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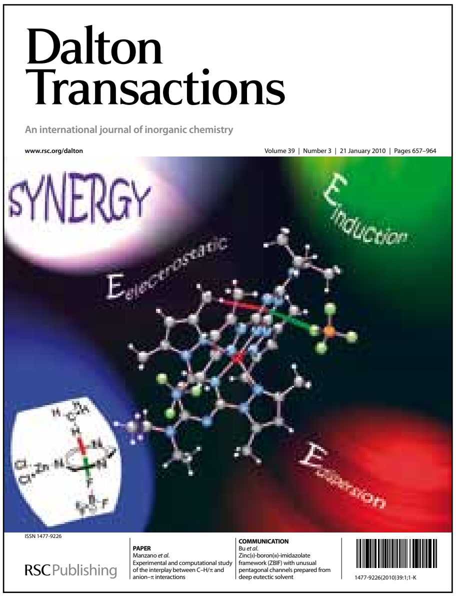
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**COMMUNICATION**
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# Five metal–organic frameworks from 3,4-dimethylphenyl substituted imidazole dicarboxylate: Syntheses, structures and properties

**Hongliang Jia,[a,b] Yanlin Li,[a] Zhifang Xiong,[a] Chengjie wang,[a] Gang Li[*a]**

**ABSTRACT:** Five metal-organic frameworks, namely, $[Mn_3(H_2DMPhIDC)_2(HDMPhIDC)_2(bpp)]_n$ ($H_3DMPhIDC$ = 2-(3,4-dimethylphenyl)-1*H*-imidazole-4,5-dicarboxylic acid, bpp = 1,3-di(4-pyridyl)propane) (**1**), $[Pb_4(DMPhIDC)_2(OH)_2]_n$ (**2**), $[Cd(HDMPhIDC)(en)]_n$ (en = ethylenediamine) (**3**), $[Cu_3(HDMPhIDC)_3(Py)_3]_n$ (Py = pyridine) (**4**) and $\{[Zn_2(HDMPhIDC)_2(Phen)_2]_2\cdot H_2O\}_n$ (Phen = 1,10-phenanthroline) (**5**) have been hydro(solvo)thermally synthesized and structurally characterized by single-crystal X-ray diffraction, elemental and thermal analyses and IR spectra. Polymer **1** displays a 3D noninterpenetrated framework with 1D open channels. Polymer **2** exhibits a stepped (4, 4, 4, 4, 6, 6)-connect 2D topology. Polymer **3** is a left-handed helix chain. Polymers **4** and **5** arrange the 3D supramolecular networks containing 1D corrugated chain *via* the π···π stacking or hydrogen bond interactions. In these MOFs, the imidazole dicarboxylate ligand shows various coordination modes and strong coordination ability. Furthermore, solid-state luminescent properties of the polymers have also been discussed.

## Introduction

Metal-organic frameworks (MOFs) have emerged as the unique crystalline materials because of their potential applications as functional materials. To get such materials, it is the most common form to employ the well-designed organic ligands as well as appropriate metal ions. So far, thousands of structurally characterized MOFs have been obtained by metal ions and

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† Electronic supplementary information (ESI) available: The X-ray crystallographic files in CIF format. CCDC reference numbers 937411 – 937415 are for **1-5**, respectively.

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organic ligands linked *via* coordination bonds taking advantage of the principles of network-based crystal engineering, which are discussed in several comprehensive reviews published.[1-3] However, formulating a precise methodology of controllable structures with desired properties is fraught with difficulty. Because the process of aggregation is frequently modulated by various factors such as metal source, ligands, solvents, templates, pH value, temperature, metal-ligand ratio, and so on,[4,5] and the same reactants can usually result in completely different structures because of the extreme sensitivity of self-assembly to reaction conditions. Among all factors, the judicious selection of appropriate organic ligands is proved to be one of the most effective ways to manipulate the versatile structures, and the length, rigidity, coordination modes, functional groups, or substituents of the organic ligands can bring about consequential effects on the final structures. In addition, the conformational freedom nature of the semirigid ligand may provide more possibility for the construction of nontrivial topology structures and microporous MOFs.

Up to now, the semirigid ligand, 2-(3,4-dimethylphenyl)-1*H*-imidazole-4,5-dicarboxylic acid ($H_3DMPhIDC$) has been documented as an fashion and versatile organic building unit in constructing coordination architectures by our group,[6] however, we believe that the MOFs of this ligand with aesthetic architectures and peculiar topologies could still be constructed by changing assembly environments and strategies. Because of the strong coordination flexibility and capability of satisfying and mediating the geometric need of metal centers, it is also effective to introduce auxiliary ligands in preparing MOFs with novel topologies.[7-9] Thereby, more systematic research on coordination chemistry of this ligand is worthy of being done, which is significant contributory to not only understanding the control of structure and topology of MOFs but also enriching its coordination chemistry.

On the basis of aforementioned understanding the coordination chemistry of this versatile ligand, we consider that the simultaneous employment of $H_3DMPhIDC$ ligand and three auxiliary linkers (Scheme 1) will contribute to the formation of various architectures and help chemists understand the process of self-assembly. As anticipated, we successfully apply this strategy and obtain five MOFs, namely, $[Mn_3(H_2DMPhIDC)_2(HDMPhIDC)_2(bpp)]_n$ (bpp = 1,3-di(4-pyridyl)propane) (**1**), $[Pb_4(DMPhIDC)_2(OH)_2]_n$ (**2**), $[Cd(HDMPhIDC)(en)]_n$ (en = ethylenediamine) (**3**), $[Cu_3(HDMPhIDC)_3(Py)_3]_n$ (Py = pyridine) (**4**) and

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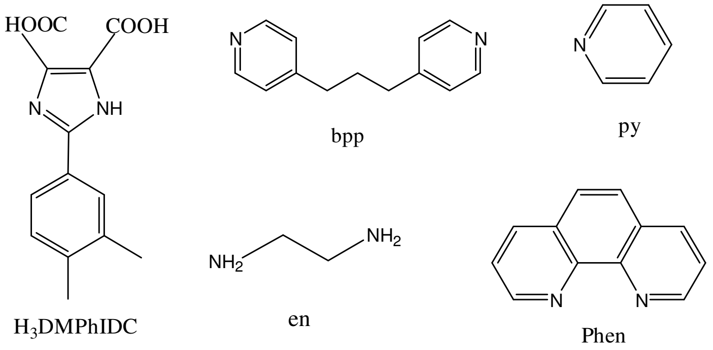
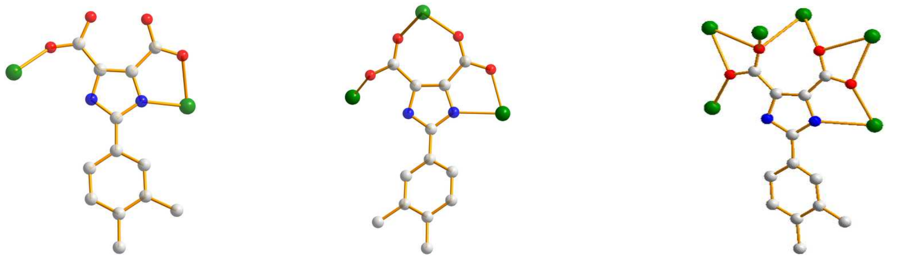
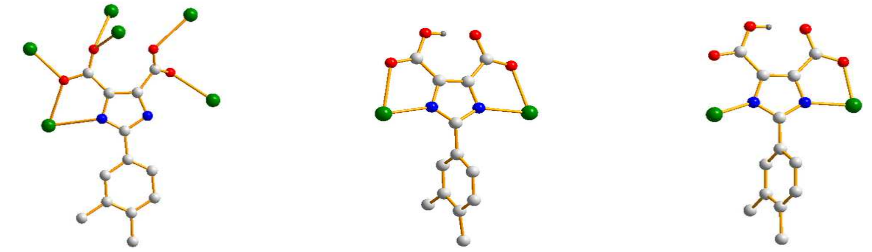
$\{[Zn_2(HDMPhIDC)_2(Phen)_2]_2\cdot H_2O\}_n$ (Phen = 1,10-phenanthroline) (**5**). The five compounds have been characterized by elemental analyses, IR spectra, thermal analyses, and single-crystal X-ray diffraction. The crystal structures, topological analyses, photoluminescence and thermal properties have been studied in detail.



**Scheme 1**. Ligands used in this work



(a) $\mu_2$-*k*N,O:*k*O' (b) $\mu_3$-*k*N,O:*k*O',O'':*k*O''' (c) $\mu_6$-*k*N,O:*k*O,O':*k*O',O'':*k*O'',*k*O''':*k*O'':*k*O'''



(d) $\mu_6$-*k*N,O:*k*O:*k*O':*k*O':*k*O'':*k*O''' (e) $\mu_2$-*k*N,O:*k*N',O' (f) $\mu_2$-*k*N,O:*k*N'

**Scheme 2.** Coordination modes of the $H_3$DMPhIDC ligand

## Experimental section

### Materials

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. The organic ligand $H_3$DMPhIDC was prepared according to the literature procedure.[10]

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The C, H and N microanalyses were carried out on a FLASH EA 1112 analyzer. IR spectra were recorded on a Nicolet NEXUS 470-FTIR spectrophotometer as KBr pellets in the 400-4000 $cm^{-1}$ region. TG measurements were performed by heating the crystalline samples from 20 to 900 °C at a rate of 10 $°C\cdot min^{-1}$ in air on a Netzsch STA 409PC differential thermal analyzer. Fluorescence spectra were characterized at room temperature by a F-4500 fluorescence spectrophotometer.

**Preparation of crystalline polymer $[Mn_3(H_2DMPhIDC)_2(HDMPhIDC)_2(bpp)]_n$ (1)**

A mixture of $MnCl_2\cdot 4H_2O$ (0.1 mmol, 19.8 mg), $H_3DMPhIDC$ (0.1 mmol, 26.0 mg), bpp (0.1 mmol, 19.8 mg), $CH_3OH/H_2O$ (4/4, 8 mL) and $Et_3N$ (0.6 mmol, 0.084 mL) was sealed in a 25 mL Teflon-lined stainless steel autoclave, heated at 150 °C for 132 h, and then cooled to room temperature. The colorless cubic crystals of **1** were isolated, washed with distilled water, and dried in air (59% yield based on Mn). Anal. Calcd. for $C_{65}N_{10}O_{16}H_{55}Mn_3$: C, 55.83; H, 3.94; N, 10.02%. Found: 55.79; H, 4.01; N, 10.35%. IR ($cm^{-1}$, KBr): 3556 (m), 3432 (m), 2921 (w), 1640 (w), 1573 (s), 1463 (m), 1431 (s), 1393 (m), 1286 (m), 1261 (m), 1124 (s), 1026 (w), 904 (m), 835 (m), 763 (m), 741 (w), 561 (w).

**Preparation of crystalline polymer $[Pb_4(DMPhIDC)_2(OH)_2]_n$ (2)**

A mixture of $Pb(NO_3)_2$ (0.1 mmol, 33.1 mg), $H_3DMPhIDC$ (0.1 mmol, 26.0 mg), $CH_3OH/H_2O$ (3/4, 7 mL), $Et_3N$ (0.028 mL, 0.2 mmol) was sealed in a 25 mL Teflon-lined stainless steel autoclave, heated at 160°C for 72 h, and then cooled to room temperature. The colorless long strips of crystals of **2** were isolated, washed with distilled water, and dried in air (31% yield based on Pb). Anal. Calcd. for $C_{26}H_{20}N_4O_{10}Pb_4$: C, 22.67; H, 1.46; N, 4.07%. Found: C, 22.31; H, 1.61; N, 4.18%. IR ($cm^{-1}$, KBr): 3434 (m), 2966 (w), 2924 (w), 1633 (w), 1548 (m), 1509 (s), 1460 (m), 1416 (s), 1388 (m), 1276 (m), 1253 (m), 1135 (w), 1114 (s), 983 (w), 892 (w), 825 (m), 804 (m), 747 (m), 659 (w), 563 (w).

**Preparation of Crystalline Polymer $[Cd(HDMPhIDC)(en)]_n$ (3)**

A mixture of $Cd(NO_3)_2\cdot 4H_2O$ (0.1 mmol, 30.8 mg), $H_3DMPhIDC$ (0.1 mmol, 26.0 mg),

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$CH_3OH/H_2O$ (3/4, 7 mL), en (0.30 mmol, 0.042 mL) was sealed in a 25 mL Teflon-lined stainless steel autoclave, heated at 150°C for 96 h, and then cooled to room temperature. Light-yellow square blocks crystals of **3** were isolated, washed with distilled water, and dried in air (71% yield based on Cd). Anal. Calcd. for $CdC_{15}N_4O_4H_{18}$: C, 41.79; H, 4.18; N, 13.0%. Found: C, 41.31; H, 4.23; N, 13.15%. IR ($cm^{-1}$, KBr): 3375 (m), 3342 (m), 2923 (w), 2889 (w), 1686 (m), 1588 (s), 1542 (s), 1493 (s), 1398 (m), 1275 (s), 1130 (m), 995 (w), 959 (m), 833 (w), 793 (m), 738 (w), 555 (w), 489 (w), 443 (w).

**Preparation of crystalline polymer $[Cu_3(HDMPhIDC)_3(Py)_3]_n$ (4)**

A mixture of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.1 mmol, 37.1 mg), $H_3DMPhIDC$ (0.1 mmol, 26.0 mg), $H_2O$ (7 mL), and Py ( 0.4 mmol, 0.056 mL) was sealed in a 25 mL Teflon-lined stainless steel autoclave, heated at 160°C for 72 h, and then cooled to room temperature. Dark green color acicular-shaped crystals of **4** were isolated, washed with distilled water, and dried in air (58% yield based on Cu). Anal. Calcd. for $C_{54}H_{45}N_9O_{12}Cu_3$: C, 53.93; H, 3.77; N, 10.48%. Found: C, 53.71; H, 3.83; N, 10.21%. IR ($cm^{-1}$, KBr): 3471 (m), 2920 (w), 1694 (s), 1591 (s), 1553 (s), 1450 (s), 1396 (m), 1256 (s), 1122 (m), 1024 (m), 896 (m), 844 (s), 760 (s), 701 (m), 442 (m).

**Preparation of crystalline polymer $\{[Zn_2(HDMPhIDC)_2(Phen)_2]_2 \cdot H_2O\}_n$ (5)**

A mixture of $Zn(ClO_4)_2 \cdot 6H_2O$ (0.1 mmol, 37.2mg), $H_3DMPhIDC$ (0.1 mmol, 26.0 mg), Phen (0.1 mmol, 26.0 mg), $H_2O$ (7 mL), and $Et_3N$ (0.1 mmol, 0.014 mL) was sealed in a 25 mL Teflon-lined stainless steel autoclave, heated at 160°C for 72 h, and then cooled to room temperature. Colorless and transparent bulk-shaped of crystals of **5** were isolated, washed with distilled water, and dried in air (55% yield based on Zn). Anal. Calcd. for $C_{100}H_{74}N_{16}O_{17}Zn_4$: C, 59.07; H, 3.67; N, 11.02%. Found: C, 58.85; H, 3.83; N, 11.15%. IR ($cm^{-1}$, KBr): 3446 (w), 2917 (w), 1630 (m), 1564 (s), 1452 (m), 1349 (m), 1274 (s), 1133 (s), 1025 (m), 907 (s), 898 (m), 845 (s), 731 (s), 646 (m), 557 (w), 515 (w), 427 (w).

**Crystal structure determinations**

Crystal data and experimental details for polymers **1**-**5** are contained in Table 1. Measurements of **1**-**5** were made on a Bruker smart APEXII CCD diffractometer with a

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graphite-monochromated Mo-$K\alpha$ radiation ($\lambda$ = 0.710 73 Å). Single crystals of **1**-**5** were selected and mounted on a glass fiber. All data were collected at room temperature using the $\omega$-$2\theta$ scan technique and corrected for Lorenz-polarization effects. A correction for secondary extinction was applied.

The five structures were solved by direct methods and expanded using the Fourier technique. The hydrogen atoms on C were positioned geometrically and refined using a riding model. The hydrogen atoms on O were found at reasonable positions in the differential Fourier map and located there. All the hydrogen atoms were included in the final refinement. All calculations were performed using the SHELXL-97 crystallographic software package.[11] Selected bond lengths and bond angles and the parameters of hydrogen bonds are listed in Tables 2 and 3, respectively.

## Results and discussion

### Crystal structure of crystalline polymer $[Mn_3(H_2DMPhIDC)_2(HDMPhIDC)_2(bpp)]_n$ (1)

The X-ray structural analysis suggests that the 3D framework of **1** can be described as a (2,3,3)-connected topology with the point symbol of $\{10^3\}4\{10\}$.

As depicted in Figure 1a, the asymmetric unit consists of two crystallographically independent Mn(II) atoms, two singly deprotonated $H_2DMPhIDC^-$ ligands, two doubly deprotonated $HDMPhIDC^{2-}$ ligands, as well as one bpp molecule. Mn1 is located in a distorted octahedral coordination environment, in which the equatorial plane is composed of two carboxylate oxygen atoms (O1 and O3a) and two nitrogen atoms (N1 and N5), and the apical positions are situated by two oxygen atoms. The O1, O2a, O3a, O5 and N1 are from one individual $H_2DMPhIDC^-$ and two $HDMPhIDC^{2-}$ anions, respectively, while the N5 atom comes from bpp. Mn2 is hexacoordinated with two nitrogen atoms (N4, N4a) occupying *cis* positions and with two oxygen atoms (O4a, O4) from two bidentate bridging $H_2DMPhIDC^-$ ligands in equatorial *cis* geometry, and the axial positions are occupied by two carboxylate oxygen atoms (O8A and O8) of two monodentate $HDMPhIDC^{2-}$ anions. Mn1 and Mn2 are bridged by $H_2DMPhIDC^-$ ligands to form a dimer with Mn1···Mn2 separation of 7.9679(10)

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Å (Figure 1a). The Mn-O/N bond lengths are in the range of 2.108(4)-2.320(4) Å, and the O/N –Mn– O/N angles range from 73.44(16)-180.000(1)°, all of which fall within the normal values.[12]

The $H_3$DMPhIDC ligand in **1** adopts two coordination modes: one imidzole and carboxyl groups adopt a bidentate and monodentate coordination mode to bridge two Mn atoms (Scheme 2a); the other imidzole and carboxyl groups adopt the di(bidentate) and monodentate coordination modes to bridge three Mn atoms with dihedral angles of 13.41, 42.37 and 43.02°, respectively (Scheme 2b). From the *c*-direction, Mn(II) ions are bridged by imidazole dicarboxylate ligands to self-assembly into a lemniscate meso helix, and pyridine rings are located on both sides of the chain. The pyridine rings distance of the same side is 7.55 Å. In the *ac* plane, adjacent chains are connected *via* Mn(II) ions into a two-dimensional expansion surface (Figure 1b). The layers are catenated by bpp to form a 3D structure (Figure 1c).

A better insight into the nature of this intricate framework can be achieved by the application of a topological approach, reducing multidimensional structures to simple node and connection nets. The $H_3$DMPhIDC ligand, Mn(II) atom and bpp can be regarded as 3-, 3- and 2-connected nodes, respectively. According to the simplification principle, the resulting topological structure of **1** is a (2,3,3)-connected gra net (Figure 1d).

Until now, there are only one 3D polymer $\{[Mn_3(\mu_3\text{-DMPhIDC})_2(H_2O)_6]\cdot 2H_2O\}_n$ (A) and one 2D left- and right-handed helical polymer $\{[Mn_5(\mu_3\text{-DMPhIDC})_2(\mu_2\text{-HDMPhIDC})_2(Phen)_5]\cdot 2CH_3OH\cdot 3H_2O\}_n$ (B) constructed from $H_3$DMPhIDC ligand.[6b,6c] Although the synthetic approach of polymer **1** is similar with A, except bpp was used, a completely different product of **1** is obtained, which could help us deeply understand the nature of polymeric frameworks. Polymer **1** is the second example of 3D coordination polymer from the $H_3$DMPhIDC ligand and it has evoked increasing interest in devising more fascinating MOFs.

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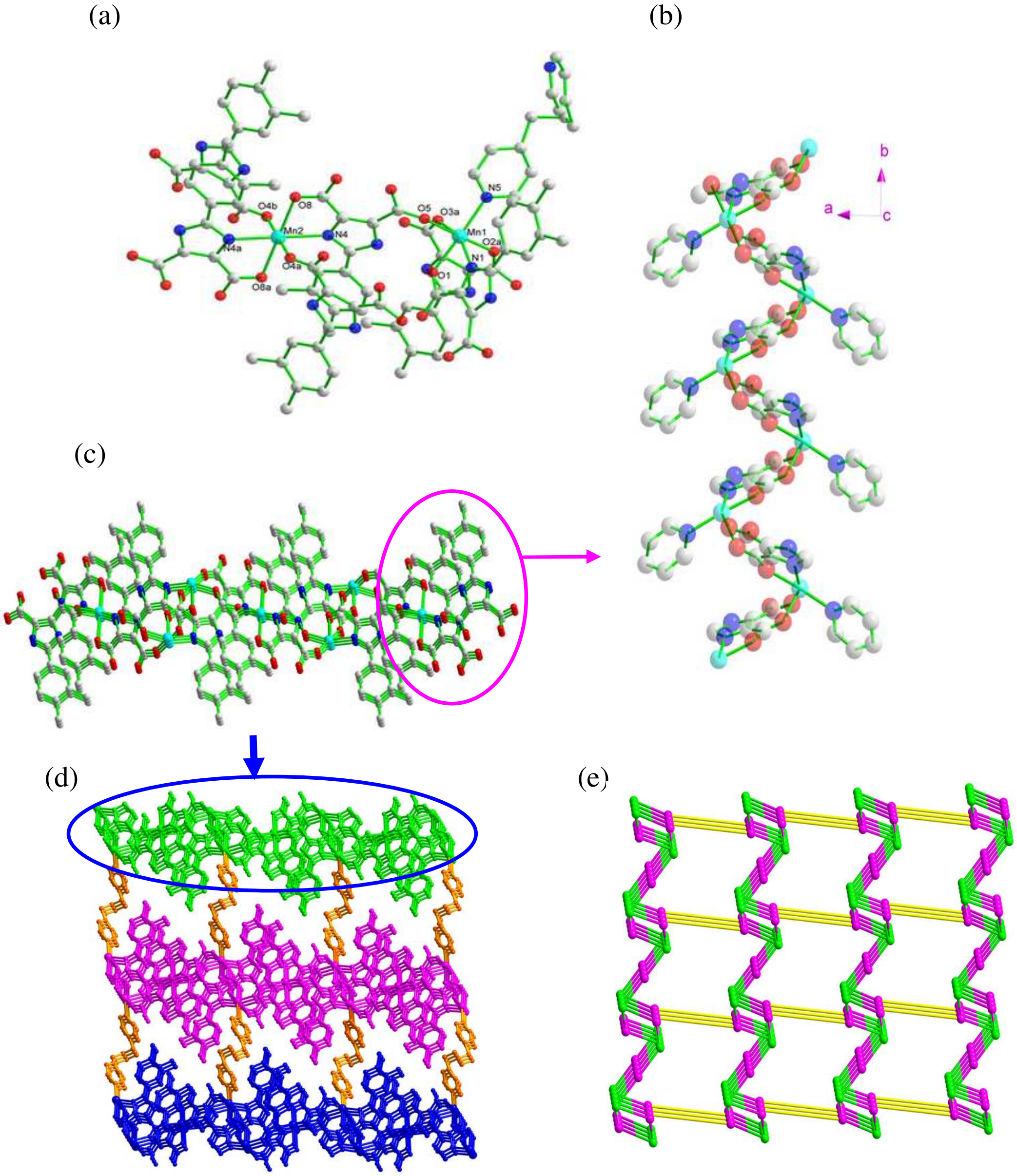

Figure 1. (a) View of the coordination environments of the Mn centers in **1**. (b) One-dimensional meso-helical chain. (c) Side view of the two-dimensional sheet. (d) Three-dimensional structure of **1**. (e) Schematic representation of **1**.

### Crystal structure of crystalline polymer $[Pb_4(DMPhIDC)_2(OH)_2]_n$ (2)

Single crystal X-ray structural analysis reveals that **2** exhibits a unique 2D framework with the stepped one-dimensional chains.

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As illustrated in Figure 2a, the coordination subunit of **2** is composed of four crystallographically independent Pb(II) cations, two DMPhIDC$^{3-}$ ligands and two OH$^{-}$ anions. The four Pb(II) atoms have two different coordination environments: three of which are five-coordinated, the other one is six-coordinated. The coordination environments of Pb1 and Pb2 are similar and in distorted trigonal bipyramidal environments, each of which is bound by three carboxyl oxygen and one nitrogen atoms from DMPhIDC$^{3-}$ anions and the other oxygen atoms from hydroxyl units. The coordination environment around the Pb3 center is best portrayed as the distorted [PbO6] octahedral geometry, ligated by five oxygen atoms from three different DMPhIDC$^{3-}$ anions as well as one oxygen atoms from one water (Figure 2a). The Pb4 atom is in a distorted trigonal bipyramidal environment, in which five coordination sites are all occupied by oxygen atoms. The O4C, O6B, O10 are in the triangular plane and O5, O3C are in axial positions. The Pb-O bond lengths are varying from 2.235 (13)-2.724 (13) Å, while Pb-N bond lengths are from 2.235 (12) to 2.699 (13) Å, in accordance with those previous values.[14,15]

The completely deprotonated DMPhIDC$^{3-}$ anion shows two quite distinctive coordination modes, namely $\mu_6$-*k*N,O: *k*O: *k*O′: *k*O″: *k*O″: *k*O‴ (Scheme 2c) and $\mu_6$-*k*N,O:*k*O,O':*k*O',O":*k*O",*k*O'":*k*O":*k*O'" (Scheme 2d). One Pb(II) atom connects other three Pb(II) atoms *via* DMPhIDC$^{3-}$ ligands to from a quadrate with the closest Pb···Pb distances being Pb1···Pb3 = 4.7634(10) Å, Pb4···Pb2 = 4.2366(10) Å, Pb1···Pb4 =3.8634(10) Å and Pb2···Pb3 = 3.9736(10)Å, which are considerably shortened by the presence of a Pb-O-Pb linkage. The Pb-Pb-Pb angles range from 84.63 (19) to 94.07 (19)° indicating a unobvious distortion from the ideal quadrate angle of 90°. These quadrangles further extended to bring about a infinite 1D chain, in which individual parallelogram as the secondary building unit is presented clearly with two side lengths being 3.9736 and 4.8470Å, respectively (Figure 2b). Furthermore, these infinite chains are linked by the DMPhIDC$^{3-}$ ligands to build up layers. Of particular interest, the most striking feature of complex **2** is the high coordination numbers of DMPhIDC$^{3-}$ ligand, which adopts its nitrogen and oxygen atoms coordinate to six lead atoms, which has never been observed previously.

To fully appreciate the structure, topology should be invoked. It is necessary to consider Pb atom as one kind of linker, $H_3$DMPhIDC and OH$^{-}$ ligands as other two kinds of linkers. Each

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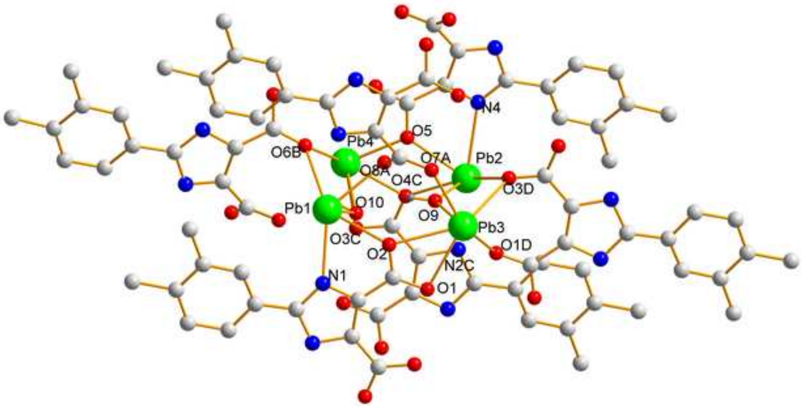
$H_3$DMPhIDC ligand connects six Pb atoms, while each Pb(II) atom also links three $H_3$DMPhIDC ligands. Thus, the $H_3$DMPhIC and Pb can be acted as a 6-connected node, and 3-connected node, respectively. According to this simplification, overall framework of **2** has a stepped (4,4,4,4,6,6)-connect two-dimensional topology as schematically illustrated in Fig. 2c, topology symbol is {3.4.64}{3.43.52}{3.44.52.68}.

Polymer **2** is the first example of 2D Pb(II) coordination polymer built by the $H_3$DMPhIDC ligand. The successful preparation of polymer **2** manifest that $H_3$DMPhIDC ligand displays a remarkable capacity for binding more kinds metals in terms of both the variety of coordination modes and the number of metals, as exemplified in its lead salt, which create chance and driving force for exploiting and expanding $H_3$DMPhIDC ligand more unique properties to us.

(a)



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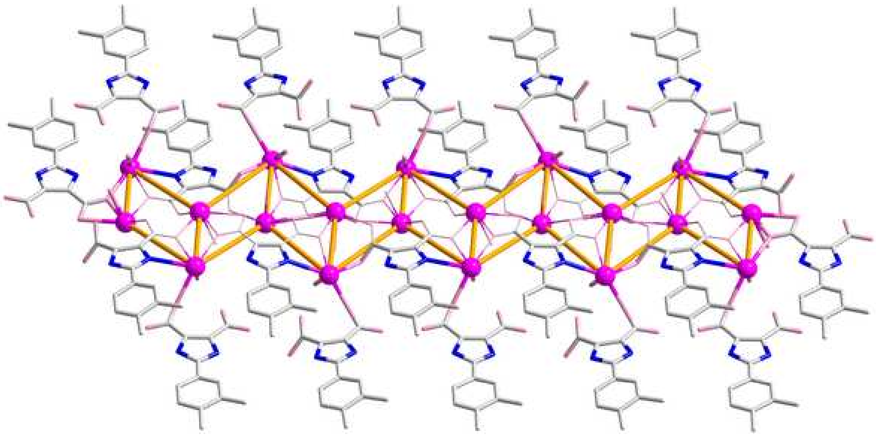

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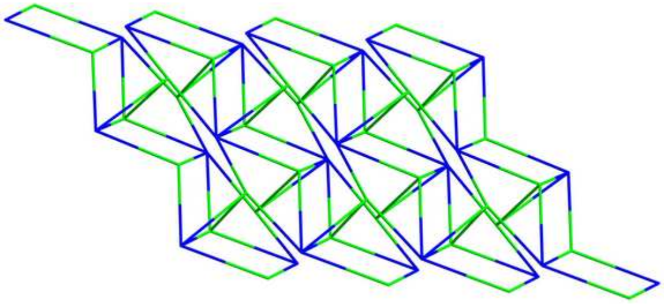

**Fig. 2** (a) Coordination environments of Pb(II) atoms in polymer **2** (H atoms omitted for clarity). (b) The chain constructed from DMPhIDC$^{3-}$ and Pb(II) atoms. (c) The new (4,4,4,4,6,6)-connected topologic structure of **2** with a {3.4.64}{3.43.52}{3.44.52.68 } network in the Schlafli notation.

### Crystal structure of crystalline polymer [Cd(HDMPhIDC)(en)]$_n$ (3)

Complex **3** features a one-dimensional left-handed helix chain structure. The coordination geometry of Cd$^{2+}$ center can be described as distorted {CdN$_4$O$_2$} octahedral (Figure 3a), in which the equatorial plane is composed of one nitrogen atom (N2A) and two chelating carboxylate oxygen atoms (O1 and O4A) of different HDMPhIDC$^{2-}$ ligands and the other nitrogen atoms (N4) from en, and the apical positions are situated by two nitrogen atoms (N1 and N3) from HDMPhIDC$^{2-}$ ligands and en. The Cd-N distances range from 2.244(8) to 2.412(8) Å and Cd-O distances are from 2.412(8)-2.539(7) Å, which are consistent with the previous values.[16-19]

The HDMPhIDC$^{2}$ ligand shows one type of coordination mode, namely $\mu_2$-*k*N, O: *k*N′, O′ (Scheme 2e). As shown in Figure 3b, the most interesting structural feature of **3** is that two kinds of helical chains in a (1D/1D) parallel fashion to give rise to a 2D undulating layer by hydrogen bonds, which extends parallel to the (010) crystallographic plane. (Figure 3c) The neighboring sheets are linked to each other with the weak π-π stacking interactions to generate a 3D supramolecular framework with 1D channel (Figure 3d). Additionally, the classical hydrogen bonding form between nitrogen-atoms and the carboxylate oxygen atoms (N4···O3 = 3.106 Å, N3···O1 = 3.026 Å and N3···O2 = 3.209 Å) reinforce the resulting 3D supramolecula

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framework. Intermolecular interactions have been successfully used to bring the single-stranded helices close to each other to create the stable structure.

Careful inspection of the structure of complex **3** suggests that due to metal ions are chelated tightly by ethylenediamine, the whole molecule only can infinite extends along certain direction forming a 1D chain (figure 3b) with pitch length of 14.51 (16) Å.

To the best of our knowledge, only one example of the Cd(II) coordination polymer $[Cd(\mu_2\text{-HDMPhIDC})(Py)]_n$ constructed from the $H_3DMPhIDC$ ligands can be found,[6b] which is a meso-compound and displays a 3D non-interpenetrated framework with 1D open channels and $[Cd_2(HDMPhIDC)_3(Py)_2]_4$ cages, which are composed of left- and right-handed helices pillared by $Cd^{2+}$ linkages. In polymer **3**, we use different reaction conditions to possess a one-dimension left-handed helix chain structure. This difference of conformation confirmed that the process of self-assembly is extreme sensitive to reaction conditions.

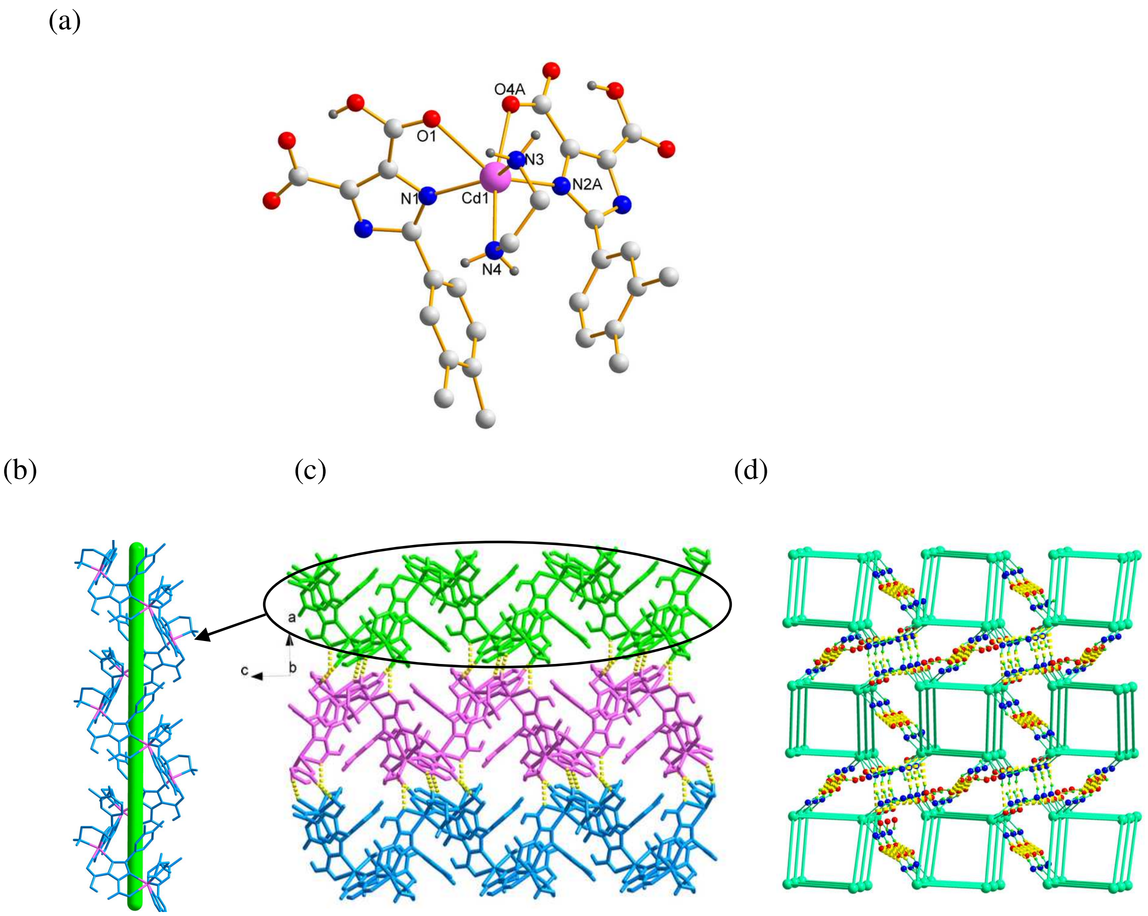

**Fig. 3** (a) Coordination environment of Cd(II) atom in polymer **3** (H atoms omitted for clarity). (b) The helix chain along the *b*-axis. (c) The layer constructed by hydrogen bonds. (d) Simplified 3D

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supramolecular framework of **3**.

### Crystal structure of crystalline polymer $[Cu_3(HDMPhIDC)_3(Py)_3]_n$ (4)

The crystal structure determination reveals that the coordination subunit in complex **4** is composed of three independent Cu(II) ions, three $HDMPhIDC^{2-}$ anions and three Py units. In the subunit, three Cu atoms lie in a approximate isosceles triangle with two symmetry-related Cu atoms, and the adjacent Cu···Cu interatomic distances are Cu1···Cu2 = 6.18(16) Å, Cu1···Cu3 = 6.22(21) Å and Cu2···Cu3 = 8.97(21)Å. The local coordination geometry around the $Cu^{2+}$ atom is depicted in Figure 4a. The Cu1, Cu2 and Cu3 atoms are 5-coordinated, and Cu(II) atoms are located in $[CuN_3O_2]$ coordination environments. They are surrounded by two carboxylate oxygen atoms and three nitrogen atoms from two $HDMPhIDC^{2-}$ ligands and one py molecule. The addison parameter ($\tau = 0.157$) of Cu1 ($\tau = 0.129$ of Cu2; $\tau = 0.195$ of Cu3) reveals that the geometry around the Cu(II) atom is a slightly distorted square-pyramidal geometry with one oxygen atom in the apical position. The equatorial plane is much distorted with the mean deviation of 0.3539 Å. The Cu-O bond lengths are 1.964(7) and 2.422(8) Å, respectively, while the Cu-N bond length range from 1.949(7) to 2.052(8), these values fall within the normal limits for such bonding interactions.[20]

The $H_3DMPhIDC$ ligand adopts one kind of coordination mode to that in compound **3**. Each partly deprotonated $HDMPhIDC^{2-}$ ligand displays the di(bidentate) coordinated mode, and forms two “double-bridges” (Scheme 2e). Then the trinuclear groups are further bridged by the $HDMPhIDC^{2-}$ anions to form undulating chains (Figure 4b), and further conjoined to 2D sheets by π···π weak stacking interactions of the Py rings. The classical hydrogen bonding form between the carboxylate oxygen atoms (O8···O9 = 2.559 Å and O4···O5 = 2.580 Å), which combine with π-π stacking interaction as supramolecular force to govern the process of self-assembly form 2D network.

Further structural analysis reveals that the dihedral angle which is defined by the stacked imidazole and benzene rings is 43.303(509)°, which indicates that there are no π…π stacking interactions between the 2D sheets. The 3D framework is generated, likely due to the electrostatic and vander Waals interactions (Fig. 4c). As evidenced by single-crystal X-ray diffraction studies, the porous structure is architecturally robust.

Polymer **4** is the first example of MOFs built by the $H_3DMPhIDC$ ligand. The successful

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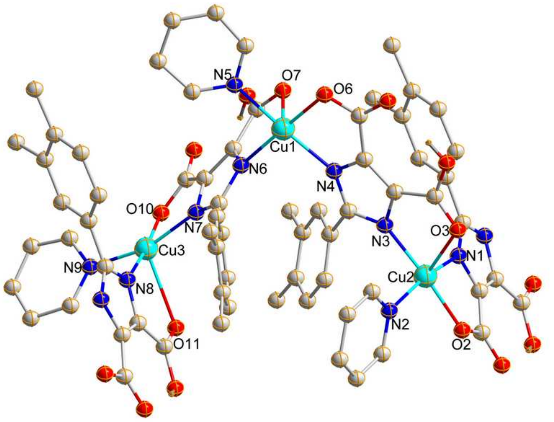
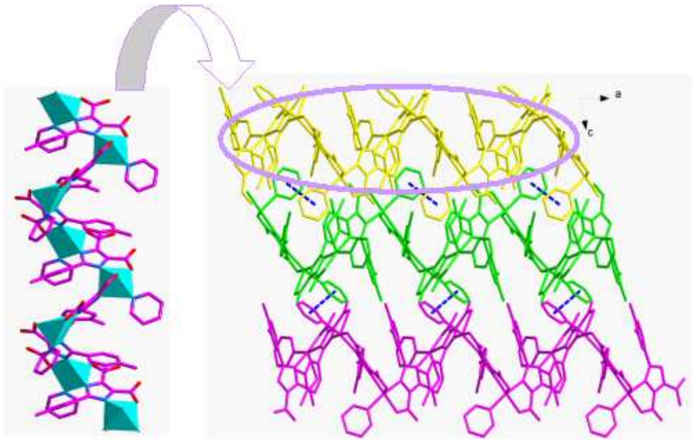
preparation of it make we more convinced that this ligand is capable of binding a wide variety of metals, and is suggestive of having more chance to study its properties.

(a)



(b) (c)



(d)

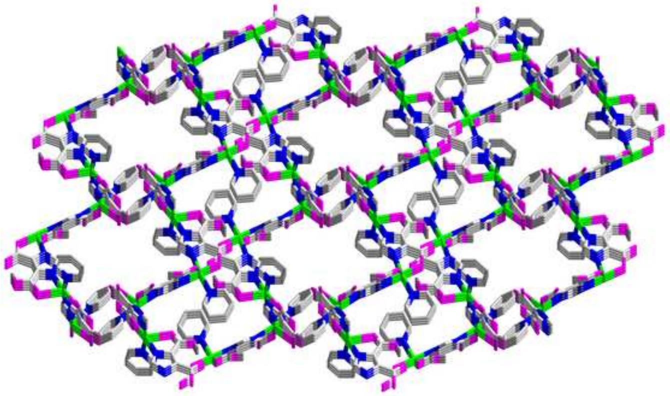


**Fig. 4** (a) Coordination environments of Cu(II) atoms in polymer **4** (H atoms omitted for clarity). (b) The waving-like chain along the *b*-axis. (c) The 2D framework supported by π···π stacking. (d) The 3D

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framework along the *b*-axis built by π···π stacking interactions (partial H, C, O atoms omitted for clarity).

## Crystal structure of crystalline ploymer $\{[Zn_2(HDMPhIDC)_2(Phen)_2]_2{\cdot}H_2O\}_n$ (5)

In complex **5**, the asymmetric unit has two independent Zn(II) ions, three $HDMPhIDC^{2-}$ anions, two phen units and one lattice water molecule. The coordination environment around the Zn(II) atom is exhibited in Figure 5a along with the atom numbering scheme. The Zn(II) atoms have two different coordination environments: $[Zn(imidazole)_2(CO_2)(Phen)]$ and $[Zn(imidazole)_2(CO_2)_2(Phen)]$. The Zn1 atom is five-coordinated showing the distorted trigonal bipyramid geometry, ligated by four nitrogen atoms (N4, N7) from two $HDMPhIDC^{2-}$ anions and (N5, N6) from one Phen molecule and the other oxygen atoms (O5) from the carboxyl group. The N4, N6 and O5 atoms are in the triangle plane and N5 and N7 occupy the axial positions, and the axial angle N5-Zn1-N7 is 148.3 (3)°. The geometry around Zn2 ion can be visualized as a slightly distorted octahedral $ZnO_2N_4$ geometry, in which two donor oxygen atoms are provided by the two deprotonated carboxylate groups, and two nitrogen atoms from the chelating phen ligand occupying the equatorial plane, and two nitrogen atoms are gave by the imidazolyl ring occupying the axial positions (Figure 4a). Deviations from the 180° and 90° bond angles for a regular octahedral geometry are observed as a result of the N3-Zn2-N8A = 155.8(3)°, N1–Zn2–O8A = 159.8(3)°, and O1-Zn2-N1 = 94.0(3)° in **5**. The Zn1–O and Zn2–O bond lengths are varying from 2.115(6) to 2.206(6) Å, which are comparable to the previous values.[21]

As shown in Figure 5b, the $HDMPhIDC^{2-}$ ligands adopt two types of coordination modes, namely $\mu_2$-*k*N, O: *k*N', O' and $\mu_2$-*k*N, O: *k*N' (Scheme 2e and 2f). Zn1 and Zn2 ions are bridged by $HDMPhIDC^{2-}$ forming a dimer with the Zn···Zn distance of 6.2776(17) Å. These dinuclear building blocks can self-assemble into a perfectly wavelike chain along the *c*-axis linked by the $HDMPhIDC^{2-}$ ligands. One fascinating structural feature of complex **5** is the Phen ligands are paralleled each other and decorated on the two sides of the chain. The adjacent chains align to build up undulated 2D grid structures through facial π-π stacking between Phen rings. (face-to-face separation 3.83(5) Å). The classical hydrogen bonds are formed between the carboxylate oxygen atoms (O3···O2 = 2.509 Å and O7···O6 = 2.479 Å), which combine with π-π stacking (3.47(15) Å) between imidazole and phenyl rings of $HDMPhIDC^{2-}$ to stabilize the

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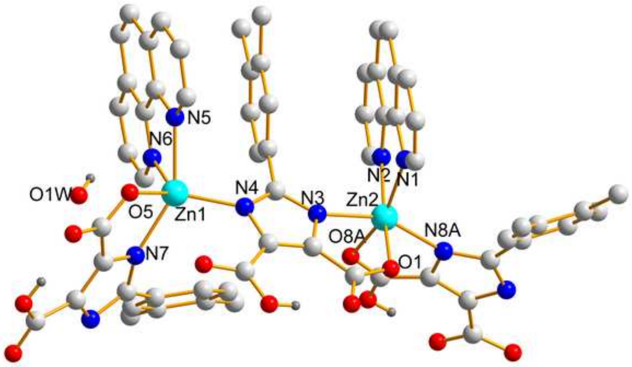
resulting supramolecular framework.

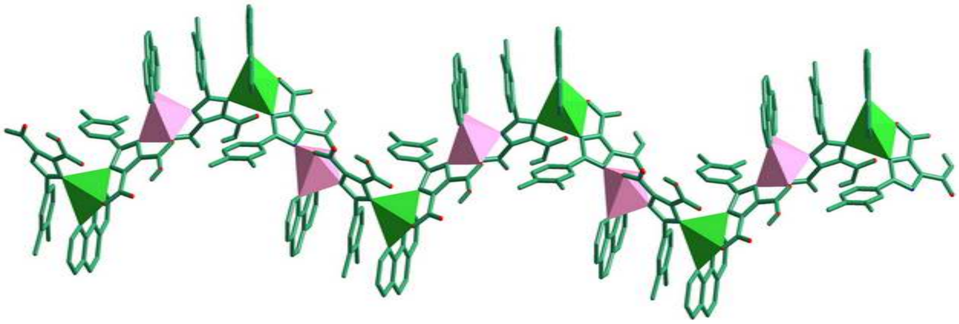
Careful inspection of the structure of complex **5** suggests that due to Phen molecules have a very strong chelation, Zn1 and Zn2 atoms only can be bridged by HDMPhIDC$^{2-}$ ligand along certain direction to form a 1D chain.

There is only one Zn(II) coordination polymer has been constructed from $H_3$DMPhIDC ligands by hydrothermally synthesized.[6b] Polymer **5** has similar synthetic approach with it, but one-dimensional corrugated chain be achieved owing to Phen participating, which is a recognition of auxiliary links playing a crucial role in the manipulation of the crystal resulting structure. This result gives us more chance to explore the rational molecular design and an effective mechanism explanation.

(a)



(b)



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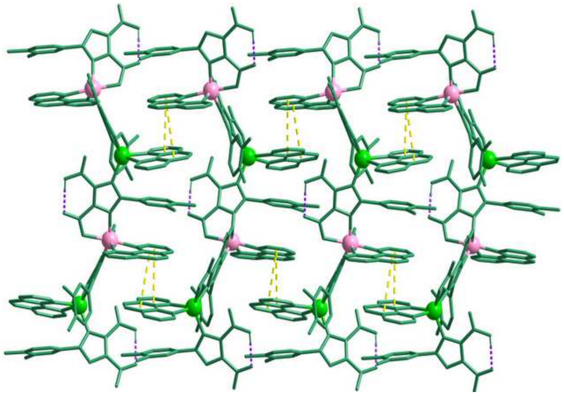
(c)



(d)

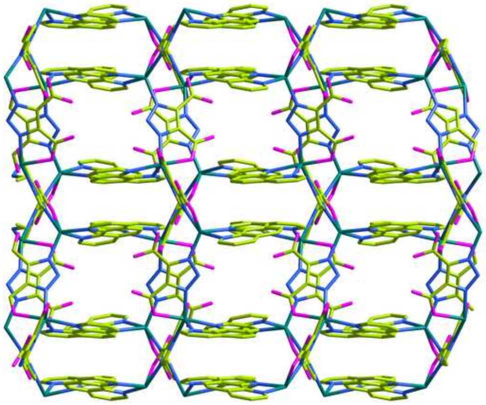


**Fig. 5** (a) Coordination environments of Zn(II) atoms in polymer **5** (H atoms omitted for clarity). (b) The linear-like chain along the *b*-axis. (c) The layer along the *b*-axis constructed by π-π stacking and C-H···π interactions (d) The 3D framework along the *c*-axis (partial H, C, O atoms omitted for clarity).

## Infrared spectra, thermal analyses and luminescent properties

The IR spectra displays characteristic absorption bands for water molecules, carboxylate, imidazole anand phenyl units. The strong and broad absorption bands in the range of 3400 – 3500 cm$^{-1}$ indicate the presence of $\nu_{N–H}$ and the $\nu_{O–H}$ stretching frequencies of imidazole ring and water molecules. The carboxyl can be observed from the absorption bands in the frequency range 1357-1669 cm$^{-1}$ as a result of $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ vibrations, respectively. The characteristic IR band of the phenyl ring at 840–860 cm$^{-1}$ due to $\delta_{=C–H}$ vibrations, which can be found at 835 cm$^{-1}$ for **1**; 825 cm$^{-1}$ for **2**; 833 cm$^{-1}$ for **3**; 842 cm$^{-1}$ for **4;** 845 cm$^{-1}$ for **5**.

Thermogravimetric analyses (TGA) of the five complexes were carried out to investigate the thermal stabilities within the range of 20.0 to 850 °C in air (See Figure 6).

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Polymer **1** is thermally stable up to 67.5 °C. From that point on, there are two consecutive process steps between 67.5 and 257.5 °C, both of them total mass loss of 15.59% can be attributed to the decomposition of bpp molecules (calculated 14.17%). The weight loss of 53.05% in the region of 257.5 -497.5 °C corresponds to the collapse of the $HDMPhIDC^{2-}$ and $H_2DMPhIDC^-$ groups (calculated 53.39%). Decomposition is complete at 589.98°C. The final residue of 31.36% is $2Mn_3O_4$.

Polymer **2** is stable up to 290.3°C, then loses weight from 290.3 to 407.7°C (observed 18.48%, calculated 17.76%) corresponding to the decomposition of dimethylphenyl and hydroxy groups. Subsequently, it keeps losing weight from 321.6 to 451.3°C corresponding to the decomposition of the remaining parts of $DMPhIDC^{3-}$ units (observed 18.22%, calculated 17.37%). The remaining weight of 63.30% corresponds to the percentage (calculated 64.87%) of the Pb and O components, indicating that the final product is 2PbO.

For polymer **3**, the weight loss corresponding to the release of en molecules is observed from 322.5 to 365.4°C (observed 22.88%, calculated 20.93%). Then an advanced degradation process takes place after 365.4 °C. It continues to decompose upon further heating and undergoes a slow weight loss of 48.07% covering the temperature from 365.4 to 520.4 °C, which corresponds to the other part destruction of $HDMPhIDC^{2-}$. Finally, a plateau region is observed from 520.4 to 900.0 °C. A mahogany amorphous residue of CdO (observed 29.05%; calculated 29.81%) remained.

Polymer **4** exhibits an initial weight loss from 87.5 to 277.5 °C, with the observed weight loss of 8.47% corresponding to the release of the coordinate water. The further weight loss of 19.42% in the temperature range of 277.5-302.5°C can be attributed to the decomposition of three py molecules (calculated 19.46%). After that, an additional weight loss of 57.73% up to 515.8°C shall be attributed to the gradual decomposition of the organic ligand. Finally, a plateau region is observed from 515.8 to 900 °C. The final black residue is 3CuO (observed 20.99%, calculated 19.48%).

Polymer **5** is stable up to 31°C, then loses weight from 31 to 433.5°C (observed 21.47%, calculated 21.97%) corresponding to 0.6Phen. The weight loss of 62.43% in the region of 433.5-703.5 °C corresponds to the other part collapse of Phen and the decomposition of $HDMPhIDC^{2-}$ group (calculated 60.33%). Finally, a plateau region is observed after 703.5°C.

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The final white residue of 14.72% is close to the calculated 15.18% based on ZnO (observed 16.1%, calculated 17.7%).

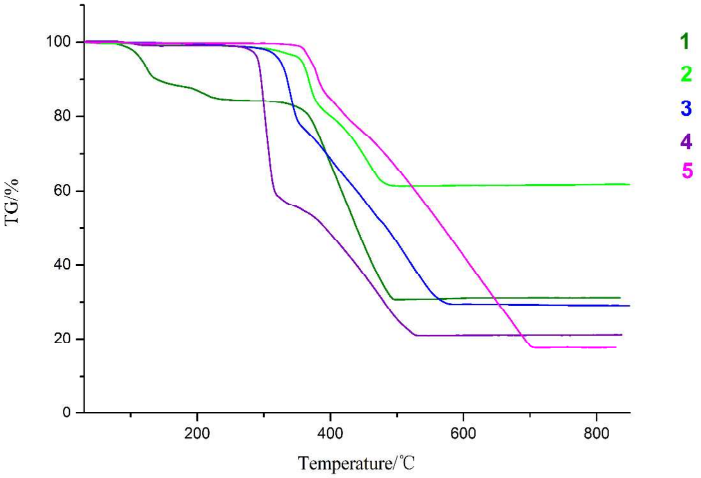

**Fig. 6** The TG curves for complexes **1-5**.

Luminescent properties of coordination polymers are promising candidates for potential applications, such as chemical sensors, white light-emitting diodes (LEDs), and electroluminescent materials (OLEDs) for displays.[22] The solid-state luminescent emission spectra of the polymers were studied at room temperature.

As reported in literature,[6b] the free $H_3DMPhIDC$ ligand displays emission with the maxima at *ca.* 396 nm when excited at 328 nm wavelength, which may be likely ascribed to $\pi^*$ - $\pi$ and/or $\pi^*$ - n transitions of $H_3DMPhIDC$. It can be observed that complex **3** exhibits an intense emission band with a maximum at 382 nm upon excitation at 273 nm. Compared with the free ligand, blue shift in **3** can be observed 396 to 382 nm. The emission of **5** ($\lambda$em = 455 nm, $\lambda$ex = 277 nm) undergoes a red-shift from 396 to 455 nm. These emissions are neither metal-to-ligand charge transfer (MLCT) nor ligand to-metal transfer (LMCT) in nature since the $Zn^{2+}$ or $Cd^{2+}$ ions are difficult to oxidize or to reduce due to their d10 configuration which can probably be assigned to the intraligand ($\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$) fluorescent emission, as reported for other similar complexes with N-donor ligands[23]. However, the emission intensity of **3** is much weaker than that of the free ligand, indicating that the energy transfer is inefficient, and the quenching effect is due to O-H vibrations of uncoordinated free carboxyl

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groups. For **5**, a luminescence emission may be attributed to the rigidity of the phen ligand, with regard to the metal clusters, which effectively increases the rigidity and then affects the loss of energy *via* a radiationless pathway of the intraligand ($\pi^*\rightarrow n$ or $\pi^*\rightarrow\pi$) excited state. Unfortunately, the polymers **1**, **2** and **4** show very weak emissions, it is visible that these metal ions show strong fluorescence quenching for the $H_3$DMPhIDC ligand.

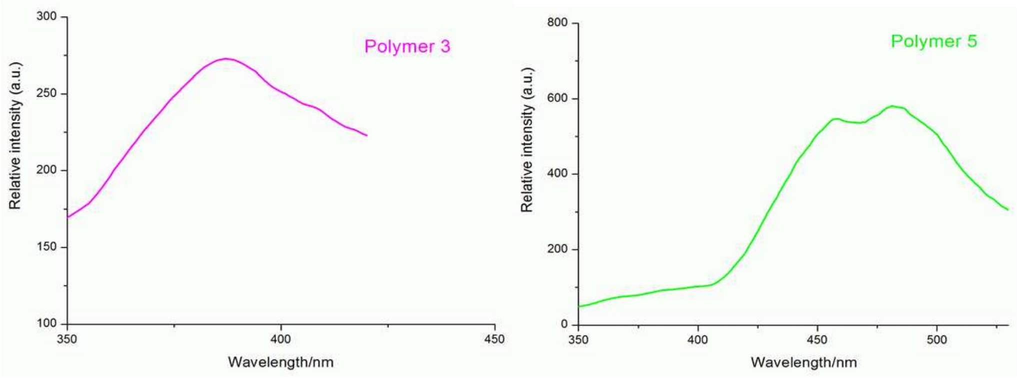

**Fig. 7** The solid-state photoluminescent spectra of the polymers **3** and **5**.

## Conclusions

In summary, five compounds **1-5** were constructed from the $H_3$DMPhIDC ligand under hydro(solvo)thermal conditions. Their molecular structures have been characterized by single-crystal X-ray diffraction, EA and IR spectra. Their thermal behaviors have been studied by thermal gravimetric analyses. Polymer **1** shows a 3D framework, and complex **2** is a unique 2D coordination framework with the stepped 1D chains. As for polymers **3-5**, it is easy to find that when the *N*-containing chelating auxiliary ligands were introduced, 1D structure can be usually obtained. The results demonstrate that the “old” organic ligand can fine-tune its configuration properly to meet the geometric requirement of many central metal atoms/clusters, which comes into being more fascinating coordination polymers and intriguing topologies could be formed by incorporating additional links. The choice of reaction conditions is also critically important to the nature of the product. Anyway, these findings obviously further enrich the library of MOFs molecules and provide a new platform to design more potential functional aggregates.

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## Acknowledgments

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**Table 1.** Crystal data and structure refinement information for compounds **1-5**

| | **1** | **2** | **3** | **4** | **5** |
|---|---|---|---|---|---|
| formula | $C_{65}H_{55}Mn_3N_{10}O_{16}$ | $C_{26}H_{20}N_4O_{10}Pb_4$ | $C_{15}H_{18}CdN_4O_4$ | $C_{54}H_{45}Cu_3N_9O_{12}$ | $C_{100}H_{74}N_{16}O_{17}Zn_4$ |
| fw | 1397.01 | 1377.22 | 430.73 | 1202.64 | 2033.23 |
| crystal system | Monoclinic | Triclinic | Tetragonal | Triclinic | Orthorhombic |
| crystal size, mm | 0.25 × 0.22 × 0.18 | 0.23 × 0.25 × 0.18 | 0.40 ×0.30 × 0.20 | 0.21 × 0.18 × 0.16 | 0.30 × 0.20 ×0.10 |
| space group | $C2/C$ | $P\bar{1}$ | $I4_1/a$ | $P\bar{1}$ | $Pbca$ |
| $a$, Å | 33.287(4) | 6.91220(10) | 22.0941(10) | 11.1070(16) | 18.737(2) |
| $b$, Å | 7.5503(8) | 13.2192(3) | 22.0941(10) | 13.386(2) | 20.667(3) |
| $c$, Å | 25.231(3) | 16.6432(4) | 14.5099(14) | 18.061(3) | 23.441(3) |
| $\alpha$, ° | 90.00 | 69.1940(10) | 90 | 88.704(2) | 90 |
| $\beta$, ° | 95.425(2) | 86.754(2) | 90 | 77.557(2) | 90 |
| $\gamma$, ° | 90.00 | 79.3670(10) | 90 | 81.910(2) | 90 |
| $V$, Å$^3$ | 6312.8(12) | 1397.11(5) | 7083.0(8) | 2596.1(7) | 9077(2) |
| $D$c, Mg m$^{-3}$ | 1.470 | 3.274 | 1.616 | 1.539 | 1.488 |
| Z | 4 | 2 | 16 | 2 | 4 |
| $\mu$, mm$^{-1}$ | 0.669 | 24.095 | 1.259 | 1.291 | 1.103 |
| reflns collected/unique | 15090 / 5524<br>[$R$(int) = 0.0478] | 7574 / 4842<br>[$R$(int) = 0.0359] | 15669 / 3662<br>[$R$(int) = 0.0492] | 13117 / 8937<br>[$R$(int) = 0.0438] | 44063 / 7931<br>[$R$(int) = 0.1954] |
| data/restraints/parameters | 5524 / 0 / 501 | 4842 / 0 / 395 | 3662 / 0 / 290 | 8937 / 0 / 723 | 7931 / 0 / 625 |
| final $R$ indices [$I>2\sigma(I)$] | $R_1 = 0.0738$, w$R_2 = 0.1664$ | $R_1 = 0.0593$, w$R_2 = 0.1766$ | $R_1 = 0.0824$ w$R_2 = 0.1996$ | $R_1 = 0.0992$, w$R_2 = 0.1952$ | $R_1 = 0.0828$, w$R_2 = 0.1536$ |
| $R$ indices (all data) | $R_1 = 0.1121$, w$R_2 = 0.1885$ | $R_1 = 0.0688$, w$R_2 = 0.1864$ | $R_1 = 0.1030$, w$R_2 = 0.2071$ | $R_1 = 0.1631$, w$R_2 = 0.2206$ | $R_1 = 0.1901$, w$R_2 = 0.1990$ |
| GOF on $F^2$ | 1.046 | 1.063 | 1.239 | 1.066 | 1.103 |
| $\Delta\rho_{min}$ and $\Delta\rho_{max}$, e Å$^{-3}$ | -2.063 and 0.891 | -4.521 and 5.299 | -2.196 and 1.224 | -2.547 and 1.354 | -2.255 and 0.788 |

$^a R = \Sigma[|Fo|-|Fc|]/\Sigma|Fo|$ $^b R_w = [\Sigma(|Fo|-|Fc|)^2 / \Sigma|Fo|^2]^{1/2}$

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**Table 2.** Selected bond distances (Å) and angles (deg) for compounds **1-5**

| | | | | | |
|---|---|---|---|---|---|
| **1** | | | | | |
| Mn(1)-O(2)#1 | 2.122(4) | Mn(1)-O(3)#1 | 2.139(4) | Mn(1)-O(1) | 2.158(4) |
| Mn(1)-O(5) | 2.172(4) | Mn(1)-N(5) | 2.229(6) | Mn(1)-N(1) | 2.320(4) |
| Mn(2)-O(4)#2 | 2.108(4) | Mn(2)-O(8) | 2.252(5) | Mn(2)-N(4) | 2.241(5) |
| O(2)#1-Mn(1)-O(3)#1 | 86.5(2) | O(2)#1-Mn(1)-O(1) | 90.3(2) | O(3)#1-Mn(1)-O(1) | 84.3(2) |
| O(2)#1-Mn(1)-O(5) | 176.6(2) | O(3)#1-Mn(1)-O(5) | 90.4(2) | O(1)-Mn(1)-O(5) | 90.9(2) |
| O(2)#1-Mn(1)-N(5) | 88.0(2) | O(3)#1-Mn(1)-N(5) | 89.2(2) | O(1)-Mn(1)-N(5) | 173.4(2) |
| O(5)-Mn(1)-N(5) | 90.5(2) | O(2)#1-Mn(1)-N(1) | 93.3(2) | O(3)#1-Mn(1)-N(1) | 157.8(2) |
| O(1)-Mn(1)-N(1) | 73.4(2) | O(5)-Mn(1)-N(1) | 90.1(2) | N(5)-Mn(1)-N(1) | 113.0(2) |
| O(4)#2-Mn(2)-O(4)#3 | 180.0(1) | N(4)-Mn(2)-O(8)#4 | 105.6(2) | O(4)#3-Mn(2)-N(4) | 88.5(2) |
| O(4)#3-Mn(2)-N(4)#4 | 91.5(2) | O(4)#2-Mn(2)-O(8) | 89.2(2) | N(4)-Mn(2)-N(4)#4 | 180.0(1) |
| O(8)-Mn(2)-O(8)#4 | 180.0(1) | O(4)#3-Mn(2)-O(8) | 90.8(2) | O(4)#3-Mn(2)-O(8)#4 | 89.2(2) |
| N(4)-Mn(2)-O(8) | 74.4(2) | N(4)#4-Mn(2)-O(8) | 105.6(2) | | |
| **2** | | | | | |
| Pb(1)-O(10) | 2.265(1) | Pb(1)-O(2) | 2.504(11) | Pb(1)-O(8)#1 | 2.573(1) |
| Pb(1)-N(1) | 2.581(1) | Pb(1)-O(6)#2 | 2.699(11) | Pb(2)-N(4) | 2.724(1) |
| Pb(2)-O(9) | 2.235(1) | Pb(2)-O(5) | 2.533(10) | Pb(2)-O(4)#3 | 2.448(1) |
| Pb(2)-O(3)#4 | 2.682(1) | Pb(3)-O(3)#4 | 2.683(12) | Pb(3)-O(7)#1 | 2.574(1) |
| Pb(3)-O(1) | 2.631(1) | Pb(3)-O(2) | 2.649(12) | Pb(3)-O(1)#4 | 2.670(1) |
| Pb(3)-O(3)#4 | 2.683(1) | Pb(4)-O(10) | 2.280(12) | Pb(4)-O(5) | 2.397(1) |
| Pb(4)-O(4)#3 | 2.523(1) | Pb(4)-O(6)#2 | 2.624(12) | O(10)-Pb(1)-O(2) | 75.5(4) |
| O(2)-Pb(1)-O(8)#1 | 68.9(3) | O(10)-Pb(1)-N(1) | 84.6(4) | O(2)-Pb(1)-N(1) | 65.1(4) |
| O(8)#1-Pb(1)-N(1) | 133.1(4) | O(10)-Pb(1)-O(6)#2 | 74.2(4) | O(2)-Pb(1)-O(6)#2 | 137.0(4) |
| O(8)#1-Pb(1)-O(6)#2 | 74.2(4) | N(1)-Pb(1)-O(6)#2 | 140.0(4) | O(9)-Pb(2)-O(4)#3 | 80.5(4) |
| O(9)-Pb(2)-O(5) | 70.6(4) | O(4)#3-Pb(2)-O(5) | 60.6(3) | O(9)-Pb(2)-O(3)#4 | 66.6(4) |
| O(4)#3-Pb(2)-O(3)#4 | 147.0(4) | O(5)-Pb(2)-O(3)#4 | 108.1(4) | O(9)-Pb(2)-N(4) | 104.5(4) |
| O(4)#3-Pb(2)-N(4) | 117.3(4) | O(5)-Pb(2)-N(4) | 62.9(4) | O(3)#4-Pb(2)-N(4) | 75.5(4) |
| O(9)-Pb(3)-O(7)#1 | 85.7(4) | O(9)-Pb(3)-O(1) | 84.1(4) | O(7)#1-Pb(3)-O(1) | 124.7(4) |
| O(9)-Pb(3)-O(2) | 71.9(4) | O(7)#1-Pb(3)-O(2) | 76.3(4) | O(1)-Pb(3)-O(2) | 48.9(3) |
| O(9)-Pb(3)-O(1)#4 | 69.5(4) | O(7)#1-Pb(3)-O(1)#4 | 149.5(4) | O(1)-Pb(3)-O(1)#4 | 71.4(4) |
| O(2)-Pb(3)-O(1)#4 | 110.4(3) | O(9)-Pb(3)-O(3)#4 | 66.5(4) | O(7)#1-Pb(3)-O(3)#4 | 92.1(4) |
| O(1)-Pb(3)-O(3)#4 | 131.3(4) | O(2)-Pb(3)-O(3)#4 | 137.5(3) | O(1)#4-Pb(3)-O(3)#4 | 62.4(3) |
| O(10)-Pb(4)-O(5) | 88.5(4) | O(10)-Pb(4)-O(4)#3 | 74.0(4) | O(5)-Pb(4)-O(4)#3 | 61.4(3) |
| O(10)-Pb(4)-O(6)#2 | 75.9(4) | O(5)-Pb(4)-O(6)#2 | 100.4(4) | O(4)#3-Pb(4)-O(6)#2 | 144.9(4) |

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**3**

| | | | | | |
|---|---|---|---|---|---|
| N(1)-Cd(1) | 2.244(8) | N(2)-Cd(1)#1 | 2.296(7) | N(3)-Cd(1) | 2.278(8) |
| N(4)-Cd(1) | 2.379(10) | O(4)-Cd(1)#1 | 2.412(8) | Cd(1)-N(2)#2 | 2.296(7) |
| Cd(1)-O(4)#2 | 2.412(8) | N(1)-Cd(1)-N(3) | 135.0(3) | N(1)-Cd(1)-N(2)#2 | 113.9(3) |
| N(3)-Cd(1)-N(2)#2 | 110.7(3) | N(1)-Cd(1)-N(4) | 90.8(4) | N(3)-Cd(1)-N(4) | 74.3(4) |
| N(2)#2-Cd(1)-N(4) | 101.5(3) | N(1)-Cd(1)-O(4)#2 | 97.7(3) | N(3)-Cd(1)-O(4)#2 | 102.4(3) |
| N(2)#2-Cd(1)-O(4)#2 | 70.8(2) | N(4)-Cd(1)-O(4)#2 | 170.3(3) | N(1)-Cd(1)-O(1) | 70.1(3) |
| N(3)-Cd(1)-O(1) | 78.7(3) | N(2)#2-Cd(1)-O(1) | 142.4(3) | N(4)-Cd(1)-O(1) | 116.0(3) |
| O(4)#2-Cd(1)-O(1) | 71.7(3) | | | | |

**4**

| | | | | | |
|---|---|---|---|---|---|
| Cu(1)-O(6) | 1.964(4) | Cu(1)-N(6) | 1.988(8) | Cu(1)-N(4) | 2.006(7) |
| Cu(1)-N(5) | 2.052(8) | Cu(1)-O(7) | 2.422(8) | Cu(2)-N(3) | 1.965(8) |
| Cu(2)-O(2) | 1.985(7) | Cu(2)-N(1) | 1.996(7) | Cu(2)-N(2) | 2.021(8) |
| Cu(2)-O(3) | 2.401(7) | Cu(3)-N(8) | 1.949(7) | Cu(3)-O(10) | 1.965(7) |
| Cu(3)-N(9) | 2.023(9) | Cu(3)-N(7) | 2.036(8) | O(6)-Cu(1)-N(6) | 177.7(3) |
| O(6)-Cu(1)-N(4) | 82.6(3) | N(6)-Cu(1)-N(4) | 96.1(3) | O(6)-Cu(1)-N(5) | 89.2(3) |
| N(6)-Cu(1)-N(5) | 91.8(3) | N(4)-Cu(1)-N(5) | 168.8(3) | O(6)-Cu(1)-O(7) | 104.8(3) |
| N(6)-Cu(1)-O(7) | 77.3(3) | N(4)-Cu(1)-O(7) | 103.9(3) | N(5)-Cu(1)-O(7) | 85.5(3) |
| N(3)-Cu(2)-O(2) | 173.1(3) | N(3)-Cu(2)-N(1) | 95.8(3) | O(2)-Cu(2)-N(1) | 82.4(3) |
| N(3)-Cu(2)-N(2) | 92.3(3) | O(2)-Cu(2)-N(2) | 88.1(3) | N(1)-Cu(2)-N(2) | 165.1(3) |
| N(3)-Cu(2)-O(3) | 77.1(3) | O(2)-Cu(2)-O(3) | 109.8(3) | N(1)-Cu(2)-O(3) | 101.0(3) |
| N(2)-Cu(2)-O(3) | 92.9(3) | N(8)-Cu(3)-O(10) | 174.7(4) | N(8)-Cu(3)-N(9) | 92.4(2) |
| O(10)-Cu(3)-N(9) | 86.8(4) | N(8)-Cu(3)-N(7) | 97.4(3) | O(10)-Cu(3)-N(7) | 82.1(3) |
| N(9)-Cu(3)-N(7) | 162.5(4) | | | | |

**5**

| | | | | | |
|---|---|---|---|---|---|
| Zn(1)-N(4) | 2.020(7) | Zn(1)-N(7) | 2.118(5) | Zn(1)-O(5) | 2.115(6) |
| Zn(1)-N(6) | 2.165(8) | Zn(1)-N(5) | 2.212(8) | Zn(2)-N(8)#1 | 2.121(7) |
| Zn(2)-N(3) | 2.124(8) | Zn(2)-N(1) | 2.138(8) | Zn(2)-O(1) | 2.146(6) |
| Zn(2)-N(2) | 2.179(7) | Zn(2)-O(8)#1 | 2.206(6) | N(4)-Zn(1)-N(7) | 110.2(3) |
| N(4)-Zn(1)-O(5) | 128.3(3) | N(7)-Zn(1)-O(5) | 79.4(3) | N(4)-Zn(1)-N(6) | 110.6(3) |
| N(7)-Zn(1)-N(6) | 95.4(3) | O(5)-Zn(1)-N(6) | 119.0(3) | N(4)-Zn(1)-N(5) | 101.4(3) |
| N(7)-Zn(1)-N(5) | 148.3(3) | O(5)-Zn(1)-N(5) | 78.9(3) | N(6)-Zn(1)-N(5) | 75.5(3) |
| N(8)#1-Zn(2)-N(3) | 155.8(3) | N(8)#1-Zn(2)-N(1) | 111.8(3) | N(3)-Zn(2)-N(1) | 87.2(3) |
| N(8)#1-Zn(2)-O(1) | 86.0(3) | N(3)-Zn(2)-O(1) | 77.6(3) | N(1)-Zn(2)-O(1) | 94.0(3) |
| N(8)#1-Zn(2)-N(2) | 97.3(3) | N(3)-Zn(2)-N(2) | 101.7(3) | N(1)-Zn(2)-N(2) | 76.9(3) |

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| | | | | | |
|---|---|---|---|---|---|
| O(1)-Zn(2)-N(2) | 170.9(3) | N(8)#1-Zn(2)-O(8)#1 | 78.8(3) | N(3)-Zn(2)-O(8)#1 | 88.1(3) |
| N(1)-Zn(2)-O(8)#1 | 159.8(3) | O(1)-Zn(2)-O(8)#1 | 104.1(3) | N(2)-Zn(2)-O(8)#1 | 84.9(3) |

Symmetry transformations used to generate equivalent atoms: For **1**: #1: -x+1/2, y-1/2, -z+1/2; #2: x, -y+1, z+1/2; #3: -x+1/2, y+1/2, -z+1/2; #4: -x+1/2, -y+3/2, -z+1; #5: -x, y, -z+1/2. For **2**: #1 -x+1, -y+1, -z+2; #2 -x, -y+1, -z+2; #3 -x,-y,-z+2; #4 -x+1, -y, -z+2. For **3**: #1 y+1/4, -x+5/4, z+1/4; #2 -y+5/4, x-1/4, z-1/4. For **4**: #1 x-1, y, z; #2 x+1, y, z. For **5**: #1 -x+1, y+1/2, -z+3/2; #2 -x+1, y-1/2, -z+3/2.

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**Table 3.** Hydrogen bonds distances (Å) and angles (deg) for **4** and **5.**

**3**

| D-H...A | d(H...A) | d(D...A) | ∠(DHA) |
|---|---|---|---|
| N3-H3A...O1#1 | 2.154 | 3.026 | 163.07 |
| N3-H3A...O2#1 | 2.558 | 3.209 | 129.69 |
| N3-H3B...O1#2 | 2.386 | 3.174 | 146.35 |
| N3-H4A...O3#3 | 2.267 | 3.106 | 155.04 |
| O2-H2...O3 | 1.636 | 2.450 | 171.71 |

**4**

| D-H...A | d(H...A) | d(D...A) | ∠(DHA) |
|---|---|---|---|
| O8-H8...O9 | 1.76 | 2.559(1) | 163.7 |
| O4-H4...O5 | 1.76 | 2.580(1) | 177.1 |

**5**

| D-H...A | d(H...A) | d(D...A) | ∠(DHA) |
|---|---|---|---|
| O3-H3A...O2 | 1.69 | 2.509(1) | 173.9 |
| O7-H7A...O6 | 1.66 | 2.479(1) | 174.5 |

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Illustration

# Five metal–organic frameworks from 3,4-dimethylphenyl substituted imidazole dicarboxylate: Syntheses, structures and properties

**Hongliang Jia, Yanlin Li, Zhifang Xiong, Chengjie Wang, Gang Li ***

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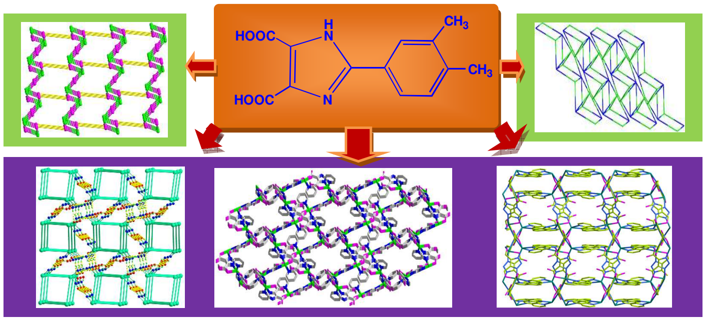
A graphical contents entry



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Five metal-organic frameworks, $[[Mn_3(H_2DMPhIDC)_2(HDMPhIDC)_2(bpp)]_n$ ($H_3DMPhIDC$ = 2-(3,4-dimethylphenyl)-1*H*-imidazole-4,5-dicarboxylic acid, bpp = 1,3-di(4-pyridyl)propane) (**1**), $[Pb_4(DMPhIDC)_2(OH)_2]_n$ (**2**), $[Cd(HDMPhIDC)(en)]_n$ (en = ethylenediamine) (**3**), $[Cu_3(HDMPhIDC)_3(Py)_3]_n$ (Py = pyridine) (**4**) and $\{[Zn_2(HDMPhIDC)_2(Phen)_2]_2\cdot H_2O\}_n$ (Phen = 1,10-phenanthroline) (**5**) have been hydrothermally synthesized and structurally characterized.

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