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Five diverse bivalent metal coordination polymers based on benzene dicarboxylate and bent dipyridyl ligands: syntheses, structures, and photoluminescent properties

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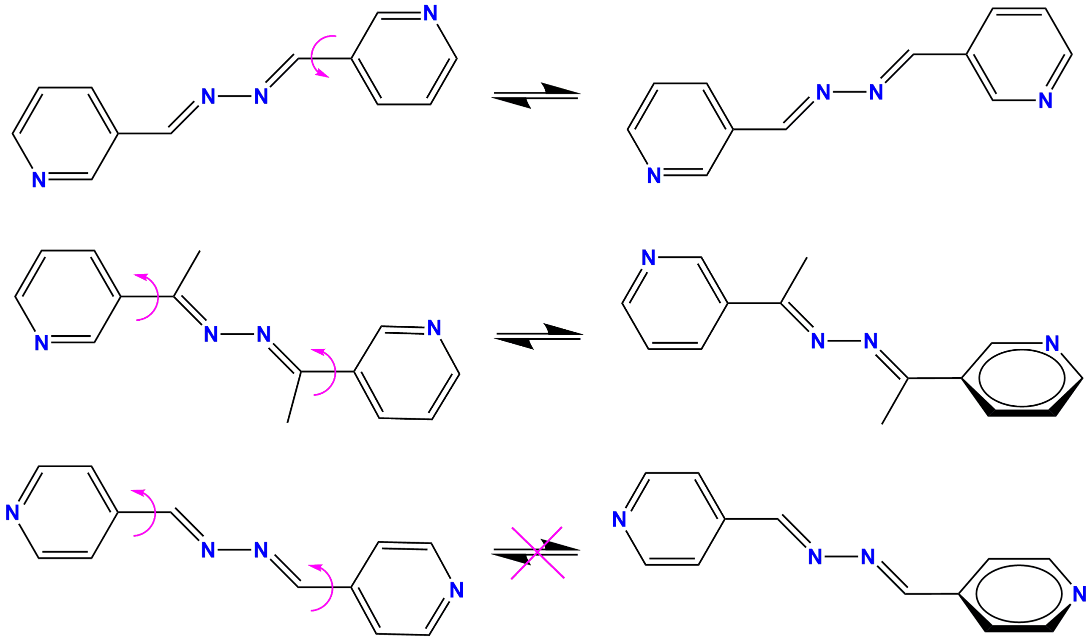
Abstract

Five new mixed ligand coordination polymers, $\{[Co_{0.5}(H_2O)(1,4\text{-bdc})(3\text{-bpdb})Co_{0.5}(H_2O)_2].(H_2O)_3\}_n$ **(1)**, $[Co(3\text{-bpdh})(1,4\text{-bdc})(H_2O)_2]_n$ (**2**), $[Zn(3\text{-bpdb})(1,4\text{-bdc})]_n$ (**3**), $\{[Zn(3\text{-bpdh})(1,4\text{-bdc})].(3\text{-bpdh})_{0.5}\}_n$ (**4**) and $[Cd(3\text{-bpdb})(1,4\text{-bdc})(H_2O)]_n$ (**5**) [where 3-bpdb = 1,4-bis-(3-pyridyl)-2,3-diaza-1,3-butadiene; 3-bpdh = 2,5-bis-(3-pyridyl)-3,4-diaza-2,4-hexadiene and 1,4-bdc = benzene-1,4-dicarboxylate] have been synthesized by slow diffusion technique at room temperature. The structures of **1**–**5** have been determined by single crystal X-ray diffraction analysis and were further characterized by elemental analysis, infrared spectroscopy (IR) and powder X-ray diffraction (PXRD) technique. Compound **1** exhibits a one-dimensional (1D) chain structure with monodentate pendant 1,4-bdc ligands which further extended to three-dimensional (3D) supramolecular structure by H-bonding and π···π interactions. Compound **2** displays a 4-connected two-dimensional (2D) framework with the point symbol $\{4^4.6^2\}$. Moreover, the 2D structure of **2** is also ultimately packed into 3D supramolecular frameworks through the H-bonding and the π–π stacking interactions. Compound **3** shows a 5-fold interpenetrated diamondoid net with 6^6 topology. Compound **4** is a 2D 3-connceted net having point symbol $\{6^3\}$ and extended to supramolecular 3D structure through C-H···π and π···π interactions with lattice 3-bpdh ligands. Compound **5** features a 3-fold interpenetrated diamondoid net with 6^6 topology. The thermal stabilities and luminescent properties of **3**−**5** have also been studied in detail. The complexes exhibit ligands based photoluminescence property at room temperature.

Introduction

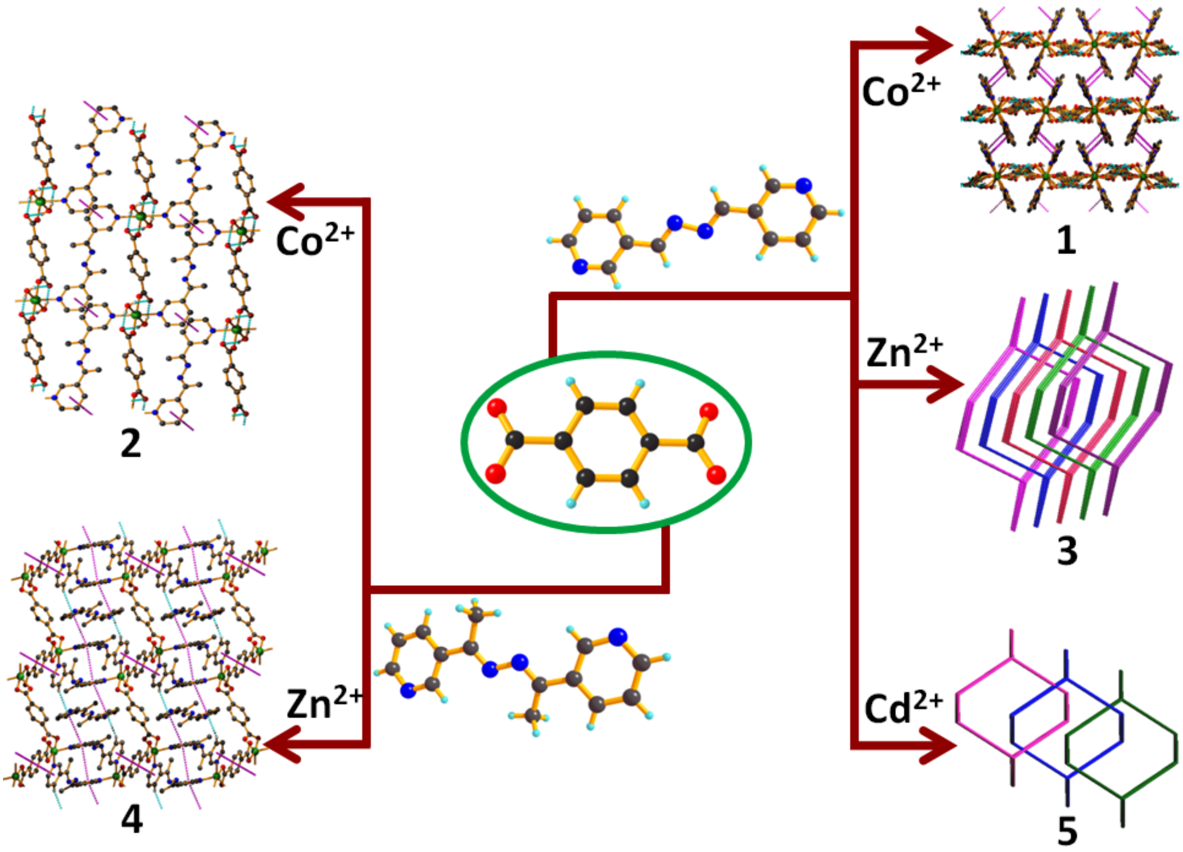
The cogent design for the fabrication of coordination polymers (CPs) based on the assembly of metal ions and multifunctional organic ligands have taken widespread attention because such CP based materials may exhibit several potential applications including gas storage,[1] magnetism,[2] separation,[3] catalysis,[4] luminescence,[5] drug delivery,[6] and many more.[7] During the synthesis of CPs, the control of their structure is one of the most fundamental aspects in determining the properties, as in most of the cases these are directly related to the topology of the network structure of CPs in solid state. Although a great variety of CPs with diverse compositions and topologies have been reported so far, however, till to date; the targeted synthesis of CPs with the predesigned structure and desired functionality remain as a major challenge in this field. This is most likely due to the involvement of self assembly process in such synthesis which is often independently influenced by several physical as well as chemical factors, such as solvents, pH of the medium, temperature, type of the ligand, metal-to-ligand ratio, chemical and geometrical preferences of the metal ions.[8] Amid them, only a careful synthetic approach balancing such parameters may able to produce a desirable MOF with the use of the properly designed organic ligands and suitable metal ions.[9]

In recent years, the judicial synthesis of mixed ligand CPs using polycarboxylates and N,N′-donor spacers have been established as a significant strategy.[10] Much efforts have been devoted using linear rod like ligands (linkers) such as, 4,4′-bipyridine; pyrazine; 4,4′-azobis(pyridine); 1,2-di(4-pyridyl)ethane; 1,2-di(4-pyridyl)ethylene; 1,3-bis(4-pyridyl)propane in combination with dicarboxylate ligands to synthesize diverse CPs ranging from 1D to 3D networks.[11] In case of designing the coordination polymers by using mixed linkers; straight N,N′-donor spacers can effectively stack the metal-carboxylate motifs to form higher dimensionality and therefore plays a crucial role in directing their structural motif in their topology. The role of the said N,N′-donor spacers in terms of their different length, flexibility, coordination ability, nature of coordination sites *etc.* are investigated thoroughly to see their diversity both in structures as well as their properties.[12] But the effect of change of the position of the coordination site of the N,N′-donor spacers (the use of bent spacers instead of straight) on the formation of networks has not been explored properly.[13] Here to observe the structural diversity in the resultant CPs; two bent pyridyl based azine linkers, namely, 1,4-bis-(3-pyridyl)-2,3-diaza-1,3-butadiene (3-bpdb) and 2,5-bis-(3-pyridyl)-3,4-diaza-2,4-hexadiene (3-bpdh) having conformational flexibility (Scheme 1), were used in combination with the rigid benzene-1,4-dicarboxylate and different divalent metal ions (Scheme 2). Moreover in spite of having strong fluorescence properties due to π conjugation effect; the above two N,N′-donor spacers are rarely used for the construction of CPs in combination with multicarboxylate ligands.[13]



Scheme 1 Representation of the conformation flexibility of 3-bpbd and 3-bpdh ligands

In this paper five interesting coordination polymers, {[Co$_{0.5}$(H$_2$O)(1,4-bdc)(3-bpdb)Co$_{0.5}$(H$_2$O)$_2$].(H$_2$O)$_3$}$_n$ **(1)**, [Co(3-bpdh)(1,4-bdc)(H$_2$O)$_2$]$_n$ (**2**), [Zn(3-bpdb)(1,4-bdc)]$_n$ (**3**), {[Zn(3-bpdh)(1,4-bdc)].(3-bpdh)$_{0.5}$}$_n$ (**4**) and [Cd(3-bpdb)(1,4-bdc)(H$_2$O)]$_n$ (**5**) [where 1,4-bdc = benzene-1,4-dicarboxylate], have been synthesized and characterized by single crystal X-ray structure and other physicochemical methods. The resultant five structures are quite different from the reported structures of mixed ligands CPs of Co(II), Zn(II) and Cd(II); which generally give pillared-layer 3D structures; when dicarboxylate and straight N,N′-donor spacers are used.[14] Recently our group has reported[15] two CPs of Zn(II), {[Zn(azpy)$_{0.5}$(terep)](H$_2$O)}$_n$ and [Zn(Meazpy)$_{0.5}$(terep)]$_n$ [azpy = *N, N′*-bis-pyridin-4-ylmethylene-hydrazine and Meazpy = *N, N′*-bis-(1-pyridin-4-yl-ethylidene)-hydrazine] by using 1,4-bdc and two different straight N, N′-donor azine ligands where the coordinated nitrogen atoms of the pyridyl groups are in 4-position. There in both cases 2D metal-dicarboxylate layers are pillared by the straight N, N′-donor azine ligand. But here by changing the position of coordinated nitrogen of two azine linkers; keeping the dicarboxylate ligands same, results a significant difference in the metal–ligand coordination environment as well as in the solid-state structures. The change of non-functionalized to methyl-functionalized N,N′-donor spacers have lead to the construction of coordination framework with different topologies and metal-ligand connectivity. Compounds **3**–**5** also show ligand based photoluminescent properties in the solid state.



Scheme 2 Synthetic scheme of compounds **1**–**5**

Experimental Section:

Materials

1,4-bis-(3-pyridyl)-2,3-diaza-1,3-butadiene (3-bpdb) and 2,5-bis-(3-pyridyl)-3,4-diaza-2,4-hexadiene (3-bpdh) were prepared according to literature procedures.[16] The starting material for these syntheses; 3-pyridinecarboxaldehyde, 3-acetyl pyridine and hydrazine hydrate were purchased from Sigma-Aldrich Chemical Co. Inc. and used as received. High purity cobalt(II) nitrate hexahydrate, zinc(II) nitrate hexahydrate, cadmium(II) nitrate tetrahydrate, benzene-1,4-

dicarboxylic acid (H_2-1,4-bdc), were also purchased from Sigma- Aldrich Chemical Co. Inc. and used as received. Na_2-1,4-bdc was synthesized by the gradual addition of Na_2CO_3 to H_2-1,4-bdc ligand in a 1:1 ratio in water and was allowed to evaporate at 90 °C until dryness. All other chemicals and solvents were AR grade and were used as received.

Physical Measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Heraeus CHNS analyzer. Infrared spectra (4000–400 cm^{-1}) were taken on KBr pellets, using a PerkinElmer Spectrum BX-II IR spectrometer. Thermal analysis (TGA) was carried out on a METTLER TOLEDO TGA 850 thermal analyzer under nitrogen atmosphere (flow rate: 50 cm^3 min^{-1}), at the temperature range 30–500 °C with a heating rate of 2 °C min^{-1}. X-ray powder diffraction (PXRD) patterns of the bulk sample were recorded in Bruker D8 Discover instrument using Cu-Kα radiation. Emission spectra were recorded on a HORIBA Jobin Yvon (Fluoromax-3) fluorescence spectrophotometer.

Crystallographic Data Collection and Refinement

Suitable single crystals of compounds **1**-**5** were mounted on the tip of thin glass fibers with commercially available super glue. X-ray single crystal data collection of all five crystals were performed at room temperature using Bruker APEX II diffractometer, equipped with a normal focus, sealed tube X-ray source with graphite monochromated Mo-Kα radiation (λ= 0.71073Å). The data were integrated using SAINT[17] program and the absorption corrections were made with SADABS.[18] All the structures were solved by SHELXS 97[19] using Patterson method and followed by successive Fourier and difference Fourier synthesis. Full matrix least-squares refinements were performed on F^2 using SHELXL-97[19] with anisotropic displacement parameters for all non-hydrogen atoms. All the hydrogen atoms were fixed geometrically by HFIX command and placed in ideal positions in case of all five structures. All calculations were carried out using SHELXS 97, SHELXL 97, PLATON v1.15,[20] ORTEP-3v2,[21] and WinGX system Ver-1.80[22] and TOPOS.[23] The coordinates, anisotropic displacement parameters, and torsion angles for all five compounds are submitted as Electronic Supporting Information in CIF format. Data collection and structure refinement parameters and crystallographic data for all compounds are given in Table 1.

Syntheses

$\{[Co_{0.5}(H_2O)(1,4\text{-bdc})(3\text{-bpdb})Co_{0.5}(H_2O)_2].(H_2O)_3\}_n$ (1). An aqueous solution (16 mL) of Na_2-1,4-bdc (1 mmol, 0.210 g) was mixed with a methanolic solution (16 mL) of 1,4-bis-(3-pyridyl)-2,3-diaza-1,3-tetradiene (3-bpdb) (1 mmol, 0.210g) and stirred for 20 min to mix it well. $Co(NO_3)_2 \cdot 6H_2O$ (1 mmol, 0.291 g) was dissolved in 16 mL of water in a separate beaker. Then in a crystal tube 3 ml of Co(II) solution was slowly and carefully layered with the 6 ml of abovementioned mixed-ligand solution using a 2 ml of buffer solution (1:1 of water and MeOH) in between the two solution. The tube was sealed and kept undisturbed at room temperature and after 5 days reddish blocked shaped single crystals suitable for X-ray diffraction analysis were obtained at the wall of the tube. The crystals were separated and washed with a methanol-water (1:1) mixture and dried under air (Yield 63%). Anal. Calc. for $C_{20}H_{26}CoN_4O_{10}$ (%): C, 44.37; H, 4.84; N, 10.35. Found (%): C, 44.51; H, 4.46; N, 10.11. IR spectra (in cm^{-1}): ν(H_2O), 3257; ν(C=N), 1632; ν(C-O), 1225; ν(CH-Ar), 3100-2900; and ν(C=C), 1606-1424.

$[Co(3\text{-bpdh})(1,4\text{-bdc})(H_2O)_2]_n$ (2). This has been synthesized by the same procedure as that of **1** using 2,5-bis-(3-pyridyl)-3,4-diaza-2,4-hexadiene (3-bpdh) (1 mmol, 0.238 g) instead of 3-bpdb. The reddish block crystals suitable for X-ray diffraction analysis were obtained after seven days. The crystals were separated and washed with a methanol-water (1:1) mixture and dried under air (Yield 71%). Anal. Calc. for $C_{22}H_{22}N_4O_6Co$ (%): C, 53.13; H, 4.46; N, 11.26. Found: C, 53.23; H,4.42; N,11.25. IR spectra (in cm^{-1}): ν(H_2O), 3370; ν(C=N), 1614; ν(C-O), 1196; ν(CH-Ar), 3074-2910 and ν(C=C), 1427-1560.

$[Zn(3\text{-bpdb})(1,4\text{-bdc})]_n$ (3). This has been synthesized by following the same procedure as for **1** using $Zn(NO_3)_2 \cdot 6H_2O$ (1 mmol, 0.297 g) instead of $Co(NO_3)_2 \cdot 6H_2O$. Yellow color single crystals suitable for X-ray diffraction analysis were obtained after two weeks. The crystals were separated and washed with a methanol-water (1:1) mixture and dried under air (yield 62%). Anal. Calc. for $C_{20}H_{14}N_4O_4Zn$ (%): C, 54.63; H, 3.21; N, 12.74. Found: C, 54.61; H, 3.19; N, 12.72. IR spectra (in cm^{-1}): ν(H_2O), 3411; ν(C=N), 1611; ν(C-O), 1230; ν(CH-Ar), 3054-2937 and ν(C=C), 1580-1425.

$\{[Zn(3\text{-bpdh})(1,4\text{-bdc})].(3\text{-bpdh})_{0.5}\}_n$ (4). This has been synthesized by the same procedure as that of **3** using 2,5-bis-(3-pyridyl)-3,4-diaza-2,4-hexadiene (3-bpdh) (1 mmol, 0.238 g) instead of 3-bpdb. The yellowish block crystals suitable for X-ray diffraction analysis were obtained after seven days. The crystals were separated and washed with a methanol−water (1:1) mixture and dried under air (Yield 70%). Anal. Calc. for $C_{29}H_{25}N_6O_4Zn$ (%): C, 59.34; H, 4.29; N,14.32. Found: C, 59.31; H, 4.31; N, 14.28. IR spectra (in cm^{-1}): ν(C=N), 1601; ν(C-O), 1195; ν(CH-Ar), 3096-3036 and ν(C=C), 1500-1475.

[Cd(3-bpdb)(1,4-bdc)(H_2O)]$_n$ (5). This has been synthesized by the same procedure as that of **3** using $Cd(NO_3)_2\cdot 4H_2O$ (1 mmol, 0.308 g) instead of $Zn(NO_3)_2\cdot 6H_2O$. The yellowish block crystals suitable for X-ray diffraction analysis were obtained after seven days. The crystals were separated and washed with a methanol-water (1:1) mixture and dried under air (Yield 65%). Anal. Calc. for $C_{20}H_{16}N_4O_5Cd$ (%): C, 47.59; H, 3.19; N, 11.1. Found: C, 47.62; H, 3.23; N, 10.97. IR spectra (in cm^{-1}): ν(H_2O), 3367; ν(C=N), 1625; ν(C-O), 1311; ν(CH-Ar), 3100-2950 and ν(C=C), 1596-1400.

The bulk compounds of all five, have been synthesized in powder form by the direct mixing of the corresponding ligands solution and M(II) salt solution in water at their equal-molar ratio. Compounds purity was verified by PXRD, which give good correspondence between simulated and bulk-phase PXRD patterns indicates the high purity of the compounds. The purity of the bulk sample was further confirmed by the results of elemental analysis and IR spectra as well, which also found in accordance with the data obtained for the single crystals.

Results and discussion

Synthesis

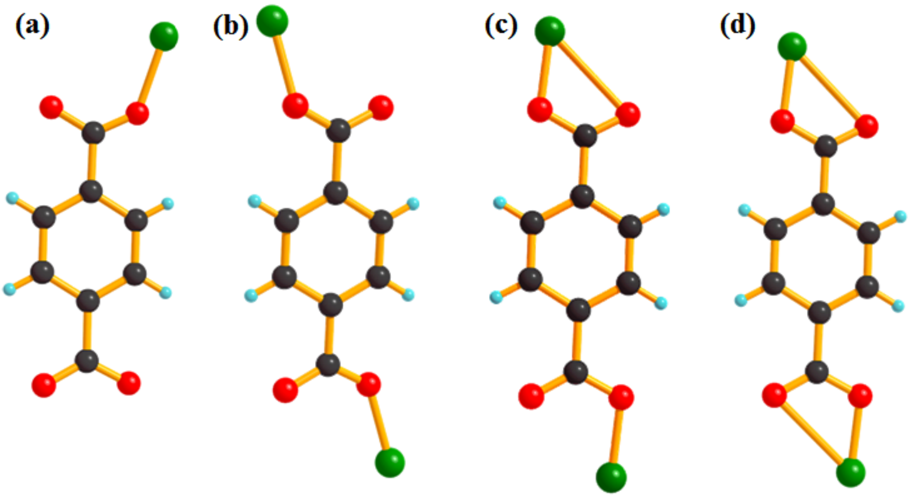
Compounds **1**−**5** were synthesized using 1,4-bdc disodium salt along with two different bent N,N′-donor such as 3-bpdb (**1**, **3** & **5**) and 3-bpdh (**2** & **4**) respectively using the corresponding metal(II) solution [Co(II), Zn(II) and Cd(II)] at room temperature (Scheme 2). The bulk powder compounds of **1-5** have been synthesized by direct mixing of aqueous solution metal salt and corresponding ligands mixture. All the products formed with high yields, and their bulk purity was confirmed through powder XRD measurements of the as-synthesized complexes (Fig. S15-19). The PXRD patterns of these compounds are in good agreement with the simulated spectra those calculated from the corresponding crystallographic data. The sharp and strong IR peaks in the 1300−1600 cm^{-1} range could be attributed to the carboxylate groups (Fig. S5-S9).

However, when we carried out the competitive reaction to evaluate the selective preference of a single metal towards any of the given ligand systems, we found that mixture of both crystals were obtained. On the other hand, where multiple metals were used in a reaction keeping a fixed ligand system a mixture of crystals (each bearing a single metal) was obtained.

This ruled out the presence of any kind of selectivity. However, it is needless to mention that the yield of the various crystals obtained in these competitive reactions was substantially low.

Crystal Structure descriptions of the CPs

The diversity of the structures of five CPs are shown in Scheme 2, originated due to various coordination modes of 1,4-bdc dianion (Scheme 3) and different orientation of neutral linkers (Scheme 1) in complexes **1-5**. Further structural details for all the complexes are described below.



Scheme 3 Various bridging modes of 1,4-bdc; (a) pendant monodendate in **1**, (b) bridging monodentate in **2** and **3**, (c) chelating-monodentate in **4**, (d) bischelating mode in **5**.

$\{[Co_{0.5}(H_2O)(1,4\text{-bdc})(3\text{-bpdb})Co_{0.5}(H_2O)_2].(H_2O)_3\}_n$ (1). Compound **1** crystallizes in the monoclinic $P2_1/n$ space group and the structure determination reveals that the formation of a one-dimensional (1D) structure of Co(II) ions linked by 3-bpdb ligands. In the asymmetric unit of **1** two crystallographically independent half occupied Co(II) centers (Co1 and Co2) are located in special positions, along with one monodentate pendant 1,4-bdc dianion, one bridging 3-bpdb, three coordinated water and three lattice water molecules. The hexa-coordinated Co1 shows distorted octahedral geometry (Fig. 1a) and is coordinated to four oxygen atoms (O3W, O3W^b, O1 and O1^b) from two coordinated water molecules and two pendant 1,4-bdc ligands (Scheme 3a), respectively; which occupy the equatorial positions. Two pyridyl nitrogen atoms, N1 and N1^b of two different bridging 3-bpdb linkers occupy the axial position of the octahedron. The Co1−O and Co1−N bond lengths are in the range of 2.073(2)−2.1195(18) Å and 2.164(2) Å, respectively (Table 2). The Co2 also shows distorted octahedral geometry (Fig. 1a) and is connected to four coordinated water molecules (O1W, O1W^{a}, O2W and O2W^{a}) sited in the equatorial position and two nitrogen atoms (N4 and N4^{a}) from two different 3-bpdb ligands present in the axial position. The Co2−O and Co2−N bond lengths are in the range of 2.074(2)−2.0874(19) Å and 2.166(2) Å, respectively (Table 2). The similar types of structures with mixed environment of Co(II) has already reported in literature.[10f, 11j, k] The overall structure shows a 1D pattern, which propagated in the *c* direction with the help of bridging 3-bpdb (Fig. 1b). In the crystal packing, the coordinated water molecules (O1W, O2W and O3W) are attached with the uncoordinated carboxylate oxygen atoms of 1,4-bdc ligand by means of trifurcated (with O2) and bifurcated (with O3 and O4) H-bonding interactions forming a supramolecular two-dimensional (2D) sheet (Fig. 1b) in the crystallographic *ab* plane (Table 3). These particular types of H-bonding interactions probably make O2/O3/O4 unavailable for coordination to the metal center instigating the monodentate pendant bridging mode of the 1,4-bdc dianion.[24] These 2D sheets are further stitched through intermolecular π-π interaction with the help of 3-bpdb ligands [cg…cg distance = 3.7541(15) Å] (Figs. 1c, S1 and Table 4) and H-bonding interactions between coordinated water (O1W) and carboxylate oxygen atom (O3) with crystalline lattice water molecules (O4W and O5W, Table 3) resulting in a supramolecular three-dimensional (3D) structure, which is shown in Fig. 1c.

[Co(3-bpdh)(1,4-bdc)(H_2O)$_2$]$_n$ (2)

When a new type of N,N′-donor linker, 3-bpdh (instead of 3-bpdb), was introduced in same experimental conditions as **1**, **2** was obtained. Compound **2** crystallizes in the triclinic *P*1̄ space group and the structure determination reveals that the formation of a two-dimensional (2D) structure of Co(II) ions linked by 3-bpdh and 1,4-bdc ligands. The asymmetric unit of **2** is composed of one half occupied Co(II) center situated at special position, half 1,4-bdc dianion; half 3-bpdh and one coordinated water molecule. The central Co(II) ion (Co1) adopts a distorted octahedral geometry (Fig. 2a) surrounded by four oxygen atoms (O2, O2^{a}, O2W and O2W^{a}) from two different 1,4-bdc ligands and two coordinated water in the equatorial plane. Two symmetry related nitrogen atoms from two different 3-bpdh ligands are placed in the axial position. The Co1–O bond lengths ranges from 2.0690(11) to 2.1354(12) Å and the Co1–N bond lengths are 2.1679(13) Å (Table 5). Here, the 1,4-bdc ligand binds in a bridging monodentate fashion (Scheme 3b) and each 1,4-bdc ligand connects two Co(II) centers to form a 1D metal-carboxylate chain. Such 1D chains are further connected by 3-bpdh ligands, leading to the formation of a 2D network (Fig. 2b). Topologically, if the Co(II) ions can be defined as 4-connected nodes, 1,4-bdc dianions and 3-bpdh ligands both can be considered as linkers, thus, the 2D framework of **2** can be simplified by TOPOS[23] software, as a (4)-connected uninodal net with the Schläfli symbol $\{4^4.6^2\}$ (Fig. 2c). In the crystal packing, these 2D grids are further stitched with the help of coordinated water molecule (O1W), by means of intermolecular H-bonding with the uncoordinated carboxylate oxygen atom (O1) (Fig. 3a and Table 3). This H-bonding makes these 2D grids to expand into a three-dimensional (3D) supramolecular structure (Fig. 3b). Apart from H-bonding, there are also intramolecular π-π interactions within the 2D sheets (Fig. 3b and Table 4) of **2**; strengthening the stability of 3D supramolecular construction [cg…cg distance = 3.6118(10) Å].

[Zn(3-bpdb)(1,4-bdc)]*n* (3)

To study the effect of metal centre on structure formation, Co(II) metal was replaced by Zn(II) which yielded **3** under the identical reaction conditions (like **1**). Compound **3** crystallizes in monoclinic system with space group *C*2/*c*. Single-crystal X-ray diffraction analysis reveals that **3** is a three-dimensional (3D) 5-fold interpenetrating diamondoid network made up Zn(II), 3-bpdb and 1,4-bdc ligands. As shown in Fig. 4a, each Zn(II) center is coordinated with two nitrogen atoms (N1 and $N1^a$) from different 3-bpdb ligand and two carboxylate oxygen atoms (O1 and $O1^a$) from two different 1,4-bdc showing a distorted tetrahedral geometry. The Zn1-N and Zn1-O distances are 2.062(2) and 1.9476(16) Å, respectively (Table 6). Here, each 1,4-bdc dianions connects the adjacent Zn(II) centers through a bridging monodentate fashion (Scheme 3b) to form $[Zn(1,4\text{-bdc})]_n$ chains (Fig. S2) that are further connected by 3-bpdb ligands, resulting the formation of a 3D diamondoid network (Fig. 4b and 4c). Topological analysis of **3** with TOPOS[23] suggests that each Zn(II) centers acts as a 4-connecting node (Fig. 5c), and the overall structure has 6^6-*dia* net topology. Here each metal center node is linked to four neighbors, generating an adamantane-like cage, which is the characteristic building unit for the diamondoid net (Fig. 5a,b,c). The Zn···Zn separation along Zn···1,4-bdc···Zn and Zn···3-bpdb···Zn are 10.994 and 14.094 Å, respectively. Due to these considerably high Zn-Zn separations, there are very large cavities which are formed within each network (Fig. 5d). In order to minimize the big voids in the framework, five independent equivalent framework interpenetrates each other for the effective filling of the voids; resulting a 5-fold interpenetrating three-dimensional architecture

(Fig. 5e). Interpenetration analysis with TOPOS[23] suggests the presence of Class Ia interpenetration with Zt = 5 and Zn = 1.

$\{[Zn(3\text{-bpdh})(1,4\text{-bdc})].(3\text{-bpdh})_{0.5}\}_n$ (4)

On search of the effect of change of metal ion on the overall structures of the CPs, when Co(II) of **2** was replaced by Zn(II), compound **4** was obtained. Compound **4** crystallizes in the triclinic *P*ī space group and the structure determination reveals that the formation of a two-dimensional (2D) structure of Zn(II) ions linked by 3-bpdh and 1,4-bdc ligands with 3-bpdh guest molecule. The asymmetric unit consists of one Zn(II) atom, one 1,4-bdc dianion, one bridging 3-bpdh ligand and half guest 3-bpdh ligand. As shown in Fig. 6a, each Zn(II) ion is five-coordinated in a distorted trigonal bipyramidal coordination geometry with Addison parameter (tau) value of 0.76.[25] The coordination environment is furnished by two nitrogen atoms from two distinct 3-bpdh ligands (N1 and N4^a) and three oxygen atoms from two different 1,4-bdc dianions (O1, O3 and O4). The Zn1-N and Zn1-O distances are 2.064(2)- 2.077(2) Å and 1.9533(19)-2.727(2) Å, respectively (Table 7). Here, the bridging 3-bpdh ligand adopts an *anti*-conformation with the dihedral angle between two pyridine rings being 58.3° whereas guest 3-bpdh ligand present in the *syn*-conformation. Each 1,4-bdc dianions connects the adjacent Zn(II) centers through chelating-mondentate fashion (Scheme 3c) to form $[Zn(1,4\text{-bdc})]_n$ chains (Fig. S3), which are further connected by bridging 3-bpdh ligands extending into a 2D layer structure (Fig. 6b). The uncoordinated 3-bpdh molecules are accommodated inside the framework to fill the void space (Fig. 6c). In the crystal packing, the bridging 3-bpdh ligands are involved in π–π interactions with 1,4-bdc and lattice 3-bpdh ligands. Furthermore, lattice 3-bpdh ligands are locked by C–H···π interaction with bridging 3-bpdh ligands (Table 4). This intermolecular π–π interaction fabricates a 3D supramolecular arrangement by locking the 2D layer along the *bc* plane (Fig. 6c, Table 4 and S6). Topologically, the Zn(II) ions can be defined as 3-connected nodes, the 1,4-bdc dianions and 3-bpdh ligands both can be regarded as linkers. Thus, the structure of **4** can be described as a (3)-connected net with the Schläfli symbol $\{6^3\}$ (Fig. 6d).

$[Cd(3\text{-bpdb})(1,4\text{-bdc})(H_2O)]_n$ (5)

With the change of Co(II) to Cd(II) under uniform reaction conditions, a structurally different compound, **5**, was obtained. Compound **5** is a three-dimensional 3-fold interpenetrating diamondoid network and crystallizes in the monoclinic space group *C*2/*c*. Each Cd(II) centers in **5** are seven coordinated with distorted pentagonal-bipyramidal geometry (Fig. 7a) resulting by the coordination to two pyridyl nitrogen atoms (N1 and N1^{a}), four carboxylate oxygen atoms (O1, O1^{a}, O2 and O2^{a}) and one coordinated water molecule, O1W. The Cd1-O distances fall in the range of 2.218(4)-2.446(3) Å and Cd1-N is 2.374(3) Å (Table 8). Here, each 1,4-bdc dianions connects the adjacent Cd(II) centers through a bischelating fashion (Scheme 3d) to form $[Cd(1,4\text{-bdc})]_n$ chains (Fig. S4), which are further connected through 3-bpdb ligands extending the structure into a 3D diamondoid network (Fig. 7b, c) similar to that found in **3**. Topological analysis of **5** with TOPOS[23] suggests that each Cd(II) center acts as a 4-connecting node (Fig. 7 c), and the overall structure has 6^6-*dia* net topology very similar to that of **3**. Each 4-connecting node is connected to four neighbors in a tetrahedral fashion, which gives rise to a diamondoid network composed of large adamantanoid cages (Fig. 8a, b, c). The Cd···Cd separation along Cd···1,4-bdc···Cd and Cd···3-bpdb···Cd are 11.160 and 12.961 Å, respectively. Owing to different metal coordination environments in **5** in comparison to **3**, here relatively small cavities are formed within each diamondoid network in **5** and naturally to minimize the voids in the diamondoid cages (Fig. 8d) and to stabilize the whole framework, a 3-fold interpenetrating diamondoid framework is generated (Fig. 8e). Interpenetration analysis with TOPOS[23] suggests the presence of Class Ia interpenetration with $Z_t = 3$ and $Z_n = 1$. The entangled nets are assisted by hydrogen bonding interactions between carboxylate oxygen atom (O2) from the 1,4-bdc ligand and coordinated water molecule (Table 3). This hydrogen-bonding interaction together with the coordinate-covalent interactions between metal ions and organic ligands mutually stabilizes the present interpenetrating diamondoid networks.

Thermal Stability and Powder X-ray Diffraction

TGA were carried out for compounds **1**−**5** in order to characterize the compounds in terms of thermal stability. The experiments were performed on polycrystalline samples in nitrogen atmosphere with a heating rate of 2 °C min^{-1}. The TGA curves for compounds **1**−**5** are shown in Figures S10-14. Compound **1** reveals a stepwise release of water molecules which can be correlated by the different H-bonding strength exist within the compound. The first step indicates the release of three lattice water and a loosely H-bonded coordinated water molecules (calcd wt loss = 13.3%; exptl wt loss = 13.9%) at 135 °C, and the second one corresponds to the release of the other two strongly tri-furcated H-bonded coordinated water molecules at 215 °C (total calcd wt loss for 6 molecules = 19.94%, total exptl wt loss = 20.4%) (Fig. S10). After that, its gradually decomposes into unidentified products. In case of **2**, it releases two coordinated water molecules at 135°C (calcd wt loss of 7.24%; exptl wt loss = 7.7%) and the desolvated framework is stable up to 260 °C without further weight loss (Fig. S11). It decomposes to unidentified product after 260 °C in two steps. For **3**, TGA shows no significant weight loss up to 350 °C owing to the absence of guest solvent molecules. It decomposes to unidentified product after 350 °C (Fig. S12). Similarly to compound **4** also thermally stable up to 225 °C without any significant weight loss and then decompose to unidentified product in two overlapping steps (Fig. S13). In case of **5** the loss of a coordinated water molecule (calcd 3.57 %; exptl wt 3.8 %) was observed at 165 ºC and the dehydrated structure is stable up to 360 ˚C without any further weight loss (Fig. S14).

To confirm the phase purity of the bulk materials, powder X-ray diffraction (PXRD) analysis was performed for all the compounds at room temperature. The experimental PXRD patterns from the samples of compounds **1**−**5** are in agreement with the simulated ones from their respective single crystal structures (Fig. S15-19), confirming the phase purity of the compounds.

Luminescent Properties

Apart from the conventional applications, CPs have often been used as photoluminescent materials, owing to their high thermal stability. Coordination polymers with d^{10} metals display interesting luminescent properties.[26] Therefore, to see their luminescent behavior, the emission properties of 3-bpdb and 3-bpdh ligands along with compounds **3**−**5** have been investigated in the solid state at room temperature (Fig. 9). The solid-state fluorescence maxima of 3-bpdb and 3-bpdh were observed at 363 and 362 nm respectively, when excited at 241 nm. The ligand emission peaks may be attributed to the π*–n or π*–π transition. The emission peak positions of compounds **3** and **5** are the same at 363 nm as that of the free 3-bpdb ligand on excitation at 247 nm and 240 nm, respectively. The intensities of emission for both the compounds were different. For compound **4**, it can be observed that weak emission occurs at 365 nm when excited at 245 nm, which exhibits slight red shift comparing with the free 3-bpdh ligand. It has observed that for d^{10} complexes, no emission originates from metal-centered MLCT/LMCT excited states, since the d^{10} metal ions are difficult to be oxidized or reduced.[27] Thus the emission bands of the three compounds can be attributed to the intra-ligand fluorescent emission. The enhancement of luminescence intensity for compounds **3**−**5** compared to the free ligands is perhaps a result of the metal−ligand coordination, which effectively increases the rigidity of the ligand and the reduction of energy loss by nonradiative decay.[28]

Conclusion

By the use of two bent N,N′-donor azine ligands (3-bpdb and 3-bpdh) in combination with benzene-1,4-dicarboxylate as mixed ligands, five transition metals [Co(II)/Zn(II)/Cd(II)] coordination polymers have been successfully synthesized. Compounds **1-5** display diverse structural variations from 1D to 3D which are distinctly different from the structures obtained by the use of straight N,N′-donor azine ligands. The change of non functionalized (3-bpdb) to methyl-functionalized (3-bpdh) bent azine N,N′-donor spacers along with the rigid 1,4-bdc ligand produced distinctly different topological networks even with the same metal ion; which is not so, in case of the straight N,N′-donor azine ligands. This is possibly due to the greater steric hindrance exerts by the substituted bent linkers in comparison to the straight one. Thus it may be concluded that the effect of substitution on bent linkers, become more important in directing the structures of CPs. Moreover, compounds **3−5** display strong emission properties and high thermal stability, which may potentially useful in the development of new optical materials. In summary, this work provides a new promising methodology for fabricating functional CPs with bent linkers having new structures and properties for the enrichment of understanding in the area of designed synthesis of CPs.

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Electronic supplementary information (ESI) available:

The IR, PXRD patterns, TGA and excitation spectra of compounds **1-5** (Figs. S5-S19) along with different structural figures related to the crystal structures reported in this paper are available as ESI. The structure reported in this paper having the CCDC reference numbers 1000608-1000612. For ESI and crystallographic data in CIF or other electronic format see DOI:

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Figures

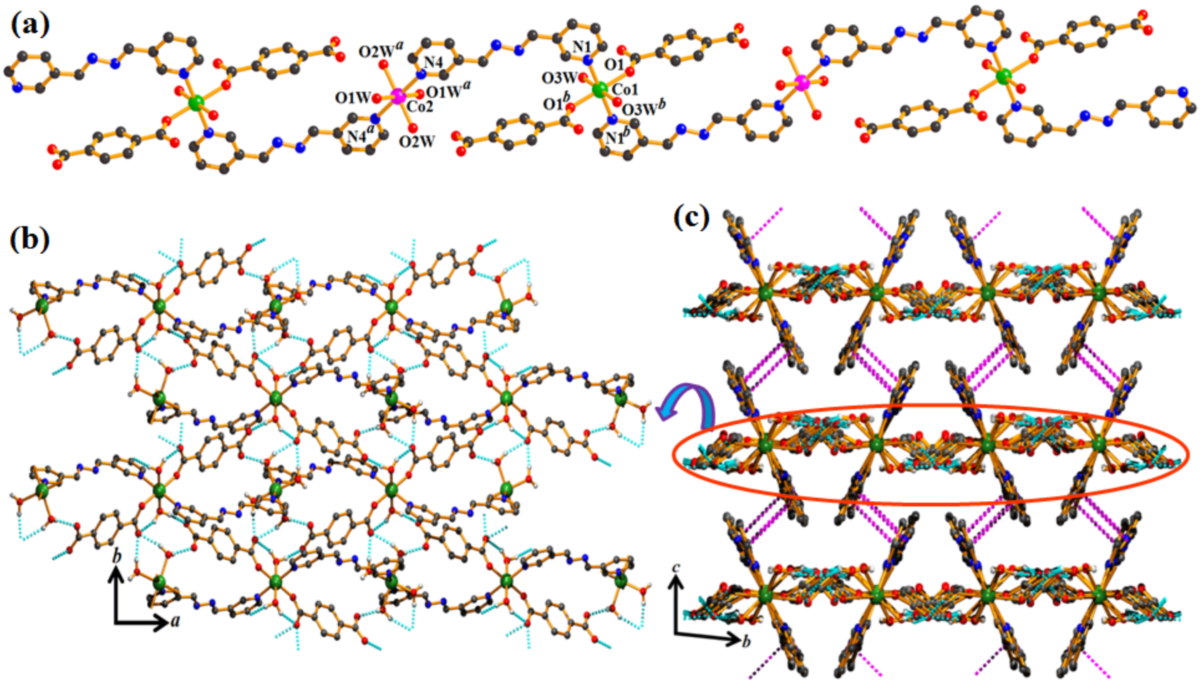

Fig. 1 (a) Coordination environment around Co(II) ions in the fragment of the one dimensional chain of **1**; Co (green), N (blue), O (red), C (gray). (b) View of the 2D sheet in **1** constructed by bi-furcated and tri-furcated H-bonding, between coordinated water molecules and free carboxylate oxygen atoms. (c) Supramolecular 3D arrangements in **1** by locking of 1D chains by H-bonding and π-π interaction (π-π interaction: pink dotted lines & H-bonding: cyan dotted lines).

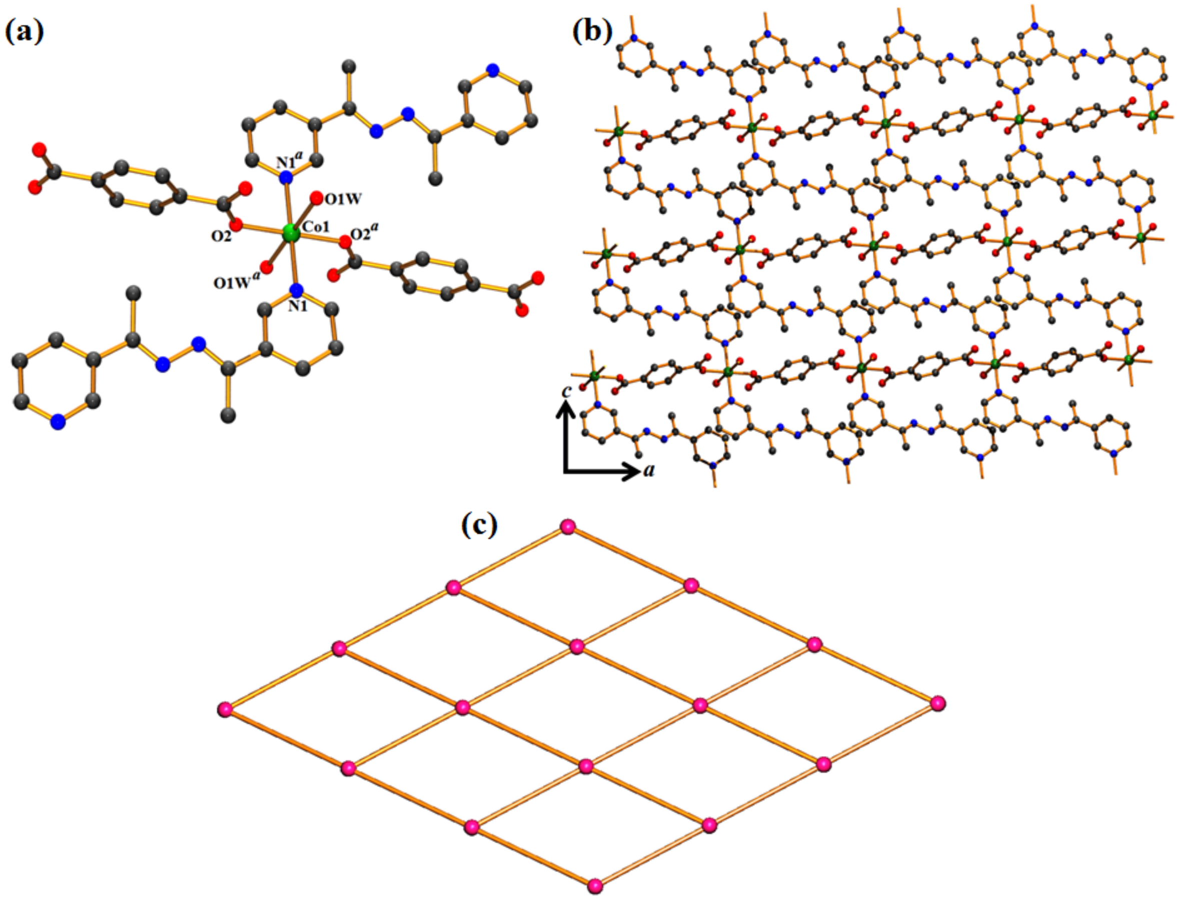

Fig. 2 (a) Coordination environment around Co(II) ions in **2**; Co (green), N (blue), O (red), C (gray). (b) Two-dimensional sheet structure in **2** constructed by benzene-1,4-dicarboxylate and 3-bpdh ligand. (c) 4-Connected 2D net in **2**.

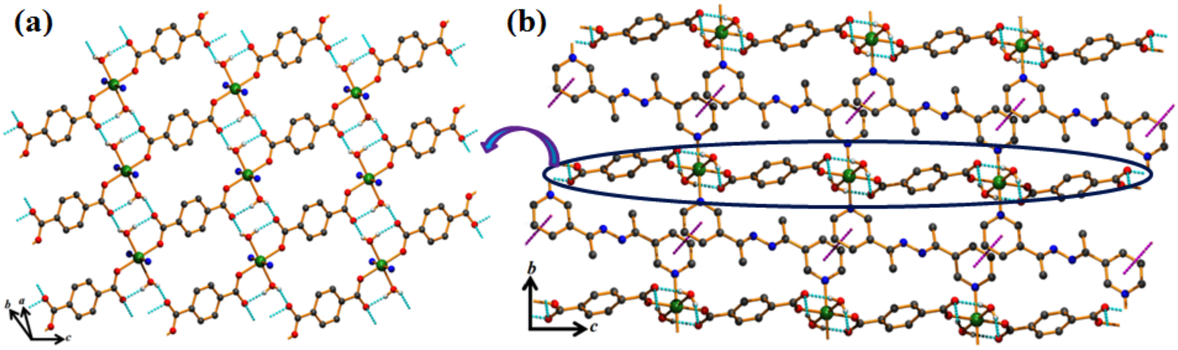

Fig. 3 (a) 1D metal carboxylate chains stitched by coordinated water molecules through bi-furcated H-bonding in **2**. (b) Supramolecular 3D arrangement in **2** by locking of 2D sheets by H-bonding and π-π interaction (π-π interaction: pink dotted lines & H-bonding: cyan dotted lines).

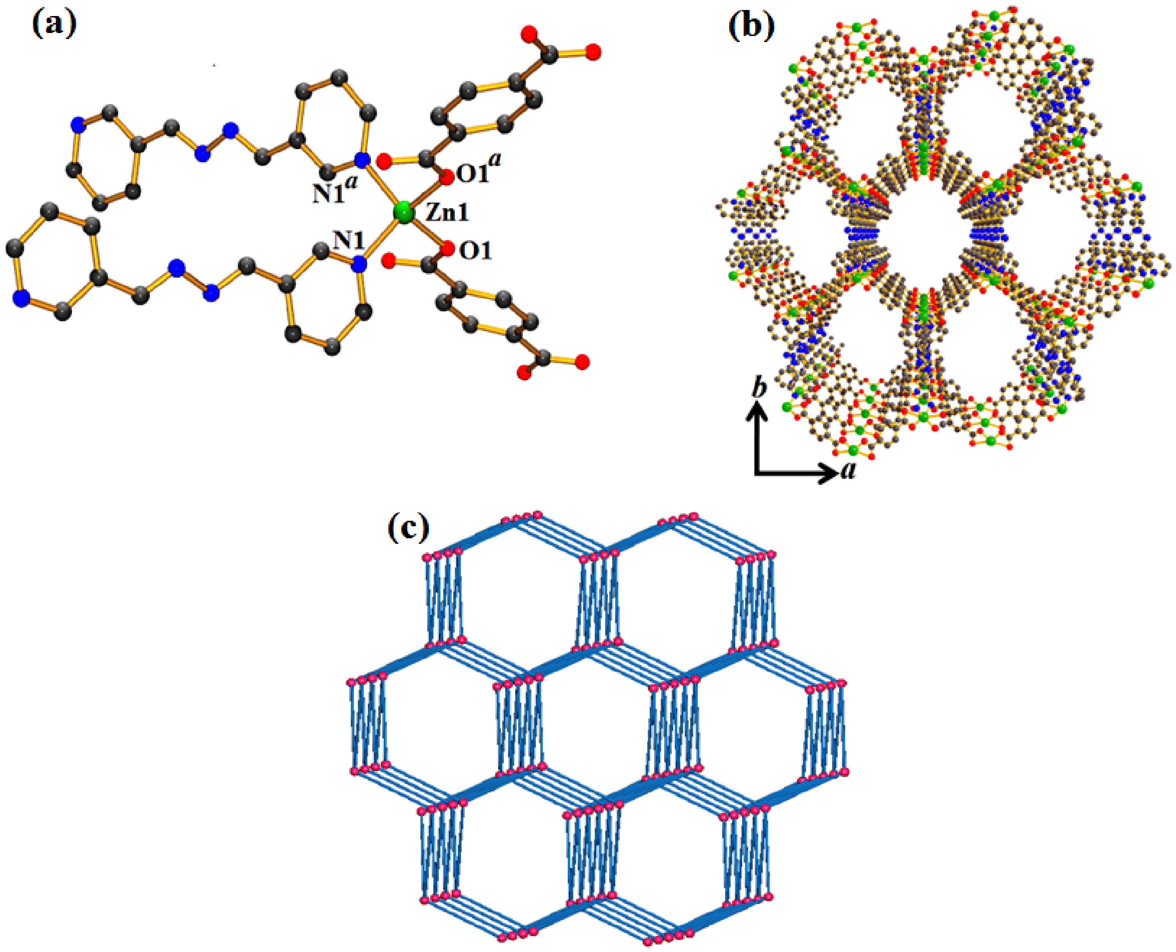

Fig. 4 (a) Coordination environment around Zn(II) ions in **3**; Zn (green), N (blue), O (red), C (gray). (b, c) A single 3D-diamondoid network showing large voids in **3**;

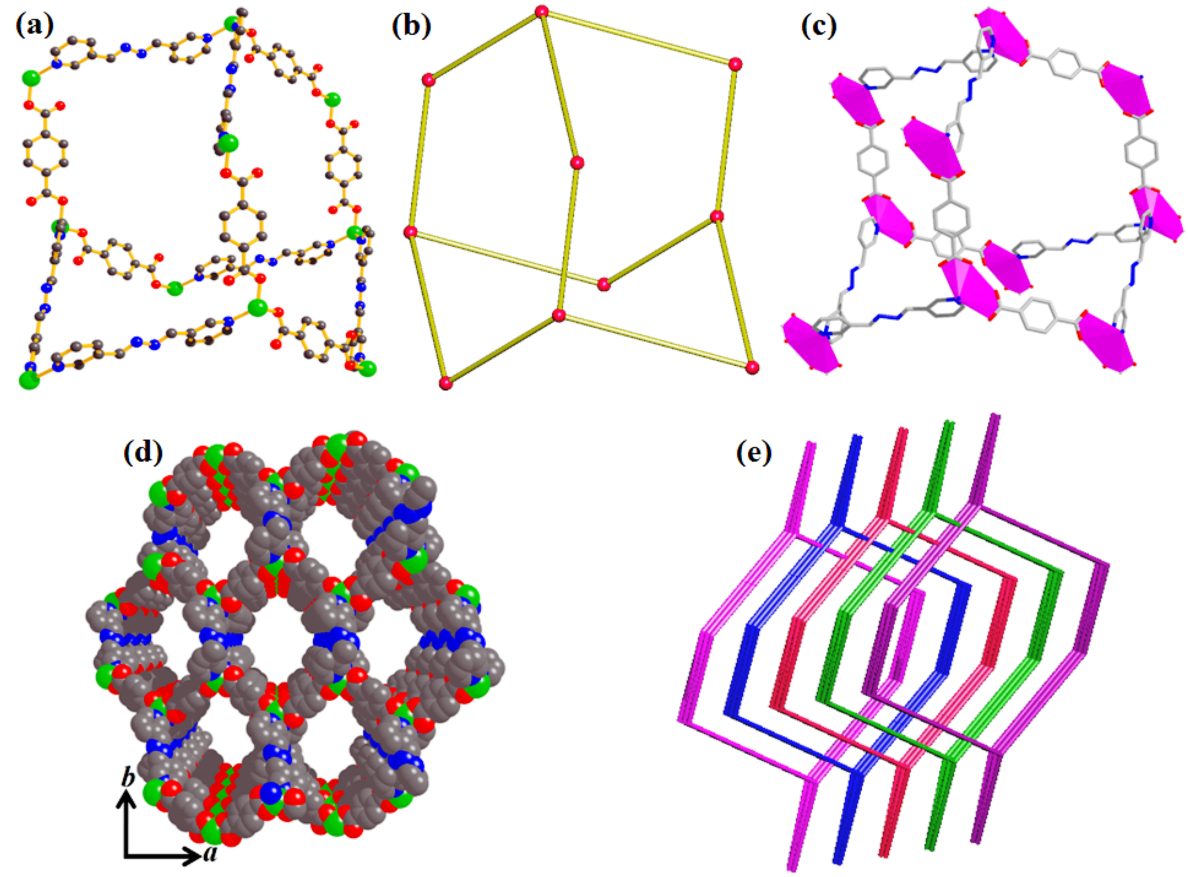

Fig. 5 (a, b, c) Perspective view of a single adamantoid cage generated through six 3-bpdb and six 1,4-bdc bridging ten Zn(II) centres in **3**. (d) Space filling model of a single 3D-diamondoid framework of **3**. (e) Topological representation of the five-fold interpenetrating diamondoid networks in **3**.

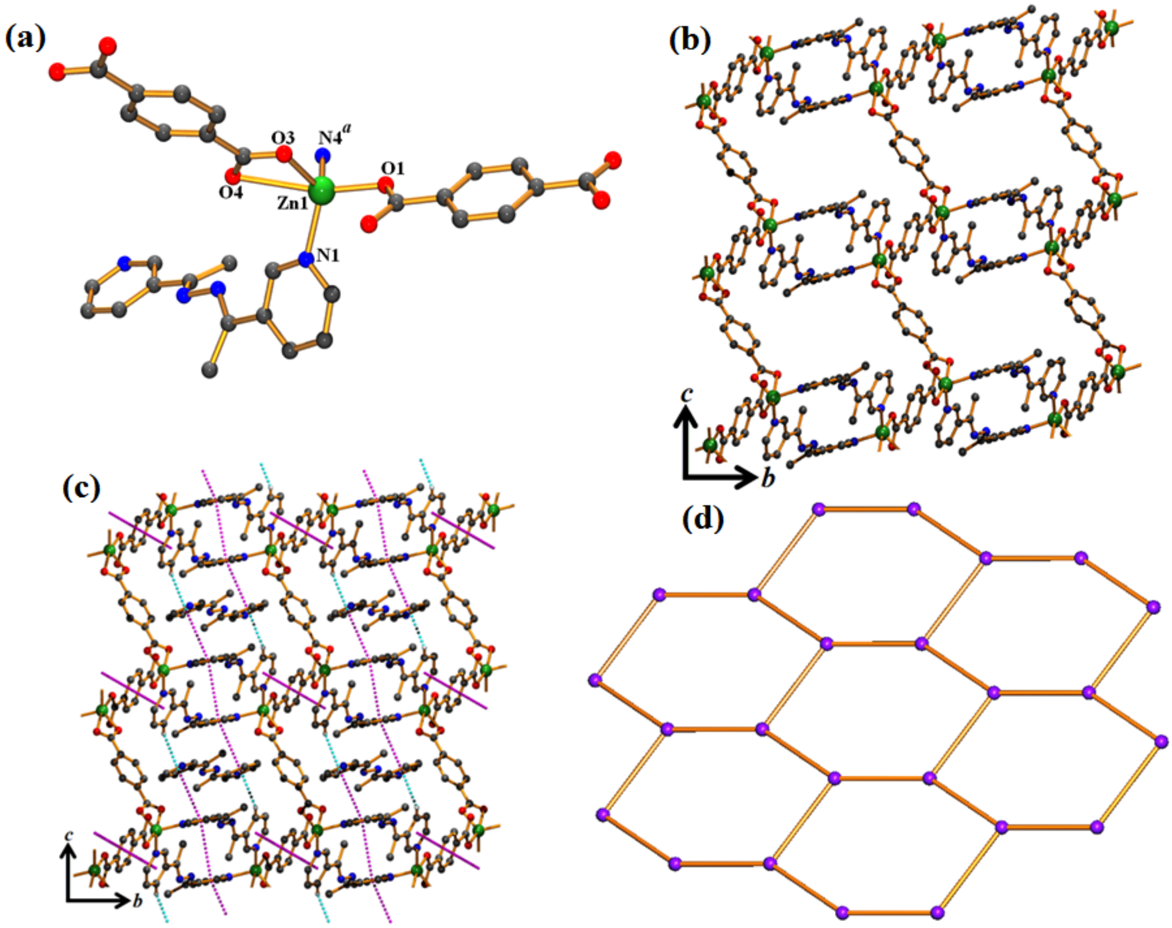

Fig. 6 (a) Coordination environment around Zn(II) ions in **4**; Zn (green), N (blue), O (red), C (gray). (b) Two-dimensional sheet structure in **4** constructed by benzene-1,4-bdc and 3-bpdh ligand. (c) Supramolecular 3D arrangement in **4** (π-π interaction: pink dotted lines & C-H-π: cyan dotted lines). (d) 3-Connected 2D net in **4**.

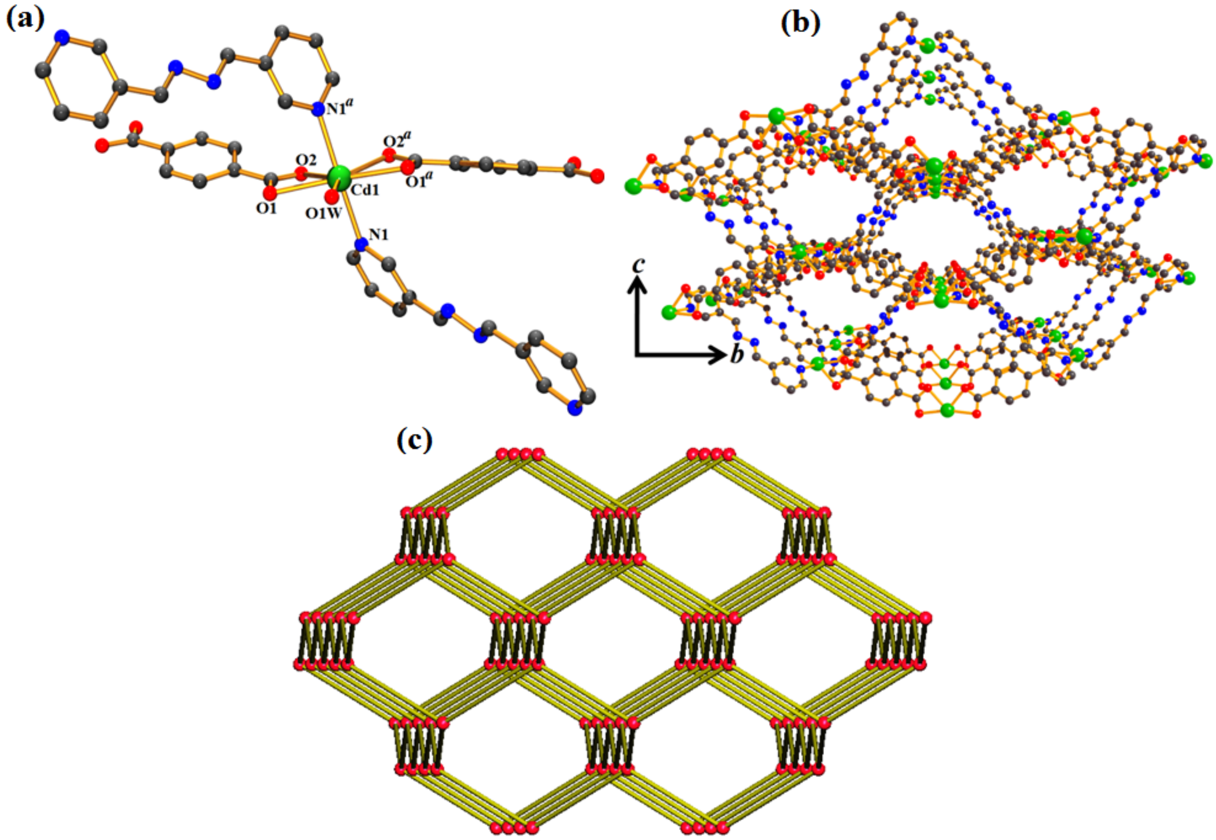

Fig. 7 (a) Coordination environment around Cd(II) ions in **5**; Cd (green), N (blue), O (red), C (gray). (b, c) A single 3D-diamondoid network showing large voids in **5**.

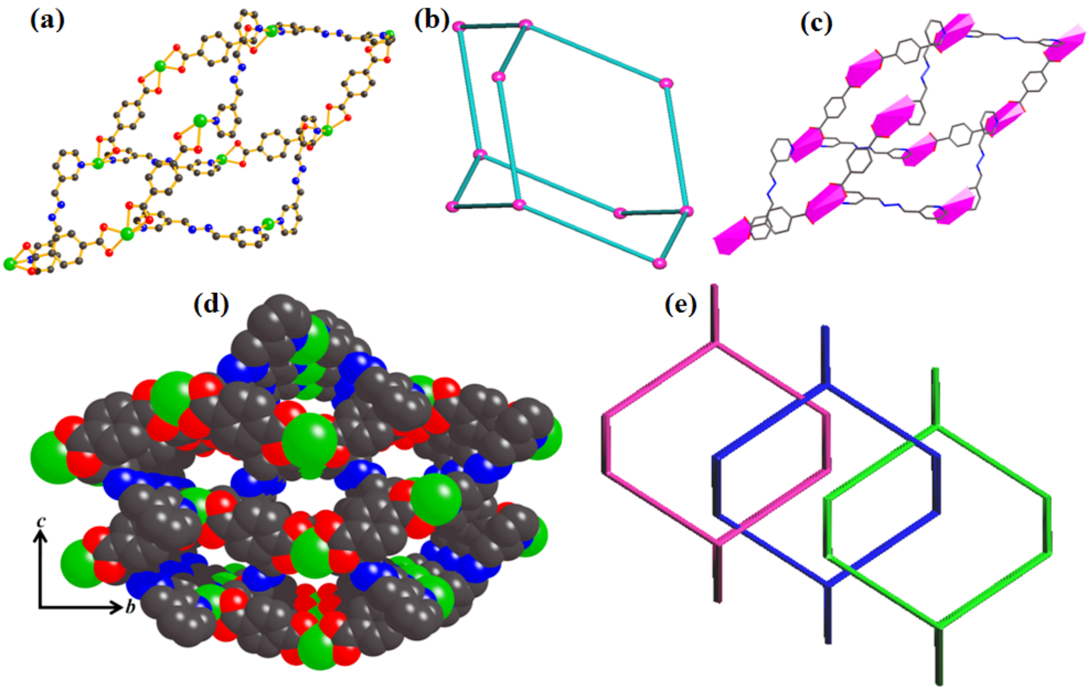

Fig. 8 (a, b, c) Perspective view of a single adamantoid cage generated through six 3-bpdb and six 1,4-bdc bridging ten Cd(II) centres in **5**. (d) Space filling model of a single 3D-diamondoid framework of **5**. (e) Topological representation of the three-fold interpenetrating diamondoid networks in **5**.

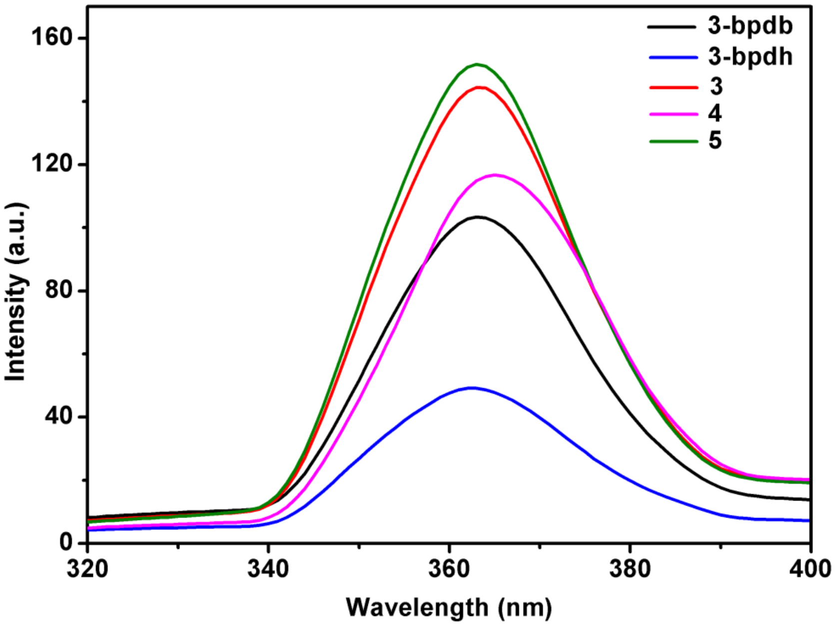

Fig. 9 The emission spectra for the free 3-bpdb, 3-bpdh ligands and compounds **3-5** in the solid state at room temperature.

Tables

Table 1 Crystallographic and structural refinement parameters for compounds **1-5**

	1	**2**	**3**	**4**	**5**
Formula	$C_{20}H_{26}CoN_4O_{10}$	$C_{22}H_{22}CoN_4O_6$	$C_{20}H_{14}N_4O_4Zn$	$C_{29}H_{25}N_6O_4Zn$	$C_{20}H_{16}Cd\,N_4O_5$
Formula Weight	541.38	497.37	439.74	586.94	504.78
Crystal System	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$C2/c$	$P\bar{1}$	$C2/c$
a/ Å	14.2985(4)	6.7280(2)	19.0040(4)	10.088(5)	15.976(5)
b/Å	12.5882(3)	8.6182(2)	6.6043(1)	12.001(5)	6.097(5)
c/ Å	14.4371(4)	10.0558(3)	15.8025(4)	12.044(5)	20.824(5)
α/°	90	97.302(1)	90	84.583(5)	90
β/°	112.007	97.195(1)	111.595(2)	67.262(5)	100.578(5)
γ/°	90	92.055(1)	90	82.802(5)	90
V/ Å3	2409.23(11)	572.99(3)	1844.13(7)	1332.5(10)	1993.9(18)
Z	4	1	4	2	4
D_c/ g cm^{-3}	1.482	1.441	1.584	1.463	1.682
μ /mm^{-1}	0.773	0.794	1.368	0.969	1.136
F(000)	1108	257	896	606	1008
θ range/°	1.7-27.5	2.1- 27.5	2.3-27.5	1.7-27.5	2.0-27.5
Reflections collected	39620	9701	14437	22008	15976
Unique reflections	5542	2626	2112	6082	2295
Reflections $I > 2\sigma(I)$	4208	2532	1897	4680	2088
R_{int}	0.022	0.017	0.028	0.033	0.037
goodness-of-fit (F^2)	1.06	1.08	1.09	1.05	1.04
$R1$ ($I > 2\sigma(I)$) ^{a}	0.0424	0.0295	0.0316	0.0396	0.0258
$wR2(I > 2\sigma(I))$ ^{a}	0.1347	0.0861	0.0907	0.0947	0.0580
Δρ max/min/e Å^3	-0.52, 0.79	-0.31, 0.76	-0.27, 0.41	-0.27,0.30	-0.28, 0.36

$^a R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma(w(F_o^{\,2} - F_c^{\,2})^2)/\Sigma w(F_o^{\,2})^2]^{½}$.

Table 2 Selected bond lengths (Å) and bond angles (°) for **1**

Co1-O1	2.0742(18)	Co1-O3W	2.1239(19)
Co1-N1	2.159(2)	Co1-O1^{b}	2.0742(18)
Co1-O3W^{b}	2.1239(19)	Co1-N1^{b}	2.159(2)
Co2-O1W	2.059(2)	Co2-O2W	2.081(2)
Co2-N4	2.176(2)	Co2-O1W^{a}	2.059(2)
Co2-O2W^{a}	2.081(2)	Co2-N4^{a}	2.176(2)
O1-Co1-O3W	93.66(7)	O1-Co1-N1	91.60(8)
O1-Co1-O1^{b}	180.00	O1-Co1-O3W^{b}	86.34(7)
O1-Co1-N1^{b}	88.40(8)	O3W-Co1-N1	92.14(8)
O1^{b}-Co1-O3W	86.34(7)	O3W-Co1-O3W^{b}	180.00
O3W-Co1-N1^{b}	87.86(8)	O1b-Co1-N1	88.40(8)
O3W^{b}-Co1-N1	87.86(8)	N1-Co1-N1^{b}	180.00
O1^{b}-Co1-O3W^{b}	93.66(7)	O1^{b}-Co1-N1^{b}	91.60(8)
O3W^{b}-Co1-N1^{b}	92.14(8)	O1W-Co2-O2W	88.19(9)
O1W-Co2-N4	90.20(8)	O1W-Co2-O1W^{a}	180.00
O1W-Co2-O2W^{a}	91.81(9)	O1W-Co2-N4^{a}	89.80(8)
O2W-Co2-N4	94.13(9)	O1W^{a}-Co2-O2W	91.81(9)
O2W-Co2-O2W^{a}	180.00	O2W-Co2-N4^{a}	85.87(9)
O1W^{a}-Co2-N4	89.80(8)	O2W^{a}-Co2-N4	85.87(9)
N4-Co2-N4^{a}	180.00	O1W^{a}-Co2-O2W^{a}	88.19(9)
O1W^{a}-Co2-N4^{a}	90.20(8)	O2W^{a}-Co2-N4^{a}	94.13(9)

Symmetry code: *a* = 3-x, 1-y, -z; *b* = 2-x, 1-y, 1-z.

Table 3 Hydrogen bonding interactions (Å, °) of **1**, **2** and **5**.

	D-H···A	D-H	H···A	D···A	∠D-H···A
1	O4W-H4WA···O5W^{i}	0.8500	1.8200	2.630(5)	159.00
	O4W-H4WB···O3	0.8500	1.9100	2.721(5)	160.00
	O1W-H1WA···O2^{ii}	0.80(4)	1.89(4)	2.671(3)	164(5)
	O1W-H1WB···O5W	0.81(4)	1.79(4)	2.578(4)	163(4)
	O2W-H2WA···O4^{iii}	0.87(4)	1.73(4)	2.576(4)	163(4)
	O2W-H2WB···O2^{ii}	0.80(5)	2.23(5)	2.927(3)	145(4)
	O3W-H3WA···O3^{iv}	0.75(4)	1.99(4)	2.747(3)	178(5)
	O3W-H3WB···O2	0.85(4)	1.99(4)	2.789(3)	157(3)
2					
	O1W-H1W···O1^{v}	0.80(3)	2.12(3)	2.8622(19)	155(3)
	O1W-H2W···O1	0.82(3)	1.84(3)	2.6442(18)	167(3)
5					
	O1W-H1W···O2^{vi}	0.79(4)	1.92(4)	2.659(4)	155(4)

Symmetry code: i = -3/2+x, 1/2-y, 1/2+z; ii = 5/2-x, 1/2+y, 1/2-z; iii = 2-x, 1-y, 1-z; iv = -1/2+x, 1/2-y, -1/2+z; v = -x, 1-y, 1-z; vi = x, -1+y, z.

Table 4 π-π interactions in **1**, **2**, **4** and C-H... π interaction in **4**.

	ring(i) → ring(j)	distance of centroid(i) from ring(j),(Å)	dihedral angle (i,j) (deg)	distance between the (i,j) ring centroids,(Å)
1	R(1)→ R(2)^{i}	3.7541(15)	5.82(12)	3.3547(10)
	R(2)→ R(1)^{i}	3.7541(15)	5.82(12)	3.4911(10)
2				
	R(1)→ R(1)^{ii}	3.6118(10)	0	3.2526(7)
4	R(1)→ R(1)^{ii}	4.227(2)	0	4.2131(10)
	R(1)→ R(5)^{iii}	3.928(2)	13.05(13)	3.7221(10)
	R(3)→ R(4)^{iv}	3.968(2)	8.00(10)	3.4427(9)
	R(3)→ R(4)^{ii}	3.968(2)	8.00(10)	3.4427(9)
	R(4)→ R(3)^{v}	3.968(2)	8.00(10)	3.6625(9)
	R(4)→ R(3)^{ii}	3.968(2)	8.00(10)	3.6625(9)
	R(5)→ R(1)^{iii}	3.928(2)	13.05(13)	3.7190(12)
4	C-H→ ring(j)	H...R distance (Å)	C-H...R angle (deg)	C...R distance (Å)
	C(14)-H(14)→R(4)^{vi}	2.83	124	3.435(3)

Symmetry code: i = 1-x, 1-y, 2-z; ii = 1-x, -y, 1-z; iii = x, y, z; iv = 1+x, -1+y, z; v = -1+x, 1+y, z; vi = 2-x, -y, -z.

R(i)/R(j) denotes the ith/jth rings in the corresponding structures: R(1)=N(1)/C(1)/C(2)/C(3)/C(4)/C(5); R(2)=N(4)/C(8)/C(9)/C(10)/C(11)/C(12); R(3)=N(4)/C(10)/C(11)/C(12)/C(13)/C(14); R(4)=C(16)/C(17)/C(18)/C(16a)/C(17a)/C(18a); R(5)=N(5)/C(23)/C(24)/C(25)/C(26)/C(27).

Table 5 Selected bond lengths (Å) and bond angles (°) for **2**

Co1-O1W	2.1354(12)	Co1-O2	2.0690(11)
Co1-N1	2.1679(13)	Co1-O1W^{a}	2.1354(12)
Co1-O2^{a}	2.0690(11)	Co1-N1^{a}	2.1679(13)
O1W-Co1-O2	90.78(5)	O1W-Co1-N1	91.27(5)
O1W-Co1-O1W^{a}	180.00	O1W-Co1-O2^{a}	89.22(5)
O1W-Co1-N1^{a}	88.73(5)	O2-Co1-N1	89.55(5)
O1W^{a}-Co1-O2	89.22(5)	O2-Co1-O2^{a}	180.00
O2-Co1-N1^{a}	90.45(5)	O1W^{a}-Co1-N1	88.73(5)
O2^{a}-Co1-N1	90.45(5)	N1-Co1-N1^{a}	180.00
O1W^{a}-Co1-O2^{a}	90.78(5)	O1W^{a}-Co1-N1^{a}	91.27(5)
O2^{a}-Co1-N1^{a}	89.55(5)		

Symmery code: *a* = 1-x ,1-y,1-z.

Table 6 Selected bond lengths (Å) and bond angles (°) for **3**

Zn1-O1	1.9476(16)	Zn1-N1	2.062(2)
Zn1-O1^{a}	1.9476(16)	Zn1-N1^{a}	2.062(2)
O1-Zn1-N1	105.20(7)	O1-Zn1-O1^{a}	99.73(6)
O1-Zn1-N1^{a}	122.54(7)	O1^{a}-Zn1-N1	122.54(7)
N1-Zn1-N1^{a}	103.28(8)	O1^{a}-Zn1-N1^{a}	105.20(7)

Symmetry code: *a* = 1-x, y, 1/2-z.

Table 7 Selected bond lengths (Å) and bond angles (°) for **4**

Zn1-O1	1.960(2)	Zn1-O3	1.9533(19)
Zn1-O4	2.727(2)	Zn1-N1	2.064(2)
Zn1-N4^{a}	2.077(2)		
O1-Zn1-O3	113.95(7)	O1-Zn1-O4	165.48(6)
O1-Zn1-N1	109.71(7)	O1-Zn1-N4^{a}	95.94(7)
O3-Zn1-O4	53.54(6)	O3-Zn1-N1	119.96(7)
O3-Zn1-N4^{a}	107.48(7)	O4-Zn1-N1	84.42(7)
O4-Zn1-N1^{a}	82.66(7)	N1-Zn1-N4^{a}	106.75(7)

Symmetry code: *a* = 2-x,-y,1-z.

Table 8 Selected bond lengths (Å) and bond angles (°) for **5**

Cd1-O1	2.446(3)	Cd1-O1^{a}	2.446(3)
Cd1-O1W	2.218(4)	Cd1-O2^{a}	2.381(3)
Cd1-O2	2.381(3)	Cd1-N1^{a}	2.374(3)
Cd1-N1	2.374(3)	O1^{a}-Cd1-O2	138.58(6)
O1-Cd1-O1W	83.78(4)	O1W-Cd1-N1^{a}	93.38(4)
O1-Cd1-O2	53.85(6)	O2-Cd1-N1	91.18(7)
O1-Cd1-N1	96.96(6)	O2^{a}-Cd1-N1^{a}	91.18(7)
O1-Cd1-O1^{a}	167.57(6)	O2-Cd1-O2^{a}	84.76(6)
O1-Cd1-O2^{a}	138.58(6)	O2-Cd1-N1^{a}	83.82(7)
O1-Cd1-N1^{a}	83.77(6)	O1^{a}-Cd1-N1	83.77(6)
O1W-Cd1-O2	137.62(4)	O2^{a}-Cd1-N1	83.82(7)
O1W-Cd1-N1	93.38(4)	N1-Cd1-N1^{a}	173.24(6)
O1^{a}-Cd1-O1W	83.78(4)	O1^{a}-Cd1-N1^{a}	96.96(6)
O1W-Cd1-O2^{a}	137.62(4)		

Symmetry code: *a* = 2-x, y, 3/2-z.

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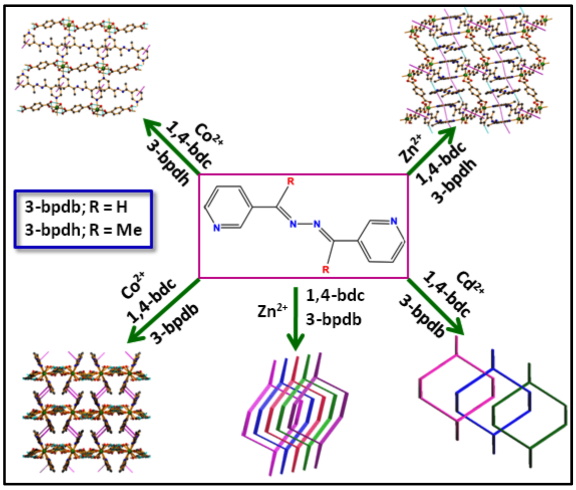

Five divalent metal coordination polymers based on two different azine based bent N,N′-donor ligand and 1,4-benzene dicarboxylate have been synthesized and characterized.