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## Introduction

Assembly of a series of MOFs based on the 2-(*m*-methoxyphenyl)imidazole dicarboxylate ligand†

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The coordination features of an imidazole dicarboxylate ligand, 2-(3-methoxyphenyl)-1*H*-imidazole-4,5dicarboxylic acid (*m*-H<sub>3</sub>MOPhIDC) has been explored. Consequently, seven coordination polymers, namely [Sr(*m*-HMOPhIDC)(H<sub>2</sub>O)]<sub>*n*</sub> (**1**), [Sr(*m*-H<sub>2</sub>MOPhIDC)<sub>2</sub>]<sub>*n*</sub> (**2**), [Cd<sub>3</sub>(*m*-H<sub>2</sub>MOPhIDC)<sub>2</sub>(*m*-HMOPhIDC) (phen)<sub>2</sub>]<sub>*n*</sub> (**3**), [Cu(*m*-HMOPhIDC)(phen)]<sub>*n*</sub> (phen = 1,10-phenanthroline) (**4**), [Cd<sub>2</sub>(*m*-HMOPhIDC)<sub>2</sub>-(phen)<sub>2</sub>]<sub>*n*</sub> (**5**) [Cd<sub>2</sub>(*m*-HMOPhIDC)<sub>2</sub>(2,2'-bipy)<sub>2</sub>]<sub>*n*</sub> (2,2'-bipy = 2,2'-bipyridine) (**6**) and [Co(*m*-HMOPhIDC) (H<sub>2</sub>O)<sub>2</sub>]<sub>*n*</sub> (**7**) have been hydro(solvo)thermally synthesized by fine control over synthetic conditions, and structurally characterized. X-ray single-crystal analyses reveal that these polymers indicate rich structural chemistry ranging from one-dimensional (**4**–**7**), two-dimensional (**1** and **3**) to three-dimensional (**2**) structures, and the *m*-H<sub>3</sub>MOPhIDC ligand in these polymers can be singly deprotonated or doubly deprotonated, and coordinates to metal ions by various modes. The thermal and fluorescence properties of the complexes **1–7** have been determined as well.

The construction of metal-organic frameworks (MOFs) has grown rapidly in chemistry and material science fields over the past two decades because of their promising applications in gas storage and capture, heterogeneous catalysis materials and so on.<sup>1,2</sup> To date, although people have been making dramatic progress in the research of the optimum strategy and manipulation in the self-assembly of MOFs,<sup>3-5</sup> it is still a big challenge to achieve target MOFs which are designed in advance. Many factors such as the organic ligands, coordination preference of the central metal ion, crystallization conditions, metal/ligand ratio and the reaction solvent system can significantly influence the final products of MOFs. Among them, the organic ligands play an extremely important role in directing the extended structure of the resulting complexes. Thus, considerable efforts have been devoted to design or choose the multifunctional bridging ligands.<sup>6</sup>

Recently, the *N*-heterocyclic dicarboxylate ligands have attracted much interest in the preparation of new MOFs under hydro(solvo)thermal conditions due to their versatile coordination modes and potential hydrogen-bonding donors and acceptors.<sup>5,7–11</sup> In this context, imidazole-4,5-dicarboxylic acid (H<sub>3</sub>IDC) is an excellent candidate for assembling novel MOFs.<sup>12-20</sup> Besides being partially or fully deprotonated to  $H_2IDC^-$ ,  $HIDC^{2-}$  and  $IDC^{3-}$  anions, the ligand  $H_3IDC$  also exhibits flexible coordination modes.<sup>21</sup> Recently, people have had great interest in introducing different substituent units into the 2-position of H<sub>3</sub>IDC, such as ethyl,<sup>22,23</sup> propyl,<sup>24</sup> phenyl,<sup>25</sup> hydroxymethyl,<sup>26</sup> or pyridyl<sup>27-33</sup> groups, and studied the influence of the substituent on the coordination abilities of the corresponding imidazole dicarboxylate ligands. More recently, based on our previous attractive results of MOFs bearing 2-phenyl-1H-imidazole-4,5-dicarboxylic acid,<sup>25</sup> we adopted the methoxyl unit to modify the phenyl group, and further explored the coordination features of the related ligand.9ef The studies showed that 2-(4-methoxyphenyl)-1Himidazole-4,5-dicarboxylic acid (p-H<sub>3</sub>MOPhIDC) can build up interesting MOFs.<sup>9e,f</sup> Prompted by these findings, we hope to probe the substituent effect of the methoxyl unit on the 3-position of the phenyl group (2-(3-methoxyphenyl)-1H-imidazole-4,5-dicarboxylic acid  $(m-H_3MOPhIDC)$ ) from both theoretical and experimental aspects.

At the same time, there are no reports of MOFs constructed from the *m*-H<sub>3</sub>MOPhIDC ligand. Herein, we will report the hydro(solvo)thermal syntheses and structural determinations of one 2D polymer  $[Sr(m-HMOPhIDC)(H_2O)]_n$ (1), one 3D polymer  $[Sr(m-H_2MOPhIDC)_2]_n$  (2), one 2D polymer  $[Cd_3(m-H_2MOPhIDC)_2(\mu_3-HMOPhIDC)_2(H_2O)_2]_n$  (3), and four 1D polymers  $[Cu(HMOPhIDC)(phen)]_n$  (phen = 1,10phenanthroline) (4),  $[Cd_2(m-HMOPhIDC)_2(phen)_2]_n$  (5),

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<sup>†</sup>Electronic supplementary information (ESI) available: The X-ray crystallographic files in CIF format. CCDC 895949–895953 for 1–5, 903675 and 903676 for complexes 6, and 7, respectively. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt32727a



 $[Cd_2(m-HMOPhIDC)_2(2,2'-bipy)_2]_n$  (2,2'-bipy = 2,2'-bipyridine) (6) and  $[Co(m-HMOPhIDC)(H_2O)_2]_n$  (7). Single crystal X-ray diffractions reveal that one or two hydrogen atoms can be removed from the ligand m-H<sub>3</sub>MOPhIDC forming m-H<sub>2</sub>MOPhIDC<sup>-</sup> and m-HMOPhIDC<sup>2-</sup> anions, and the deprotonated m-H<sub>3-n</sub>MOPhIDC<sup>n-</sup> (n = 1 or 2) could coordinate to metal ions in various modes (Scheme 1).

## **Experimental section**

### **General details**

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. The organic ligand m-H<sub>3</sub>MOPhIDC was prepared according to the literature procedure.<sup>34</sup>

C, H and N microanalyses were carried out on a FLASH EA 1112 analyzer. IR data were recorded on a BRUKER TENSOR 27 spectrophotometer with KBr pellets in the 400–4000 cm<sup>-1</sup> region. TG-DSC measurements were performed by heating the crystalline sample from 20 to 850 °C at a rate of 10 °C min<sup>-1</sup> in the 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 $[Sr(m-HMOPhIDC)(H_2O)]_n$ (1)

A mixture of *m*-H<sub>3</sub>MOPhIDC (52.4 mg, 0.2 mmol), Sr(NO<sub>3</sub>)<sub>2</sub> (42.3 mg, 0.2 mmol), Et<sub>3</sub>N (0.056 mL, 0.4 mmol) and CH<sub>3</sub>CN-H<sub>2</sub>O (3:4, 7 mL) was sealed in a 25 mL Teflon-lined bomb and heated at 150 °C for 96 h. The reaction mixture was then allowed to cool to room temperature. Block-shaped crystals of 1 were collected, washed with acetonitrile and dried in air. Yield: 86% (based on Sr). Anal. calcd for  $C_{12}H_{10}N_2O_6Sr$ : C, 39.40; H, 2.73; N, 7.66%. Found: C, 39.82; H, 2.91; N, 7.48%. IR (cm<sup>-1</sup>, KBr): 3620 s, 3225 w, 1593 s, 1529 s, 1262 s, 1178 w, 867 m, 800 w, 727 s, 472 m.

## Preparation of crystalline $[Sr(m-H_2MOPhIDC)_2]_n$ (2)

A mixture of *m*-H<sub>3</sub>MOPhIDC (52.4 mg, 0.2 mmol), Sr(NO<sub>3</sub>)<sub>2</sub> (42.3 mg, 0.2 mmol), Et<sub>3</sub>N (0.056 mL, 0.4 mmol) and CH<sub>3</sub>OH-H<sub>2</sub>O (3:4, 7 mL) was sealed in a 25 mL Teflon-lined bomb, which was heated to 150 °C for 96 h. After the mixture was cooled to room temperature, yellow crystals of 2 were obtained, washed with methanol and water, and dried in air. Yield: 64% (based on Sr). Anal. calcd for  $C_{24}H_{16}N_4O_{10}Sr$ : C, 47.41; H, 2.65; N, 9.22%. Found: C, 47.82; H, 2.43; N, 9.07%. IR (cm<sup>-1</sup>, KBr): 3621 m, 3223 w, 2963 m, 1593 s, 1556 w, 1490 s, 1420 w, 1384 w, 1261 s, 1056 w, 800 s, 628 m.

## Preparation of crystalline [Cd<sub>3</sub>(*m*-H<sub>2</sub>MOPhIDC)<sub>2</sub>-(*m*-HMOPhIDC)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>*n*</sub> (3)

A mixture of *m*-H<sub>3</sub>MOPhIDC (52.4 mg, 0.2 mmol), Cd  $(NO_3)_2$ ·4H<sub>2</sub>O (61.6 mg, 0.2 mmol), pyridine (0.2 mL), and deionized water (7 mL) was sealed in a 25 mL Teflon-lined bomb and heated at 160 °C for 96 h, and then cooled to room temperature. Colorless strip-shaped crystals of **3** were collected, washed with distilled water and dried in air. Yield: 53% (based on Cd). Anal. calcd for C<sub>24</sub>H<sub>19</sub>N<sub>4</sub>O<sub>11</sub>Cd<sub>1.5</sub>: C, 40.70; H, 2.70; N, 7.91%. Found: C, 40.58; H, 2.82; N, 8.22%. IR (cm<sup>-1</sup>, KBr): 3440 s, 2847 w, 1570 s, 1446 w, 1374 w, 1245 w, 1221 w, 837 s, 699 s.

### Preparation of crystalline [Cu(m-HMOPhIDC)(phen)]<sub>n</sub> (4)

A mixture of *m*-H<sub>3</sub>MOPhIDC (52.4 mg, 0.2 mmol), Cu(ClO<sub>4</sub>)<sub>2</sub> (52.4 mg, 0.2 mmol), phen (39.6 mg, 0.2 mmol) and Et<sub>3</sub>N (0.056 mL, 0.4 mmol) and CH<sub>3</sub>OH-H<sub>2</sub>O (3:4, 7 mL) was sealed in a 25 mL Teflon-lined bomb and heated at 160 °C for 72 h, and then cooled to room temperature. Blue crystals of 4 were collected, washed with distilled water and dried in air. Yield: 53% (based on Cu). Anal. calcd for C<sub>24</sub>H<sub>16</sub>N<sub>4</sub>O<sub>5</sub>Cu: C, 57.19; H, 3.20; N, 11.12%. Found: C, 57.48; H, 3.02; N, 11.21%. IR (cm<sup>-1</sup>, KBr): 3423 w, 3036 w, 1588 s, 1445 w, 1423 s, 1221 w, 839 s, 722 s.

## Preparation of crystalline $[Cd_2(m-HMOPhIDC)_2(phen)_2]_n$ (5)

A mixture of *m*-H<sub>3</sub>MOPhIDC (52.4 mg, 0.2 mmol), Cd-(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (61.6 mg, 0.2 mmol), phen (39.6 mg, 0.2 mmol) and Et<sub>3</sub>N (0.056 mL, 0.4 mmol) and CH<sub>3</sub>OH-H<sub>2</sub>O (3 : 4, 7 mL) was sealed in a 25 mL Teflon-lined bomb and heated at 155 °C for 96 h, and then cooled to room temperature. Colorless stripshaped crystals of 5 were collected, washed with distilled water and dried in air. Yield: 53% (based on Cd). Anal. calcd for C<sub>48</sub>H<sub>32</sub>N<sub>8</sub>O<sub>10</sub>Cd<sub>2</sub>: C, 52.14; H, 2.89; N, 10.13%. Found: C, 52.48; H, 2.52; N, 10.42%. IR (cm<sup>-1</sup>, KBr): 3446 m, 2834 m, 1635 s, 1471 s, 1386 s, 1234 s, 1123 s, 846 s, 709 m.

## Preparation of crystalline $[Cd_2(m-HMOPhIDC)_2(2,2'-bipy)_2]_n$ (6)

A mixture of  $Cd(NO_3)_2$ · $GH_2O$  (30.8 mg, 0.1 mmol), *m*- $H_3MOPhIDC$  (26.2 mg, 0.1 mmol), 2,2'-bipy (15.6 mg, 0.1 mmol) and  $CH_3OH-H_2O$  (3:4, 7 mL), Et<sub>3</sub>N (0.056 mL, 0.4 mmol) was sealed in a 25 mL Teflon-lined bomb and heated at 155 °C for 120 h, and then cooled to room

temperature. Colorless strip-shaped crystals of **6** were collected, washed with distilled water and dried in air. Yield: 53% (based on Cd). Anal. calcd for  $C_{44}H_{32}N_8O_{10}Cd_2$ : C, 49.97; H, 3.02; N, 15.12%. Found: C, 49.78; H, 2.76; N, 15.42%. IR (cm<sup>-1</sup>, KBr): 3445 m, 2832 m, 1593 s, 1471 w, 1388 s, 1235 s, 1123 s, 835 w, 764 s.

## Preparation of crystalline $[Co(m-HMOPhIDC)(H_2O)_2]_n$ (7)

A mixture of *m*-H<sub>3</sub>MOPhIDC (26.2 mg, 0.2 mmol), CoCl<sub>2</sub>·6H<sub>2</sub>O (23.8 mg, 0.1 mmol) Et<sub>3</sub>N (0.056 mL, 0.4 mmol) and CH<sub>3</sub>CN-H<sub>2</sub>O (3 : 4, 7 mL) was sealed in a 25 mL Teflon-lined bomb and heated at 155 °C for 120 h, and then cooled to room temperature. Pink crystals of 7 were collected, washed with distilled water and dried in air. Yield: 53% (based on Co). Anal. calcd for C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>O<sub>7</sub>Co: C, 40.58; H, 3.43; N, 7.93%. Found: C, 40.78; H, 3.52; N, 7.63%. IR (cm<sup>-1</sup>, KBr): 3364 w, 2835 w, 1574 s, 1467 s, 1405 m, 1233 s, 1125 s, 848 m, 709 w.

### X-ray crystallography

Crystal data for compounds 1–7 are contained in Table 1. Single crystals of 1–7 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 seven structures were solved by direct methods and expanded using the Fourier technique. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included but not refined. The final cycle of full-matrix least squares refinement was based on 3033 observed reflections and 200 variable parameters for **1**, 2803 observed reflections and 179 variable parameters for **2**, 4835 observed reflections and 381 variable parameters for **3**, 5322 observed reflections and 309 variable parameters for **4**, 8932 observed reflections and 591 variable parameters for **5**, 6013 observed reflections and 580 variable parameters for **6**, 3201 observed reflections and 209 variable parameters for **7**. All calculations were performed using the SHELX-97 crystallographic software package.<sup>9a</sup> Selected bond lengths and bond angles, and hydrogen bond parameters for **1**–7 are listed in Tables S1 and S2,<sup>†</sup> respectively.

### Quantum chemical calculation

The optimized geometry, NBO charge distributions of the free ligand *m*-H<sub>3</sub>MOPhIDC were given by the GAUSSIAN 03 suite of programs.<sup>35</sup> And all calculations were carried out at the B3LYP/ 6-311++G(d, p) level of theory.

# **Results and discussion**

## Synthesis

The deprotonation process and diversity of the coordination modes of the ligand *p*-H<sub>3</sub>MOPhIDC have been discussed previously and eleven corresponding fascinating polymers have been reported by our laboratory.<sup>9e,f</sup> It was found that the position and type of functional groups of this kind of organic ligand are crucial for the generation of frameworks. To further predict the *m*-methoxyl substituent effect on the *m*-H<sub>3</sub>MOPhIDC ligand, we calculated the optimized geometries and NBO charge distributions of the free ligand *m*-H<sub>3</sub>MOPhIDC on the B3LYP/6-311++G(d, p) level of theory.<sup>35</sup> The computed results reveal that the negative NBO charges are mainly distributed on the oxygen and nitrogen atoms in the

	1	2	3	4	5	6	7
Formula	$\mathrm{C_{12}H_{10}N_2O_6Sr}$	$C_{24}H_{18}N_4O_{10}Sr$	$C_{48}H_{38}N_8O_{22}Cd_3$	$\mathrm{C}_{24}\mathrm{H}_{16}\mathrm{N}_{4}\mathrm{O}_{5}\mathrm{Cu}$	$C_{48}H_{32}N_8O_{10}Cd_2\\$	$C_{44}H_{32}N_8O_{10}Cd_2\\$	C <sub>12</sub> H <sub>12</sub> N <sub>2</sub> O <sub>7</sub> Co
fw	365.84	610.04	1416.06	503.95	1105.62	1057.58	355.17
Crystal system	Monoclinic	Tetragonal	Triclinic	Orthorhombic	Orthorhombic	Monoclinic	Triclinic
Crystal size	0.20  imes 0.18  imes	0.20 imes 0.18 imes	0.23  imes 0.22  imes	0.18 imes 0.18 imes	0.40  imes 0.30  imes	0.30  imes 0.20  imes	0.20  imes 0.18  imes
(mm)	0.16	0.16	0.21	0.16	0.20	0.10	0.16
Space group	$P2_1/c$	$I4_1/a$	$P\bar{1}$	Pbcn	Pbca	$P2_1$	$P\bar{1}$
a (Å)	16.085(3)	16.7894(12)	9.145(3)	16.936(6)	19.014(2)	9.3619(6) A	8.0394(14)
b (Å)	6.6736(10)	16.7894(12)	10.039(3)	12.348(5)	21.244(2)	22.6503(15)	8.8500(15)
c (Å)	12.681(2)	17.349(3)	14.935(4)	20.245(8)	25.136(3)	9.6061(6)	9.4594(16)
α (°)	90	90	70.431(3)	90	90	90	90.930(2)
$\beta$ (°)	111.524(2)	90	72.443(4)	90	90	94.8710(10)	97.192(2)
γ (°)	90	90	73.837(3)	90	90	90	102.019(2)
$V(Å^3)$	1266.3(3)	4890.4(9)	1207.5(6)	4234(3)	10 153.5(19)	2029.6(2)	652.47(19)
$D_{\rm c}$ (Mg m <sup>-3</sup> )	1.919	1.657	1.947	1.581	1.447	1.731	1.808
Z	4	8	1	8	8	2	2
$\mu ({\rm mm}^{-1})$	4.289	2.272	1.407	1.078	0.899	1.120	1.356
Reflns	11 482/3033	14 668/2803	6067/4171	27 074/5322	48 939/8922	10 798/6013	8956/3201
collected/	R(int) = 0.0480	R(int) = 0.0843	R(int) = 0.0689	R(int) = 0.0747	R(int) = 0.0700	R(int) = 0.0193	R(int) = 0.0342
unique							
Data/restraints/ parameters	3033/0/200	2803/0/179	4171/0/370	5322/0/309	8922/0/591	6013/2/588	3201/0/214
R	0.0351	0.0468	0.0487	0.0407	0.0676	0.0188	0.0362
$R_{\rm w}$	0.0852	0.1074	0.1109	0.1123	0.1894	0.0439	0.0901
GOF on $F^2$	0.985	1.051	0.916	0.768	1.037	1.032	1.042



**Scheme 2** The optimized geometries of the free ligands p-H<sub>3</sub>MOPhIDC and m-H<sub>3</sub>MOPhIDC (the blue ball represents N atom, the red ball represents O atom and the gray ball represents C atom).

free ligand m-H<sub>3</sub>MOPhIDC. The NBO charges are -0.0637 for O1, -0.647 for O2, -0.665 for O3, -0.597 for O4, -0.463 for N6, and -0.496 for N7 in the free ligand m-H<sub>3</sub>MOPhIDC (Scheme 2). The methoxyl group plays the role of electron donor and the oxygen has a wealth of electron. In comparison with the free ligand p-H<sub>3</sub>MOPhIDC,<sup>9e</sup> the NBO charge distributions of carboxyl oxygen and imidazole nitrogen atoms all slightly increase because of the introduction of a methoxyl group into the meta position of the benzene ring. These values indicate that the oxygen and nitrogen atoms of the *m*-H<sub>3</sub>MOPhIDC ligand also have potential coordination ability and various coordination modes under appropriate reaction conditions. This can be confirmed by our present experimental results. In polymers 1, 3-7, the imidazole-H and COO-H are removed from the organic ligand m-H<sub>3</sub>MOPhIDC to form a *m*-HMOPhIDC<sup>2-</sup> unit. The singly deprotonated *m*-H<sub>2</sub>MOPhIDC<sup>-</sup> and doubly deprotonated m-HMOPhIDC<sup>2-</sup> can be found in polymer 2. Our experimental results demonstrate that the organic compound *m*-H<sub>3</sub>MOPhIDC is also a promising ligand like p-H<sub>3</sub>MOPhIDC to build amazing MOFs, which show various coordination modes (Scheme 1) and strong coordination ability. To understand the coordination modes of *m*-H<sub>3</sub>MOPhIDC, we have analyzed the Cambridge Structure Database, and found about more than four hundred complexes bearing H<sub>3</sub>IDC and its 2-position-substituted derivatives. Through comparison of the similarities and differences of the coordination modes about the imidazole dicarboxylate ligands in CCDC, we found that each coordination mode of *m*-H<sub>3</sub>MOPhIDC can be found in previous different imidazole dicarboxylate-based complexes.9,22-27 This suggests that no matter what kinds of 2-position substituent the derivatives of H<sub>3</sub>IDC contain, they all show diversity of coordination modes.

The different structural complexes 1 and 2 have been obtained in high yield by hydrothermal reaction of  $Sr(NO_3)_2$  with  $H_3MOPhIDC$  in different solvents. This indicates that solvent is crucial for the formation of the two complexes. However, the role of solvent in the construction of polymers 1 and 2 is ambiguous.

The amount of pyridine is important for the formation of complex **3**. The addition of pyridine (2.5 mmol) has produced crystals of **3** successfully, while a different amount of pyridine has failed to produce suitable crystals or has given products with low yield. We have also attempted to replace pyridine with  $Et_3N$  (2.5 mmol or 0.4 mmol) in the synthesis of **3**, only leading to the formation of some unidentified powder. This fact implies that pyridine has been adopted mainly to adjust pH values and benefit the crystallization of complex **3**.

When auxiliary ligands phen and 2,2'-bipy were introduced into the reaction system, three chain polymers **4**, **5** and **6** can be obtained. Obviously, these chelating ligands coordinate to the metal ions and occupy some coordination sites. Thus, a similar situation has been observed in the previous coordination polymer  $[Cd_2(\mu_2-PhHIDC)_2(phen)_2]_n^{25}$  (PhH<sub>3</sub>IDC = 2-phenyl-1*H*-imidazole-4,5-dicarboxylic acid).

The pH values of the reaction solution are adjusted by  $Et_3N$ , however pyridine is more suitable for preparation of **3**. The reactions of metal salt and the imidazole dicarboxylate ligand all in a molar ratio of 1:1 have produced crystals of **1**–7 successfully, while other stoichiometries have failed to produce suitable crystals or have given products with low yields (about 2.5%).

In conclusion, through the careful control of reaction condition, such as pH values, solvent, metal-to-ligand molar ratio, *etc.*, the reproducibility of our experiment is good.

The IR spectra reveal characteristic absorption bands for water molecules, carboxyl groups, phenyl, imidazolyl and pyridyl rings. Polymers **1–7** exhibit strong characteristic absorption bands in the range of 1384–1610 cm<sup>-1</sup> due to  $\nu_{\rm as}(\rm COO^-)$  and  $\nu_{\rm s}(\rm COO^-)$  vibrations. The strong and broad bands centered at 3620 and 3440 cm<sup>-1</sup> are attributed to the  $\nu_{\rm O-H}$  stretching of coordinated water in polymers **1** and **3**. The frame vibrations of the phenyl ring in **1–7** vary from 1400 to 1700 cm<sup>-1</sup>. The strong bands between 1588 cm<sup>-1</sup> and 1670 cm<sup>-1</sup> in all these polymers imply the C=N and C=C stretching bands of imidazole ring.

# Crystal structure of crystalline polymer $[Sr(m-HMOPhIDC)-(H_2O)]_n$ (1)

Complex **1** exhibits a 2D framework, which is constructed from alternate 1D helical chains bridged by the carboxyl groups.

It is worth noting that each *m*-HMOPhIDC<sup>2–</sup> anion in **1** shows an uncommon coordination mode, namely  $\mu_5$ -*k*O:*k*O,O': *k*O',O'':*k*O'',O''':*k*O''' (Scheme 1a), which is different from the  $\mu_2$ -*k*O:*k*O' coordination mode in the previous polymer [Sr( $\mu_5$ -H<sub>2</sub>PhIDC)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]·2H<sub>2</sub>O.<sup>9a</sup> As shown in Fig. S1,<sup>†</sup> the asymmetric unit of **1** consists of one Sr( $\pi$ ) ion, five *m*-HMOPhIDC<sup>2–</sup> anions, one coordinated water molecule. Each Sr( $\pi$ ) ion is coordinated by nine oxygen atoms from five share  $\mu_5$ -*m*-HMO-PhIDC<sup>2–</sup> anions and one water molecule showing a polyhedron coordination geometry. Neighboring Sr atoms are linked by *m*-HMOPhIDC<sup>2–</sup> anions to form the 1D left-handed and 1D right-handed helical chains. The distance of the two adjacent intrachain Sr...Sr is 4.4593 Å. Surprisingly, the left-and right-handed helix chains are hierarchical helix of the



**Fig. 1** The layer structure of polymer **1** constructed by the left- and righthanded helix chains (benzene rings omitted for clarity).

helix, and very like a DNA double helix (Fig. 1a). As shown in Fig. 1b, six Sr(n) atoms and six *m*-HMOPhIDC<sup>2–</sup> units compose a distorted hexagonal ring. Consequently, these distorted hexagonal rings are connected into a grid sheet by two oxygen atoms from the carboxyl groups.

The Sr–O bond lengths vary from 2.4828(18)–2.803(2) Å, which are comparable to the previously reported values.<sup>12</sup> The bond angles around each Sr( $\pi$ ) ion vary from 47.05(6) to 171.81(7)°. The *m*-HMOPhIDC<sup>2–</sup> ligands link neighbor Sr( $\pi$ ) ions forming helical chains along the crystallographic *a*-axis. The other oxygen atoms of the *m*-HMOPhIDC<sup>2–</sup> ligands bridge these helices to get a sheet structure. Moreover, the hydrogen bonds (Table S2†) occurring at O(2)–H(1W)…N(3)#6 and N(2)–H(2W)…O(2)#1 enhance the stability of complex **1**.

#### Crystal structure of crystalline polymer $[Sr(m-H_2MOPhIDC)_2]_n$ (2)

Complex 2 features a 3D framework. The central Sr(II) ion is eight-coordinated with six oxygen (O2B, O2C, O2D, O2E, O4 and O4A) and two nitrogen atoms (N1 and N1A) from six individual  $\mu_3$ -*m*-H<sub>2</sub>MOPhIDC<sup>-</sup> anions (Fig. S2†). The Sr–O bond distances ranging from 2.488(3) to 2.773(3) Å and Sr–N bond distance being 2.737(3) Å are consistent with the previously reported values.<sup>36–38</sup> Obviously, the metal sites in 2 also exhibit polyhedron coordination geometry.

Interestingly, the organic ligand exhibits a different coordination mode from that in polymer 1. They all adopt one type of coordination mode, namely  $\mu_3$ -kN,O:kO':kO' (Scheme 1b) in 2. The coordination mode for the imidazole dicarboxylate ligand in polymer 2 is rather unusual. One imidazole nitrogen atom takes part in the coordination to the  $Sr(\pi)$  atom. So far, only three related reports have been found in the literature.<sup>36-38</sup> As shown in Fig. 2a, each *m*-HMOPhIDC<sup>2-</sup> anion bridges three Sr(II) atoms to form step-shaped infinite chains (Fig. 2a). The four strontium atoms form a parallelogram in which the two side lengths are 3.6072 and 9.4490 Å, respectively, and one of the interior angles is 62.676°. These parallelograms with a common edge connection form a ladder-like 1D chain. Furthermore, these infinite chains are linked by  $\mu_3$ -*m*-H<sub>2</sub>MOPhIDC<sup>-</sup> ligands to build up many layers (Fig. 2b). It is noteworthy that adjacent layers are pillared by the  $\mu_3$ -*m*-H<sub>2</sub>MOPhIDC<sup>-</sup> ligands to result in a three-dimensional supramolecular structure with microporous channels (Fig. 2c). The microporous channel diameter is about 6.2122 Å  $\times$ 



**Fig. 2** (a) The ladder-like chain along the *b*-axis. (b) The layer constructed from *m*-HMOPhIDC<sup>2–</sup> and Sr( $\mathfrak{n}$ ) atoms. (c) The 3D framework along the *b*-axis built by the layers and *m*-HMOPhIDC<sup>2–</sup> units (H atoms omitted for clarity). (d) Schematic illustrating the topology of the 3D framework of compound **2**. (The organic ligands are represented by pink spheres, Sr ions by green.)

11.2672 Å. Finally,  $\pi$ - $\pi$  interactions of the parallel benzene rings between layers increase the stability of complex 2.

From a topological viewpoint, the *m*-HMOPhIDC<sup>2–</sup> and the two Sr ions can be viewed as a 2-connected node and a 8-connected node. Thus, the 3D framework of 2 can be described as a (2,8)-connected topology with the point symbol of  $(4^4.12^{24})$ - $(4)_4$  (Fig. 2d).

## Crystal structure of crystalline polymer [Cd<sub>3</sub>(*m*-H<sub>2</sub>MOPhIDC)<sub>2</sub>-(*m*-HMOPhIDC)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>*n*</sub> (3)

Single-crystal X-ray diffraction studies reveal that the architecture of **3** is a sheet structure. As illustrated in Fig. 3a, it contains two crystallographically independent Cd( $\pi$ ) ions and six organic ligands per asymmetric unit. Interestingly, singly deprotonated *m*-H<sub>2</sub>MOPhIDC<sup>-</sup> and doubly deprotonated *m*-HMOPhIDC<sup>2-</sup> coexist in **3**, and they adopt two types of coordination modes, namely  $\mu_3$ -*k*N,O:*k*O (Scheme 1c) and  $\mu_2$ -*k*N,O:*k*O (Scheme 1d), respectively. Each organic ligand serves as bridges to link Cd atoms by *N*,*O*-chelating, *O*-bridging and *N'*,*O'*-chelating coordination modes into a sheet structure. Although both Cd1 and Cd2 are six-coordinated, their



Fig. 3 (a) Coordination environments of Cd(II) atom in polymer 3 (H atoms omitted for clarity). (b) The chain along the *a*-axis based on Cd(II) and *m*-HMO-PhIDC<sup>2-</sup> units. (c) The layer constructed from  $\mu_3$ -*m*-HMOPhIDC<sup>2-</sup> and the chain (H atoms and benzene ring omitted for clarity). (d) The 3-D supramolecular network of 3. (e) The simplified topological consideration of 3.

coordination environments are slightly different. The Cd1 is chelated by two *m*-HMOPhIDC<sup>2-</sup> ligands (Fig. 3a) with O,Nchelating donors (N3C, O6C, N3 and O6) to form two fivemembered chelating rings. The Cd1 center displays a distorted octahedral environment, in which the equatorial plane comprises two nitrogen atoms and two carboxylate oxygen atoms from two distinct doubly deprotonated *m*-HMOPhIDC<sup>2-</sup> ligands, and two oxygen atoms from the other two m-HMO-PhIDC<sup>2-</sup> ligands occupy the apical sites. For Cd2, there is a little difference: water molecules participate in the coordination by providing an oxygen atom instead of one hydroxyl group. It should be noted that the chelating effects of both organic ligands are the main effect responsible for the distortion in the coordination geometries of both two Cd(II) atoms. The Cd(1)–O(1) (2.363(5) Å) and Cd(1)–O(6) (2.387(4) Å) bond distances are longer than that of Cd(2)-O(9)#4 (2.283(4) Å) and Cd(2)-O(2) (2.299(4) Å), and slightly shorter than that of Cd(2)-O(9)#1 (2.408(4) Å). Both Cd1 and Cd2 are held together by the imidazole ring and one carboxylate group. The N and O atoms behave as a bidentate ligand to yield a binuclear metallocycle. The organic ligand likes one bridge. Each binuclear unit is surrounded via five organic ligands. These binuclear units are connected into a layer by N and O atoms chelating as double bridges (Fig. 3c). Two bond angles (N3C-Cd1-O6 and N4-Cd2-O9A being 107.02(16)° and 71.43(16)°, respectively) are responsible for the obvious distortion from the octahedral environment. The Cd-L (L = O or N) distances are in the range of 2.283(4)–2.408(4) Å. The *m*-HMOPhIDC<sup>2–</sup> ligands link neighboring Cd(II) ions to form a 1-D wavy chain (Fig. 3b), which comprise a plane like paper cut for a window decoration along the *b*-axis, as shown in Fig. 3c. Within the same  $[Cd_3(\mu_2-m_2)]$  $H_2MOPhIDC)_2(\mu_3-m-HMOPhIDC)_2(H_2O)_2]_n$  chain, the dihedral angles between phenyl ring C6-C11 (the mean deviation from the plane is 0.000 Å) and imidazole ring N1–N2 (the mean deviation from the plane is 0.0195 Å), and the phenyl ring C18-C23 and other imidazole ring N3-N4 (the mean deviation from the plane is 0.0378 Å) are 57.417° and 27.603°, respectively. Finally, such layers are packaged into an interpenetrating 3D supramolecular architecture through weak  $\pi$ - $\pi$  interactions and hydrogen bond (Fig. 3d).

# Crystal structure of crystalline polymer [Cu(*m*-HMOPhIDC)-(phen)]<sub>n</sub> (4)

Single crystal X-ray diffraction studies reveal that **4** is an infinite chain structure. As illustrated in Fig. S3,<sup>†</sup> the asymmetrical unit of **4** comprises one Cu<sup>2+</sup> cation, one phen unit and one singly deprotonated  $\mu_2$ -*m*-HMOPhIDC<sup>2-</sup> anion. The *m*-HMOPhIDC<sup>2-</sup> ligand adopts one type of coordination mode, namely  $\mu_2$ -*k*N,O:*k*N',O' (Scheme 1e). The central Cu<sup>2+</sup> cation is six-coordinated by two nitrogen atoms (N1 and N2) from phen, two oxygen atoms (O3 and O6A) from carboxylate groups and another two nitrogen atoms (N3 and N4A), showing a slightly distorted octahedral geometry. The bond distances of Cu–N vary from 1.987(2) to 2.2853(18) Å while the Cu–O length is 1.9966(16) Å, which are partially different from the previously

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**Fig. 4** (a) The chain along the *a*-axis based on Cu(II) and *m*-HMOPhIDC<sup>2-</sup> units. (b) The 3D supramolecular structure of polymer **4** supported by  $\pi$ - $\pi$  interactions and hydrogen bonds.

reported values.<sup>39</sup> The bond angles around the central  $Cu^{2+}$  atom are in the range of 83.12(6) to 177.25(7)°.

The adjacent organic  $\mu_2$ -*m*-HMOPhIDC<sup>2-</sup> units are almost vertical in the infinite uniform chain of **4**. Each  $\mu_2$ -*m*-HMO-PhIDC<sup>2-</sup> anion connects the neighboring Cu(n) ions in *N*,*O*-chelation or *N'*,*O'*-chelation to obtain a chain along the *b*-axis with auxiliary ligand 1,10-phenanthroline arranged regularly in the side chain (Fig. 4a). The intrachain neighboring Cu···Cu distance is 6.1740(25) Å. Each chain packs with the others through  $\pi$ - $\pi$  interactions (the dihedral angle between the two phen rings being 0.000°) to extend a layer along the *ab* axes. Furthermore, the layers are further assembled into a 3D supramolecular structure, with  $\pi$ - $\pi$  interactions and hydrogen bonds increasing structural stability (Fig. 4b).

# Crystal structure of crystalline polymers $[Cd_2(m-HMOPhIDC)_2 - (phen)_2]_n$ (5) and $[Cd_2(m-HMOPhIDC)_2(2,2'-bipy)_2]_n$ (6)

Polymers 5 and 6 are 1-D zigzag chains and contain very similar compositions: Cd(II) ions, *m*-HMOPhHIDC<sup>2-</sup> anions, chelating *N*-containing ligands, phen or 2,2'-bipy. Therefore, the structure of 5 was selected and described in detail and pertinent points for the polymer 6 will be just mentioned wherever appropriate.

In polymer 5, the asymmetric unit consists of two Cd( $\pi$ ) ions, two phen units and two individual  $\mu_2$ -*m*-HMOPhIDC<sup>2-</sup> anions (Fig. 5). Each imidazole dicarboxylate ligand adopts  $\mu_2$ *k*N,O:*k*N',O' mode (Scheme 1e), connecting two Cd( $\pi$ ) ions to generate a zigzag chain. The two Cd( $\pi$ ) ions assume similar distorted octahedral environments. Cd1 is coordinated by two nitrogen atoms (N3 and N4) from a phen unit, two carboxylato oxygen atoms (O4 and O6) and two nitrogen atoms (N2 and N8) from two imidazole rings. N3, N8, O4 and O6 occupy the equatorial sites, and N2, O6 are located at the axial positions.



**Fig. 5** (a) Coordination environments of Cd(II) atoms in polymer **5** (H atoms omitted for clarity). (b) 1D chain along the *a*-axis based on Cu(II) and *m*-HMO-PhIDC<sup>2–</sup> units. (c) The 3D supramolecular structure of **5** supported by the  $\pi$ - $\pi$  interactions.

The Cd2 atom is also six-coordinated by two phen nitrogen atoms (N5 and N6), two nitrogen atoms (N1 and N9) and two oxygen atoms (O9 and O1) from two  $\mu_2$ -*m*-HMOPhIDC<sup>2-</sup> anions. The Cd–O and Cd–N bond lengths are in the range of 2.379(7)–2.416(8) Å and 2.243(8)–2.381(9) Å, respectively, which are consistent with the previous values.<sup>22</sup> The bond angles around the central Cd(II) ion vary from 71.0(3) to 170.5(3)°.

It is noteworthy that the Cd atoms are joined by the doubly deprotonated  $\mu_2$ -*m*-HMOPhIDC<sup>2-</sup> ligands to generate an infinite corrugated-shaped chain along the *a*-axis (Fig. 5b). The intrachain Cd…Cd separations are 6.3948 Å and 6.4333 Å, respectively. Notably, a layer is constructed by  $\pi$ - $\pi$  interactions between the chains. The two phen rings are approximately parallel and the distance between them is 3.7052 Å. Finally, intermolecular  $\pi$ - $\pi$  interactions and hydrogen bonds lead to the formation of a 3D network (Fig. 5c).



**Fig. 6** (a) Coordination environments of Cd( $\mathfrak{n}$ ) atoms in polymer **6** (H atoms omitted for clarity). (b) 1D chain along the c-axis based on Cd( $\mathfrak{n}$ ) and *m*-HMO-PhIDC<sup>2-</sup> units. (c) The 3D supramolecular structure of **6**.

Complex 6 is assembled in a 1D chain with two  $Cd(\pi)$ atoms, two *m*-HMOPhHIDC<sup>2-</sup> anions and two 2,2'-bipy in each asymmetric unit. As shown in Fig. 6a, Cd1 is ligated by two nitrogen atoms (N3 and N4) from 2,2'-bipy and two oxygen atoms (O3 and O10) from two individual  $\mu_2$ -m-HMOPhHIDC<sup>2-</sup> units in the quasi-plane, and two nitrogen atoms (N2 and N8) from two individual  $\mu_2$ -*m*-HMOPhHIDC<sup>2-</sup> in axial positions. Cd2 has a similar coordination environment to Cd1. The bond angles around Cd(II) ion range from 69.47(13) to 166.96(15)°. Therefore the two  $Cd(\pi)$  ions are both in seriously distorted octahedral geometries. Interestingly, the doubly deprotonated *m*-HMOPhHIDC<sup>2–</sup> anions all adopt  $\mu_2$ -*k*N,O:*k*N',O' (Scheme 1e) in 5 and 6. And the 2,2'-bipy ligands are arranged alternately beside the chain (Fig. 6b), and the dihedral angle between two adjacent 2,2'-bipy rings is 33.419°. Similar to 5, intermolecular hydrogen bonds link infinite parallel chains to form the layers, which assemble in a 3D structure through weak  $\pi$ - $\pi$  stacking interactions (the distance between two staggered phenyl rings of *m*-HMOPhHIDC<sup>2–</sup> anion is 7.1661 Å) (Fig. 6c).

# Crystal structure of crystalline polymer $[Co(m-HMOPhIDC)-(H_2O)_2]_n$ (7)

Single-crystal X-ray structural analysis reveals that 7 is a 1D chain. As illustrated in Fig. S3,<sup>†</sup> the asymmetric unit of 7 comprises one  $Co^{2+}$  cation, one double deprotonated  $\mu_2$ -*m*-HMO-PhIDC<sup>2-</sup> anion. The ligand adopts one type of coordination mode, namely  $\mu_2$ -kN,O:kN',O' (Scheme 1e). The Co(II) atom is six-coordinated, adopting a slightly distorted octahedral geometry (Fig. S4<sup>†</sup>). The equatorial plane is defined by two nitrogen atoms (N1, N1B) and two oxygen atoms (O5, O5B) from two individual m-HMOPhIDC<sup>2-</sup> ligands. The axial positions are occupied by two water molecules. The bond distances of Co-O/N vary from 2.0648 (2)-2.207(2) Å, which are partially different from the previously reported values.9c The bond angles around the central  $Co^{2+}$  atom are in the range of 78.64(7) to 180.00°. Each  $\mu_2$ -*m*-HMOPhIDC<sup>2-</sup> anion connects the neighboring Co(II) ions in N,O-chelation or N',O'-chelation to obtain a chain along the *b*-axis (Fig. 7a). In addition, the neighboring Co…Co separation is 6.5794(8) Å within the chain. Finally, such 1-D infinite chains are further connected and assembled into an interpenetrating 3-D solid-state network through the  $\pi$ - $\pi$  interactions and hydrogen bonds (Fig. 7b).

### Thermogravimetric analyses

To characterize the polymers more fully in terms of thermal stability, their thermal behaviors were studied by the thermogravimetric analysis (TGA). The TG curves have been obtained



**Fig. 7** (a) 1D chain along the *b*-axis based on Co(II) and *m*-HMOPhIDC<sup>2-</sup> units. (b) The 3D supramolecular structure of **7**.



under flowing air for the crystalline samples of polymers 1–7 (Fig. 8).

For polymer 1, the first weight loss of 5.14% (calculated 4.93%) occurs at about between 164.4 °C and 373.9 °C, which is attributed to the loss of coordinated water molecules. The second weight loss of 59.37% between 373.9 °C and 560 °C corresponds to the loss of the *m*-HMOPhIDC<sup>2–</sup> unit. The remaining weight of 36.32% corresponds to the percentage (calculated 35.49%) of the Sr and O components, indicating that the final product is SrO.

Polymer 2 is stable up to 161 °C, then loses weight from 161 to 198.5 °C (observed 10.2%, calculated 10%) corresponding to two methoxy groups. Subsequently, a plateau region is observed from 198.5 to 373.0 °C. It keeps losing weight from 373.0 to 567.3 °C corresponding to the decomposition of the remaining group of *m*-HMOPhIDC<sup>2–</sup> units (observed 23.50%, calculated 22.88%). A white amorphous residue is 2SrO (observed 35.4%, calculated 34.10%).

For polymer 3, the weight loss corresponding to the release of two methoxyphenyl units is observed from 157.8 to 259.2 °C (observed 7.92%, calculated 8.72%). Then an advanced degradation process takes place after 259.2 °C. It continues to decompose upon further heating and undergoes a slow weight loss of 46.00% covering the temperature from 259.2 to 418.6 °C, which corresponds to the destruction of two phen molecules and four carboxyl groups. It keeps losing weight from 418.6 to 490.5 °C corresponding to decomposition of the remaining groups of the imidazole dicarboxylate ligand (observed 19.56%, calculated 18.36%). Finally, a plateau region is observed from 490.5 to 840 °C. The remaining weight corresponds to the formation of 1.5CdO (observed 26.52%, calculated 27.2%).

Polymer 4 exhibits an initial weight loss from 247.4 to 397.8 °C, with the observed weight loss of 42.27% corresponding to the release of one phen molecule and one carboxyl group (observed 22.24%, calculated 21.26%). After that an additional weight loss of 41.43% up to 542 °C shall be attributed to the gradual decomposition of other parts of the organic ligand. Finally, a plateau region is observed from 640 to

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840 °C. The final blue residue is CuO (observed 15.44%, calculated 15.78%).

For polymer 5, the first weight loss of 2.24% in the region of 32.8–323.7 °C corresponds to the loss of the *m*-methoxyphenyl group (calculated 2.81%). The further weight loss of 37.49% in the temperature range of 32.3.7–410.4 °C can be attributed to the decomposition of phen molecule. It keeps losing weight from 410.4 to 540.3 °C corresponding to the collapse of other parts of *m*-HMOPhIDC<sup>2–</sup> units (observed 36.69%, calculated 36.42%) remaining parts of *m*-HMOPhIDC<sup>2–</sup> unit. The final white residue of 23.58% is close to the calculated 23.23% based on 2CdO.

For polymer 6, the first weight loss of 49.69% (calculated 49.54%) in the region of 341.2-442.3 °C can be attributed to the decomposition of the collapse of *m*-methoxyphenyl group. The further weight loss of 25.84% corresponds to the two 2,2′-bipy molecules in the temperature range of 442.3–500 °C (observed 25.84%, calculated 29.53%). The final white residue of 24.47% is close to the calculated 24.28% based on 2CdO.

For polymer 7, the first weight loss of 12.29% in the region of 44.6–170 °C corresponds to the loss of the carboxyl group (calculated 12.67%). The further weight loss of 3.77% in the temperature range of 170–278.9 °C can be attributed to the water molecule. It keeps losing weight from 278.9 to 480 °C corresponding to the collapse of other parts of *m*-HMOPhIDC<sup>2–</sup> units (observed 56.12%, calculated 61.18%). The final rose residue of 21.25% is close to the calculated value of 21.09% based on CoO.

In conclusion, the thermal data of complexes 1–7 are in reasonable agreement with the crystal structure analyses.

#### Photoluminescent properties

Metal–organic coordination complexes constructed from metal atoms and conjugated organic ligands are candidates for hybrid photoactive materials with potential applications.<sup>40</sup> The solid-state luminescent emission spectra of polymers **1–7** and the free *m*-H<sub>3</sub>MOPhIDC ligand were studied at room temperature. As shown in Fig. 9, the free *m*-H<sub>3</sub>MOPhIDC ligand shows



Fig. 9 The solid-state photoluminescent spectra of the free  $m-H_3MOPhIDC$  ligand and polymers 1, 2, 3, 5, and 6.

luminescence with the emission maximum at 376 nm by selective excitation at 280 nm, which may be attributed to the ligand-centered  $\pi^* \rightarrow n$  electronic transitions. The emission spectra of 1 ( $\lambda_{em}$  = 360 nm,  $\lambda_{ex}$  = 300 nm), 2 ( $\lambda_{em}$  = 360 nm,  $\lambda_{ex}$ = 300 nm), 3 ( $\lambda_{em}$  = 393 nm,  $\lambda_{ex}$  = 295 nm), 5 ( $\lambda_{em}$  = 441 nm,  $\lambda_{ex}$ = 280 nm) and 6 ( $\lambda_{em}$  = 464 nm,  $\lambda_{ex}$  = 336 nm) show luminescent properties. Compared with the free m-H<sub>3</sub>DMPhIDC ligand, blue shifts of 16 nm in 1 and 2 have been observed. We can presume that these emissions are neither ligand-to-ligand charge transfer (LLCT) nor metal-to-ligand charge transfer (MLCT) in nature. Therefore, the emission of 1 and 2 may be ascribed to a charge transfer transition between ligands and metal centers, namely ligand-to-metal charge transfer (LMCT), similar to the reported results on coordination polymers with benzene dicarboxylate ligands.<sup>39</sup> Further, it can be observed that the emission spectra for 3, 5 and 6 exhibit red-shifts with respect to the free ligand may be due to the chelating and/or bridging effect of the deprotonated m-HMOPhIDC<sup>2-</sup> ligands. At the same time, a luminescence emission may be attributed to the rigidity of the phen ligands with regard to the metal clusters, which effectively increases the rigidity and conjugation upon metal coordination and then affects the loss of energy *via* a radiationless pathway of the intra-ligand ( $\pi^* \rightarrow n$ or  $\pi^* \to \pi$ ) excited state. Complexes 4 and 7 exhibit very weak emissions. It is visible that Cu<sup>2+</sup> and Co<sup>2+</sup> ions show fluorescence quenching for the *m*-H<sub>3</sub>MOPhIDC ligand.

## Conclusions

In summary, a series of metal-organic complexes with architectures diversity have been successfully synthesized under hydro(solvo)thermal conditions by fine control over solvent and pH values. The organic ligand m-H<sub>3</sub>MOPhIDC displays various coordination modes, which can generate interesting structures with metal ions ranging from one-dimensional chain, two-dimensional sheet to three-dimensional pillaredlayer structures. The results show that the structures of the complexes are affected by reaction conditions, the core metal ions and auxiliary ligands. From the structural differences of 1 and 2, we know that the solvent has a huge impact on the crystal structures. As for polymers 4-6, it is easy to find that when the N-containing chelating auxiliary ligands were introduced, one-dimensional structures can be usually obtained. Current beautiful structures further confirm the stirring coordination features of the ligand m-H<sub>3</sub>MOPHIDC. We believe that one desirable organic linkage has been found for assembling novel MOFs. Obviously, to study its coordination features and obtain more novel MOFs, much work needs to be done using the organic imidazole dicarboxylate ligand.

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