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ARTICLE

Synthesis, crystal structure, and luminescence properties of seven tripodal imidazole-based Zn/Cd(II) coordination polymers induced by tricarboxylates

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2014,
Accepted 00th January 2014

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Seven tripodal imidazole-based metal coordination polymers including $[\text{Zn}_3(\text{L}^1)_2(\text{tib})_2]_n \cdot (\text{H}_2\text{O})_{4n}$ (**1**), $[\text{Cd}_3(\text{L}^1)_2(\text{tib})_2(\text{H}_2\text{O})_2]_n \cdot (\text{H}_2\text{O})_{6n}$ (**2**), $[\text{Zn}_3(\text{L}^2)_2(\text{tib})_2]_n \cdot (\text{H}_2\text{O})_n$ (**3**), $[\text{Cd}_3(\text{L}^2)_2(\text{tib})_2]_n \cdot (\text{H}_2\text{O})_{6n}$ (**4**), $[\text{Zn}_3(\text{L}^3)_2(\text{tib})_2]_n \cdot (\text{H}_2\text{O})_{4.5n}$ (**5**), $[\text{Zn}_2(\text{HL}^3)_2(\text{tib})_2]_n \cdot (\text{H}_2\text{O})_n$ (**6**), and $[\text{Cd}_3(\text{L}^3)_2(\text{tib})_2(\text{H}_2\text{O})_2]_n \cdot (\text{H}_2\text{O})_{4n}$ (**7**) with different structures have been designed and prepared based on the hydrothermal reaction between $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ or $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ and tib ligands in the presence of three asymmetric semi-rigid V-shaped tricarboxylate ligands H_3L^{1-3} , where tib, H_3L^1 , H_3L^2 , and H_3L^3 ligands represent 1,3,5-tris(1-imidazolyl)benzene, 3-(2-carboxyphenoxy)phthalic acid, 4-(2-carboxyphenoxy)phthalic acid, and 3-(4-carboxyphenoxy)phthalic acid, respectively. All these compounds sharing three-dimensional (3D) networks have been clearly revealed by the single crystal X-ray diffraction analysis. Among these complexes **1-7** (except **6**), their common 3D skeleton are composed of tib N-donor ligands bridging two-dimensional (2D) sheets made of L^{1-3} ligands and metal ions. Compound **6** also exhibits a 3D network constructed by partly deprotonated L^3 ligands attached on the right- and left-helices made of tib ligands and Zn ions. In these compounds, the diversity of the tib ligand-based metal building units is tuned by the coordination molecular conformation of tricarboxylates and coordination geometry of metal ion. In addition, the thermal stability and emission spectroscopy for the series of seven complexes have also been investigated.

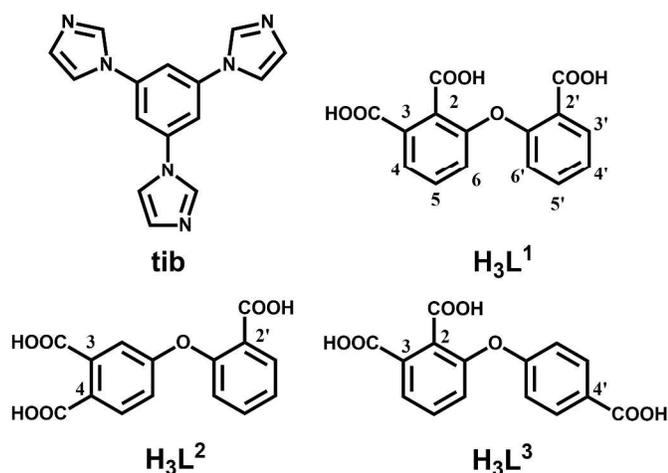
Introduction,

Rational design and synthesis of functional coordination polymers (CPs) inspired a wide range of research interests over the past few decades due to their rich structural diversities and important industrial application potentials.^{1,2} Considerable efforts dedicated in the coordination chemistry and crystal engineering gave birth to a great many CPs to correlate the relationship between structure and property for enabling the realization of potential usage.³ It is also true for the complexes based d¹⁰ metals, such as Zn(II) and Cd(II) ions, due to their attractive luminescence functionality and potential applications.⁴ However, exact prediction in the crystal structure and property of coordination polymers based on organic ligands, especially without well-defined shape, is very impossible because of the diverse structural geometries induced by supramolecular interaction and reaction conditions as well as the influence in the feasible secondary unit by metal ions (node), main ligand (linker), and secondary ligand (linker) involved in the formation and crystallization process of CPs.⁵ As a result, it is still necessary to synthesize the coordination polymers by using not only the “new-fashioned” but also “old-

fashioned” ligands and explore more assembly principle of node and linker. In this regards, various of N-donor ligands are popular to be employed to fabricate the coordination polymers because of the excellent crystalline ability and relatively simple coordination geometry of the coordinated nitrogen atom(s).⁶ In recent years, rigid tripodal N-donor ligand, 1,3,5-tris(1-imidazolyl)benzene (tib) and derivatives, Scheme 1, have been revealed efficient and versatile to help multidentate organic carboxylate for building coordination architectures with interesting topology and excellent functionality.⁷ However, the binding mode and corresponding constructed secondary units by these N-donor ligands in CPs seems boundless and thus incompletely elaborated, which still can be varied by selecting of different organic ligands and metals.⁸

In the present case, three isomeric V-shaped multidentate O-donor ligands of 3-(2-carboxyphenoxy)phthalic acid (H_3L^1) and its two derivatives 4-(2-carboxyphenoxy)phthalic acid (H_3L^2) and 3-(4-carboxyphenoxy)phthalic acid (H_3L^3), Scheme 1, were used to induce the different binding modes and secondary units of tib ligand. These three O-donor ligands without well-defined shape commonly include a semi-rigid molecular framework containing free rotated two benzene rings

around an oxygen atom and different carboxyl group(s) attached on these two benzene rings. Fortunately, seven tib ligand involved metal coordination polymers with three-dimensional (3D) networks including $[\text{Zn}_3(\text{L}^1)_2(\text{tib})_2]_n \cdot (\text{H}_2\text{O})_{4n}$ (**1**), $[\text{Cd}_3(\text{L}^1)_2(\text{tib})_2(\text{H}_2\text{O})_2]_n \cdot (\text{H}_2\text{O})_{6n}$ (**2**), $[\text{Zn}_3(\text{L}^2)_2(\text{tib})_2]_n \cdot (\text{H}_2\text{O})_n$ (**3**), $[\text{Cd}_3(\text{L}^2)_2(\text{tib})_2]_n \cdot (\text{H}_2\text{O})_{6n}$ (**4**), $[\text{Zn}_3(\text{L}^3)_2(\text{tib})_2]_n \cdot (\text{H}_2\text{O})_{4.5n}$ (**5**), $[\text{Zn}_2(\text{HL}^3)_2(\text{tib})_2]_n \cdot (\text{H}_2\text{O})_n$ (**6**), and $[\text{Cd}_3(\text{L}^3)_2(\text{tib})_2(\text{H}_2\text{O})_2]_n \cdot (\text{H}_2\text{O})_{4n}$ (**7**) have been successfully prepared in the presence of these three multidentate semi-rigid organic carboxylates. Systematical and comparative studies on the structures reveal that the diversity in the building subunits formed by tib ligands and metal ions in **1-7** actually are induced by the three asymmetric V-shaped tricarboxylate ligands together with the used metals. The thermal stability and luminescent properties of these seven metal coordination polymers have also been comparatively investigated.



Scheme 1. Schematic molecular structures of tib and H_3L^{1-3} ligands.

Results and discussion

Synthesis of the Complexes 1-7. In the present case, the N-donor ligand, 1,3,5-tris(1-imidazolyl)benzene (tib), was chosen and used to assemble complexes with help of three tricarboxylate ligands (H_3L^1 , H_3L^2 , and H_3L^3). Complexes **1-7** (except **5** and **6**) were successfully obtained from the hydrothermal reaction with the starting materials of N-donor ligand (tib), metal salt and three asymmetric V-shaped tricarboxylate ligands in molar ratio of both 1:2:1 and 1:1:1. However, the reaction between tib ligand and $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ in the presence of H_3L^3 ligand in molar ratio of 1:2:1 and 1:1:1 gave different structural complexes **5** and **6**, respectively. These results reveal the effect of starting materials in different molar ratio on the structure of CPs. In addition, introduction of the alkali (NaOH and KOH) with a molar ratio 3:1 to the tricarboxylate ligands was introduced for the purpose of deprotonating protons in the presence of tib ligands led to the isolation of all these complexes (except **6**) but with reduced yield and poor crystal quality, indicating the important role of pH value on the formation and the crystallization of coordination polymers. This is also true for the reaction temperature. Actually, compounds **1-7** only can be obtained only at a relative lower temperature below 130°C , higher than this temperature only gave some amorphous powders.

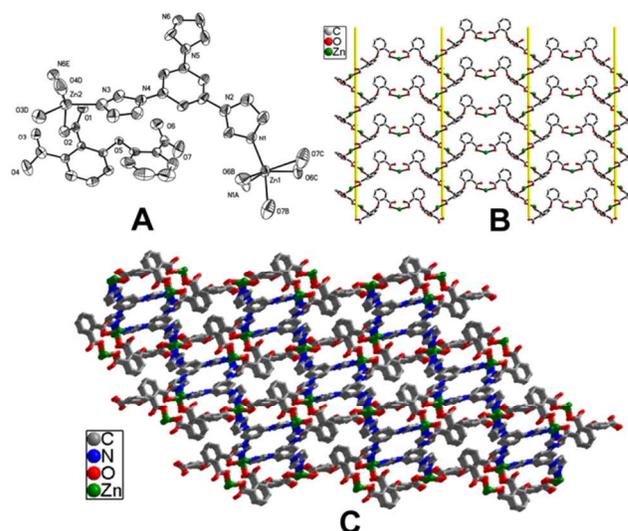


Fig. 1 (A) The coordination geometry for Zn(II) atoms in **1** with the 30% probability level, all hydrogen atoms and solvent water molecules have been omitted for clarity. (B) 2D sheet in **1** comprised of right- and left-helices. (C) The 3D framework of **1**. [Symmetry codes: (i) $1 - x, y, -0.5 - z$ for N1A; (ii) $x, 1 + y, z$ for O6B and O7B; (iii) $1 - x, 1 + y, -0.5 - z$ for O6C and O7C; (iv) $-1.5 - x, 0.5 + y, 0.5 - z$ for O3D and O4D; (v) $1 - x, 1 - y, -z$ for N6E]

Crystal Structure of Complexes 1 and 2. Compounds **1** and **2** both crystallize in the monoclinic system and $C2/c$ space group. These two almost isostructural complexes exhibit complicated 3D structures with secondary building units of adjacent sheets connected by tib ligands. The detailed crystal structures of **1** and **2** have been described with the former one as representative. As shown in Fig. 1A, there are two kinds of crystallographically independent Zn(II) ions in **1**. Zn1 ion is located in a six-coordinated environment built from four oxygen atoms of two pairs of carboxylic groups in bidentate chelating mode and two nitrogen atoms of two tib ligands. Zn2 ion is five-coordinated by two nitrogen atoms of tib ligands, two oxygen atoms of bidentate chelating carboxylic group, and one oxygen atom of carboxylic group in a monodentate mode. In comparison with the five- and six-coordinated Zn ions sharing relative smaller ionic radius in **1**, both Cd ions with bigger ionic radius in **2** are six-coordinated, which subsequently lead to the more one coordination water molecule than that in **1**, Fig. S1A†. The bond length of M-O (M = Zn and Cd) or M-N are in consistent with those in the segment containing corresponding coordination bonds.^{9,10} In addition, the L^1 ligands in **1** and **2** exhibit different coordination modes towards metal ions and the molecular conformation with *cis*-type in the former compound and *trans*-type in the latter species. Herein, the *cis*-type molecular configuration of L^1 ligand is defined that the one isolated carboxyl group points out of the plane composed of the benzene ring with two neighboring carboxyl groups towards right direction, while the reverse is defined as *trans*-kind mode. This is also true for the L^2 ligand. In the present case, with the Zn or Cd ions in **1** or **2** as node and only L^1 ligands as linker, a 2D sheet is formed composed of racemic helices built by the neighboring carboxylic groups connecting the Zn/Cd ions, Figs. 1B and S1B†. The adjacent sheets are further linked into the 3D crystal structure by virtue of the tib ligands, Fig. 1C.

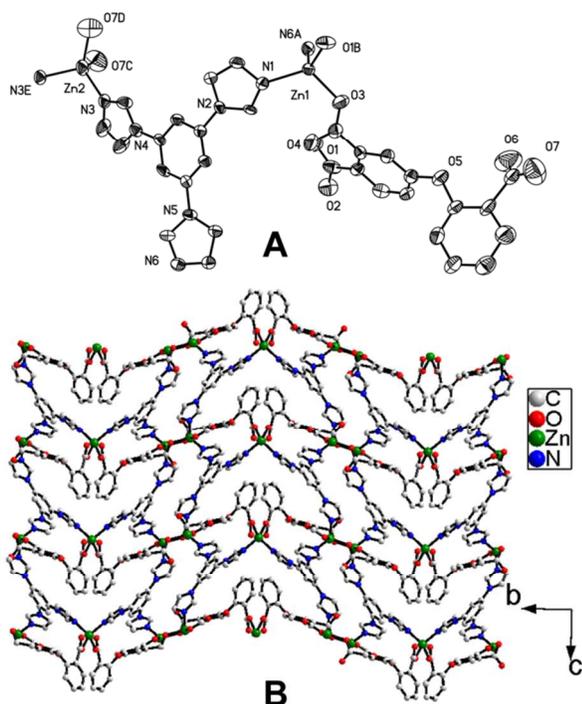


Fig. 2 (A) The coordination environment for Zn(II) atoms in **3** with 30% probability level, all hydrogen atoms and solvent water molecules have been omitted for clarity. (B) 3D packing structure of this compound in view of *bc* plane. [Symmetry code: (i) $-0.5 - x, y, 0.5 - z$ for N6A; (ii) $0.5 + x, -y, 0.5 - z$ for O1B; (iii) $-x, 0.5 + y, 0.5 - z$ for O7C; (iv) $-1.5 + x, -y, 0.5 - z$ for O7D; (iv) $-1.5 - x, 0.5 - y, 0.5 - z$ for N3E]

Crystal Structures of Complexes 3 and 4. Similar with compounds **1** and **2**, isostructural compounds **3** and **4** still have slight structural differences due to the involved metal ions with different ionic radius, they feature 3D architecture completed by the 2D sheets linked by tib ligands. There are two kinds of crystallographically different M(II) ($M = \text{Zn}$ and Cd) ions, one tib molecule, and one L^2 ligand, and one solvent water molecule in the asymmetric unit of **3** but two solvent and one coordination water molecules in **4**. As can be found in Fig. 2A, the Zn1 and Zn2 ions in **3** locate in a distorted tetrahedral coordination geometry completed by two nitrogen atoms from tib ligands and two oxygen atoms from three carboxylic groups of L^2 ligands. However, due to the increased ionic radius from Zn(II) to Cd(II) ions, coordination number of metal ions in **4** has changed into six, and both Cd1 and Cd2 ions are surrounded by the distorted coordination sphere completed by the two nitrogen atoms and four oxygen atoms from two carboxylic groups in bidentate chelating coordination mode, Fig. S2†. Despite the L^2 ligands in **3** and **4** exhibit different coordination mode towards metal ions, but the ligands in these two compounds show the same *cis*-type molecular conformation. The 2-, 3-, and 4-carboxyl groups of this ligand binding the metal ions of **3** and **4** form a 2D sheet unit, Figs. S2 and S3B †. The adjacent sheets are associated by the tib ligands connecting the metal ions, giving a 3D sheet in the *ac* plane, Fig. 2C.

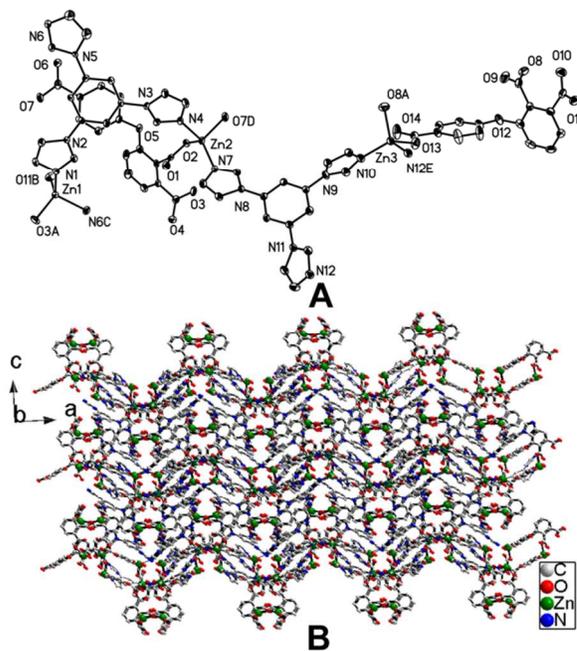


Fig. 3 (A) The coordination sphere for Zn(II) atoms in **5** with the 30% probability level, all hydrogen atoms and water molecules have been omitted for clarity. (B) complicated 3D molecular framework in **5**. [Symmetry codes: (i) $1.5 - x, -0.5 + y, z$ for O3A and O8A; (ii) $1.5 - x, 3 - y, -0.5 + z$ for O11B; (iii) $0.5 + x, y, 0.5 - z$ for N6C; (iv) $1 - x, 0.5 + y, 0.5 - z$ for O7D; (v) $2 - x, 3 - y, 1 - z$ for O11B; (v) $1.5 - x, 3 - y, -0.5 + z$ for N12E]

Crystal Structure of Complexes 5 and 6. Complexes **5** and **6** are obtained due to the different molar ratio 1:1:2 and 1:1:1 for tib, H_3L^3 ligands and zinc acetate as starting materials, respectively. The structure of **5** features a complicated 3D framework with the two kinds of sheets composed of sole L^3 and tib ligands, respectively. There are three types of crystallographically independent Zn(II) ions, two kinds of tib ligand, and two types of L^3 ligand in this compound, Fig. 3A. Three crystallographically independent Zn ions all are located in a distorted tetrahedron coordination environment completed by two nitrogen atoms from tib ligands and two oxygen atoms of different monodentate carboxylic groups. The complexation of L^3 ligands and Zn ions gives a 2D sheet in the *ab* plane, Fig. S4†, and the tib ligands binding Zn ions lead to the other 2D sheet in the *bc* plane. These two kinds of coordination sheets associate together, forming a complicated 3D framework of **5**, Fig. 3B.

Compound **6** exhibits a 3D molecular structure composed of right- and left-helices made of tib ligands and Zn ions. Both the Zn ions in this compound are four-coordinated by three nitrogen atoms of tib ligands and one oxygen atom of partly deprotonated L^3 ligands, Fig. 4A. The tib ligands bind zinc ions to give helix units with right- or left-conformation, which form the achiral 3D skeleton of **6**. The partly deprotonated L^3 ligand coordinate the Zn ion to fill in the cavity of the helices, Fig. 4B.

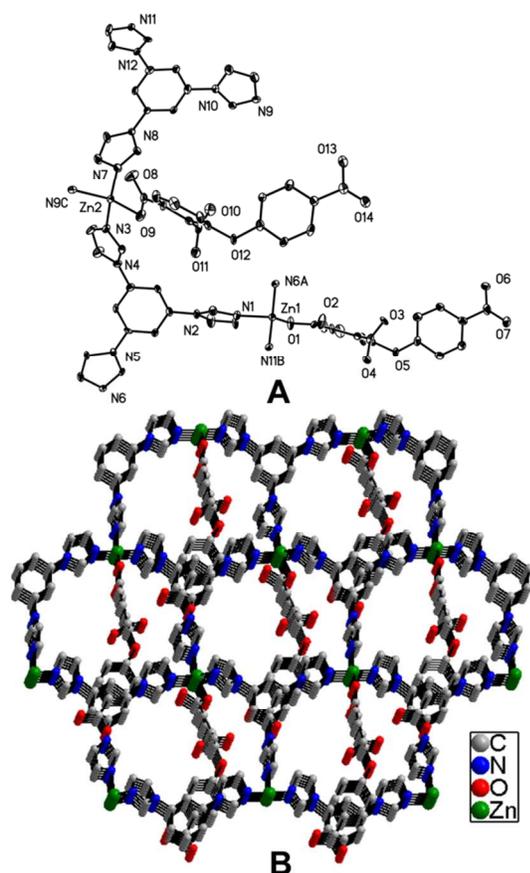


Fig. 4 (A) The asymmetric unit of **6** with the 30% probability level, all hydrogen atoms and water molecules were omitted for clarity. (B) A 3D coordination framework in **6**. [Symmetry codes: (i) $1 + x, -1 + y, z$ for N6A; (ii) $x, y, 1 + z$ for N11B; (iii) $x, 1 + y, z$ for N9C]

Crystal Structure of Complex 7. The complex **7** was prepared by the same experimental procedure of **5** only with cadmium acetate instead of zinc acetate as starting material. The asymmetric unit of **7** comprises of one and half Cd(II) ions, one tib ligand, and one L^3 ligands, two coordination and solvent water molecules. For these two crystallographically independent Cd(II) ions, the coordination geometry of Cd1 ion is seven-coordinated completed by two nitrogen atoms of tib ligands, four oxygen atoms from two bidentate chelating carboxylic groups, and one oxygen atoms of water molecule, Fig. 5A. The coordination environment of Cd2 is similar that of Cd1 ion only without the coordination water molecule. The L^3 ligands of **7** binding Cd ions form a 2D sheet containing right- and left-helices secondary units built from the 2- and 3-carboxylic group, Fig. 5B. The adjacent sheets are further connected into a 3D framework of **7**, Fig. 5C.

Thermal Stability and Emission Spectroscopy. The purity of **1-7** was determined on the basis of powder X-ray diffraction pattern, Fig S5†. The thermal behaviors for these new obtained compounds **1-7** were studied to reveal their thermal stability. Thermogravimetric analysis (TGA) experiments were performed on pure single crystal sample of **1-7** under air atmosphere with a heating rate of $10^\circ\text{C}/\text{min}$ in the range of $30-650^\circ\text{C}$.

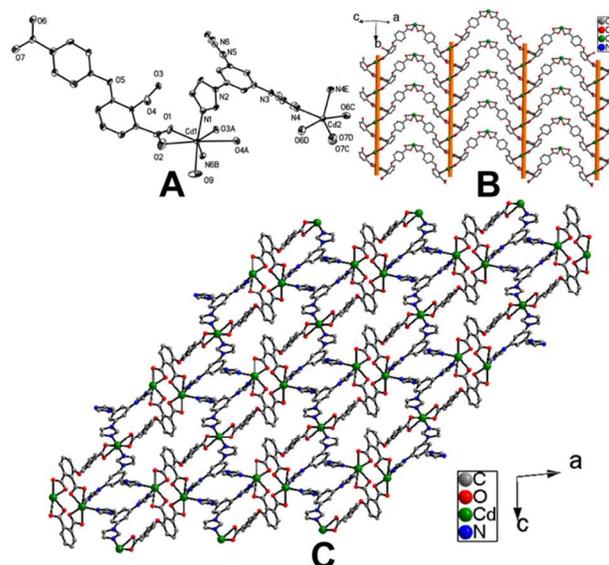


Fig. 5 (A) The asymmetric unit of **7** with the 30% probability level, all hydrogen atoms and water molecules have been omitted for clarity. (B) 2D coordination sheet in **7** composed of right- and left-helices. (C) 3D packing structure of **6** in ac plane. [Symmetry codes: (i) $1.5 - x, 0.5 + y, -1 - z$ for O3A and O4A; (ii) $1 - x, y, -z$ for N6B, $-0.5 + x, 1.5 + y, 1 + z$ for O6C and O7C; (iii) $1.5 - x, 1.5 + y, -1 - z$ for O6D and O7D; (iv) $1 - x, y, -z$ for N4E]

The thermal curves are shown in Fig. S6†. The slight weight loss of complex **1** was found in the temperature range from 30°C to 250°C owing to the release of two crystalline water molecules (obsd. 5.1%, calcd. 4.9%). The organic linkers then decompose from $330-500^\circ\text{C}$ (obsd. 77.8%, calcd. 77.7%). For **2**, the solvent water molecules are seen to be lost in the range of $30-260^\circ\text{C}$ (obsd. 6.9%, calcd. 6.6%). For compound **3**, the slightly changed TGA curve indicates that the few solvent water molecules lost from room temperature to 151°C (obsd. 1.4%, calcd. 1.3%), and the organic components are then desposed in the range of $330-510^\circ\text{C}$. According to the TGA curve of **4**, the crystalline water molecules are lost in the range of $275-300^\circ\text{C}$ (obsd. 6.5%, calcd. 6.8%). The tib and L ligands organic components break down in the range of $286-550^\circ\text{C}$. The release of water molecules in **5** was observed at 293°C (obsd. 6.1%, calcd. 5.7%). Similar with **3**, the few solvent water molecules of **6** are found lost relatively low temperature range from 30 to 100°C (obsd. 1.3%, calcd. 1.4%). One serious weight loss is observed from 248 to 485°C , which should be attributed to the decomposition of organic components of tib and L^3 ligands. For compound **7**, the first stage of weight loss are ascribed to the total release of coordination and solvent water molecules (obsd. 6.4%, calcd. 6.8%) in the temperature range of $30-217^\circ\text{C}$, and the further weight loss from 388 to 488°C corresponds to the organic ligands deposited, leading to the CdO as residue.

The luminescence spectra of **1-7** have been recorded in the solid state at room temperature with the excitation wavelength $\lambda_{\text{ex}} = 350 \text{ nm}$ for the all seven complexes. Despite different tricarboxylic ligands and metal ion were employed for these complexes **1-7**, their solid emission spectra are very similar with the wide emission band observed at $400-442 \text{ nm}$, Fig. S7†. On the basis of previous result reported on the emission of

metal-free H_3L^{1-3} and tib ligands, the present emission of these complexes around 400 nm should originate from the emission of L ligand.¹¹

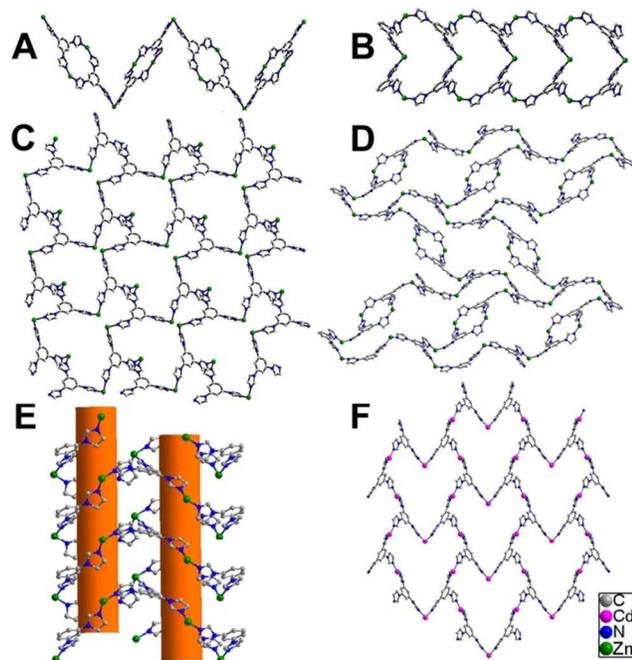


Fig. 6 The secondary structure composed of tib ligands in **1-7** (A for **1** and **2**, B and C for **3** and **4**, D for **5**, E for **6**, and F for **7**).

The Various Patterns Comprised of Tib N-donor Ligands of 1-7. In the present case, the tib N-donor ligand was used to synthesize the metal coordination polymers in the presence of the semi-rigid V-shape ligand. All coordination polymers (except **6**) are 3D frameworks composed of the 2D sheets pillared by the tib ligands, Fig. 6. Interestingly, the diverse motif built from the tib ligands and metal ions are found in the analyzing the crystal structure. In a word, the tib ligand coordinating with the metals exhibits two kinds of bind mode with metals, including A and B type, Fig. S8†. In comparison with those reported tib-based secondary unit,^{7,8,12} the common 1D chain unit is observed in **1** and **2**. However, four new and different tib-based metal 2D networks are found in compounds **3-7**. The 2D patterns in **3** and **4** look like puppet configuration, 2D sheet of **5** exhibits a bird-shaped pattern, helix secondary unit are observed in **6**, and 2D network of **7** shows a heart-shape diagram. These diverse subunits built from the ligands seem to be induced by the three asymmetric V-shaped tricarboxylate ligands and metals.

Experimental

All the reagents and solvents employed in the present work were obtained from commercial source and used directly without further purification. The tib ligand and three H_3L^{1-3} linkers were synthesized according to the reported procedure.^{7a,13}

Table 1. Crystal data and structure refinements of **1-7**.

Complex	1	2	3
Formula.	$C_{60}H_{46}N_{12}O_{18}Zn_3$	$C_{60}H_{54}N_{12}O_{22}Cd_3$	$C_{60}H_{40}N_{12}O_{15}Zn_3$
F.W.	1419.3	1632.4	1363.2
Crystal system	Monoclinic	Monoclinic	Orthorhombic
space group	$C2/c$	$C2/c$	$Pccn$
<i>A</i>	37.342(7)	38.1051(19)	10.1513(15)
<i>B</i>	8.2819(4)	8.0262(2)	32.003(6)
<i>C</i>	26.577(9)	26.1036(12)	18.417(4)
α	90.00	90.00	90.00
β	134.36(3)	130.755(8)	90.00
γ	90.00	90.00	90.00
volume	5877(2)	6047.6(4)	5983.3(19)
<i>Z</i>	4	4	4
$D_{\text{calc}}/\text{g cm}^{-3}$	1.604	1.793	1.513
μ/mm^{-1}	1.301	1.139	1.271
<i>F</i> 000	2896	3272	2768
R_1 $I > 2\theta$	0.0794	0.0531	0.0987
R_w $I > 2\theta$	0.1381	0.0977	0.2535
R_1^a	0.1415	0.0772	0.1961
R_w^b	0.1575	0.1049	0.3063
<i>S</i>	1.043	1.084	0.952

4	5	6	7
$C_{60}H_{50}N_{12}O_{20}Cd_3$	$C_{60}H_{47}N_{12}O_{18.5}Zn_3$	$C_{60}H_{42}N_{12}O_{15}Zn_2$	$C_{60}H_{50}N_{12}O_{20}Cd_3$
1594.3	1428.3	1301.9	1596.4
Orthorhombic	Orthorhombic	Triclinic	Monoclinic
$Pccn$	$Pbca$	$P1$	$C2$
32.5833(8)	19.9674(5)	7.5481(6)	27.4177(12)
10.1910(3)	18.9868(5)	10.8878(10)	8.2315(3)
19.1380(5)	30.7298(11)	19.0460(18)	13.7691(7)
90.00	90.00	79.948(8)	90.00
90.00	90.00	79.570(8)	94.263(5)
90.00	90.00	73.077(8)	90.00
6354.9(3)	11650.2(6)	1460.3(2)	3098.9(2)
4	8	2	2
1.685	1.634	1.480	1.711
1.081	1.315	0.901	1.107
3224	5840	666	1596
0.0466	0.0628	0.0617	0.0464
0.1035	0.1361	0.1591	0.1002
0.0621	0.1234	0.0740	0.0583
0.1093	0.1615	0.1680	0.1043
1.072	0.988	1.049	1.044

$$^a R_1 = \sum |F_o - F_c| / \sum |F_o|, \quad ^b R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

[Zn₃(L¹)₂(tib)₂]_n·(H₂O)_{4n} (1**).** A mixture of tib (0.0276 g, 0.1 mmol), H_3L^1 (0.0302 g, 0.1 mmol), $Zn(OAc)_2 \cdot 2H_2O$ (0.0439 g, 0.2 mmol) and H_2O (15 mL) were sealed in 25 mL teflon-lined stainless steel reactor, heated at 120°C for 72 hours. After being cooled to 50°C at a descent rate of 10°C/h, the oven was cut off and kept for another 10 hours, leading to the separation of perfect colorless block-shaped crystals suitable for X-ray diffraction by filtration with the yield of 0.058 g, 81% (based on L^1 ligand). Anal. Calcd. for $C_{30}H_{23}N_6O_9Zn_{1.5}$: C 50.77, H 3.27, N 11.84. Found: C 50.90, H 3.22, N 11.81. IR / cm^{-1} (KBr): 3387(m), 3124(m), 1618(s), 1512(s), 1384(s), 1238(s), 1080(s), 825(s).

[Cd₃(L¹)₂(tib)₂(H₂O)₂]_n·(H₂O)_{6n} (2**).** A mixture of $Cd(OAc)_2 \cdot 2H_2O$ (0.0533 g, 0.2 mmol), tib (0.0276 g, 0.1 mmol), H_3L^1 (0.0302 g, 0.1 mmol), and H_2O (15 mL) was sealed in 25 mL teflon-lined stainless steel reactor, which was heated for 72 hours at 120°C, then cooled to 50°C at a descent rate of 10°C/h. Finally, the oven was cut off and kept for another 10 hours, perfect colorless block-shaped crystals suitable for X-ray diffraction analysis were separated by filtration with the yield of 0.064 g, 79% (based on L^1 ligand). Anal. Calcd. for $C_{30}H_{27}N_6O_{11}Cd_{1.5}$: C 44.15, H 3.33, N 10.30.

Found: C 44.45, H 3.39, N 10.25. IR /cm⁻¹ (KBr): 3421(m), 3115(m), 1579(s), 1508(s), 1392(s), 1236(s), 1072(s), 827(s).

[Zn₃(L²)₂(tib)₂]_n·(H₂O)_n (**3**). The complex **3** was synthesized by the same procedure used for **1** except that H₃L¹ was replaced by H₃L² (0.0302 g, 0.1 mmol) as starting material, colorless blocked crystals suitable for X-ray diffraction analysis were obtained with the yield of 0.051 g, 75% (based on L² ligand). Anal. Calcd. for C₃₀H₂₀N₆O_{7.5}Zn_{1.5}: C 52.78, H 2.95, N 12.31. Found: C 52.76, H 2.92, N 12.29. IR /cm⁻¹ (KBr): 3429(m), 3142(m), 1620(s), 1514(s), 1396(s), 1261(s), 1074(s), 846(s).

[Cd₃(L²)₂(tib)₂]_n·(H₂O)_{6n} (**4**). The title compound was obtained by the same procedures as that of **2** except that H₃L¹ was replaced by H₃L² (0.0302 g, 0.1 mmol). After the reactor was cooled to room temperature from 120°C colorless blocked crystals suitable for X-ray diffraction analysis were collected with the yield of 0.063 g, 79% (based on L² ligand). Anal. Calcd. for C₃₀H₂₅N₆O₁₀Cd_{1.5}: C 45.14, H 3.16, N 10.53. Found: C 45.06, H 3.11, N 10.51. IR /cm⁻¹ (KBr): 3435(m), 3124(m), 1622(s), 1548(s), 1404(s), 1232(s), 1072(s), 856(s).

[Zn₃(L³)₂(tib)₂]_n·(H₂O)_{4.5n} (**5**). By utilizing the above described procedure used to prepare **1** with H₃L³ (0.0302 g, 0.1 mmol) instead of H₃L¹. Colorless blocked crystals suitable for X-ray diffraction analysis were collected after the reactor was cooled to room temperature from reaction temperature with the yield of 0.059 g, 82% (based on L³ ligand). Anal. Calcd. for C₆₀H₄₇N₁₂O_{18.5}Zn₃: C 50.45, H 3.32, N 11.77. Found: C 50.41, H 3.37, N 11.71. IR /cm⁻¹ (KBr): 3413(m), 3136(m), 1620(s), 1514(s), 1381(s), 1238(s), 1070(s), 850(s).

[Zn₂(HL³)₂(tib)₂]_n·(H₂O)_n (**6**). The preparation of **6** is similar to that of **5** except that the quantity of Zn(OAc)₂·2H₂O was decrease to 0.1 mmol. Colorless blocked crystals suitable for X-ray diffraction analysis were obtained with the yield of 0.052 g, 80% (based on L¹ ligand). Anal. Calcd. for C₆₀H₄₂N₁₂O₁₅Zn₂: C 55.35, H 3.25, N 12.91. Found: C 55.26, H 3.22, N 12.95. IR /cm⁻¹ (KBr): 3419(m), 3130(m), 1616(s), 1516(s), 1384(s), 1247(s), 1076(s), 858(s).

[Cd₃(L³)₂(tib)₂(H₂O)₂]_n·(H₂O)_{4n} (**7**). The similar procedure used for preparation of **7** was followed to prepare **2** except that H₃L¹ was replaced by H₃L³ (0.0302 g, 0.1 mmol). Colorless blocked crystals suitable for X-ray diffraction analysis were obtained with the yield of 0.066 g, 83% (based on L³ ligand). Anal. Calcd. for C₃₀H₂₅N₆O₁₀Cd_{1.5}: C 45.14, H 3.16, N 10.53. Found: C 45.20, H 3.13, N 10.55. IR /cm⁻¹ (KBr): 3410(m), 3111(m), 1619(s), 1502(s), 1396(s), 1247(s), 1076(s), 831(s).

Physical Measurements. Elemental analyses were carried out with an Elementary Vario El. The infrared spectroscopy on KBr pellets was performed on a Bruker Tensor-37 spectrophotometer in the region of 4000-400 cm⁻¹. TGA was measured on a Perkin-Elmer TG-7 analyzer heated from 30-800°C under air. Steady-state fluorescence spectroscopic studies were performed on an F 4500 (Hitachi). The slit width was 5.0 nm for excitation and 2.5 nm for emission. The photon multiplier voltage was 700 V.

Single Crystal X-ray Diffraction Determination. Data were collected on a Oxford Diffraction Gemini E system with Mo K α radiation ($\lambda = 0.71073$ Å). Final unit cell parameters were

derived by global refinements of reflections obtained from integration of all the frame data. The collected frames were integrated by using the preliminary cell-orientation matrix. CrysAlisPro Agilent Technologies software was used for collecting frames of data, indexing reflections, and determining the lattice constants; CrysAlisPro Agilent Technologies for integration of intensity of reflections and SCALE3 ABSPACK for absorption correction. The structures were solved by the direct method (SHELXS-97) and refined by full-matrix least-squares (SHELXL-97) on F².¹⁴ Anisotropic thermal parameters were used for the nonhydrogen atoms and isotropic parameters for the hydrogen atoms. Hydrogen atoms were added geometrically and refined using a riding model. 'DFIX' command was used to restrain the hydrogen atoms of water molecules in complexes **1-7**. Crystallographic data and other pertinent information for all the complexes are summarized in Table 1. Selected bond distances and bond angles with their estimated standard deviation are listed in Table S1†. CCDC 983513-983519 for **1-7**, respectively, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Conclusions

In summary, "old-fashioned" ligand of 1,3,5-tris(1-imidazolyl)benzene (tib) have been further exploited to construct seven various zinc/cadmium coordination polymers in the presence of three asymmetric semirigid V-shaped tricarboxylate ligands. Systematic and comparative studies on the structures reveal that the diversity in the new formed pattern made of tib ligands and metal ions in these polymers actually are induced by the three asymmetric V-shaped tricarboxylate ligands together with used metals.

Acknowledgements

Financial support from the National Key Basic Research Program of China (Grant Nos. 2013CB933402 and 2012CB224801), Natural Science Foundation of China, Beijing Municipal Commission of Education, and University of Science and Technology Beijing is gratefully acknowledged.

Notes and references

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† Electronic Supplementary Information (ESI) available: [X-ray crystallographic files (CIF), pdf of check-cif, diagrams of the structures of **2-5**, tib coordination mode, power X-ray diffraction analysis (PXRD), TGA, and luminescence curves, and selected bond distances and angles of compounds **1-7**.]. See DOI: 10.1039/b000000x/

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Graphic Abstract**Synthesis, Crystal Structure, and Luminescence Properties of Seven Tripodal Imidazole-based Zn/Cd(II) Coordination Polymers Induced by Tricarboxylates**

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New structural patterns made of “old-fashioned” ligand of 1,3,5-tris(1-imidazolyl)benzene have been obtained by using the three asymmetric V-shaped tricarboxylate ligands together with different metals.

