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Design and construction of coordination polymers based on 2,2'-dinitro-4,4'biphenyldicarboxylate and semi-rigid N-donor ligands: diverse structures and magnetic properties[†]

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Eight 2D and 3D coordination polymers, $[Mn(NBPDC)(1,4-bimb)]_n$ (1), $[Zn(NBPDC)(1,4-bimb)]_n$ (2), $[Cd(NBPDC)(1,4-bimb)]_n$ (3), $[Mn_2(NBPDC)_2(1,3-bimb)(H_2O)]_n$ (4), $\{Zn(NBPDC)(1,3-bimb)\}_n$ (5), $[Cd_2(NBPDC)_2(1,3-bimb)_2(H_2O)]_n$ (6), $[Mn(NBPDC)(4,4'-bimbp)]_n$ (7), and $[Cd_2(NBPDC)_2(4,4'-bimbp)_2]_n$ (8), (NBPDC = 2,2'-dinitro-4,4'-biphenyldicarboxyl acid, 1,4-bimb = 1,4-bis(imidazol-1-ylmethyl) benzene, 1,3-bimb = 1,3-bis(imidazol-1-ylmethyl) benzene, and 4,4'-bimbp = 4,4'- (bis(imidazol-1-ylmethyl) biphenyl), have been prepared and structurally characterized. In these coordination polymers, NBPDC and three N-donor ligands link different metal ions and SBUs to construct diverse architectures. Compounds 1 and 3 are isomorphic, showing a two-fold interpenetrating pcu topology. Compound 2 presents a 2D (4, 4) net. Compound 4 is a hex framework built by the linkage of ligands with infinite rod-shaped SBUs. Compound 5 presents a unprecedented eight-fold interpenetrating structure. Compound 7 presents a 3D hex topology, and compound 8 shows a (4, 4) net. The magnetic properties of compounds 1, 4, and 7 have been characterized. Compound 7 exhibits spin-canting antiferromagnetism.

Introduction

The design and construction of coordination polymers have attracted increasing attention in the field of crystal engineering due to their novel and diverse topologies and potential applications in many areas such as catalysis, gas adsorption and separation, optics, and magnetism.¹⁻⁵ An important task of crystal engineering is to synthesize coordination polymers with targeted structure and expected properties. However, the investigation into factors influencing the structural construction of functional compounds has been a challenge because too many factors can influence the structures of coordination polymers. These factors mainly include organic ligands, metal ions, pH value of solution and solvent effect, the ratio of metal-to-ligand and so on.⁶⁻⁹ Among these factors, the organic ligand is one of the most important factors because its length, flexibility, steric effects and angle of coordination atoms will lead in diverse structures of coordination polymers.¹⁰

Recently, coordination polymers based on two ligands such as polycarboxylate and N-donor ligands have attracted lasting research interest because of the possibility to easily obtain a controlled architecture by changing one of the two ligands.¹¹ In previous work, we have used the rigid NBPDC (NBPDC = 2.2'dinitro-4,4'-biphenyldicarboxyl acid) and the flexible ligands bpp (bpp = 1,3-bi(4-pyridyl)propane), bib (bib = 1,4-bis (imidazol)butane), and bip (bip = 1.5-bis(imidazol)pentane) to construct a series of coordination polymers.¹² In order to investigate the effect of length, flexibility, and angle of N-donor ligand on the structures of the coordination polymers, we chose three semi-rigid N-donor ligands 1,4-bis(imidazol-1-ylmethyl) benzene (1,4-bimb),¹³ 1,3-bis(imidazol-1-ylmethyl) benzene (1,3-bimb),^{13b,13h,14} 4,4'-(bis(imidazol-l-ylmethylene)) and biphenyl $(4,4'-bimbp)^{131,15}$ with different features as one of the mix ligands to construct coordination polymers (Scheme 1).

In this paper, eight coordination polymers exhibiting 2D or 3D structures were synthesized by reacting NBPDC and three



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Scheme 2 Schematic representation of the diverse coordination modes of NBPDC.

different N-donor ligands with different metal ions including Mn^{2+} , Zn^{2+} , and Cd^{2+} . The magnetic properties of compounds 1, 4, 7 have also been investigated.

Results and discussion

Description of crystal structures

Structure of [Mn(NBPDC)(1,4-bimb)]_n (1). The asymmetry unit of crystal 1 consists of one Mn(II) atom, one NBPDC molecule, and one 1,4- bimb molecule. The Mn(II) atom lies in a distorted octahedral coordination sphere occupied by four oxygen atoms from three different NBPDC molecules (Mn-O = 2.142-2.320 Å), and two nitrogen atoms of two 1,4-bimb molecules (Mn–N = 2.243-2.307 Å) (Fig. S1[†]). Two adjacent Mn(II) atoms are linked by a carboxyl group to form a Mn_2 unit. Each Mn2 unit links four Mn2 units around it through four NBPDC with mode A (Scheme 2) to construct a 2D layer along the bc plane (Fig. 1a). Two adjacent layers are interconnected through 1,4-bimb molecules along the *a* axis direction to build a 3D net (Fig. 1b). It is interesting that two identical 3D nets are interweaved together to form a two-fold interpenetrating network structure (Fig. 1c). From the view of topology, if Mn₂ clusters are viewed as nodes and the ligands as spacers, then crystal 1 will exhibit a pcu topology (Fig. S2[†]).

Structure of $[Zn(NBPDC)(1,4-bimb)]_n$ (2). The asymmetry unit of crystal 2 includes one Zn(II) atom, one NBPDC molecule, and one 1,4-bimb molecule. The Zn(II) atom is in tetrahedral configuration coordinated by two oxygen atoms from two different NBPDC molecules (Zn-O = 1.965-2.001 Å) and two nitrogen atoms of two 1,4-bimb (Zn-N = 1.993-2.038 Å) (Fig. S3†). NBPDC links two adjacent Zn(II) atoms with mode B (Scheme 2) along the *c* axis direction to construct a 1D zigzag chain (Fig. 2a). Two 1D chains are interconnected through 1,4bimb molecules to form a 2D wave-shaped layer with (4, 4) net (Fig. 2b, S4†). These layers construct the structure of compound 1 by weak interactions (Fig. S5†). The distance between the hydrogen atoms of methylene in 1,4-bimb and the carboxyl oxygen atoms of NBPDC is 2.68 Å.

Structure of [Cd(NBPDC)(1,4-bimb)]_n (3). Crystal 3 has the same structure as 1 except different metal atoms, so the structure of crystal 3 will not be depicted here.



Fig. 1 (a) 2D layer of crystal 1 (nitro groups of NBPDC and hydrogen atoms have been omitted for clarity), (b) 3D framework of crystal 1 (green: 1,4-bimb molecules; nitro groups of NBPDC and hydrogen atoms have been omitted for clarity), (c) two-fold interpenetrating network of crystal 1 (nitro groups of NBPDC and hydrogen atoms have been omitted for clarity).



Fig. 2 (a) 1D chain of crystal 2 (nitro groups of NBPDC and hydrogen atoms have been omitted for clarity), (b) 2D layer of crystal 2 (green: 1,4-bimb molecules; nitro groups of NBPDC and hydrogen atoms have been omitted for clarity).

O N C



Fig. 3 (a) 1D rod-shaped SBU of crystal 4, (b) 3D subnet of crystal 4 (nitro groups of NBPDC, hydrogen atoms, and free water molecules have been omitted for clarity), (c) 3D structure of crystal 4 (green and purple: 1,3-bimb molecules; nitro groups of NBPDC, hydrogen atoms, and free water molecules have been omitted for clarity).

Structure of $[Mn_2(NBPDC)_2(1,3-bimb)(H_2O)]_n$ (4). There are one Mn(II) atom, one NBPDC molecule, half of a 1,3-bimb molecule, and half of a free water molecule in the asymmetry unit of crystal 4. The Mn(II) is in a trigonal bipyramid geometry consisting of four oxygen atoms of NBPDC (Mn–O = 2.082–2.153 Å) and one nitrogen atom of the 1,3-bimb molecule (Mn–N = 2.190 Å) (Fig. S6†). Adjacent Mn(II) atoms are interconnected through carboxyl group oxygen atoms to form a 1D rod-shaped SBU (Fig. 3a). Each rod-shaped SBU links four adjacent rodshaped SBUs constructing a 3D subnet (Fig. 3b). NBPDC molecules exhibit mode C in crystal 4 (Scheme 2). 1,3-bimb molecules link two rod-shaped chains along the *a* axis direction to construct an extended 3D framework with hex topology (Fig. 3c, S7†).

Structure of {Zn(NBPDC)(1,3-bimb)}_{*n*} (5). Single crystal Xray analysis revealed that the asymmetric unit of 5 consists of one Zn(II) atom, one NBPDC molecule, and two half 1,3-bimb molecules. The Zn(II) atom is in a tetrahedral coordination sphere coordinated by two oxygen atoms (Zn–O = 1.966–1.968 Å) from two distinct NBPDC molecules and two nitrogen atoms (Zn–N = 2.004–2.006 Å) of two 1,3-bimb molecules (Fig. S8†). NBPDC molecules with mode B (Scheme 2) link two adjacent Zn(II) atoms to form a 1D zigzag chain along the *c* axis direction (Fig. 4a). Each 1D chain links three identical 1D chains through 1,3-bimb molecules to form a 3D framework with sra topology (Fig. 4b, 4c). An interesting feature of crystal



Fig. 4 (a) 1D chain of crystal 5 (nitro groups of NBPDC and hydrogen atoms have been omitted for clarity), (b) 3D framework of crystal 5 (purple: 1,3-bimb molecules; nitro groups of NBPDC, hydrogen atoms, and some disordered atoms have been omitted for clarity), (c) sra topology of crystal 5, (d) eight-fold interpenetrating sra topology of crystal 5.

5 is that eight identical 3D frameworks are interweaved together to form an eight-fold interpenetrating structure (Fig. 4d). To the best of our knowledge, a compound with eight-fold interpenetrating sra topology is unprecedented.

Structure of $[Cd_2(NBPDC)_2(1,3-bimb)_2(H_2O)]_n$ (6). The asymmetry unit of crystal 6 consists of two Cd(II) atoms, two NBPDC molecules, two 1,3-bimb molecules and one free water molecule. As shown in Fig. S9,† the two Cd(II) atoms are both



Fig. 5 (a) 1D chain of crystal 6 (nitro groups of NBPDC and hydrogen atoms have been omitted for clarity), (b) 2D layer of crystal 6 (green: 1,3-bimb molecules; nitro groups of NBPDC, hydrogen atoms, and free water molecules have been omitted for clarity), (c) four-fold interpenetrating network of crystal 6 (nitro groups of NBPDC, hydrogen atoms, and free water molecules have been omitted for clarity).

in distorted octahedral coordination spheres coordinated by four oxygen atoms of NBPDC (Cd–O = 2.284-2.501 Å) and two nitrogen atoms of 1,3-bimb molecules (Cd–N = 2.222-2.266 Å), respectively. Two adjacent Cd(II) atoms are interconnected by NBPDC molecules with mode D (Scheme 2) to construct a 1D zigzag chain along the *b* direction (Fig. 5a). The 1D chains are bridged by 1,3-bimb molecules to form a 2D layer (Fig. 5b). If Cd(II) atoms are viewed as nodes, the crystal will exhibit a rare (3, 4)-connected net with point (Schlafli) symbol for net: {6³} {6⁵.8}. It is interesting to note that each 2D layer interweaves with three adjacent layers to form a four-fold interpenetrating net (Fig. 5c, S10†). Free water molecules fill in the framework through H-bond interactions.

Structure of [Mn(NBPDC)(4,4'-bimbp)]_n (7). The asymmetry unit of crystal 7 includes two half Mn(II) atoms, one NBPDC molecule, and one 4,4'-bimbp molecule. Two Mn(II) atoms are both in octahedral configurations in which the six coordination sites of the Mn(II) atom are occupied by four oxygen atoms of four different NBPDC molecules (Mn–O = 2.191–2.220 Å) and two nitrogen atoms of 4,4'-bimbp molecules (Mn–N = 2.223–2.240 Å), respectively (Fig. S11†). Adjacent Mn(II) atoms are bridged by carboxyl group oxygen atoms to form a 1D rod-shaped SBU along the *a* direction (Fig. 6a). Two 1D chains are interconnected by biphenyl parts of NBPDC to form a 2D layer along the *ab* plane (Fig. 6b). Similar to crystal **4**, NBPDC





Fig. 6 (a) 1D rod-shaped SBU of crystal 7, (b) 2D layer of crystal 7 (nitro groups of NBPDC and hydrogen atoms have been omitted for clarity), (c) 3D framework of crystal 7 (purple: 4,4'-bimbp molecules; nitro groups of NBPDC and hydrogen atoms have been omitted for clarity).

molecules exhibit mode C in crystal 7. 4,4'-bimbp molecules link two adjacent layers constructing a 3D framework (Fig. 6c). From the view of topology, each rod-shaped SBU links six rodshaped SBUs around it through NBPDC and 4,4'-bimbp molecules to form a hex topology (Fig. S12†).

Structure of [Cd₂(NBPDC)₂(4,4'-bimbp)₂]_n (8). Crystal 8 possesses an asymmetry unit consisting of two Cd(II) atoms, two NBPDC molecules, and two 4,4'-bimbp molecules. The two Cd(II) atoms are both in distorted octahedral coordination environments coordinated by four oxygen atoms of NBPDC molecules (Cd–O = 2.328–2.423 Å) and two nitrogen atoms of 4,4'-bimbp molecules (Cd–N = 2.216–2.236 Å), respectively (Fig. S13†). NBPDC molecules with mode D bridge Cd(II) atoms to form a 1D chain along the *c* axis direction, which is further linked through 4,4'-bimbp molecules to construct a 2D layer along the *ac* plane with (4, 4) topology (Fig. 7, S14†). Two adjacent layers are linked through weak interactions to build a 3D supermolecular net. The distance between the hydrogen atoms of methylene in 4,4'-bimbp and the carboxyl oxygen atoms of NBPDC is 2.73 or 2.80 Å.

Effects of ligands and metal ions on the structure of compounds. As discussed above, NBPDC presents four different coordination modes, which link different metal ions to form various inorganic building blocks. NBPDC with mode A or C is inclined to construct clusters or infinite SBUs, whereas NBPDC with mode B or D tends to yield single metal atom building



Fig. 7 2D layer of crystal 8 (blue: 4,4'-bimbp molecules; nitro groups of NBPDC and hydrogen atoms have been omitted for clarity).

blocks. For example, the building blocks are clusters in crystals 1 and 3, and infinite rod-shaped SBUs in crystals 4 and 7; for the other compounds, the building blocks are single metal ions. The difference in building blocks is an important factor affecting the structural diversity of coordination polymers due to different coordination directions and coordination numbers. Another important factor is the three N-donor ligands (1,4-bimb, 1,3bimb, 4,4'-bimbp) with different bridging length and angle of the coordination atoms. This conclusion can be drawn by comparing the structures of crystal 2 and crystal 5. In the structures of crystals 2 and 5, NBPDC molecules with the same coordination modes bridge Zn(II) ions with the same configurations to construct similar 1D chains. However, they give different structures including (4, 4) and sra topologies due to different linking directions of two N-donor ligands. A similar conclusion can be achieved by comparing crystal 6 and crystal 8. The diverse structures afforded by different N-donor ligands may be attributed to spatial effect, linking length, angle of coordination atoms, matching of NBPDC and N-donor, etc. In addition, the metal centres also play an important role in constructing coordination polymers. The frameworks of the final compounds are related to coordination configurations of metal ions, metal radii, coordination environments, etc. A clear example is compounds 5 and 6. They have the same ligands but different structures because of different metal ions.

Magnetic properties. Variable temperature d.c. magnetic susceptibility data were measured at 1000 Oe in the temperature range 2–300 K. For 1, the $\chi_{\rm M}T$ value of approximately 4.61 cm³ K mol⁻¹ at room temperature is close to the expected spin-only value for an isolated Mn^{2+} ion (4.38 cm³ K mol⁻¹, g = 2.0) (Fig. 8). The value of $\chi_M T$ remains almost constant as the temperature is decreased until 120 K, then decreases very slowly to a minimum of 4.40 cm³ K mol⁻¹ at 54 K, then increases up to 6.7 cm³ K mol⁻¹ at 38 K and finally drops sharply upon further cooling. The Curie-Weiss fits above 54 K give Weiss constants of -2.17 K, demonstrating the presence of a very weak antiferromagnetic interaction between spin centres. The magnetic data above 54 K were fitted to the Hamilton equation $\hat{H} = -J\hat{S}_1\hat{S}_2$ with the best parameters g = 2.08 and J = -0.98 cm⁻¹. The negative value of J confirms the weak antiferromagnetic interaction again. The magnetic behavior below 54 K may be due to spin canting as described below.



Fig. 8 Temperature dependence of $\chi_m T$ and χ_m^{-1} of 1 at H = 1 kOe from 2 to 300 K.



Fig. 9 ZFC and FC curves at H = 100 Oe from 2 to 80 K of 1.

As shown in Fig. 9, the field-cooled (FC) and zero-fieldcooled (ZFC) susceptibities (100 Oe) diverge at about 50 K, indicating the irreversible transition of the weak ferromagnetism. Furthermore, the susceptibility in low temperature range is field dependent, as shown in Fig. S15,† which is consistent with spin canting. Further experimental evidence for the spin-canted weak ferromagnetism and magnetic phase transition in **1** comes from field-dependent isothermal magnetization measurements (Fig. 10). The magnetization value at 2 K and 5 T amounts to



Fig. 10 Plots of the magnetization (M) vs. H of 1 at 2 K. The inset shows the derivative of M at 2 K against H.



Fig. 11 Temperature dependence of $\chi_m T$ and χ_m^{-1} of **4** at H = 1 kOe from 2 to 300 K.

4.5 N β , which is smaller than the theoretical saturation value $(M_s = 5 \text{ N}\beta)$. A hysteresis loop (Fig. S16[†]) is observed with a coercive field of 150 Oe and a remnant magnetization of 0.014 N β . The respective canting angle, calculated from tan⁻¹ (M_r/M_s) , where M_r is the remnant magnetization, which is about 0.16°. Notably, the field-dependent magnetization at 2 K for compound 1 has an S-shaped curve, suggesting a metamagnetic behavior. The dM/dH *versus* H curve displays a relative maximum, implying the field-induced metamagnetic transition and the critical field is 20.1 kOe.

For 4, the $\chi_{\rm M}T$ value of approximately 4.00 cm³ K mol⁻¹ at room temperature is smaller than the spin-only one expected for a bivalent uncorrelated manganese ion (4.38 cm³ K mol⁻¹, g =2.0) (Fig. 11). The deviation from the expected value of $\chi_{\rm M}T$ at room temperature may be due to intramolecular antiferromagnetic interactions. A gradual decrease is observed from room temperature to 100 K, and below this temperature the $\chi_{\rm M}T$ value falls very sharply. The best fit with the Curie–Weiss law gives C= 4.20 cm³ mol⁻¹ K and θ = -12.87 K. The negative value of θ indicates the interaction between the spin centres is antiferromagnetic. The magnetic data over the whole temperature range could be well fitted by a Fisher 1D Heisenberg chain model (S = 5/2, $\hat{H} = -2J\hat{S}_{i}\hat{S}_{i}$ resulting in J = -2.32 cm⁻¹, g = 2.03 and R = 1.32 $\times 10^{-6}$ (*R* is defined as $[(\chi_{\rm M}) \text{obs} - (\chi_{\rm M}) \text{calcd}]^2 / [(\chi_{\rm M}) \text{obs}]^2$). We also present the isothermal magnetization curve (2 K) here (Fig. S17[†]). The magnetization value increases almost linearly with the applied magnetic field and reaches a value of 0.86 NB at 50 kOe, far from the saturation (5 N β) for an spin-only Mn²⁺ ion, confirming the antiferromagnetic interaction again.

For 7, at room temperature, the $\chi_M T$ value is about 4.00 cm³ K mol⁻¹, which is somewhat below the expected value for an isolated manganese ion and nearly keeps constant to 150 K. Below this temperature the $\chi_M T$ decreases smoothly and reaches a minimum value of 3.54 cm³ K mol⁻¹ at 50 K, then increases sharply to a maximum value of 4.62 cm³ K mol⁻¹ at 40 K, and finally drops rapidly upon further cooling (Fig. 12). The temperature dependence of the reciprocal susceptibility (χ^{-1}) above 54 K obeys the Curie–Weiss law with a Weiss constant of -2.93 K, indicating a weak intrachain antiferromagnetic interaction between the Mn²⁺ ions. The magnetic data above 54 K could be fitted by a Fisher 1D Heisenberg chain model (S = 5/2, $\hat{H} = -2J\hat{S}_i\hat{S}_j$) very well, resulting in J = -1.10 cm⁻¹, g = 2.00 and $R = 1.04 \times 10^{-7}$ (*R* is defined above).



Fig. 12 Temperature dependence of $\chi_m T$ and χ_m^{-1} of 7 at H = 1 kOe from 2 to 300 K.



Fig. 13 ZFC and FC curves at H = 100 Oe from 2 to 80 K of 7.

The low-temperature ferromagnetic-like behavior of 7 may be due to spin canting. The field-cooled (FC) and zero-field-cooled (ZFC) susceptibities are measured at 100 Oe in the range 2-80 K (Fig. 13). The divergence indicates the existence of weak ferromagnetism. Furthermore, the field dependence of the magnetization, M(H) at 2 K (Fig. S18⁺), shows a steady increase to 1.52 NB at 50 kOe, much less than the expected saturation value of 5 N β for one Mn²⁺ ion with S = 5/2 and g = 2, consistent with its observed spin-canted behavior. The hysteresis loop measured at 2 K is consistent with a weak ferromagnetism (Fig. S19[†]). The remnant magnetization is 0.0074 NB, and the coercive field is ca. 110 Oe. This confirms the behavior of weak ferromagnetism due to spin canting again, and the canting angle giving by the equation $\varphi = \tan^{-1}(M_r/M_s)$ is about 0.086°, where $M_{\rm r}$ is the remnant magnetization and $M_{\rm s} = gS$ is the expected saturation magnetization if all of the spins are aligned ferromagnetically.

Conclusions

Eight new coordination polymers exhibiting diverse structures have been synthesized by reacting NBPDC molecules and three N-donor ligands (1,4-bimb, 1,3-bimb, 4,4'-bimbp) with different metal ions. The diverse architectures and other interesting features of these compounds have been identified, such as different dimensional frameworks, molecular topology, interpenetration, and weak interactions (hydrogen bonding, π – π stacking interactions, *etc.*). The structural diversity indicates that organic ligands and metal ions can exert great influence on the structure of the final assembly. The magnetic properties of compounds 1, 4, and 7 have been studied.

Experimental

Materials and physical measurements

All reagents and solvents were commercially available except for NBPDC, (1,4-bimb), (1,3-bimb), and (4,4'-bimbp), which were synthesized according to the literature.¹⁶ Elemental analyses were performed on a Perkin-Elmer 2400 element analyzer. IR spectra were recorded on a Nicolet Impact 410 FTIR spectrometer using KBr pellet. PXRD data were collected on a Rigaku D/max 2550 X-ray Powder Diffractometer. Variabletemperature magnetic susceptibility data were obtained with SQUID magnetometer (Quantum Design, MPMS-5) in the temperature range 2-300 K by using an applied field of 1000Oe. Pascal's constants were used to estimate the diamagnetic corrections, which were subtracted from the experimental susceptibility to give the molar paramagnetic susceptibility (χ_m). Fluorescent emission spectra for the solid samples were recorded on a Perkin-Elmer LS 55 luminescence spectrometer. TG analysis was performed on a TGA Q500 V20.10 Build 36.

Synthesis of [Mn(NBPDC)(1,4-bimb)]_n (1). A mixture of NBPDC (0.054 g, 0.16 mmol), 1,4-bimb (0.072 g, 0.30 mmol), Mn(AC)₂ (0.061 g, 0.18 mmol), and H₂O (5 mL) was heated in a 20 mL Teflon-lined autoclave at 160 °C for 3 d, followed by slow cooling (5 °C h⁻¹) to room temperature. The resulting mixture was washed with water, and colorless block crystals were collected and dried in air. Yield: 28% (based on Mn). Elemental analysis (%): Calcd for 1: C 53.89, H 3.20, N 13.47. Found: C 54.01, H 3.15, N 13.42. IR (KBr, cm⁻¹): 3609(m), 3467(m), 3117(m), 1624(s), 1530(s), 1405(s), 1347(s), 1085(s), 781(s).

Synthesis of $[Zn(NBPDC)(1,4-bimb)]_n$ (2). The same synthetic procedure as for 1 was used except that $Mn(AC)_2$ was replaced by ZnCl₂, giving colorless block crystals. Yield: 35% (based on Zn). Elemental analysis (%): Calcd for 2: C 53.01, H 3.16, N 13.25. Found: C 53.22, H 3.09, N 13.24. IR (KBr, cm⁻¹): 3472 (m), 3132(m), 1697(m), 1619(s), 1525(s), 1384(s), 1336(s), 1242(s), 1096(s), 954(m), 761(m).

Synthesis of [Cd(NBPDC)(1,4-bimb)]_n (3). The same synthetic procedure as for 1 was used except that $Mn(AC)_2$ was replaced by Cd(NO₃)₂·4H₂O, giving colorless block crystals. Yield: 39% (based on Cd). Elemental analysis (%): Calcd for 3: C 49.35, H 2.94, N 12.34. Found: C 49.42, H 3.88, N 12.42. IR (KBr, cm⁻¹): 3483(m), 3106(s), 1975(w), 1609(s), 1530(s), 1394(s), 1352(s), 1090(s), 917(s), 786(s).

Synthesis of $[Mn_2(NBPDC)_2(1,3-bimb)(H_2O)]_n$ (4). The same synthetic procedure as for 1 was used except that 1,4-bimb was replaced by 1,3-bimb, giving colorless block crystals. Yield: 28% (based on Mn). Elemental analysis (%): Calcd for 4: C 49.09, H 2.27, N 10.91. Found: C 49.21, H 2.18, N 10.83. IR

(KBr, cm⁻¹): 3462(w), 3127(w), 3080(w), 1640(s), 1598(s), 1525(s), 1409(s), 1342(s), 1085(m), 781(s), 656(m).

Synthesis of $\{Zn(NBPDC)(1,3-bimb)\}_n$ (5). The same synthetic procedure as for 4 was used except that $Mn(AC)_2$ was replaced by $ZnSO_4 \cdot 7H_2O$, giving colorless block crystals. Yield: 32% (based on Zn). Elemental analysis (%): Calcd for 5: C 53.01, H 3.16, N 13.25. Found: C 53.32, H 3.02, N 13.21. IR (KBr, cm⁻¹): 3378(m), 3138(s), 1619(s), 1530(s), 1488(s), 1378 (s), 1242(s), 1117(s), 828(s), 786(s).

Synthesis of $[Cd_2(NBPDC)_2(1,3-bimb)_2(H_2O)]_n$ (6). The same synthetic procedure as for 4 was used except that $Mn(AC)_2$ was replaced by $Cd(AC)_2 \cdot 2H_2O$, giving colorless block crystals. Yield: 22% (based on Cd). Elemental analysis (%): Calcd for 6: C 48.70, H 3.04, N 12.18. Found: C 48.82, H 2.96, N 12.06. IR (KBr, cm⁻¹): 3541(m), 3132(m), 1588(s), 1525(s), 1478(m), 1405(s), 1347(s), 1237(m), 1090(s), 828(s), 729(s).

Synthesis of [Mn(NBPDC)(4,4'-bimbp)]_n (7). The same synthetic procedure as for 1 was used except that 1,4-bimb was replaced by 4,4'-bimbp, giving colorless block crystals. Yield: 35% (based on Mn). Elemental analysis (%): Calcd for 7: C 58.32, H 3.43, N 12.01. Found: C 58.25, H 3.48, N 12.06. IR (KBr, cm⁻¹): 3436(w), 3143(w), 1645(s), 1614(s), 1530(s), 1399 (s), 1342(s), 1085(m), 938(w), 823(w), 791(m).

Synthesis of $[Cd_2(NBPDC)_2(4,4'-bimbp)_2]_n$ (8). The same synthetic procedure as for 7 was used except that $Mn(AC)_2$ was replaced by $CdCl_2$, giving colorless block crystals. Yield: 41% (based on Cd). Elemental analysis (%): Calcd for 8: C 53.90, H 3.17, N 11.10. Found: C 53.85, H 3.28, N 11.02. IR (KBr, cm⁻¹): 3436(w), 3138(w), 1703(w), 1588(s), 1530(s), 1399(s), 1347(s), 1237(m), 1090(m), 833(m), 781(m).

X-Ray structure determinations. The data collection and structural analysis of crystals 1-3, 7, and 8 were performed on a Rigaku RAXIS-RAPID equipped with a narrow-focus, 5.4 kW sealed tube X-ray source (graphite-monochromated Mo-Ka radiation, $\lambda = 0.71073$ Å). The data processing was accomplished with the PROCESS-AUTO processing program. The data collection and structural analysis of crystals 4-6 were performed on a Bruker SMART CCD diffractometer equipped with a graphite monochromator. The SMART software was used for data collection, for indexing the reflections and for determining the unit cell parameters; the collected data were integrated by using the SAINT software. All data were collected at a temperature of 20 \pm 2 °C. Direct methods were used to solve the structure using the SHELXL crystallographic software package. All non-hydrogen atoms were easily found from the difference Fourier map. All non-hydrogen atoms were refined anisotropically. Basic information pertaining to crystal parameters and structure refinement is summarized in Table S1.[†]

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