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Syntheses and crystal structures of 1D tubular chains and 2D polycatenanes built from the asymmetric 1-(1-imidazolyl)-4-(imidazol-1-ylmethyl)benzene ligand with metal salts†

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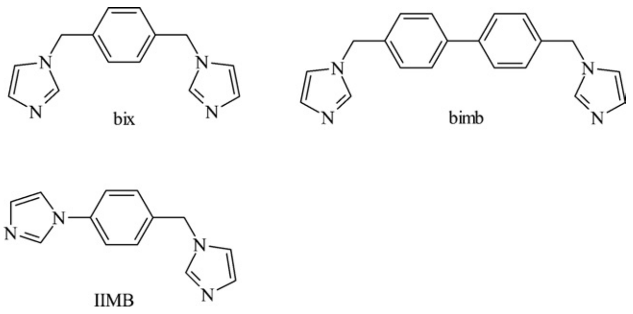
Reactions of a new asymmetric ligand, 1-(1-imidazolyl)-4-(imidazol-1-ylmethyl)benzene (IIMB), with various metal [Cd(II), Mn(II), Zn(II)] salts led to the formation of molecular, one- (1D) and two-dimensional (2D) architectures $[Cd(IIMB)_2(H_2O)(SO_4)]\cdot 7.5H_2O$ **1**, $[Cd(IIMB)_2Cl_2]\cdot H_2O$ **2**, $[Cd(IIMB)_4(H_2O)_2](NO_3)_2\cdot 5H_2O$ **3**, $[Cd(IIMB)(OAc)_2]\cdot H_2O$ **4**, $[Mn(IIMB)_2(SO_4)(H_2O)]\cdot 8.2H_2O$ **5**, $[Mn(IIMB)_4(H_2O)_2]Cl_2\cdot 5H_2O$ **6** and $[Zn(IIMB)_2]_4(NO_3)_8\cdot 13.5H_2O$ **7**. All the structures were established by single-crystal X-ray diffraction analysis. Both compounds **1** and **5** with sulfate anion are 2D polycatenanes formed by the interlocking of 1D double-stranded chains, while **2** and **4** with chloride and acetate anions are 1D chains. The results provide nice examples of topologies of metal-organic frameworks controlled by the counter anions. Interestingly, **3** and **6** are discrete molecular complexes with monometallic cores and form 2D networks through strong intermolecular hydrogen bonds. Complex **7**, obtained under the same conditions as **3**, is a 1D tubular chain. The structural difference between **3** and **7** suggests the metal ions also have a significant effect on the construction of supramolecular architectures. Furthermore, the photoluminescence properties of these compounds were investigated in the solid state at room temperature.

Introduction

Construction of supramolecules with novel structures and topologies have attracted great interest from chemists because of their potential applications in material science, medicine, chemical technology, *etc.*[1] In the previous reports, there are several strategies to construct pre-designed metal-organic frameworks (MOFs),[2] for example using rationally designed organic ligands and/or elaborately chosen metal salts with defined coordination geometries, introducing non-covalent weak interactions such as hydrogen bonds, π-π interactions or even hydrophobic forces.[3] However, the self-assembly process is complex and frequently influenced by factors such as solvent, template, pH of solution, geometric requirements of the metal ions, counter ions and even the synthesis conditions.[4] Therefore, much more work is required to achieve information of the relevant structural types and establish the proper relationship between the structures and properties. In the past decades, extensive work has been carried out and a variety of one- (1D), two- (2D) and three-dimensional (3D) frameworks with specific topologies and interesting properties have been obtained. It has been recognized that the use of bridging ligands to tune the supramolecular architectures has become a key step during the self-assembly process. For example, the flexible bridging ligand 1,4-bis(imidazole-1-ylmethyl)benzene (bix, Scheme 1) gave an infinite 2D polyrotaxane network by reaction with silver(I) nitrate or zinc(II) nitrate hexahydrate, and an infinite 1D chain with manganese(II) nitrite.[5] Recently, an infinite 3D entanglement network was obtained by the reaction of bix and cobalt sulfate.[5d]



Scheme 1 Ditopic ligands bix, bimb and IIMB.

We focus our attention on the design and synthesis of MOFs with specific topologies and properties by using flexible imidazole-containing ligands such as 4,4′-bis(imidazole-1-ylmethyl)-biphenyl (bimb), 1,3,5-tris(imidazol-1-ylmethyl)benzene (TIB) and 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (TITMB).[6] In our previous studies, the ligand bimb was synthesized to detect the effect of π-π interactions on the formation of the supramolecular architectures and to study the influence of the spacer group on the MOFs.[6a,b] As an extension of our studies,[6,7] we have designed and prepared a new imidazole-containing ligand, 1-(1-imidazolyl)-4-(imidazol-1-ylmethyl)-benzene (IIMB), and its reactions with various metal salts were carried out. In this paper, we report the syntheses, crystal structures and photoluminescence properties of complexes $[Cd(IIMB)_2(H_2O)(SO_4)]\cdot 7.5H_2O$ (**1**), $[Cd(IIMB)_2Cl_2]\cdot H_2O$ (**2**),

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† Electronic supplementary information (ESI) available: tables of bonding parameters for compounds **1**–**7**; additional figures of the crystal structures; the excitation and emission spectra of compounds **1**–**4** and **7**. See http://www.rsc.org/suppdata/nj/b3/b315842j/

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$[Cd(IIMB)_4(H_2O)_2](NO_3)_2\cdot5H_2O$ (**3**), $[Cd(IIMB)(OAc)_2]\cdot H_2O$ (**4**), $[Mn(IIMB)_2(SO_4)(H_2O)]\cdot8.2H_2O$ (**5**), $[Mn(IIMB)_4(H_2O)_2]Cl_2\cdot5H_2O$ (**6**) and $[Zn(IIMB)_2]_4(NO_3)_8\cdot13.5H_2O$ (**7**) obtained by reactions of IIMB with the corresponding metal salts. To the best of our knowledge, compounds **1** and **5** are the first examples of 2D polycatenanes formed by interlocking of 1D double-stranded chains.

Experimental

Materials and measurements

All commercially available chemicals are of reagent grade and used as received without further purification. Solvents were purified by standard methods prior to use. Elemental analyses of C, H and N were taken on a Perkin–Elmer 240C elemental analyzer, at the Center of Materials Analysis, Nanjing University. 500 MHz ^1H NMR spectra were measured on a Bruker DRX-500 NMR spectrometer at room temperature. The luminescent spectra for the powdered solid samples were recorded at room temperature on an Aminco Bowman Series 2 spectrofluorometer with a xenon arc lamp as the light source. In the measurements of emission and excitation spectra the pass width was 5.0 nm. All the measurements were carried out under the same experimental conditions.

Syntheses

Synthesis of IIMB. The ligand 1-(1-imidazolyl)-4-(imidazol-1-ylmethyl)benzene (IIMB) was synthesized by the Ullmann condensation method between imidazole and 1-bromo-4-(imidazol-1-ylmethyl)benzene, which was prepared by reaction of 4-bromobenzyl bromide with imidazole under alkaline conditions.[8] Reaction of imidazole (4.1 g, 60 mmol), sodium hydroxide (2.6 g, 65 mmol) and 4-bromobenzyl bromide (15.0 g, 60 mmol) in dimethylsulfoxide (DMSO; 80 mL) solution was carried out following the procedures reported for preparation of TITMB as described previously,[8b] to give 12.1 g (85%) 1-bromo-4-(imidazol-1-ylmethyl)benzene. 1-Bromo-4-(imidazol-1-ylmethyl)benzene (12.1 g, 51 mmol), imidazole (3.0 g, 56 mmol), K_2CO_3 (7.8 g, 56 mmol) and $CuSO_4$ (1.25 g, 5 mmol) were mixed and heated at 180 °C for 12 h under a nitrogen atmosphere. After being cooled to room temperature, the reaction mixture was washed by water and the residue was extracted by CH_2Cl_2 (5×30 mL). The organic layer was separated, dried over sodium sulfate and evaporated to dryness to give the crude product of IIMB, which was recrystallized from dichloromethane and petroleum ether. Yield: 8.11 g (71%). ^1H NMR (500 MHz, D_2O): δ 7.89 (s, 1H), 7.65 (s, 1H), 7.34 (s, 1H), 7.32 (d, 2H), 7.23 (d, 2H), 7.02 (s, 1H), 7.01 (s, 1H), 6.90 (s, 1H), 5.12 (s, 2H). Anal. Calcd for $C_{13}H_{12}N_4$: C, 69.62; H, 5.39; N, 24.98. Found: C, 69.68; H, 5.50; N, 25.03.

$[Cd(IIMB)_2(H_2O)(SO_4)]\cdot7.5H_2O$, 1. A solution of IIMB (67.2 mg, 0.3 mmol) and $CdSO_4\cdot2.7H_2O$ (38.5 mg, 0.15 mmol) in water (15 mL) was sealed in a stainless steel vessel and placed in an oven at 120 °C for 3 days. The resulting colorless crystals of **1** were collected in 81% yield. Anal. Calcd for $C_{26}H_{41}CdN_8O_{12.50}S$: C, 38.55; H, 5.10; N, 13.83. Found: C, 38.56; H, 4.96; N, 13.79%.

$[Cd(IIMB)_2Cl_2]\cdot H_2O$, 2. A solution of IIMB (44.8 mg, 0.2 mmol) in ethanol (7 mL) was layered over a solution of $CdCl_2\cdot2.5H_2O$ (22.8 mg, 0.1 mmol) in water (5 mL). Colorless single crystals of **2** suitable for X-ray diffraction analysis were obtained by slow inter-layer diffusion in 45% yield. Anal. Calcd for $C_{26}H_{26}CdCl_2N_8O$: C, 48.00; H, 4.06; N, 17.21. Found: C, 48.05; H, 4.03; N, 17.24%.

$[Cd(IIMB)_4(H_2O)_2](NO_3)_2\cdot5H_2O$, 3. A solution of $Cd(NO_3)_2\cdot4H_2O$ (23.1 mg, 0.075 mmol) in water (10 mL) was added to a solution of IIMB (67.2 mg, 0.3 mmol) in MeOH (20 mL). The mixture was stirred for *ca.* 10 min, then filtered. The compound **3** was obtained by slow evaporation of the filtrate at room temperature in 54% yield. Anal. Calcd for $C_{52}H_{62}CdN_{18}O_{13}$: C, 49.59; H, 4.96; N, 20.02. Found: C, 49.63; H, 5.01; N, 19.98%.

$[Cd(IIMB)(OAc)_2]\cdot H_2O$, 4. A solution of IIMB (44.8 mg, 0.2 mmol) and $Cd(OAc)_2\cdot2H_2O$ (53.3 mg, 0.2 mmol) in water (20 mL) was stirred for *ca.* 1.5 h at room temperature. Then the solvent was removed under reduced pressure and the residue was dissolved in *N*,*N*-dimethylformamide (DMF; 10 mL) and filtered. Colorless single crystals of **4** suitable for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into the above filtrate at room temperature over several days. The yield was *ca.* 51%. Anal. Calcd for $C_{17}H_{20}CdN_4O_5$: C, 43.19; H, 4.26; N, 11.85. Found: C, 43.33; H, 4.31; N, 11.86%.

$[Mn(IIMB)_2(SO_4)(H_2O)]\cdot8.2H_2O$, 5. A solution of $MnSO_4\cdot H_2O$ (16.9 mg, 0.1 mmol) in water (10 mL) was added to a solution of IIMB (44.8 mg, 0.2 mmol) in water (10 mL). The mixture was stirred for *ca.* 20 min, then filtered. The compound **5** was obtained by slow evaporation of the filtrate at room temperature in 75% yield. Anal. Calcd for $C_{26}H_{42.43}N_8MnO_{13.22}S$: C, 40.79; H, 5.59; N, 14.64. Found: C, 40.79; H, 5.53; N, 14.75%.

$[Mn(IIMB)_4(H_2O)_2]Cl_2\cdot5H_2O$, 6. A solution of $MnCl_2\cdot4H_2O$ (9.9 mg, 0.05 mmol) in water (10 mL) was added to a solution of IIMB (44.8 mg, 0.2 mmol) in water (10 mL). The mixture was stirred for *ca.* 20 min, then filtered. The compound **6** was obtained by slow evaporation of the filtrate at room temperature in 63% yield. Anal. Calcd For $C_{52}H_{62}Cl_2N_{16}MnO_7$: C, 54.36; H, 5.44; N, 19.50. Found: C, 54.15; H, 5.52; N, 19.47%.

$[Zn(IIMB)_2]_4(NO_3)_8\cdot13.5H_2O$, 7. A solution of $Zn(NO_3)_2\cdot6H_2O$ (29.7 mg, 0.1 mmol) in water (20 mL) was added to a solution of IIMB (44.8 mg, 0.2 mmol) in MeOH (10 mL). The mixture was stirred for *ca.* 10 min, then filtered. The compound **7** was obtained by slow evaporation of the filtrate at room temperature in 48% yield. Anal. Calcd for $C_{104}H_{123}N_{40}O_{37.50}Zn_4$: C, 44.69; H, 4.44; N, 20.05. Found: C, 44.75; H, 4.57; N, 19.86%.

Crystallographic analyses

The X-ray diffraction measurements for compounds **1**–**7** were carried out on a Rigaku RAXIS-RAPID imaging plate diffractometer at 200 K, using graphite-monochromated Mo-Kα radiation ($\lambda = 0.7107$ Å). The structures were solved by direct methods using SIR92[9] and expanded using Fourier techniques.[10] One of the lattice water molecules with the O6 atom in **3** was disordered into two positions with site occupation factors of 0.672(11) and 0.328(11). The O3 atom (from one of the uncoordinated water molecules) in **6** has two positions with site occupation factors of 0.68(3) and 0.32(3). The O41, O42, O43 atoms in **7** are part of one nitrate ion and have two positions with site occupation factors of 0.640(8) and 0.360(8). The O83 and N8 atoms in **7** are part of one nitrate ion and have two positions with site occupation factors of 0.640(8) and 0.360(8). The nitrate ion with O71, O72, O73 and N7 atoms in **7** is disordered into two positions with site occupation factors of 0.515(9) and 0.485(9). In addition, two imidazole groups and two nitrate anions of **7** are also disordered into two positions. All the non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method except for the O43, N8, N8B atoms in **7**, which were refined isotropically. The crystal parameters, data collection and refinement results for the compounds **1**–**7** are summarized in Table 1. Selected

Table 1 Crystal data and refinement parameters for compounds **1–7**

	1	**2**	**3**	**4**	**5**	**6**	**7**
Empirical formula	$C_{26}H_{41}CdN_8O_{12.5}S$	$C_{26}H_{26}CdCl_2N_8O$	$C_{52}H_{62}CdN_{18}O_{13}$	$C_{17}H_{20}CdN_4O_5$	$C_{26}H_{42.43}N_8MnO_{13.22}S$	$C_{52}H_{62}Cl_2N_{16}MnO_7$	$C_{104}H_{123}N_{40}O_{37.50}Zn_4$
Formula weight	810.13	649.85	1259.60	472.77	765.56	1149.02	2794.90
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$C2/c$	P-1	Cc	$P2_1/n$	$C2/c$	$C2/c$	P-1
a/Å	19.5212(13)	8.8980(5)	29.0122(9)	8.8280(4)	19.26(2)	28.14(3)	14.8166(3)
b/Å	13.7568(11)	12.7568(5)	12.1985(4)	9.2669(3)	14.45(2)	12.158(11)	18.2768(4)
c/Å	26.832(2)	14.3176(3)	16.5499(6)	23.8138(9)	26.80(6)	16.671(14)	24.8929(6)
α/deg	90.00	63.556(2)	90.00	90.00	90.00	90.00	69.9171(5)
β/deg	111.705(3)	80.625(2)	104.8848(8)	91.6407(13)	111.39(11)	103.24(8)	75.1473(7)
γ/deg	90.00	70.607(2)	90.00	90.00	90.00	90.00	88.2844(9)
U/Å^3	6694.8(9)	1372.37(10)	5660.6(3)	1947.37(13)	6944(20)	5553(9)	6107.1(2)
Z	8	2	4	4	8	4	2
T/K	200	200	200	200	200	200	200
μ/mm^{-1}	0.789	1.026	0.466	1.156	0.514	0.400	0.875
Data collected	25 589	13 243	27 476	18 748	32 105	25 099	58 919
Indep. reflections	7477	6250	12 738	4442	7919	6349	27 718
R_{int}	0.0962	0.0611	0.0650	0.0665	0.0883	0.0700	0.0569
Obs. reflections	4803	3916	7024	3078	4558	3414	14 007
R [$I > 2\sigma(I)$]	0.0616	0.0424	0.0487	0.0360	0.0580	0.0607	0.1005
wR [$I > 2\sigma(I)$]	0.1457[a]	0.0630[b]	0.1124[c]	0.0605[d]	0.1605[e]	0.1571[f]	0.2823[g]
R (all data)	0.1038	0.0941	0.0852	0.0691	0.0949	0.1081	0.1777
wR (all data)	0.1577	0.0715	0.1206	0.0657	0.1735	0.1765	0.3211

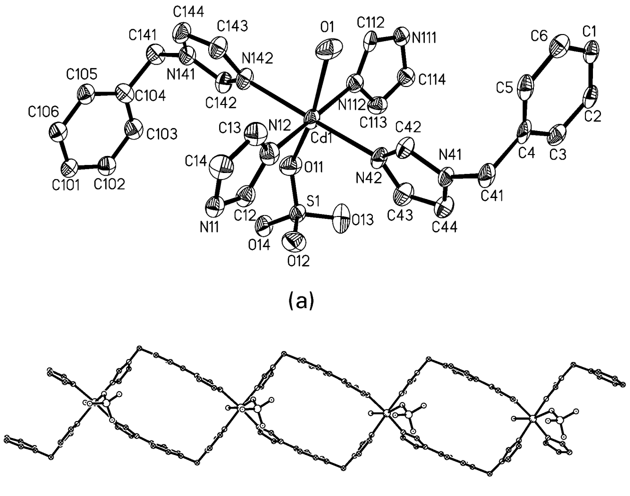
[a] $w = 1/[\sigma^2(F_o^2) + (0.0829P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. [b] $w = 1/[\sigma^2(F_o^2) + (0.0279P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. [c] $w = 1/[\sigma^2(F_o^2) + (0.0638P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. [d] $w = 1/[\sigma^2(F_o^2) + (0.0293P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. [e] $w = 1/[\sigma^2(F_o^2) + (0.0986P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. [f] $w = 1/[\sigma^2(F_o^2) + (0.1020P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. [g] $w = 1/[\sigma^2(F_o^2) + (0.1414P)^2 + 20.4991P]$, where $P = (F_o^2 + 2F_c^2)/3$.

bond length and angles are listed in Table S1 [Electronic supplementary information (ESI)]. Further details are provided in the ESI.‡

Results

Description of crystal structures

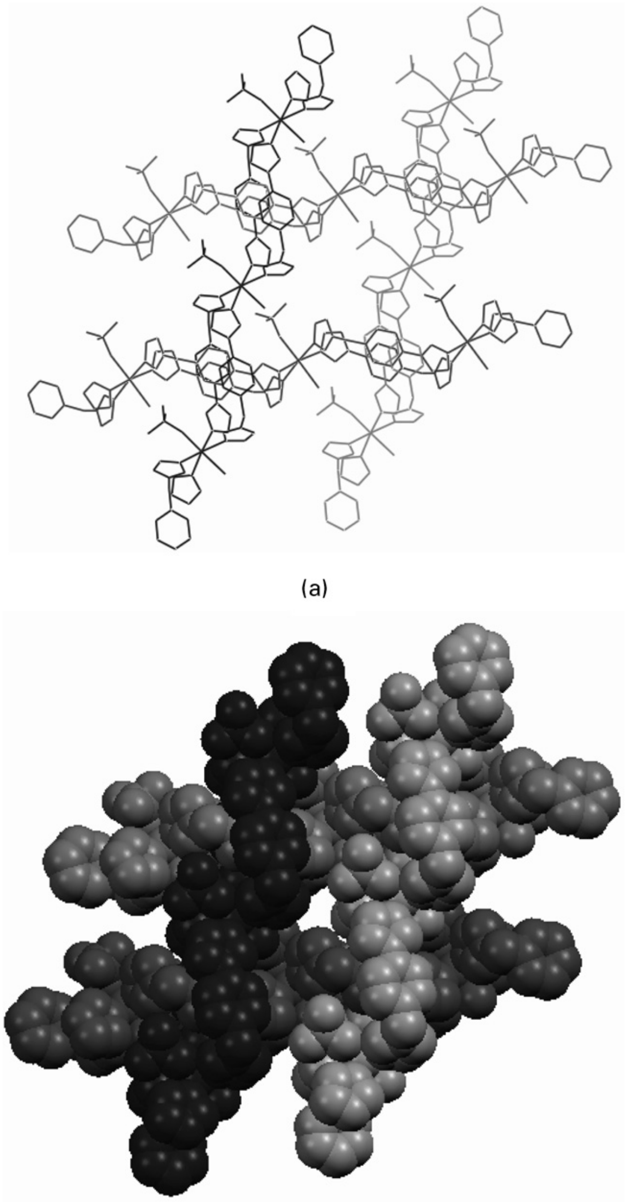
[Cd(IIMB)$_2$(H$_2$O)(SO$_4$)]·7.5H$_2$O, 1. In contrast to the symmetric ligands bix and bimb (Scheme 1), IIMB is asymmetric since one imidazole group is attached to the benzene group *via* a methylene group and the other one is directly attached to the benzene group. Novel MOFs with different structures and topologies from those with bix and bimb ligands can be expected by assembly reactions of IIMB with metal salts. As illustrated in Fig. 1(a), each Cd^{II} center in compound **1** has a slightly distorted octahedral environment and is coordinated by four imidazole groups of four IIMB ligands with Cd1–N bond lengths in the range of 2.291(4)–2.327(4) Å [Cd1–N$_{av}$ = 2.310(15) Å].[11] The Cd^{II} atom lies 0.11 Å out from the N$_4$ plane towards the O11 atom; such a deviation may be attributed to the different axial ligands (water molecule and sulfate anion). Each IIMB ligand links two Cd^{II} atoms to form a double-stranded 1D chain containing 24-membered rings with a Cd···Cd intra-chain distance of 11.94 Å [Fig. 1(b)]. In each ring, the two benzene ring planes are parallel to each other and are almost perpendicular to the chain plane defined by the cadmium and methylene carbon atoms [Fig. 1(b)], since the dihedral angles between them are 87.7 and 85.4°, respectively. The distance between the two benzene ring planes within one 24-membered ring is 6.65 Å, which makes it possible for an aromatic ring from another ligand to pass through the ring. Therefore, the remarkable feature of **1** is that the 1D chains are interlaced with each other to generate a 2D polycatenane network structure (Fig. 2). In the interlocked 2D structure, there are face-to-face π-π interactions between the benzene ring planes with centroid-centroid separations ranging from 3.67 to 3.75 Å (Fig. S1 in ESI). In addition, the oxygen atoms of the coordinated SO$_4^{2-}$ anion form hydrogen bonds with the coordinated water and with the imidazole ring C–H from the adjacent interlaced chains. In addition, there are a lot of O–H···O hydrogen bonding interactions between the SO$_4^{2-}$ and water molecules, water and water molecules, and C-H···O hydrogen bonds between the imidazole ring C–H and water molecules. The data on the hydrogen bonds are summarized in Table S2 in the ESI. Such hydrogen bonds, as well as π-π interactions, stabilize the interpenetrated structure and link the 2D sheets into a 3D structure (Fig. S2, ESI).



(a)

(b)

Fig. 1 (a) A view of **1** showing the coordination environment around the Cd^{II} center (ellipsoids at 30% probability). (b) A view of the double-stranded 1D chain of **1**. The hydrogen atoms and solvent molecules are omitted for clarity.



(a)

(b)

Fig. 2 (a) Wire-frame and (b) space-filling views of the 2D polycatenane network formed from independent double-stranded 1D chains in **1**.

[Cd(IIMB)$_2$Cl$_2$]·H$_2$O, 2. When IIMB reacts with cadmium chloride, instead of the sulfate salt, complex **2** was obtained. Crystallographic study shows that the Cd^{II} center in **2** has a similar coordination environment as that in **1** except two chloride ions, rather than sulfate anion and water molecule, occupying the axial positions with a Cl1–Cd–Cl2 angle of 176.67(4)° [Fig. 3(a) and Table S1). The Cd1–N bond lengths range from 2.313(3) to 2.371(3) Å with Cd1–N$_{av}$ of 2.343(29) Å, which is slightly longer than that in compound **1** (Table S1). Complex **2** is also a hinged 1D chain containing

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‡ CCDC reference numbers 204243–204244 and 225285–225289. See http://www.rsc.org/suppdata/nj/b3/b315842j/ for crystallographic data in .cif or other electronic format.

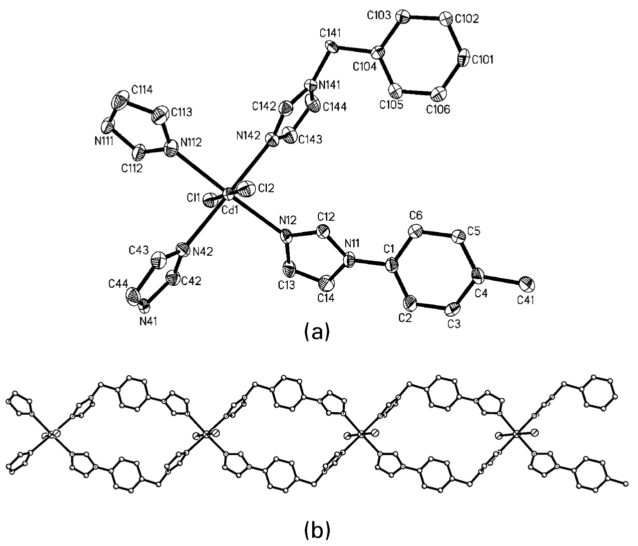


Fig. 3 (a) Crystal structure of compound **2** with atom numbering scheme. The thermal ellipsoids are drawn at 30% probability. (b) Infinite hinged 1D chain structure of **2**. The hydrogen atoms and solvent molecules are omitted for clarity.

24-membered rings with a Cd···Cd intra-chain distance of 12.91 Å, which is longer than that in **1** [Fig. 3(b)]. However, there are definite differences between complexes **1** and **2**. In contrast to the near perpendicular orientation of the benzene ring planes to the chain plane in **1**, the benzene ring planes in **2** are nearly parallel to the chain plane since the dihedral angles between the benzene ring plane and the chain plane defined by cadmium and methylene carbon atoms are 13.0 and 11.5°, respectively. And the shortest H···H distance between two benzene rings within the 24-membered ring is 2.94 Å, which is too narrow for another ligand to pass through the ring. As a result, the structure of **2** is a hinged 1D chain; no interpenetration of 1D chains was observed. Instead, the 1D chains are linked by two O–H···Cl, two C–H···O and one C–H···Cl hydrogen bonding interactions (Table S2) and weak π-π interactions (the shortest centroid-centroid separation is 4.26 Å) to form a 3D structure (Fig. S3, ESI).

[Cd(IIMB)$_4$(H$_2$O)$_2$](NO$_3$)$_2$·5H$_2$O, 3. It is interesting that a mononuclear complex **3** was obtained when cadmium nitrate was used to react with IIMB. Fig. 4(a) shows a view of the coordination environment of the metal atom in **3** with the atom numbering scheme. It is clear that only the imidazole group connected to the benzene ring through the methylene group coordinates to the Cd^{II} atom, while the one connected directly to the benzene ring is uncoordinated. In the complexes **1** and **2**, each cadmium atom is coordinated by four N atoms, two of which are from imidazole groups attached to the benzene ring directly and the other two are from ones attached to the benzene ring *via* the methylene group. The coordination geometry around the Cd^{II} atom is distorted octahedral with a N$_4$O$_2$ binding set. The Cd1–N bond lengths range from 2.289(10) to 2.343(10) Å [Cd1–N$_{av}$ = 2.318(23) Å], and two water molecules coordinated to the Cd^{II} atom are in a *trans* arrangement with bond lengths of Cd1–O1 = 2.399(8), Cd1–O2 = 2.335(7) Å (Table S1). Fig. 4(b) exhibits the infinite 2D network structure of **3** formed by intermolecular O–H···N hydrogen bonds, indicated by dashed lines, with O···N distances of 2.76(1) Å (Table S2). The oxygen and nitrogen atoms are from a coordinated water molecule and uncoordinated imidazole group, respectively. The nitrate anions and lattice water molecules are located in the voids formed between two adjacent cationic layers, held there by eight C–H···O hydrogen bonds; the C···O distances range from 3.02(2) to 3.440(14) Å (Fig. S4 and Table S2). The distances of 2.099 to 2.998 Å between the O atoms of water molecules or between the O atoms of a water molecule and the O atom of a nitrate anion indicate the formation of O–H···O hydrogen bonds (Table S2), although the hydrogen atoms of the water molecules could not be found. The center-to-center distance of 4.17 Å between the two nearest benzene ring planes indicates the presence of weak π-π interactions in **3**.

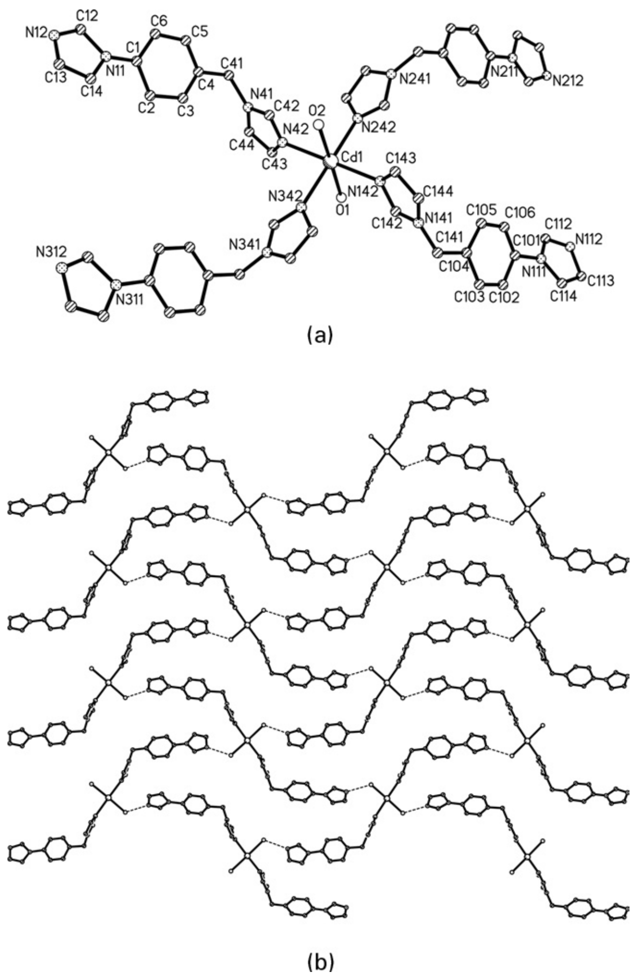


Fig. 4 (a) Crystal structure of compound **3**. (b) 2D network structure of **3** with hydrogen bonds indicated by the dashed lines. The IIMB ligands that do not participate in the formation of O–H···N hydrogen bonds are omitted for clarity.

[Cd(IIMB)(OAc)$_2$]·H$_2$O, 4. To further examine the impact of the anion on the self-assembled structures, the reaction of IIMB with cadmium acetate was carried out and a different 1D chain complex **4** was isolated. Fig. 5(a) exhibits the crystal structure of **4** together with the atom numbering scheme. Each Cd^{II} atom is six-coordinated with a N$_2$O$_4$, rather than N$_4$O$_2$, donor set from two N atoms of imidazole groups from two different IIMB ligands and two acetate anions in η^2-coordination mode. Each IIMB ligand in turn links two Cd^{II} atoms to generate a 1D sawtooth chain. The Cd1–N bond lengths are 2.246(2) and 2.259(2) Å, and the Cd1–O bond lengths are in the range of 2.311(2)–2.413(2) Å with a Cd1–O$_{av}$ of 2.362(54) Å. The crystal packing diagram of **4** shows that the 1D chains pack together through six C–H···O hydrogen bonds and two O–H···O hydrogen bonds [Fig. 5(b) and Table S2].

[Mn(IIMB)$_2$(SO$_4$)(H$_2$O)]·8.2H$_2$O, 5. In addition to the above mentioned cadmium(II) complexes, reactions of IIMB with other metal salts were carried out to elucidate the influence of the metal ion on the structures of the assemblies.

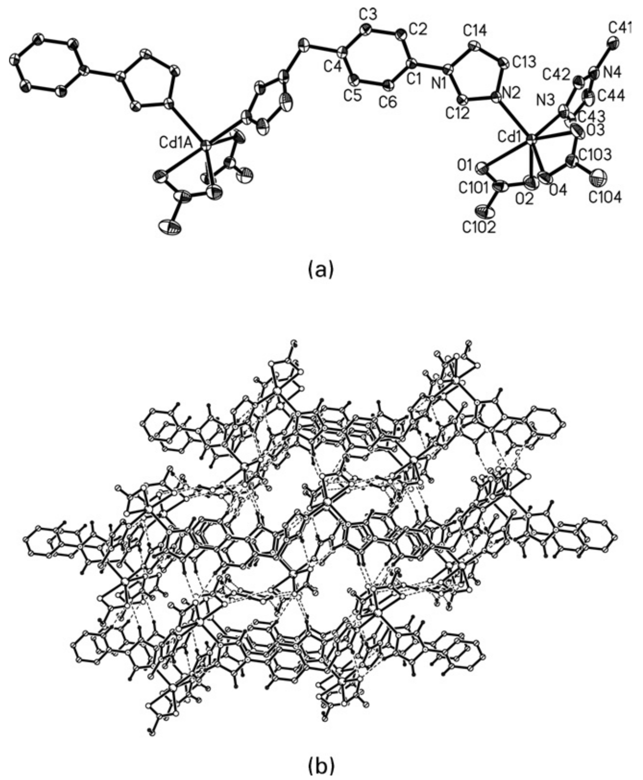


Fig. 5 (a) Infinite 1D chain structure of **4**. The solvent molecules and hydrogen atoms are omitted for clarity. (b) 3D structure of **4** linked by hydrogen bonds.

Complex **5** was obtained by reaction of IIMB with manganese(II) sulfate and its structure, evidenced by crystallographic analysis, is similar to that of **1** (Table 1), namely, a 2D polycatenane composed of a slant interpenetrated 1D double-stranded chains (Fig. 6). Each $\mathrm{Mn^{II}}$ center with distorted octahedral geometry is coordinated by four imidazole groups of four IIMB ligands with an average bond length of $\mathrm{Mn1{-}N_{av}} = 2.256(4)$ Å, and by two O atoms from one water molecule and a sulfate anion. The $\mathrm{Mn^{II}}$ atom is displaced by 0.03 Å from the plane formed by the N_4 donor set. Each IIMB ligand links two $\mathrm{Mn^{II}}$ centers to form a 1D chain with Mn···Mn intra-chain distance of 12.04 Å. The dihedral angles between the benzene ring plane and the chain plane defined by manganese and methylene carbon atoms are 86.5° and 84.3°, which are similar to those observed in **1**. The distance between the two benzene ring planes within the ring is 6.75 Å, which is a little longer than that in **1** (6.65 Å). There are many hydrogen bonds stabilizing the interpenetrated structure and linking the 2D sheets into a 3D structure (Table S2). In addition, similar face-to-face π-π interactions, with centroid-centroid separations ranging from 3.63 to 3.88 Å, were also detected for **5** such as those in **1**.

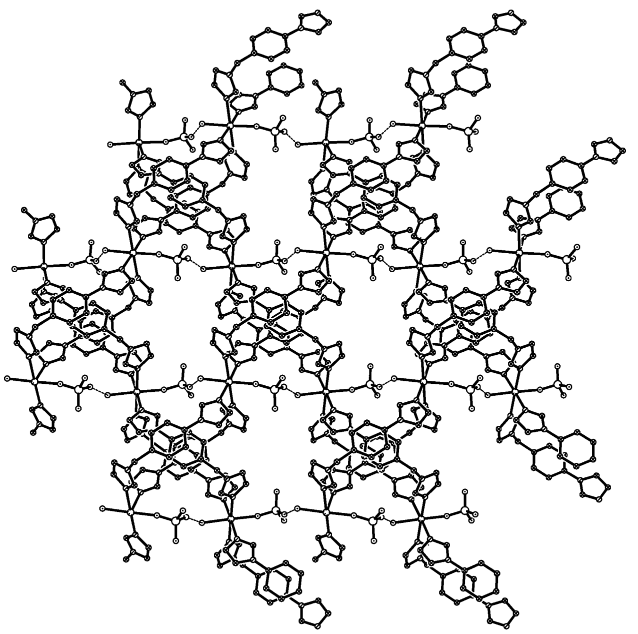


Fig. 6 A view of the 2D polycatenane network structure of **5** showing the interpenetrated 1D chains with O–H···O hydrogen bonds indicated by the dashed lines.

$[\mathrm{Mn(IIMB)_4(H_2O)_2}]\mathrm{Cl_2{\cdot}5H_2O}$, 6. When manganese chloride was employed to react with IIMB, complex **6** was formed. The X-ray crystallographic analysis revealed that the structure of **6** is mononuclear as that of **3**, but different from that of **2**. The coordination environment and average bond length of $\mathrm{Mn{-}N_{av}}$ are similar to those of the reported compound $\mathrm{Mn(bix)_3(NO_2)_2{\cdot}4H_2O}$.[5c] The distorted octahedral $\mathrm{Mn^{II}}$ center with N_4O_2 binding set is coordinated by four imidazole N atoms connecting to the benzene group through the methylene groups and two O atoms from two water molecules in a *trans* arrangement. Complex **6** also forms a 2D network by an intermolecular O(coordinated water)–H···N(uncoordinated imidazole group) hydrogen bond with an O···N distance of 2.739(5) Å. The crystal packing diagram of **6** is illustrated in Fig. 7. Weak overlap occurs between the benzene ring planes from two adjacent ligands, since the center-to-center distance between the two nearest benzene ring planes is 4.17 Å. The chloride anions and lattice water molecules occupy the voids formed between 2D layers by forming hydrogen bonds (Table S2). No such π-π interactions were reported in the related complex $\mathrm{Mn(bix)_3(NO_2)_2{\cdot}4H_2O}$, which may be due to the greater flexibility of bix compared to IIMB.[5c]

$[\mathrm{Zn(IIMB)_2}]_4\mathrm{(NO_3)_8{\cdot}13.5H_2O}$, 7. The crystal structure of compound **7** is shown in Fig. 8. It is interesting that the zinc(II) atom in **7** is four-coordinated rather than six-coordinated as observed for the cadmium(II) and manganese(II) atoms in complexes **1**–**6**. Each $\mathrm{Zn^{II}}$ atom is coordinated by four N atoms of four IIMB ligands with distorted tetrahedral geometry since the N–Zn–N bond angles vary from 95.2(8)° to 123.3(4)° (Table S1). This is similar to the $\mathrm{Zn^{II}}$ atoms in $[\mathrm{Zn(bix)_2(NO_3)_2}]{\cdot}4.5\mathrm{H_2O}$,[5b] in which the N–Zn–N bond angles vary from 96.2(1)° to 125.0(1)°. It is noteworthy that there are four zinc(II) atoms in one asymmetric unit of **7** [Fig. 8(a)]. Two $\mathrm{Zn^{II}}$ atoms, *e.g.* Zn1 and Zn1B or Zn4A and Zn3B in Fig. 8(b), are linked by two IIMB ligands to form a quadrangled

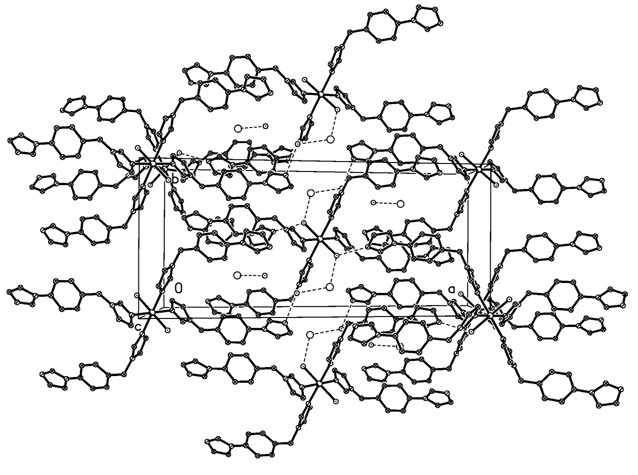


Fig. 7 Crystal packing diagram of compound **6**.

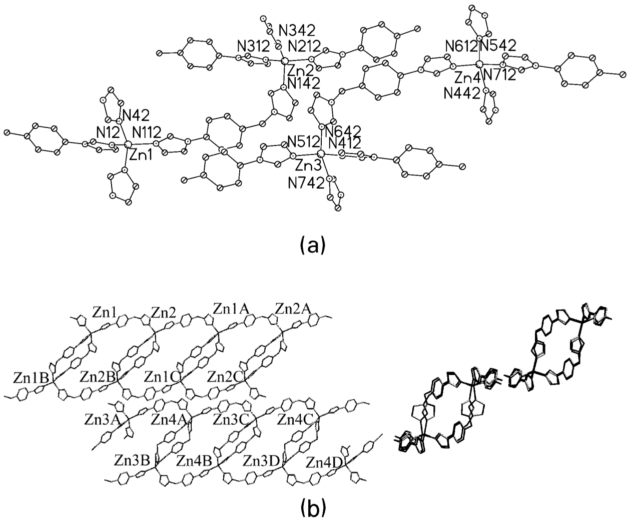


Fig. 8 (a) Independent crystal structure of compound **7**. (b) Two independent tubular 1D chains of **7**. The anions, solvent molecules and hydrogen atoms are omitted for clarity.

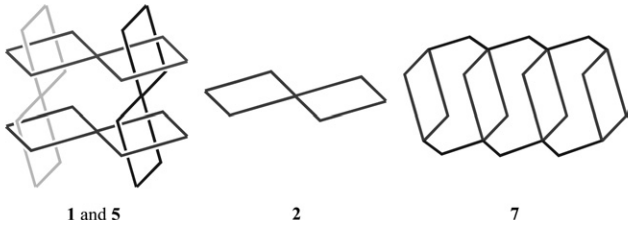
24-membered ring similar to that observed in **2**. Such macrocyclic rings are further interlinked by two IIMB ligands to form an infinite 1D tube-like chain; four independent zinc atoms in each asymmetric unit form two independent 1D chains [Fig. 8(b)]. The 1D chain structure is similar to that in the reported complex $[(CuI)_2(bpds)]_\infty$ [bpds = bis(4-pyridyl)disulfide],[12] while the structure of $[Zn(bix)_2(NO_3)_2]\cdot 4.5H_2O$ is a 2D polyrotaxane, which may be attributed to the flexibility of the bix ligand. The 1D chains are arranged in the *bc* plane to form 2D sheets, which further stack together to generate vacancies (Fig. S5 of the ESI), occupied by water molecules and uncoordinated nitrate anions. There are many C–H···O and O–H···O hydrogen bonds with C···O and O···O distances ranging from 2.812(14) to 3.490(17) Å and from 2.312 to 2.991 Å, respectively (Table S2) and weak π-π interactions with centroid-centroid separations ranging from 3.70 to 4.02 Å.

Photoluminescence properties of the compounds

The photoluminescence properties of compounds **1**–**7** were studied in the solid state at room temperature. The measurements were carried out under the same experimental conditions and the results are shown in Fig. S6 (see ESI). It is interesting that compounds **1**, **3** and **4** show luminescence with emission maxima at 455 ± 2 nm upon excitation at 396 nm, while compounds **2** and **7** exhibit photoluminescence with emission maxima around 464 ± 2 nm at the same excitation wavelength. Though the structures of **5** and **6** are similar to complexes **1** and **3**, respectively, no clear photoluminescence was observed for **5** and **6** at room temperature. The luminescence emissions of **5** and **6** are probably quenched by the Mn(II) ion. The emissions observed in compounds **1**, **2**, **3**, **4** and **7** are tentatively assigned to the π-π* intraligand fluorescence due to their close resemblance to the emission bands.[13]

Discussion

Seven new MOFs of ligand IIMB with different metal salts were successfully synthesized. The X-ray crystallographic analysis revealed that these compounds have different structures. (1) Both complexes **1** and **5** with a coordinated sulfate anion have similar 2D polycatenated structures (Scheme 2). They can be regarded as a completely new mode of 1D → 2D inclined interpenetration of double-stranded 1D chains, which was predicted by Ciani *et al.* in a review.[14] In the previously reported structures, the topology of interpenetration is that the nodes of the nets lie in the centers of the rings, while in the structures of **1** and **5**, the links of the chains pass through the rings of the interpenetrating chains.[15] The doubled-stranded 1D chains are interlaced with each other to form the 2D network with angles of 85.1° and 78.1° between the two inclined 1D chains for **1** and **5**, respectively. The coordination of sulfate anions and water molecules may probably be responsible for the formation of such a 2D polycatenated structure. On one hand, compared with chloride or nitrate anion, the sulfate anion has a large volume and its steric hindrance can subtly tune the orientation of the coordinated imidazole groups around the metal atom as well as the orientation of the benzene ring groups, which is different from those in other complexes, *e.g.* in **2** and **6**. On the other hand, the sulfate anions and water molecules act as acceptors and donors of hydrogen bonds. One O(coordinated water)–H···O(sulfate ion) hydrogen bond and one C(imidazole group)–H···O (sulfate ion) hydrogen bond play an important role in stabilizing the polycatenated structure. (2) The counter anions of complex **2**, namely two chloride ions, occupy the axial positions of the metal atom and the structure of **2** is a 1D hinged chain, which is similar to that of **1**. But the relative orientations of the benzene ring groups in the loop are different. The benzene ring planes in complex **2** are nearly parallel to the chain plane with dihedral angles of 13.0 and 11.5°, respectively. The corresponding dihedral angles in complex **1** are 87.7 and 85.4°, respectively, which indicates that the benzene ring planes are almost perpendicular to the chain plane defined by the cadmium atoms and the methylene carbon atoms. As a result, the space between the two benzene ring planes within the loop in complex **1** is significantly larger than that in complex **2**, making room for another ligand to pass through. Thus, the overall structures of **1** and **2** are obviously different (Scheme 2). (3) Complexes **3** and **6** are both discrete molecular complexes with a monometallic core, though they have different counter ions. The counter anions, nitrate ions (**3**) and chloride ions (**6**), did not participate in the coordination with the metal atoms and exist in the structure by forming hydrogen bonds. (4) The acetate ions of complex **4** adopt a η^2 coordination mode to coordinate to the metal atom, the structure is a single 1D chain. (5) The zinc(II) atom in complex **7** has a tetrahedral coordination environment and is coordinated by four IIMB ligands; the structure is a tubular 1D chain (Scheme 2). Furthermore, it has been confirmed that the complexes can be obtained under the same metal:ligand molar ratios of 1:2. That is, the metal-to-ligand molar ratios did not affect the structure greatly in this system. The different structures of complexes **5** and **6**, as well as **3** and **7**, which were prepared under the same experimental conditions, indicate that the nature of the counter anions and the geometric requirements of the metal atoms play important roles in determining the structure and topology of MOFs.[4e]



Scheme 2 Schematic drawing of the structures of complexes **1** and **5**, **2**, and **7**.

In addition, in the complexes with six-coordinated metal atoms, the four equatorial N atoms are from four distinct IIMB ligands while the two axial positions are occupied by two O atoms in **1**, **3**, **5** and **6** or by two chloride anions in **2**, except for complex **4**, which is different due to the coordination of acetate anions in bidentate mode [Fig. 5(a)]. In complex **7** with four-coordinated Zn(II) atoms, all the coordinated N atoms are from IIMB ligands with no coordination of O atoms from water or nitrate anion. The structures of **1**, **2**, **5** and **7** are schematically shown in Scheme 2, in which the axial ligands in **1**, **2** and **5** were omitted for clarity. It is clear that there are $M_2(IIMB)_2$ loops in these complexes. In **1**, **2** and **5**, the loops are joined together by six-coordinated metal atoms to give 1D hinged chains, which are further interlaced with each other to form a 2D polycatenane for **1** and **5**. While in the case of **7**, the loops are connected by IIMB ligands to produce a 1D chain and, as a result, each Zn(II) atom is coordinated by four IIMB ligands, two of which form a loop and two of which link the loops. The reactions of IIMB with other metal salts having square planar or triangular coordination geometries are now undergoing in our lab.

It is worthy to note that reactions of $Zn(NO_3)_2{\cdot}6H_2O$ with IIMB and bix generated complexes with 1D tubular chain (**7**) and 2D polyrotaxane structures,[5b] respectively. The zinc(II) atoms in both complexes have the same tetrahedral coordination geometry with a N_4 donor set and the difference between bix and IIMB is just that there is one more methylene group in bix. The results imply that subtle changes in the ligand may have a great impact on the structure of MOFs. In the case of the Mn(II) complexes **5**, **6** and $Mn(bix)_3(NO_2)_2{\cdot}4H_2O$,[5c] all the Mn(II) atoms in these three complexes are six-coordinated with N_4O_2 binding set. However, they have different structures, which are attributed to the different structures of the IIMB and bix ligands as well as different anions. Reaction of manganese(II) perchlorate with bimb gave an infinite 1D chain complex, in which the Mn(II) atom has a N_6, rather than N_4O_2, donor set and a snake-like 1D chain was obtained by reaction of bimb with zinc(II) acetate, which is different from the 1D chain of **4**.[6a,6b] The differences between the complexes of bimb and IIMB are considered to be caused by the greater flexibility and larger biphenyl spacer group of bimb compared with IIMB.

Conclusions

We have assembled the first examples of 2D polycatenanes formed by the interlocking of double-stranded 1D chains. A series of relevant coordination compounds was successfully synthesized and the structures were examined. X-Ray analyses show that reactions of IIMB with seven kinds of metal salts afford molecular, 1D and 2D coordination compounds. The results indicate that the nature of counter anions, such as their coordination ability, coordination mode and size, and the geometric needs of the metal atoms can determine the topologies and properties of coordination compounds. Furthermore, the anions participating in coordination can greatly influence the structure of the compounds.

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