	0.1971	0.1057
$wR_2(I > 2\mathbf{q}(I))$	0.1050	0.1606	0.0963
Max/min residual (e <sup>-</sup> / Å <sup>3</sup> )	1.184/-1.108	0.812/-0.528	0.725/-0.514
G.O.F.	1.080	1.061	1.075

Table 1.	Crystal	and	Structure	Refinement	Data	for	1-(	6.
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Data	4	5	6
Empirical Formula	$C_{34}H_{42}Cd_2N_4O_{16}$	$C_{42}H_{56}Cd_2N_4O_{15}$	C <sub>27</sub> H <sub>30</sub> CdN <sub>4</sub> O <sub>7</sub>
Formula Weight	987.51	1081.70	634.95
Crystal system	triclinic	triclinic	triclinic
Space group	PĪ	PĪ	PĪ
a (Å)	10.2581(9)	10.0640(10)	9.1347(9)
b (Å)	10.3346(9)	10.1461(10)	10.2596(10)
c (Å)	10.9331(10)	13.2099(13)	14.7794(16)
α (°)	85.2730(10)	88.0940(10)	86.965(2)
β (°)	75.3130(10)	68.4760(10)	86.773(2)
γ (°)	61.1920(10)	72.5140(10)	76.955(3)
$V(\text{\AA}^3)$	981.34(15)	1192.3(2)	1346.1(2)
Z	1	1	2
$D (\mathrm{g} \mathrm{cm}^{-3})$	1.671	1.507	1.567
$\mu (mm^{-1})$	1.159	0.960	0.864
Min./max. transmission	0.9121	0.9043	0.9448
hkl ranges	$-12 \le h \le 11,$ $-12 \le k \le 12,$ $-13 \le l \le 13$	$-12 \le h \le 11,$ $-12 \le k \le 12,$ $-15 \le l \le 15$	$-11 \le h \le 10,$ $-12 \le k \le 12,$ $-17 \le l \le 17$
Total reflections	16455	13895	22266
Unique reflections	3605	4367	4937
R(int)	0.0369	0.0328	0.0288
Parameters	258	273	356
$R_1$ (all data)	0.0321	0.0594	0.0265
$R_1(I > 2q(I))$	0.0283	0.0533	0.0239
$wR_2$ (all data)	0.0718	0.1458	0.0586
$wR_2(I > 2q(I))$	0.0692	0.1430	0.0567
Max/min residual (e <sup>-</sup> / Å <sup>3</sup> )	0.682/-0.809	1.552/-0.688	0.908/-0.333
G.O.F.	1.102	1.221	1.063

Table 1.	Crystal	and	Structure	Refinemer	nt Data	for	1-6	Ś.
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Zn1–O1	1.9866(19)	$O4^{\#1}$ –Zn1–N1	116.4(5)
$Zn1-O4^{#1}$	1.9935(19)	O6–Zn1–O1	109.24(8)
Zn1–06	1.984(2)	$O6-Zn1-O4^{\#1}$	109.63(9)
Zn1–N1	2.04(2)	O6–Zn1–N1	113.7(5)
$O1-Zn1-O4^{#1}$	95.71(8)	O1–Zn1–N1	110.6(4)

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

Table 3. Selected Bond Distance	(Å) and Angl	e (°) Data for $2$ .
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01=2111=04	95.71(0)	OI-ZIII-INI	110.0(4)	
Symmetry trans	sformation: #	1 x + 1, y, z.		
Table 3. Selecte	ed Bond Dista	ance (Å) and Angl	e (°) Data f	for 2.
Zn1–O1	1.908(4)	O1–Zn1–N1	120.6(2)	
Zn1–O3 <sup>#1</sup>	1.935(4)	O1–Zn1–N4 <sup>#2</sup>	109.9(2)	
Zn1–N1	2.034(5)	$O3^{\#1}$ –Zn1–N1	102.8(2)	
$Zn1-N4^{#2}$	2.075(6)	$O3^{\#1}$ –Zn1–N4 <sup>#2</sup>	96.5(2)	
$O1-Zn1-O3^{\#1}$	120.41(19)	N1-Zn1-N4 <sup>#2</sup>	102.8(2)	

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

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Zn1–O1	2.064(2)	$O1^{\#1}$ –Zn1– $O6^{\#2}$	94.01(10)
Zn1–O1 <sup>#1</sup>	2.064(2)	$O1^{\#1}$ –Zn1– $O6^{\#3}$	85.99(10)
Zn1–O3 <sup>#2</sup>	2.073(3)	$O1-Zn1-O6^{#2}$	86.00(10)
$Zn1-O3^{#3}$	2.073(3)	$O3^{#3}$ –Zn1– $O3^{#2}$	180.0
Zn1–O6 <sup>#3</sup>	2.096(2)	$O3^{#3}$ –Zn1– $O6^{#2}$	87.84(9)
Zn1–O6 <sup>#2</sup>	2.096(2)	$O3-Zn1-O6^{#2}$	92.16(10)
Zn2–O2 <sup>#4</sup>	1.952(3)	$O3^{#3}$ –Zn1– $O6^{#3}$	92.16(10)
Zn2–O4	1.941(2)	$O3^{#2}$ –Zn1– $O6^{#3}$	87.84(10)
Zn2–O5	1.957(3)	$O6^{#3}$ –Zn1– $O6^{#2}$	180.0
$Zn2-N1^{#5}$	2.047(3)	$O2^{#4}$ –Zn2–O5	116.36(11)
$O1-Zn1-O1^{#1}$	180.0	$O2^{#4}$ –Zn2–N1 <sup>#5</sup>	99.26(11)
$O1^{\#1}$ -Zn1-O3 <sup>#2</sup>	91.10(10)	$O4-Zn2-O2^{#4}$	115.54(11)
$O1-Zn1-O3^{#2}$	88.90(10)	O4–Zn2–O5	116.62(11)
$O1^{\#1}$ -Zn1- $O3^{\#3}$	88.90(10)	O4–Zn2–N1 <sup>#5</sup>	99.09(11)
$O1-Zn1-O3^{#3}$	91.10(10)	$O5-Zn2-N1^{#5}$	105.85(11)
$O1-Zn1-O6^{#3}$	94.00(10)		

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

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

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

Cd101	2.316(2)	O5Cd1O2	98.79(7)
Cd1O2	2.5678(19)	O5–Cd1–O3 <sup>#1</sup>	90.37(7)
Cd1–O3 <sup>#1</sup>	2.323(2)	O5–Cd1–O4 <sup>#1</sup>	77.77(7)
Cd1O4 <sup>#1</sup>	2.616(2)	O6Cd1O1	91.75(7)
Cd105	2.313(2)	O6Cd1O2	79.82(7)
Cd106	2.303(2)	O6Cd1O3 <sup>#1</sup>	91.50(7)
Cd1–N1	2.312(2)	O6Cd1O4 <sup>#1</sup>	103.41(7)
O1Cd1O2	53.05(7)	O6Cd1O5	178.13(7)
O1–Cd1–O3 <sup>#1</sup>	85.26(7)	O6Cd1N1	88.89(8)
O1–Cd1–O4 <sup>#1</sup>	134.52(7)	N1Cd1O1	138.66(8)
O2Cd1O4 <sup>#1</sup>	170.89(6)	N1Cd1O2	86.57(7)
O3 <sup>#1</sup> -Cd1-O2	136.64(7)	N1-Cd1-O3 <sup>#1</sup>	136.06(8)
$O3^{\#1}$ -Cd1-O4 <sup>#1</sup>	52.27(7)	N1-Cd1-O4 <sup>#1</sup>	84.99(7)
O5-Cd1-O1	88.39(8)	N1Cd1O5	89.77(8)

Symmetry transformation: #1 x - 1, y, z.

Cd101	2.376(4)	O6Cd1O2	78.59(14)				
Cd1O2	2.466(4)	O6–Cd1–O3 <sup>#1</sup>	98.60(14)				
Cd1–O3 <sup>#1</sup>	2.471(3)	O6–Cd1–O4 <sup>#1</sup>	152.00(14)				
Cd1–O4 <sup>#1</sup>	2.410(4)	O6Cd1N4 <sup>#2</sup>	85.25(15)				
Cd106	2.320(4)	N1Cd1O1	105.28(17)				
Cd1–N1	2.310(5)	N1Cd1O2	86.05(18)				
Cd1-N4 <sup>#2</sup>	2.338(5)	N1–Cd1–O3 <sup>#1</sup>	91.39(16)				
O1Cd1O2	52.86(13)	N1–Cd1–O4 <sup>#1</sup>	95.35(16)				
O1–Cd1–O3 <sup>#1</sup>	130.60(12)	N1Cd1O6	86.71(17)				
O1–Cd1–O4 <sup>#1</sup>	78.48(13)	N1-Cd1-N4 <sup>#2</sup>	166.96(18)				
O2–Cd1–O3 <sup>#1</sup>	176.29(13)	N4 <sup>#2</sup> -Cd1-O1	87.76(15)				
O4 <sup>#1</sup> -Cd1-O2	129.40(13)	N4 <sup>#2</sup> -Cd1-O2	102.36(17)	6			
O4 <sup>#1</sup> -Cd1-O3 <sup>#1</sup>	53.49(12)	N4 <sup>#2</sup> -Cd1-O3 <sup>#1</sup>	79.70(15)				
O6Cd1O1	127.94(14)	$N4^{#2}$ -Cd1-O4 <sup>#1</sup>	87.03(15)				
Symmetry transformations: #1 $x$ + 1, $y$ , $z$ ; #2 $x$ + 1, $y$ + 1, $z$ - 1.							

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

Table 7. Selected Bond Distance	(Å) and	Angle (°)	Data	for 6	5
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Cd101	2.2473(15)	$O2^{\#_1}$ -Cd1-O3 $^{\#_2}$	140.84(6)
$Cd1-O2^{#1}$	2.2858(16)	$O2^{\#_1}$ -Cd1-O4 $^{\#_2}$	87.40(6)
Cd1–O3 <sup>#2</sup>	2.4422(16)	$O2^{\#_1}$ -Cd1-N1	93.45(6)
$Cd1-O4^{#2}$	2.3444(15)	$O2^{\#_1}$ -Cd1-N4 <sup>#_3</sup>	87.98(6)
Cd1–N1	2.3096(18)	$O4^{\#_2}$ -Cd1-O3 $^{\#_2}$	54.67(5)
Cd1–N4 <sup>#3</sup>	2.3347(18)	N1–Cd1–O3 <sup>#2</sup>	95.54(6)
O1–Cd1–O2 <sup>#1</sup>	132.53(6)	N1-Cd1-O4 <sup>#2</sup>	89.82(6)
$O1-Cd1-O3^{#2}$	85.88(5)	$N1-Cd1-N4^{#3}$	173.91(6)
$O1-Cd1-O4^{#2}$	140.07(6)	$N4^{#3}$ -Cd1-O3 <sup>#2</sup>	87.03(6)
01-Cd1-N1	88.02(6)	$N4^{#3}$ -Cd1-O4 $^{#2}$	96.16(6)
O1–Cd1–N4 <sup>#3</sup>	86.65(6)		

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

1
1
1
2
3
<u> </u>
5
<u> </u>

Table 8. Excitation and Emission Spectral Data for 1–6.



Scheme 1. The dicarboxylate ligands used in this study.





Figure 1. a) Coordination environment in **1**. Thermal ellipsoids are depicted at 50% probability. Symmetry codes are as in Table 2.



Figure 2. a)  $[Zn(hip)(H_2O)]_n$  coordination polymer chain in 1. b)  $[Zn_2(hip)_2(H_2O)_2(hdn)]_n$  1D coordination polymer ladder in 1 showing both disordered hdn conformations.



Figure 3. Aggregation of neighboring  $[Zn_2(hip)_2(H_2O)_2(hdn)]_n$  1D ladder motifs into supramolecular layers coincident with the *ac* crystal planes in 1.  $\pi$ – $\pi$  stacking between isophthalate ring centroids is indicated as dashed lines.



Figure 4. a) Coordination environment in **2**. Thermal ellipsoids are depicted at 50% probability. Symmetry codes are as in Table 3. b) 1D  $[Zn(nip)]_n$  coordination polymer chain in **2**. c) Face view of a  $[Zn_2(nip)_2(hdn)_2]_n$  ribbon in **2**. d) Side view of a  $[Zn_2(nip)_2(hdn)_2]_n$  ribbon in **2**.





Figure 5. a) Coordination environment in **3**. Thermal ellipsoids are depicted at 50% probability. Symmetry codes are as in Table 4. b) Trinuclear  $\{Zn_3(OCO)_6\}$  linear cluster unit in **3**.

Figure 6. a)  $[Zn_3(tbip)_2]_n$  coordination polymer layer arranged parallel to the  $(1 \ 0 \ \overline{1})$  crystal plane in **3**. The *tert*-butyl groups have been removed for clarity. In the online version of the article, the 5-position carbon atoms are rendered as purple spheres. b)  $[Zn_3(nic)_2]_n$  coordination polymer layer oriented parallel to the  $(1 \ 0 \ 1)$  crystal plane in **3**.



Figure 7. 3D  $[Zn_3(tbip)_2(nic)_2]_n$  coordination polymer network in **3**. In the online version of this article, the  $[Zn_3(tbip)_2]_n$  layer submotifs are drawn in red.



Figure 8. Schematic perspective of the  $4^{24}6^4$  **bcu** body-centered cubic topology in **3**. The spheres represent the 8-connected  $\{Zn_3(OCO)_6\}$  clusters.





Figure 9. a) Coordination environment in **4**. Thermal ellipsoids are depicted at 50% probability. Symmetry codes are as in Table 5. b)  $[Cd_2(ip)_2(H_2O)_4(hdn)]_n$  1D coordination polymer ladder in **4**.



Figure 10. a) Coordination environment in **5**. Thermal ellipsoids are depicted at 50% probability. Symmetry codes are as in Table 6. b)  $[Cd(tbip)(H_2O)_2]_n$  coordination polymer chain submotif in **5**. c)  $[Cd_2(tbip)_2(H_2O)_4(hdn)]_n$  1D coordination polymer ladder in **5**, showing both disordered hdn conformations.





Figure 11. a) Coordination environment in **6**. Thermal ellipsoids are depicted at 50% probability. Symmetry codes are as in Table 7. b)  $[Cd_2(mip)_2]$  dimeric unit in **6**.



Figure 12.  $[Cd(mip)(hdn)]_n$  coordination polymer layer in **6**.







Figure 14. Luminescence quenching of **4** in the presence of  $1 \times 10^{-4} M$  nitrobenzene in DMSO.



Figure 15. Luminescence quenching of **6** in the presence of  $1 \times 10^{-4} M$  nitrobenzene in DMSO.

#### Highlights

 $\rightarrow$  Zinc and cadmium phases with substituted isophthalate ligands

- $\rightarrow$  Long spanning *N*,*N*'-(hexane-1,6-diyl)dinicotinamide (hdn) coligands
- $\rightarrow$  1D ladder and 2D layered phases, and a 3D **bcu** topology via *in situ* ligand hydrolysis
- → Luminescent behavior in all cases, with some potential for nitrobenzene detection

#### Graphical abstract

Zinc and cadmium substituted isophthalate coordination polymers with *N*,*N*'-(hexane-1,6-diyl)dinicotinamide (hdn) coligands show a diversity of 1D ladder and 2D layer phases. In situ hydrolysis of the hdn ligands resulted in nicotinate ligands and the formation of a 3D bcu topology. All new phases showed luminescence behavior, and two exhibited potential as nitrobenzene detectors in ethanol suspension.

