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# Synthesis and characterization of $d^{10}$ metal complexes with mixed 1,3-di(1H-imidazol-4-yl)benzene and multicarboxylate ligands

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#### ABSTRACT

Seven new coordination polymers [Zn(H<sub>2</sub>L)(mbdc)] (1), [Zn(H<sub>3</sub>L)(btc)] (2), [Zn(H<sub>2</sub>L)(Hbtc)] (3), [Zn(H<sub>2</sub>L) (Hbtc)] · H<sub>2</sub>O (4), [Zn<sub>2</sub>(H<sub>2</sub>L)(btc)( $\mu_2$ -OH)] (5), [Cd(H<sub>2</sub>L)(mbdc)] (6) and [Cd<sub>3</sub>(H<sub>2</sub>L)<sub>2</sub>(btc)<sub>2</sub>(H<sub>2</sub>O)] · 5H<sub>2</sub>O (7) were synthesized by reactions of the corresponding metal salt with rigid ligand 1,3-di(1H-imidazol-4-yl) benzene (H<sub>2</sub>L) and different carboxylic acids of 1,3-benzenedicarboxylic acid (H<sub>2</sub>mbdc) and benzene-1,3,5-tricarboxylic acid (H<sub>3</sub>btc), respectively. The results of X-ray crystallographic analysis indicate that complex 1 is 1D chain while 2 is a (3,3)-connected 2D network with Point (Schläfli) symbol of (4,8<sup>2</sup>). Complexes 3 and 6 are 2D networks, 4 is a 3-fold interpenetrating 3D framework with Point (Schläfli) symbol of  $(3,4^2)_2$  ( $3^4,4^6,5^6,6^7,7^3,8$ ), while 7 is a (3,10)-connected 3D net with Schläfli symbol of (3,4,5)<sub>2</sub>( $3^4,4^8,5^{18},6^{12},7^2,8$ ). The thermal stability and photoluminescence of the complexes were investigated. Furthermore, DFT calculations were performed for **2–4** to discuss the temperature controlled self-assembly of the complexes.

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#### 1. Introduction

Metal-organic frameworks (MOFs) which consist of metal ions or clusters and organic linkers have attracted great interest from chemists in recent years [1], due to their potential application in gas storage/separation, ion exchange, magnetism, catalysis, photoactive material and so on [2–6]. In the assembly reactions of MOFs, the primary considerations are the coordination preference of ligands and the coordination geometry of metal centers, however, other factors can also play important roles in the formation of the structures, such as the choice of auxiliary ligand, pH value, template and reaction temperature [7-11]. The multidentate organic ligands with N and/or O donors as coordination sites are widely used as building blocks in the construction of MOFs. Particularly, the ditopic and tripodal imidazole-containing ligands e.g. 1,4-di(1-imidazolyl)benzene, 1,4-di(1H-imidazol-4-yl)benzene, 1,3,5-tri(imidazole-1-ylmethyl)-2,4,6-trimethyl-benzene, 1,3,5-tri (1-imidazolyl)benzene, 1,3,5-tri(1H-imidazol-4-yl)benzene, have been widely used in our studies, and the results have shown that such ligands can react with varied metal salts leading to the formation of MOFs with different structures and properties [12]. On the other hand, multicarboxylate compounds, such as benzenedicarboxylate and benzenetricarboxylate, are the most widely

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studied organic ligands in the construction of MOFs with varied coordination modes of the carboxylate group.

In this work, we focused our attention on reactions of 1,3-di (1H-imidazol-4-yl)benzene (H<sub>2</sub>L) together with different carboxylate ligands and  $d^{10}$  metal salts, and made systematic investigation on the impact of carboxylate ligands on the construction of frameworks. In addition, the effect of temperature and base on the assembly of MOFs was also studied. Herein, we report the synthesis, crystal structure and property of seven new coordination polymers  $[Zn(H_2L)(mbdc)]$  (1),  $[Zn(H_3L)(btc)]$  (2),  $[Zn(H_2L)(Hbtc)]$ (3),  $[Zn(H_2L)(Hbtc)] \cdot H_2O$  (4),  $[Zn_2(H_2L)(btc)(\mu_2-OH)]$  (5),  $[Cd(H_2L)$ (mbdc)] (6) and  $[Cd_3(H_2L)_2(btc)_2(H_2O)] \cdot 5H_2O$  (7) obtained by reactions of H<sub>2</sub>L and different carboxylic acids of benzene-1,3,5tricarboxylic acid (H<sub>3</sub>btc) and 1,3-benzenedicarboxylic acid (H<sub>2</sub>mbdc) with corresponding metal salt under hydrothermal conditions. DFT calculations for 2-4 were performed to discuss the temperature controlled self-assembly of MOFs. The thermal stability and photoluminescence of the complexes in the solid state were investigated.

#### 2. Experimental section

#### 2.1. Materials and measurements

All commercially available chemicals and solvents are of reagent grade and were used as received without further purification. The

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ligand H<sub>2</sub>L was prepared according to the literature [13]. Elemental analyses of C, H, and N were performed on a Perkin-Elmer 240C elemental analyzer at the analysis center of Nanjing University. Infrared spectra (IR) were recorded on a Bruker Vector22 FT-IR spectrophotometer by using KBr pellets. Thermogravimetric analyses (TGA) were carried out on a simultaneous SDT 2960 thermal analyzer under nitrogen at a heating rate of 10 °C min<sup>-1</sup>. The luminescence spectra for the powdered solid samples were measured on an Aminco Bowman Series 2 spectrofluorometer with a xenon arc lamp as the light source. In the measurements of emission and excitation spectra the pass width is 5 nm, and all the measurements were carried out under the same experimental conditions. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer using Cu-K $\alpha$  radiation ( $\lambda$  = 1.5418 Å), in which the X-ray tube was operated at 40 kV and 40 mA at room temperature.

#### 2.2. Syntheses

#### 2.2.1. $[Zn(H_2L)(mbdc)]$ (1)

A mixture of  $H_2L$  (21.0 mg, 0.1 mmol),  $Zn(NO_3)_2 \cdot 6H_2O$  (29.7 mg, 0.1 mmol),  $H_2mbdc$  (16.6 mg, 0.1 mmol) and NaOH

Table 1

Crystallographic data for complexes 1-7.

(8.0 mg, 0.2 mmol) in 10 mL of H<sub>2</sub>O was sealed in a 16 mL Teflon lined stainless steel container and heated at 180 °C for 3 d. After the reaction mixture was cooled to room temperature, colorless block crystals of **1** were collected with a yield of 67% by filtration and washed with water and ethanol several times. Anal. Calcd for  $C_{20}H_{14}N_4O_4Zn$ : C, 54.63, H, 3.21, N, 12.74%. Found: C, 54.32, H, 3.41, N, 12.57%. IR (KBr pellet, cm<sup>-1</sup>): 3426 (w, br), 3091–2874 (m), 1607 (s), 1567 (s), 1479 (s), 1437 (m), 1398 (s), 1371 (s), 1221 (w), 1128 (w), 1076 (m), 973 (w), 900 (w), 849 (w), 820 (m), 782 (w), 748 (m), 719 (m), 653 (w), 626 (w).

#### 2.2.2. $[Zn(H_3L)(btc)]$ (2)

A mixture of H<sub>2</sub>L (21.0 mg, 0.1 mmol),  $Zn(NO_3)_2 \cdot 6 H_2O$  (29.7 mg, 0.1 mmol), H<sub>3</sub>btc (21.0 mg, 0.1 mmol) and NaOH (8.0 mg, 0.2 mmol) in 10 mL of H<sub>2</sub>O was sealed in a 16 mL Teflon lined stainless steel container and heated at 160 °C for 3 d. After cooling to the room temperature, yellow block crystals of **2** were collected by filtration and washed with water and ethanol several times with a yield of 71%. Anal. Calcd for C<sub>21</sub>H<sub>14</sub>N<sub>4</sub>O<sub>6</sub>Zn: C, 52.14, H, 2.92, N, 11.58%. Found: C, 52.44, H, 2.81, N, 11.66%. IR (KBr pellet, cm<sup>-1</sup>): 3444 (w, br), 3122–2855 (m), 1618 (s), 1574 (s), 1533 (s),

	1	2		3	4
Empirical formula Formula weight Temperature/K Crystal system Space group a Å b Å c/Å $a ^{\circ}$ $\beta ^{\circ}$ $\gamma ^{\circ}$ $V(Å^3)$ Z $D_c/(g cm^{-3})$ $F(0 \ 0)$ $\theta$ range/ $^{\circ}$ Reflections collected Independent reflections Goodness-of-fit on $F^2$ $R_1 [I > 2\sigma (I)]^a$ $wR_2 [I > 2\sigma (I)]^b$	C <sub>20</sub> H <sub>14</sub> N <sub>4</sub> O <sub>4</sub> Zn 439,72 293(2) Triclinic <i>P</i> -1 8.8319(10) 9.7098(10) 11.5626(13) 106.277(2) 92.356(2) 111.188(2) 876.17(17) 2 1.667 448 1.86-25.10 6312 3072 1.039 0.0380 0.0874 5	$\begin{array}{c} C_{21}H_{14}N_4O_6Zn\\ 483.73\\ 293(2)\\ Monoclinic\\ P_{2,1}c\\ 15.185(3)\\ 7.5341(16)\\ 19.632(3)\\ 90\\ 126.563(10)\\ 90\\ 1804.0(6)\\ 4\\ 1.781\\ 984\\ 1.67-25.01\\ 9428\\ 3168\\ 0.943\\ 0.0372\\ 0.0660\\ \end{array}$	6	$\begin{array}{c} C_{21}H_{14}N_4O_6Zn\\ 483.73\\ 293(2)\\ Triclinic\\ P-1\\ 9.1439(3)\\ 9.2915(3)\\ 12.0125(4)\\ 110.1260(10)\\ 99.0200(10)\\ 99.3210(10)\\ 99.3210(10)\\ 943.88(5)\\ 2\\ 1.702\\ 492\\ 2.26-25.01\\ 9438\\ 3297\\ 1.096\\ 0.0245\\ 0.0642\\ \end{array}$	C <sub>21</sub> H <sub>16</sub> N <sub>4</sub> O <sub>7</sub> Zn 501.75 293(2) Orthorhombic <i>P</i> na2 <sub>1</sub> 8.4321(14) 15.064(3) 15.064(3) 90 90 90 1913.4(6) 4 1.742 1024 1.91–25.04 9037 2958 1.033 0.0306 0.0787 <b>7</b>
Empirical formula Formula weight Temperature/K Crystal system Space group a A b A c/A $a ^{\circ}$ $\beta ^{\circ}$ $\gamma ^{\circ}$ $V$ ( $A^{3}$ ) Z $D_{c}/(g \text{ cm}^{-3})$ $F(0 \ 0 \ 0)$ $\theta$ range/° Reflections collected Independent reflections Goodness-of-fit on $F^{2}$ $R_{1}$ [ $I > 2\sigma$ ( $I$ )] <sup>b</sup>	$\begin{array}{c} C_{21}H_{14}N_4O_7Zn_2\\ 565.18\\ 293(2)\\ Triclinic\\ P-1\\ 9.8679(8)\\ 10.2786(7)\\ 10.6037(8)\\ 90.5100(10)\\ 108.4710(10)\\ 106.379(3)\\ 972.99(13)\\ 2\\ 1.929\\ 568\\ 2.04-25.10\\ 4967\\ 3417\\ 1.023\\ 0.0328\\ 0.0914 \end{array}$		$\begin{array}{c} C_{20}H_{14}N_4O_4\\ 486.75\\ 293(2)\\ Triclinic\\ P-1\\ 8.3451(9)\\ 10.1109(10)\\ 11.2679(11)\\ 100.743(2)\\ 90.027(2)\\ 112.287(2)\\ 861.65(15)\\ 2\\ 1.876\\ 484\\ 1.85-25.00\\ 4312\\ 2982\\ 1.223\\ 0.0350\\ 0.0813\\ \end{array}$	Cd	$\begin{array}{c} C_{42}H_{38}N_8O_{18}Cd_3\\ 1,280.03\\ 293(2)\\ Monoclinic\\ P_{2_1/c}\\ 16.6011(12)\\ 16.2848(12)\\ 19.7529(10)\\ 90\\ 118.741(4)\\ 90\\ 4.682.2(5)\\ 4\\ 1.816\\ 2.536\\ 1.72-25.01\\ 22.935\\ 8.247\\ 1.343\\ 0.1257\\ 0.2447\\ \end{array}$

<sup>a</sup>  $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$ .

<sup>b</sup>  $wR_2 = |\Sigma w(|F_o|^2 - |F_c|^2)| / \Sigma |w(F_o)^2|^{1/2}$ , where  $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ .  $P = (F_o^2 + 2F_c^2)/3$ .

1436 (s), 1349 (s), 1145 (w), 1114 (w), 971 (w), 845 (w), 819 (m), 762 (m), 729 (m), 713 (m), 646 (w), 620 (w), 543 (w).

#### 2.2.3. $[Zn(H_2L)(Hbtc)]$ (3)

Complex **3** was synthesized by the same procedure as that used for preparation of **2**, except that the reaction mixture was heated at 65 °C. After cooling to the room temperature, colorless block crystals of **3**, which were picked out from the mixture of **2** and **3**, were washed with water and ethanol several times with a yield of 30%. Anal. Calcd for  $C_{21}H_{14}N_4O_6Zn$ : C, 52.14, H, 2.92, N, 11.58%. Found: C, 51.99, H, 2.98, N, 11.43%. IR (KBr pellet, cm<sup>-1</sup>): 3420 (w, br), 3121–2852 (m), 1681 (s), 1536 (s), 1484 (w), 1437 (s), 1348(s), 1232(w), 1176 (w), 820 (m), 763 (m), 730 (m), 714 (m), 647 (w), 620 (w), 500 (w).

#### 2.2.4. $[Zn(H_2L)(Hbtc)] \cdot H_2O(4)$

A trace amount of complex **4** was found in the synthesis of **2** at 180 °C. The yellow block crystals of **4** were difficultly separated from **2** and the yield of **4** was very poor, so only the crystal structure of **4** was obtained.

#### 2.2.5. $[Zn_2(H_2L)(btc)(\mu_2-OH)]$ (5)

A mixture of H<sub>2</sub>L (21.0 mg, 0.1 mmol),  $Zn(NO_3)_2 \cdot 6H_2O$  (29.7 mg, 0.1 mmol), H<sub>3</sub>btc (21.0 mg, 0.1 mmol) and NaOH (16.0 mg, 0.4 mmol) in 10 mL of H<sub>2</sub>O was sealed in a 16 mL Teflon lined stainless steel container and heated at 180 °C for 3 d. After the reaction mixture was cooled to room temperature, colorless block crystals of **5** were collected by filtration and washed with water and ethanol several times in 48% yield. Anal. Calcd for C<sub>21</sub>H<sub>14</sub>N<sub>4</sub>O<sub>7</sub>Zn<sub>2</sub>: C, 44.63, H, 2.50, N, 9.91%. Found: C, 44.84, H, 2.66, N, 10.06%. IR (KBr pellet, cm<sup>-1</sup>): 3428 (w), 3141–2855 (m), 1614 (s), 1573 (s), 1435 (s), 1370 (s), 1132 (w), 816 (w), 766 (m), 730 (m), 715 (m), 644 (w), 554 (w).

#### 2.2.6. $[Cd(H_2L)(mbdc)]$ (6)

Complex **6** was synthesized by the same procedure as that used for preparation of **1**, except that  $Cd(NO_3)_2 \cdot 4H_2O$  (30.8 mg, 0.1 mmol) was used instead of  $Zn(NO_3)_2 \cdot 6H_2O$ . After cooling to the room temperature, colorless block crystals of **6** were collected by filtration and washed with water and ethanol several times in 65% yield. Anal. Calcd for  $C_{20}H_{14}N_4O_4Cd$ : C, 49.35, H, 2.90, N, 11.51%. Found: C, 49.43, H, 2.75, N, 11.42%. IR (KBr pellet, cm<sup>-1</sup>): 3120–2865 (m), 1599 (s), 1547 (s), 1476 (m), 1457 (m), 1387 (s), 1114 (m), 1071 (w), 822 (w), 786 (w), 752 (m), 723 (m), 701 (w), 650 (w), 626 (w).

#### 2.2.7. $[Cd_3(H_2L)_2(btc)_2(H_2O)] \cdot 5H_2O(7)$

Complex **7** was synthesized by the same procedure as that used for preparation of **5**, except that  $Cd(NO_3)_2 \cdot 4H_2O$  (46.2 mg, 0.15 mmol) was used instead of  $Zn(NO_3)_2 \cdot 6H_2O$ . After the reaction mixture was cooled to room temperature, colorless block crystals of **7** were collected by filtration and washed with water and ethanol several times with a yield of 32%. Anal. Calcd for  $C_{42}H_{38}N_8O_{18}Cd_3$ : C, 39.41, H, 2.99, N, 8.75%. Found: C, 39.56, H, 2.78, N, 8.52%. IR (KBr pellet, cm<sup>-1</sup>): 3420–3150 (m), 1615 (s), 1546 (s), 1436 (s), 1364 (s), 1136 (m), 1077 (w), 943 (w), 829 (w), 769 (m), 733 (m), 642 (w).

#### 2.3. Crystal structure determination

The data collections for **1–7** were carried out on a Bruker Smart Apex CCD area-detector diffractometer using graphitemonochromated Mo  $K\alpha$  radiation ( $\lambda$ =0.71073 Å) at 20(2) °C. The diffraction data was integrated by using the *SAINT* program [14]. Semi-empirical absorption corrections were applied using the *SADABS* program [15]. The structures of **1–7** were solved by direct methods and all non-hydrogen atoms were refined anisotropically on  $F^2$  by the full-matrix least-squares technique using the

#### Table 2

Selected bond lengths (A	Å) and bond angles	(°) for complexes 1–7 <sup>a</sup> .
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1			
Zn(1)-O(4) Zn(1)-N(4) O(4)-Zn(1)-O(2)#1 O(2)#1-Zn(1)-N(4) O(2)#1-Zn(1)-N(1)#2	1.946(2) 2.005(2) 116.1(1) 118.7(1) 101.8(1)	$\begin{array}{l} Zn(1)-O(2)\#1\\ Zn(1)-N(1)\#2\\ O(4)-Zn(1)-N(4)\\ O(4)-Zn(1)-N(1)\#2\\ N(4)-Zn(1)-N(1)\#2\\ \end{array}$	1.960(2) 2.055(3) 99.4(1) 113.3(1) 107.9(1)
Zn(1)-O(6)#1 Zn(1)-O(3)#2 O(6)#1-Zn(1)-N(4) N(4)-Zn(1)-O(3)#2 N(4)-Zn(1)-O(4)	1.922(2) 1.973(2) 131.2(1) 104.9(1) 110.2(1)	$\begin{array}{l} Zn(1)-N(4)\\ Zn(1)-O(4)\\ O(6)\#1-Zn(1)-O(3)\#2\\ O(6)\#1-Zn(1)-O(4)\\ O(3)\#2-Zn(1)-O(4) \end{array}$	1.955(3) 1.981(3) 105.9(1) 103.6(1) 95.3(1)
Zn(1)-O(2)#1 Zn(1)-N(2)#2 O(2)#1-Zn(1)-O(4) O(4)-Zn(1)-N(2)#2 O(4)-Zn(1)-N(2)#2 O(4)-Zn(1)-N(4)	1.941(1) 1.993(2) 113.85(6) 121.05(6) 95.90(6)	Zn(1)-O(4) Zn(1)-N(4) O(2)#1-Zn(1)-N(2)#2 O(2)#1-Zn(1)-N(4) N(2)#2-Zn(1)-N(4)	1.969(1) 2.007(2) 97.39(6) 114.36(7) 115.51(6)
Zn(1)-O(4) Zn(1)-N(4) O(4)-Zn(1)-O(1)#1 O(1)#1-Zn(1)-N(4) O(1)#1-Zn(1)-N(2)#2	1.916(2) 1.955(2) 101.1(1) 112.2(1) 95.8(1)	Zn(1)-O(1)#1 Zn(1)-N(2)#2 O(4)-Zn(1)-N(4) O(4)-Zn(1)-N(2)#2 N(4)-Zn(1)-N(2)#2	1.950(2) 1.999(2) 127.5(1) 112.3(1) 103.7(1)
$\begin{array}{c} J\\ Zn(2)-O(7)\\ Zn(2)-O(3)\#2\\ Zn(2)-O(3)\#2\\ Zn(2)-O(1)\#3\\ O(7)-Zn(2)-O(6)\#1\\ O(7)-Zn(2)-O(3)\#2\\ O(6)\#1-Zn(2)-O(1)\#3\\ O(6)\#1-Zn(2)-O(1)\#3\\ O(3)\#2-Zn(2)-O(1)\#3\\ O(3)\#2-Zn(2)-O(1)\#3\\ \end{array}$	1.912(2) 1.946(2) 1.948(2) 1.948(2) 104.0(1) 112.1(1) 118.0(1) 107.8(1) 106.2(1) 108.1(1)	$\begin{array}{l} Zn(1)-O(7)\\ Zn(1)-N(4)\\ Zn(1)-N(2)\#4\\ O(7)-Zn(1)-N(4)\\ O(7)-Zn(1)-N(4)\\ O(7)-Zn(1)-O(4)\\ N(4)-Zn(1)-N(2)\#4\\ O(7)-Zn(1)-N(2)\#4\\ O(4)-Zn(1)-N(2)\#4\\ O(4)-Zn(1)-N(2)\#4\\ \end{array}$	$\begin{array}{c} 1.919(2)\\ 1.976(2)\\ 1.993(2)\\ 2.002(2)\\ 110.9(1)\\ 108.7(1)\\ 112.2(1)\\ 110.5(1)\\ 117.4(1)\\ 96.1(1) \end{array}$
$\begin{array}{c} \textbf{O}\\ Cd(1)-O(4)\\ Cd(1)-N(4)\\ Cd(1)-N(4)\\ O(4)-Cd(1)-N(4)\\ O(4)-Cd(1)-O(1)\#1\\ N(4)-Cd(1)-O(1)\#1\\ N(4)-Cd(1)-N(1)\#2\\ N(4)-Cd(1)-N(1)\#2\\ O(1)\#1-Cd(1)-N(1)\#2\\ O(4)-Cd(1)-O(2)\#1\\ N(4)-Cd(1)-O(2)\#1\\ N(4)-Cd(1)-O(2)\#1\\ \end{array}$	2.228(3) 2.231(3) 2.363(3) 138.8(1) 87.3(1) 133.8(1) 93.5(1) 96.3(1) 81.8(1) 123.9(1) 87.1(1)	$\begin{array}{c} Cd(1)-N(1)\#2\\ Cd(1)-O(2)\#1\\ Cd(1)-O(2)\#3\\ 0(1)\#1-Cd(1)-O(2)\#1\\ N(1)\#2-Cd(1)-O(2)\#1\\ O(4)-Cd(1)-O(2)\#3\\ O(1)\#1-Cd(1)-O(2)\#3\\ O(1)\#1-Cd(1)-O(2)\#3\\ N(1)\#2-Cd(1)-O(2)\#3\\ O(2)\#1-Cd(1)-O(2)\#3\\ O(2)\#1-Cd(1)-O(2)\#1\\ O(2)\#1-Cd(1)-O(2)\#1\\ O(2)\#1-Cd(1)-O(2)\#1\\ O(2)\#1-Cd(1)-O(2)\#1\\ O(2)\#1-Cd(1)-O(2)\#1\\ O(2)\#1-Cd(1)-O(2)\#1\\ O(2)\#1-Cd(1)-O(2)\#1\\ O(2)\#1-Cd(1)-O(2)\#1\\ O(2)\#1\\ O($	$\begin{array}{c} 2.372(3)\\ 2.451(3)\\ 2.590(3)\\ 54.2(1)\\ 115.4(1)\\ 80.2(1)\\ 83.8(1)\\ 105.3(1)\\ 170.2(1)\\ 74.4(1) \end{array}$
	$\begin{array}{c} 2.20(1)\\ 2.20(1)\\ 2.28(1)\\ 2.35(1)\\ 2.35(1)\\ 2.41(1)\\ 2.35(1)\\ 2.41(1)\\ 2.35(1)\\ 175.0(4)\\ 88.4(4)\\ 87.1(4)\\ 98.8(3)\\ 85.8(4)\\ 171.5(3)\\ 85.7(3)\\ 96.5(3)\\ 89.9(3)\\ 86.3(3)\\ 90.1(4)\\ 87.5(4)\\ 86.5(3)\\ 97.8(3)\\ 174.5(4)\\ 109.9(4)\\ 96.7(4)\\ 147.4(4)\\ 96.0(4)\\ 110.9(4)\\ 83.6(3)\\ 109.9(4)\\ 96.6(3)\\ 109.9(4)\\ 96.7(4)\\ 147.4(4)\\ 96.0(4)\\ 110.9(4)\\ 83.6(3)\\ 109.9(4)\\ 96.9(3)\\ 109.9(4)\\ 96.7(4)\\ 110.9(4)\\ 83.6(3)\\ 109.9(4)\\ 96.9(3)\\ 109.9(4)\\ 96.7(4)\\ 110.9(4)\\ 83.6(3)\\ 109.9(4)\\ 90.9(4)\\ 90.9(4)\\ 90.9(4)\\ 96.7(4)\\ 109.9(4)\\ 96.7(4)\\ 109.9(4)\\ 96.7(4)\\ 109.9(4)\\ 96.7(4)\\ 109.9(4)\\ 96.7(4)\\ 109.9(4)\\ 96.7(4)\\ 109.9(4)\\ 96.7(4)\\ 109.9(4)\\ 96.7(4)\\ 109.9(4)\\ 96.7(4)\\ 109.9(4)\\ 96.7(4)\\ 109.9(4)\\ 96.7(4)\\ 109.9(4)\\ 96.7(4)\\ 109.9(4)\\ 96.7(4)\\ 109.9(4)\\ 96.7(4)\\ 109.9(4)\\ 96.7(4)\\ 109.9(4)\\ 96.7(4)\\ 109.9(4)\\ 96.7(4)\\ 109.9(4)\\ 96.7(4)\\ 109.9(4)\\ 96.9(4)\\ 109.9(4)$	$\begin{array}{c} Cd(2)-O(1)\#3\\ Cd(2)-O(2)\#3\\ Cd(2)-O(2)\#3\\ Cd(3)-O(6)\#4\\ Cd(3)-O(5)\\ Cd(3)-O(12)\#6\\ Cd(3)-O(11)\#6\\ Cd(3)-O(11)\#6\\ Cd(3)-O(6)\\ O(9)-Cd(2)-O(10)\\ O(1)\#3-Cd(2)-O(2)\#3\\ N(8)-Cd(2)-O(2)\#3\\ O(9)-Cd(2)-O(2)\#3\\ O(9)-Cd(2)-O(2)\#3\\ O(1)\#3-Cd(2)-O(2)\#3\\ O(1)\#3-Cd(3)-O(12)\#6\\ O(5)-Cd(3)-O(12)\#6\\ O(2)\#5-Cd(3)-O(11)\#6\\ O(12)\#6-Cd(3)-O(11)\#6\\ N(6)\#4-Cd(3)-O(11)\#6\\ N(6)\#4-Cd(3)-O(6)\\ O(2)\#5-Cd(3)-O(6)\\ O(12)\#6-Cd(3)-O(6)\\ O(12)\#6-D(12)\#6\\ O(12)\#6\\ O(12)\#$	$\begin{array}{l} 2.35(1)\\ 2.40(1)\\ 2.50(1)\\ 2.20(1)\\ 2.27(1)\\ 2.27(1)\\ 2.27(1)\\ 2.31(1)\\ 3.38(1)\\ 2.49(1)\\ 54.5(3)\\ 54.5(3)\\ 149.4(3)\\ 85.6(4)\\ 80.1(3)\\ 53.4(3)\\ 102.2(3)\\ 80.1(3)\\ 93.7(4)\\ 100.6(3)\\ 93.7(4)\\ 127.9(4)\\ 90.3(3)\\ 92.9(4)\\ 97.5(4)\\ 142.8(3)\\ 55.2(3)\\ 86.9(4)\\ 55.2(3)\\ 86.9(4)\\ 55.2(3)\\ 86.9(4)\\ 55.2(3)\\ 86.9(4)\\ 55.2(3)\\ 86.9(4)\\ 55.2(3)\\ 86.9(4)\\ 55.2(3)\\ 86.9(4)\\ 55.2(3)\\ 86.9(4)\\ 53.7(4)\\ 112.8(3)\\ 55.2(3)\\ 10.8(4)\\$
N(8)-Cd(2)-O(10)	101.2(3)	S()"0 Ca(S)=0(0)	

<sup>a</sup> Symmetry transformations used to generate equivalent atoms: For 1: #1 x, y+1, z, #2 -x+1, -y+1, -z. For 2: #1 -x+1, -y+2, -z+1, #2 -x+1, y+1/2, -z+1/2. For 3: #1 x, y-1, z, #2 x, y, z+1. For 4: #1 -x+2, -y, z+1/2, #2 -x+1/2, y-1/2, z-1/2. For 5: #1 -x+2, -y+1, -z+1, #2 -x+1, -y+1, -z+1, #3 x, y+1, z, #4 x+1, y+1, z. For 6: #1 x, y+1, z, #2 -x+1, -y+1, -z+1, #3 -x+2, -y, -z+1. For 7: #1 x, -y+3/2, z-1/2, #2 x, -y+3/2, z+1/2, #3 -x+1, -y+1/2, -z+1/2, #4 x, y-1, z, -y+3/2, z-1/2, #2 -x+1, -y+1, -z+1, #3 -x+2, -y, -z+1. For 7: #1 x, -y+3/2, z-1/2, #2 x, -y+3/2, z+1/2, #3 -x+1, y+1/2, -z+1/2, #4 x, y-1, z, z+5 <math>-x+1, -y+1, -z+1, #6 -x, y-1/2, -z+1/2.

*SHELXL-97* crystallographic software package [16]. The hydrogen atoms on the nitrogen atom of imidazole groups in **2**, the ones of non-deprotonated carboxylic acid (–COOH) in **3** and **4**, the ones of coordinated water molecule in **7**, and the one of hydroxyl (–OH) in **5** were found directly from the differential Fourier map. All the other hydrogen atoms were generated geometrically except that the hydrogen atoms of free water molecules were not identified. The details of the crystal parameters, data collection, and refinements for the

complexes are summarized in Table 1, selected bond lengths and angles with their estimated standard deviations are listed in Table 2.

#### 2.4. DFT calculations

In order to understand the relation between structure and energy, calculations were performed for the compounds based upon the crystallographic data of  $[Zn(H_3L)(btc)]$  (2),  $[Zn(H_2L)(Hbtc)]$  (3),



**Fig. 1.** (a) The coordination environment of Zn(II) in **1** with the ellipsoids drawn at the 50% probability level. The hydrogen atoms except those on the nitrogen atom of imidazole groups are omitted for clarity. Symmetry Code: a 1–*x*, 1–*y*, –*z*, b *x*, 1+*y*, *z*. (b) The 1D chain of **1**. (c) 2D network of **1** linked by hydrogen bonds indicated by dashed line.



Scheme 1. Coordination modes of mbdc<sup>2-</sup>, Hbtc<sup>2-</sup> and btc<sup>3-</sup> ligands appeared in 1-7.

 $[Zn(H_2L)(Hbtc)] \cdot H_2O$  (4) by using the total-energy code CASTEP, which employs pseudopotentials to describe electron interactions and represents electronic wave functions using a plane-wave basis set [17]. The total energy was calculated by density functional theory (DFT) within the framework of nonlocal gradient-corrected approximations [Perdew–Burke–Ernzerhof (PBE)]. Under the periodic boundary condition (PBC) [18], different unit cells were treated by using the kinetic energy cutoff from 300 eV for plane-waves, employing also the ultrasoft pseudopotential (USP) method for the Local Density Approximations (LDA). The following orbital

electrons are treated as valence electrons: C  $2s^22p^2$ , H  $1s^1$ , N  $2s^22p^3$ , O  $2s^22p^4$ , and Zn  $3d^{10}4s^2$ .

#### 3. Results and discussion

#### 3.1. Crystal structure of $[Zn(H_2L)(mbdc)]$ (1)

Structural analysis revealed that the asymmetric unit of **1** consists of one Zn(II) atom, one  $H_2L$  and one  $mbdc^{2-}$ . Fig. 1a shows



**Fig. 2.** (a) The coordination environment of Zn(II) in **2** with the ellipsoids drawn at the 50% probability level. The hydrogen atoms except those on the nitrogen atom of imidazole groups are omitted for clarity. Symmetry Code: a 1–*x*, 0.5+*y*, 0.5–*z*, b 1–*x*, 2–*y*, 1–*z*. (b) The 2D layer of Zn(II)-btc<sup>3–</sup>. (c) The 2D network of **2**. (d) Schematic representation of the  $(4,8^2)$  topology. (e) 3D framework of **2** linked by hydrogen bonds indicated by dashed line.

that each Zn(II) atom is four-coordinated with distorted tetrahedral coordination geometry by two N (N1a, N4) atoms of two different H<sub>2</sub>L and two O (O2b, O4) atoms from two distinct mbdc<sup>2–</sup> ligands. The Zn–N bond distances are 2.055(3) and 2.005(2) Å while the Zn–O ones are 1.960(2) and 1.946(2) Å, and the coordination angles around the Zn1 are in the range of 99.37(10)–118.72 (10)° (Table 2). The mbdc<sup>2–</sup> ligand acts as a  $\mu_2$ -bridge using its two carboxylate groups with  $\mu_1 - \eta^1: \eta^0$ -monodentate mode (Type I, Scheme 1) and connects Zn(II) atoms to form an infinite onedimensional (1D) chain. Furthermore, the H<sub>2</sub>L ligands bridge the adjacent 1D chains to give a double chain (Fig. 1b). Then, the double chains are further linked together by N–H···O hydrogen bonds to generate a two-dimensional (2D) network (Fig. 1c). The hydrogen bonding data are summarized in Table S1.

#### 3.2. Crystal structure of $[Zn(H_3L)(btc)]$ (2)

When H<sub>3</sub>btc, instead of H<sub>2</sub>mbdc, was used to react with H<sub>2</sub>L and Zn(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O in the presence of NaOH, complex **2** was obtained. It is interesting that H<sub>3</sub>btc completely deprotonated to give btc<sup>3–</sup>, while one of the two imidazole of H<sub>2</sub>L is protonated to form H<sub>3</sub>L<sup>+</sup>. The Zn(II) atom in **2** has distorted tetrahedral coordination environment with three O atoms from three distinct btc<sup>3–</sup> ligands and one N atom from one H<sub>3</sub>L<sup>+</sup> ligand (Fig. 2a). Each btc<sup>3–</sup> ligand connects three Zn(II) atoms using its two of three carbox-ylate groups in  $\mu_1-\eta^1:\eta^0$ -monodentate,  $\mu_2-\eta^1:\eta^1$ -bismonodentate modes, while the third one is free of coordination (Type II,

Scheme 1). The Zn(II) atoms and  $btc^{3-}$  ligands form a 2D network via coordination interactions as shown in Fig. 2b. The H<sub>3</sub>L<sup>+</sup> coordinates with Zn(II) as terminal ligand (Fig. 2c). Because the terminal coordinated H<sub>3</sub>L<sup>+</sup> ligands bring about no change to the topology of the Zn(II)-btc<sup>3-</sup> 2D network, according to the simplification principle, the resulting structure of **2** is a binodal (3,3)-connected network with (4,8<sup>2</sup>) topology (Fig. 2d). The adjacent 2D layers are further connected together by N–H···O hydrogen bonds between the protonated imidazole and non-coordinated carboxylate groups to form a 3D framework (Fig. 2e, Table S1).

#### 3.3. Crystal structure of [Zn(H<sub>2</sub>L)(Hbtc)] (3)

When the reaction was carried out at 65 °C, complex **3** was obtained. The structure of **3** is different from that of **2** prepared by the reaction at 160 °C, implying the impact of the reaction temperature on the complexes [19]. As shown in Fig. 3a, the Zn (II) atom is four-coordinated by two N and two O atoms which is the same as that in **1**. In **3**, each Hbtc<sup>2–</sup> uses its two carboxylate groups in  $\mu_1 - \eta^1: \eta^0$ -monodentate coordination mode to link two Zn (II) atoms to form a chain, while the non-deprotonated carboxylic group is free of coordination (Type III, Scheme 1). However, the H<sub>2</sub>L ligands bridge the adjacent chains to form a 2D network of **3** (Fig. 3b), rather than the double chain of **1** (Fig. 1b). From the view of topology, the Zn(II) atom is considered as a 4-connected node, H<sub>2</sub>L and Hbtc<sup>2–</sup> ligands are regarded as linear linkers, thus, the structure of **3** can be defined as a network with (4,4)



**Fig. 3.** (a) The coordination environment of Zn(II) in **3** with the ellipsoids drawn at the 50% probability level. The hydrogen atoms except those on the nitrogen atom of imidazole groups are omitted for clarity. Symmetry Code: a x, y, 1+z, b x, -1+y, z. (b) The 2D layer of **3**. (c) 2D (4,4) network of **3** based on the binuclear subunits. (d) 3D framework of **3** linked by hydrogen bonds indicated by dashed line.

topology (Fig. 3c). Moreover, the 3D structure is generated and consolidated from the 2D networks by  $N-H \cdots O$  hydrogen bonds (Fig. 3d, Table S1).

3.4. Crystal structure of  $[Zn(H_2L)(Hbtc)] \cdot H_2O(4)$ 

Complex **4** was synthesized by the reaction at 180 °C, and it was found that **4** has similar composition with **3** except the existence of free water molecule in **4**, however, they have different structures. As shown in Fig. 4a, Zn1 atom in **4** is in a distorted tetrahedral coordination environment with N<sub>2</sub>O<sub>2</sub> donor set, and two carboxylate groups of Hbtc<sup>2-</sup> in **4** adopt  $\mu_1 - \eta^1: \eta^0$ -monodentate coordination mode and the non-deprotonated one is free of coordination (Type IV, Scheme 1), which are similar with those in **3**. In **4**, two kinds of zigzag chains are formed by the Zn(II) with H<sub>2</sub>L and Zn(II) with Hbtc<sup>2-</sup>, respectively. And such two kinds of zigzag chains connect each other to generate a 3D structure of **4** (Fig. 4b), with large channels (Fig. 4c), rather than the 2D network of **3** (Fig. 3b). The large voids allow to form interpenetrated framework to stabilize the overall structure [20], accordingly, **4** is a 3-fold interpenetrating 3D architecture (Fig. 4d), and the

Schläfli symbol of the topology is  $(6^5,8)$  since the Zn(II) is 4-connected node, and H<sub>2</sub>L and Hbtc<sup>2–</sup> ligands are linear linkers.

#### 3.5. Crystal structure of $[Zn_2(H_2L)(btc)(\mu_2-OH)]$ (5)

Increasing the amount of NaOH in the preparation reaction [21], complex **5** was isolated. The results of crystallographic analysis revealed that the asymmetric unit of 5 consists of two crystallographically independent Zn(II) atoms bridged by one OHgroup, one  $btc^{3-}$  and one  $H_2L$  (Fig. 5a). In addition to the hydroxyl bridge, Zn1 is coordinated by three carboxylate O atoms from different btc<sup>3-</sup> ligands and Zn2 is coordinated by two N atoms from two different H<sub>2</sub>L ligands and one carboxylate O atom, hence, both Zn1 and Zn2 are four coordinated with distorted tetrahedral geometry. The btc<sup>3–</sup> in **5** acts as a  $\mu_4$ -bridge to link four zinc atoms, one carboxylate group adopts a  $\mu_2 - \eta^1 : \eta^1$  bridging coordination mode connecting two zinc atoms, and the other two carboxylate groups adopt monodentate mode coordinating to one zinc atom (Type V, Scheme 1). Two [Zn<sub>2</sub>(OH)] units are bridged by carboxvlate groups to form a tetranuclear subunit (Fig. 5b, highlighted by pink circle), which is further linked through the btc<sup>3–</sup> ligands to generate a 2D network (Fig. 5b). Meanwhile, H<sub>2</sub>L ligands act as





**Fig. 5.** (a) The coordination environment of Zn(II) in **5** with the ellipsoids drawn at the 50% probability level. The hydrogen atoms except those on the nitrogen atom of imidazole groups are omitted for clarity. Symmetry Code: a 1+x, 1+y, z, bx, 1+y, z, c 1-x, 1-y, 1-z, d 2-x, 1-y, 1-z. (b) The 2D layer of Zn(II)-btc<sup>3-</sup>. (c) The 2D network of **5**. (d) Schematic representation of the  $(3,4^2)_2(3^4,4^6,5^6,6^8,7^3,8)$  topology. (e) 3D framework of **5** linked by hydrogen bonds indicated by dashed line.

hinges to connect adjacent zinc atoms of the Zn(II)-btc<sup>3–</sup> network from two sides, yet forming the final 2D network of **5** constructed by H<sub>2</sub>L and btc<sup>3–</sup> ligands (Fig. 5c). From topological view, the center of the tetranuclear unit acts as eight-connected nodes to link each other through 3-connectors of btc<sup>3–</sup> into a 2D network with a Schläfli symbol  $(3,4^2)_2(3^4,4^6,5^6,6^8,7^3,8)$  topology (Fig. 5d). Furthermore, adjacent layers in an–ABAB–arrangement are linked together by  $\pi$ – $\pi$  and N–H···O hydrogen bonding interactions to generate a 3D structure (Fig. 5e, Table S1). The distance between the nearly parallel imidazole ring planes of two adjacent H<sub>2</sub>L ligands is 3.73 Å [22].

#### 3.6. Crystal structure of [Cd(H<sub>2</sub>L)(mbdc)] (6)

The Cd(II) atom in **6** is six-coordinated by two N (N1a, N4) atoms of two different H<sub>2</sub>L ligands and four O (O1b, O2b, O2c, O4) atoms of three different mbdc<sup>2–</sup> (Fig. 6a). In **6**, each mbdc<sup>2–</sup> ligand connects three Cd(II) atoms with its carboxylate groups in  $\mu_1 - \eta^1: \eta^1$ -chelating and  $\mu_2 - \eta^2: \eta^1$ -bridging coordina-

tion modes (Type VI, Scheme 1). The Cd(II) atoms and mbdc<sup>2–</sup> ligands connect each other to form a 1D chain. Meanwhile, each pair of H<sub>2</sub>L ligands bridges two Cd(II) atoms in two adjacent chains to construct a 2D network (Fig. 6b). In addition to the coordination, there are face-to-face  $\pi$ - $\pi$  interactions between the nearly parallel imidazole ring planes of two adjacent H<sub>2</sub>L ligands from two different layers with a centroid-centroid distance of 3.52 Å. There also exists N-H···O hydrogen bonds between the adjacent layers, therefore, the  $\pi$ - $\pi$  and hydrogen bonding interactions link the 2D layers to a 3D framework of **6** (Fig. 6c).

#### 3.7. Crystal structure of $[Cd_3(H_2L)_2(btc)_2(H_2O)] \cdot 5H_2O(7)$

As show in Fig. 7a, three Cd(II) atoms in **7** are all sixcoordinated with distorted octahedral geometry. Cd1 is coordinated by two N atoms from two H<sub>2</sub>L, three O atoms from three btc<sup>3–</sup> ligands and one O atom from a coordinated water molecule, Cd2 and Cd3 are both coordinated by one N atom from one H<sub>2</sub>L and



**Fig. 6.** (a) The coordination environment of Cd(II) in **6** with the ellipsoids drawn at the 50% probability level. The hydrogen atoms except those on the nitrogen atom of imidazole groups are omitted for clarity. Symmetry Code: a 1–*x*, 1–*y*, 1–*z*, b *x*, 1+*y*, *z*, c 2–*x*, –*y*, 1–*z*. (b) The 2D layer of **6**. (c) 3D framework of **6** linked by hydrogen bonds indicated by dashed line.

five O atoms from three different btc<sup>3-</sup> ligands. In **7**, there are two kinds of btc<sup>3-</sup> with different conformations and coordination modes of the carboxylate groups:  $\mu_1 - \eta^1: \eta^0$ -monodentate,  $\mu_1 - \eta^1: \eta^1$ -chelating,  $\mu_2 - \eta^2: \eta^1$ -bridging,  $\mu_2 - \eta^1: \eta^1$ -bismonodentate (Types VII and VIII, Scheme 1). If the coordination of btc<sup>3-</sup> is ignored, H<sub>2</sub>L and Cd1 constitute a zigzag chain, while the H<sub>2</sub>L ligands and Cd2, Cd 3 only form a Cd<sub>2</sub>(H<sub>2</sub>L) unit (Fig. 7b). These zigzag chains and Cd<sub>2</sub>(H<sub>2</sub>L) units further connected by btc<sup>3-</sup> ligands to form a 3D framework (Fig. 7c).

Topological analysis has been proved to be a useful and simple method to analyze the extended frameworks, especially for the complicated 3D frameworks [23]. The Cd1, Cd2 and Cd3 atoms are bridged by carboxylate groups of btc<sup>3–</sup> ligands to form a trinuclear subunit (Fig. 7c, highlighted in pink cycle), which can be treated as a 10-connected node, while btc<sup>3–</sup> and H<sub>2</sub>L ligands are 3– and 2-connectors, respectively. Therefore, the 3D structure of **7** is a (3,10)-connected net with a Schläfli symbol  $(3,4,5)_2(3^4,4^8,5^{18},6^{12},7^2,8)$  topology (Fig. 7d).

#### 3.8. Synthesis of the complexes and comparison of the structures

Seven Zn(II) and Cd(II) coordination polymers were successfully synthesized and structurally characterized using rigid ditopic ligand  $H_2L$  and multicarboxylic acids. Among these complexes, Zn(II) and Cd(II) atoms are four- and six-coordinated, respectively. Different coordination number and geometry of the metal centers lead to the structure diversity of the complexes. For example, **1** and **6** as well as **5** and **7** were prepared under the same reaction conditions except for the different metal salt, the framework structures are 1D chain and 2D network for **1** and **6**, and 2D network and 3D net for **5** and **7**, respectively. On the other hand,  $H_2L$  serves as a neutral ligand to link two metal centers in **1** and **3**–**7**, while in **2**,  $H_2L$  is partially protonated to generate a  $H_3L^+$  as terminal ligand. The auxiliary carboxylate ligands also have different coordination modes: mbdc<sup>2–</sup>, Hbtc<sup>2–</sup> and btc<sup>3–</sup> ligands act as 2–, 3–, 4– and 5-connectors in **1–7** as illustrated in Scheme 1. In addition, the remarkable difference between the structures of **2** and **5** implies the great influence of the amount of NaOH used in the reaction [24].

It is interesting to note that there are three different complexes 2-**4** synthesized by changing the reaction temperature, implying the hydrothermal reaction temperature has great influence on the structures of the complexes [25]. Changing the reaction temperature from 180 to 65 °C leads to increasing the amount of **3** and decreasing the amount of 2. When the reaction temperature was between 65 and 85 °C. a mixture of 2 and 3 was obtained (Fig. S1). Pure 2 can be synthesized between 100 and 160 °C, while the reaction temperature is high at 180 °C, a trace of 4 can be found in 2. Table 3 shows the summary of the complexes synthesized at different temperatures. In order to get more detailed information on this, we performed periodic DFT calculations. The results are shown in Table S2. It is clear that the relative energy of the dehydrated frameworks per zinc in the order of 3 < 2 < 4 (Fig. 8). The calculations therefore show that the transformation of **3** to **2** or **4** is endothermic, indicating that **3** is the most stable among three of them. In this work, the most energetically favorable structure of 3 was obtained at lower temperature while the framework **4** with high energy can only be obtained with very low yield at higher temperature. The results indicate that thermodynamic factor is primary in dictating the formation of the complexes.



**Fig. 7.** (a) The coordination environment of Cd(II) in **7** with the ellipsoids drawn at the 50% probability level. The hydrogen atoms except those on the nitrogen atom of imidazole groups and free water molecules are omitted for clarity. Symmetry Code: a x, 1.5–y, -0.5+z, b x, 1.5–y, -0.5+z, c 1-x, 0.5+y, 0.5-z, d x, -1+y, z, e 1-x, 1-y, 1-z, f -x, -0.5+y, 0.5-z. (b) The layer of Cd(II)–H<sub>2</sub>L. (c) The 3D framework of **7**. (d) Schematic representation of the  $(3,4,5)_2(3^4,4^8,5^{18},6^{12},7^2,8)$  topology.

Table 3	
Summary of the complexes synthesized at different temperatures.	

Reaction temperature	65–85 °C	100–160 °C	180 °C
Products	<b>2</b> and <b>3</b>	2	<b>2</b> and a trace of <b>4</b>

## 3.9. Thermal stabilities and powder X-ray diffraction of the complexes

Complexes **1–3** and **5–7** were subjected to thermogravimetric analysis (TGA) to ascertain the stability of the frameworks (Fig. S2) [26]. Only complex **7** shows a weight loss of 8.51% around 210 °C for the release of the free and coordinated water molecules (calc. 8.40%) and when temperature reach 360 °C, the residue of **7** was decomposed. For the other five complexes, no obviously weight losses were found before the decomposition of the structure occurred at about 420–460 °C, which are in agreement with the crystal structures. The pure phase of the complexes was confirmed by the PXRD, where the patterns of as-synthesized **1–3** and **5–7** are consistent with the corresponding simulated ones (Fig. S3).

#### 3.10. Photoluminescence property

Inorganic-organic hybrid coordination polymers have been reported to have ability to adjust the emission wavelength of organic materials through incorporation of metal centers, especially for the  $d^{10}$ metal centers [27]. The solid-state photoluminescent properties of complexes 1-3 and 5-7, together with the free H<sub>2</sub>L, H<sub>2</sub>mbdc and H<sub>3</sub>btc, have been investigated at room temperature under the same conditions. The emission spectra of the complexes and ligands are depicted in Fig. 9. It can be seen that all of the emission bands of complexes and ligands were, respectively, observed at 413 nm  $(\lambda_{ex}=315 \text{ nm})$  for **1**, 411 nm  $(\lambda_{ex}=336 \text{ nm})$  for **2**, 419 nm  $(\lambda_{ex}=315 \text{ nm})$ 338 nm) for **3**, 454 nm ( $\lambda_{ex}$ =378 nm) for **5**, 433 nm ( $\lambda_{ex}$ =367 nm) for **6**, 458 nm ( $\lambda_{ex}$ =411 nm) for **7**, while weak emissions at 427 nm  $(\lambda_{ex}=307 \text{ nm})$  for H<sub>2</sub>L, 398 nm  $(\lambda_{ex}=349 \text{ nm})$  for H<sub>2</sub>mbdc and 416 nm  $(\lambda_{ex}=359 \text{ nm})$  for H<sub>3</sub>btc. The fluorescent emissions observed in the complexes may be tentatively assigned to the intraligand fluorescence since the free ligands (H<sub>2</sub>L, H<sub>2</sub>mbdc and H<sub>3</sub>btc) exhibit similar emissions under the same conditions [28]. The red- and blue-shifted emissions of 1-3 and 5-7 are caused by the coordination of the ligands to the metal centers [28,29]. The enhanced emissions of the complexes may mainly originate from the coordination interactions between the metal atom and the ligand [30]. Specifically, the coordination interactions enhanced the conformational rigidity of the complexes and decreased the non-radiative energy loss [31].



Fig. 8. Comparison of the absolute energy of the structures based upon per zinc(II) as a function of temperature.



Fig. 9. Emission spectra of 1-3, 5-7, H<sub>2</sub>L, H<sub>2</sub>mbdc and H<sub>3</sub>btc.

#### 4. Conclusions

Seven new coordination polymers with rigid ditopic 4-imidazole containing ligand 1,3-di(1H-imidazol-4-yl)benzene (H<sub>2</sub>L) and two multicarboxylic acids (H2mbdc and H3btc) have been obtained and found to show different structures and topologies. Complexes 1-7 have varied structures with different topologies: 1 is a 1D chain. 2. 3. 5 and 6 are a variety of 2D networks while 4 and 7 are distinctive 3D frameworks. The results of present study show that the mixed imidazole-containing ligand and multicarboxylic acid are useful in construction of MOFs and changing reaction conditions such as the amount of base, reaction temperature can further enrich the structure diversity of the complexes.

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#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jssc.2013.03.042.

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