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# Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

# Construction of several d<sup>10</sup> metal coordination polymers based on aromatic

polycarboxylate and flexible triazole-based ligand

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#### ARTICLE INFO

Article history: Received 28 June 2009 Received in revised form 3 August 2009 Accepted 6 August 2009 Available online 12 August 2009

Keywords: Aromatic polycarboxylate Triazole-based ligand Crystal structure Luminescence

# ABSTRACT

To investigate the effect of organic anions on the coordination frameworks, we synthesized five new complexes, namely,  $[[Zn_3(\mu-OH_2)_2(btc)_2(btx)_3]\cdot 4H_2O]_n$  (1),  $[Zn(bdc)(btx)]_n$  (2),  $[[Ag_8(3,5-pydc)_4(btx)_4]\cdot 8H_2O]_n$  (3),  $[Ag(2,6-Hpydc)(btx)]_n$  (4) and  $[Cd_2(\mu_2-OH_2)(2,6-pydc)_2(btx)]_n$  (5)  $(H_2bdc = 1,4-benzenedicarboxylic acid; H_3btc = 1,3,5-benzenetricarboxylate; 3,5-H_2pydc = pyridine-3,5-dicarboxylic acid; 2,6-H_2pydc = pyridine-2,6-dicarboxylic acid), which were obtained by the reactions of 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene (btx) as main ligand, and several aromatic polycarboxylate as organic anions with different d<sup>10</sup> metal salts. Single crystal structure analysis shows that complexes 1, 3 and 5 posses 3D structures, 2 takes a 2D layer motif, and 4 displays a 1D chain structure. The distinct structures indicate that polycarboxylate anions with the diverse coordination modes and coordination groups can affect the topologies of metal-organic frameworks. In addition, the luminescence measurements reveal that the complexes 1, 2 and 5 exhibit strong fluorescent emissions in the solid state at room temperature.$ 

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## 1. Introduction

Multifunctional metal-organic coordination frameworks continue to be of current interest due to the combination of the individual properties associated with inorganic and organic components [1-5]. Accordingly, the design and construction of well-regulated network structures with new functions are imperative, in which the key steps are to employ appropriate bridging ligands and to choose suitable metal ions. The ligands bearing bis(triazole) groups are good candidates for the formation of novel architectures. The ligands can adopt multiple coordination modes, such as bidentate, tridentate or tetradentate, to meet the different coordination requirements of metal centers [6,7]. As an excellent derivative of triazole, the flexible 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene (btx) not only possesses the merits of triazole, but also can freely bend and rotate to interact with metal ions. Thus, a series of metal-organic frameworks with novel topology were obtained by assembling metal salts and btx ligand. Although the ligand plays crucial role in determining these resulted polymeric structures, the effect of anions cannot be ignored as well [8-10]. In fact, the influence of inorganic anions (such as  $Cl^{-}$ ,  $SO_4^{2-}$ ,  $NO_3^{-}$ ) on the structures of complexes has been extensively studied [11-14]. By contrast, the organic anions such as polycarboxylate, which usually

possess multiform coordination fashions and structural features, may more effectively tune framework architectures [15–17]. Upon careful inspection of previous cases, we intend to probe into the influence of aromatic polycarboxylates as anionic co-ligands on the resulting complex architectures by using the btx as the main ligand. Therefore, especially rich possibilities for the construction of unique motifs with beautiful aesthetics and useful functional properties may be anticipated, because triazole of btx and aromatic polycarboxylates are complementary in their coordination preferences and may act synergetically [18–20].

Taking these into consideration, our synthetic strategy is to select neutral btx as the main ligand, in the presence of 1,3,5-benzenetricarboxylate (btc<sup>3-</sup>), pyridine-3,5-dicarboxylate (3,5-pydc<sup>2-</sup>), pyridine-2,6-dicarboxylate (2,6-pydc<sup>2-</sup>) or 1,4-benzenedicarboxyl-ate (bdc<sup>2-</sup>) anions as co-ligands and different  $d^{10}$  metal salts to construct complexes. The four polycarboxylate anionic co-ligands have rigid conformation and distinct structural features. The btc<sup>3-</sup> has three equally spaced carboxylate groups oriented in three directions, while bdc<sup>2-</sup> bears two carboxylate groups with linear conformation. The 3,5-pydc<sup>2-</sup> and 2,6-pydc<sup>2-</sup> are isomers with different orientations of the functional groups. The structural difference of anions may have different impact on the construction of frameworks in conjunction with the btx. As a result, a series of mixed-ligand coordination complexes with different structure types have been synthesized under hydrothermal conditions and structurally characterized. Their thermal and fluorescence properties were also investigated.





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# 2. Experimental

# 2.1. Materials and general methods

All chemicals were commercially available and used as purchased. 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene (btx) was synthesized according a literature method [21]. Thermogravimetric experiments were performed using a TGA/SDTA instrument. IR data were recorded on a BRUKER TENSOR 27 spectrophotometer with KBr pellets in the region of 400–4000 cm<sup>-1</sup>. Elemental analyses (C, H and N) were carried out on a Flash EA 1112 elemental analyzer. Steady state fluorescence measurements were performed using spectrofluorimeter Hitachi F–4500 at ambient temperature in solid state. The excitation and emission slit width are both 1 nm, and response time is 0.1 s.

# 2.2. Synthesis of $\{[Zn_3(\mu-OH_2)_2(btc)_2(btc)_3] \cdot 4H_2O\}_n$ (1)

A reaction mixture of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.1 mmol, 0.0297 g), btx (0.1 mmol, 0.012 g), H<sub>3</sub>BTC (0.1 mmol, 0.021 g), and water 10 mL was placed in a Teflon-lined stainless steel vessel, and then the pH was adjusted to 7 by addition of methanolic NaOCH<sub>3</sub> solution. The mixture was sealed and heated at 130 °C for three days, and then the reaction system was cooled to room temperature. Colorless crystals of **1** were obtained in yield (based on Zn): 60%. Elemental *Anal.* Calc. for ( $C_{54}H_{54}N_{18}O_{18}Zn_{3}$ ): C, 45.06; H, 3.78; N, 17.52. Found: C, 44.93; H, 3.70; N, 17.63%. IR(KBr/pellet, cm<sup>-1</sup>): 3415w, 3122w, 1626s, 1573m, 1528m, 1352s, 1281m, 1132m, 1000m, 771s, 734s, 733s.

#### 2.3. Synthesis of $[Zn(bdc)(btx)]_n$ (2)

A reaction mixture of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.1 mmol, 0.0297 g), btx (0.1 mmol, 0.012 g), H<sub>2</sub>bdc (0.1 mmol, 0.0166 g), and water 10 mL was placed in a Teflon-lined stainless steel vessel and then the pH was adjusted to 6 by addition of methanolic NaOCH<sub>3</sub> solution. The mixture was sealed and heated at 130 °C for three days, and then the reaction system was cooled to room temperature. Colorless crystals of **2** were obtained in yield (based on Zn): 55%. Elemental *Anal.* Calc. for ( $C_{20}H_{16}N_6O_4Zn$ ): C, 51.13; H, 3.43; N, 17.89. Found: C, 51.48; H, 3.44; N, 17.63%. IR(KBr/pellet, cm<sup>-1</sup>): 3117w, 1688s, 1613w, 1573w, 1352m, 1288s, 1132s, 999w, 783m, 744s, 673w.

## 2.4. Synthesis of $\{[Ag_8(3,5-pydc)_4(btx)_4] \cdot 8H_2O\}_n$ (3)

A reaction mixture of AgNO<sub>3</sub> (0.1 mmol, 0.0169 g), btx (0.1 mmol, 0.012 g), 3,5-H<sub>2</sub>pydc (0.1 mmol, 0.0167 g), and water 10 mL was placed in a Teflon-lined stainless steel vessel, and then the pH was adjusted to 6.5 by addition of methanolic NaOCH<sub>3</sub> solution. The mixture was sealed and heated at 120 °C for two days, and then the reaction system was cooled to room temperature. Colorless crystals of **3** were obtained in yield (based on Ag): 55%. Elemental *Anal.* Calc. for ( $C_{76}H_{68}Ag_8N_{28}O_{24}$ ): C, 34.83; H, 2.62; N, 14.97. Found: C, 34.58; H, 2.52; N, 14.96%. IR(KBr/pellet, cm<sup>-1</sup>): 3418w, 3107w, 1742w, 1617w, 1516s, 1384s, 1271s, 1212m, 1142s, 1014m, 827m, 729s, 676s.

#### 2.5. Synthesis of $[Ag(2,6-Hpydc)(btx)]_n$ (4)

The synthesis was similar to that described for **3** except using 2,6-H<sub>2</sub>pydc (0.1 mmol, 0.0167 g) instead of 3,5-H<sub>2</sub>pydc and heated at 120 °C for three days. Then the reaction system was cooled to room temperature. Colorless crystals of **4** were obtained in yield (based on Ag): 55%. Elemental *Anal.* Calc. for (C<sub>19</sub>H<sub>16</sub>AgN<sub>7</sub>O<sub>4</sub>): C,

44.38; H, 3.14; N, 19.07. Found: C, 44.31; H, 3.05; N, 19.22%. IR(KBr/pellet, cm<sup>-1</sup>): 3410w, 3099w, 1703w, 1621s, 1380s, 1017s, 884m, 757m, 696m.

#### 2.6. Synthesis of $[Cd_2(\mu_2-OH_2)(2,6-pydc)_2(btx)]_n$ (5)

A reaction mixture of Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (0.1 mmol, 0.0308 g), btx (0.1 mmol, 0.012 g), 2,6-H<sub>2</sub>pydc (0.1 mmol, 0.0167 g), and water 10 mL was placed in a Teflon-lined stainless steel vessel, and then the pH was adjusted to 7 by addition of methanolic NaOCH<sub>3</sub> solution. The mixture was sealed and heated at 150 °C for three days, and then the reaction system was cooled to room temperature. Colorless crystals of **5** were obtained in yield (based on Cd): 55%. Elemental *Anal.* Calc. for ( $C_{26}H_{18}Cd_2N_8O_9$ ): C, 38.49; H, 2.24; N, 13.82. Found: C, 38.72; H, 2.44; N, 13.97%. IR(KBr/pellet, cm<sup>-1</sup>): 3088w, 1649s, 1523m, 1426m, 1377s, 1346m, 1274m, 775m, 721s.

#### 2.7. Crystal structure determination

A crystal suitable for X-ray determination was mounted on a glass fiber. The data of **1–5** were collected at room temperature on a Rigaku Saturn 724 CCD with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The structures were solved by direct methods and expanded with Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on observed reflections and variable parameters. All calculations were performed with the SHELXL-97 crystallographic software package [22–24]. Table 1 showed crystallographic crystal data and processing parameters for all complexes, and Table 2 listed their selected bond lengths and bond angles.

# 3. Results and discussion

#### 3.1. Syntheses

Although some complexes based on btx ligand have been reported, the selection of counterions is mostly concentrated on inorganic anions. In this paper, we expect to investigate the influence of organic anions on the structures of complexes. As a widely used polycarboxylic acid, the H<sub>3</sub>btc has three equally spaced carboxyl groups, which can be completely or partially deprotonated. This makes it very appealing for the design of MOFs with interesting structures. Using btx in combination with H<sub>3</sub>btc under hydrothermal conditions, a 3D zinc complex 1 was obtained. When the starlike H<sub>3</sub>btc was changed to linear H<sub>2</sub>bdc containing two carboxyl groups, a 2D layer zinc complex **2** was achieved. Both complexes **1** and **2** are greatly different from previously reported 2D square grid units  $[Zn(btx)_2(NO_3)_2]_n$  with inorganic anion [25]. In contrast to the benzenecarboxylates, the heterocyclic carboxylates, such as pyridine- and imidazole-carboxylates exhibit unique features. These ligands can contribute their carboxylate oxygen as well as pyridyl nitrogen atoms to metal coordination, to construct interesting coordination networks [26,27]. The 3,5-H<sub>2</sub>pydc was employed to react with  $AgNO_3$  and btx, to form a 3D complex **3**. When 3,5-H<sub>2</sub>pydc was substituted by 2,6-H<sub>2</sub>pydc, a completely different 1D silver complex 4 was obtained under the similar conditions. To further investigate various coordination modes of 2,6-H<sub>2</sub>pydc, the reaction of 2,6-H<sub>2</sub>pydc with btx and Cd(NO<sub>3</sub>)<sub>2</sub> was carried out, to give rise to a 3D complex 5, which is greatly different from previously reported complexes [Cd(btx)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O and  $[Cd(btx)_2(H_2O)_2](BF_4)_2 \cdot 3DMF$  as well [13].

Table 1	
Crystal data and structure refinement for complexes 1–5.	

Complex	1	2	3	4	5
Formula	C <sub>54</sub> H <sub>54</sub> N <sub>18</sub> O <sub>18</sub> Zn <sub>3</sub>	$C_{20}H_{16}N_6O_4Zn$	C <sub>76</sub> H <sub>68</sub> Ag <sub>8</sub> N <sub>28</sub> O <sub>24</sub>	C <sub>19</sub> H <sub>16</sub> AgN <sub>7</sub> O <sub>4</sub>	C <sub>26</sub> H <sub>18</sub> Cd <sub>2</sub> N <sub>8</sub> O <sub>9</sub>
Formula weight	1439.26	469.78	2620.54	513.25	811.28
T (K)	293(2)	293(2)	293(2)	293(2)	293(2)
λ (Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$\begin{array}{c} P2(1)/c \\ 14.840(3) \\ 10.125(2) \\ 20.333(4) \\ 90.00 \\ 99.35(3) \\ 90.00 \end{array}$	C2/c	C2/c	C2/c	P2/c
a (Å)		18.735(4)	42.914(9)	7.6733(15)	10.331(2)
b (Å)		18.507(4)	8.7726(18)	26.592(5)	9.827(2)
c (Å)		11.587(2)	12.182(2)	9.957(2)	13.867(3)
$\alpha$ (°)		90.00	90.00	90.00	90.00
$\beta$ (°)		107.19(3)	92.22(3)	90.00(3)	90.69(3)
$\gamma$ (°)		90.00	90.00	90.00	90.00
$V(\tilde{A}^{3})$ $Z$ $2\theta_{max} (^{\circ})$ $F(0 \ 0 \ 0)$ Final $R_{1}^{a}, wR_{2}^{b}$ Goodness-of-fit (GOF) on $F^{2}$	3014.3(10)	3838.1(13)	4582.6(16)	2031.7(7)	1407.8(5)
	2	8	2	4	2
	54.00	50.00	50.00	58.00	54.98
	1472	1919	2568	1032	796
	0.070, 0.163	0.076, 0.137	0.064, 0.159	0.045, 0.103	0.023, 0.050
	1.144	1.201	1.145	1.107	1.108

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

<sup>b</sup>  $wR_2 = \left[\sum w(|F_0^2| - |F_c^2|)^2 / \sum w|F_0^2|^2\right]^{1/2}$ .  $w = 1/[\sigma^2(F_0)^2 + 0.0297P^2 + 27.5680P]$ , where  $P = (F_0^2 + 2F_c^2)/3$ .

Table 2	
Selected bond lengths and angles for complexes 1-5	5.

Complex 1			
Zn(1)-O(6)#1	1.989(3)	Zn(1)-O(2)	1.990(3)
Zn(1)-N(4)#2	2.010(4)	Zn(1)-N(7)	2.016(4)
Zn(2)-O(3)	2.086(3)	Zn(2)–O(7)	2.113(3)
N(4)#2-Zn(1)-N(7)	116.58(17)	O(7)#3-Zn(2)-O(7)	180.0
O(6)#1-Zn(1)-O(2)	96.95(12)	O(6)#1-Zn(1)-N(4)#2	103.37(16)
Complex <b>2</b>			
O(1) - Zn(1)	1.948(4)	O(3)-Zn(1)	1.975(4)
N(1) - Zn(1)	1.996(5)	N(4) - Zn(1)	2.060(5)
C(1)-O(1)-Zn(1)	109.3(4)	C(5)-O(3)-Zn(1)	110.4(3)
C(15)-N(4)-Zn(1)	130.1(4)	C(16)-N(4)-Zn(1)	122.4(4)
O(1)-Zn(1)-O(3)	105.82(16)	O(1)-Zn(1)-N(1)	120.63(17)
Complex <b>3</b>			
Ag(1) - N(1)	2.255(6)	Ag(1) - N(4) # 1	2.256(6)
Ag(1) - O(2)	2.424(6)	Ag(2)-N(5)	2.348(6)
Ag(2) - O(4)	2.517(8)	Ag(2) - O(3)	2.592(8)
N(1)-Ag(1)-O(2)	99.7(2)	N(5)-Ag(2)-O(4)	82.4(3)
N(5)-Ag(2)-O(3)	131.3(2)	O(4)-Ag(2)-O(3)	48.9(3)
Complex <b>4</b>			
Ag(1) - N(2)	2.259(3)	Ag(1) - N(1)	2,336(3)
Ag(1) - N(2) # 1	2.259(3)	N(2)#1-Ag(1)-N(1)	120.93(7)
C(2)#1-N(1)-Ag(1)	120.84(17)	C(9) - N(2) - Ag(1)	133.1(2)
N(2)-Ag(1)-N(2)#1	118.14(13)	N(2)-Ag(1)-N(1)	120.93(7)
Complex 5			
Cd(1)-N(2)	2.279(2)	Cd(1) - N(1)	2.331(2)
Cd(1) = O(5)	2.3980(18)	Cd(1) - O(3)	2.4036(18)
Cd(1) - O(1)	2.5107(18)	N(1)-Cd(1)-O(3)	68.95(5)
N(2)-Cd(1)-O(1)	86.89(6)	N(2)-Cd(1)-N(1)	93.69(8)
O(3)-Cd(1)-O(1)	136.08(5)	O(5)-Cd(1)-O(3)	152.44(5)
			. ,

Symmetry transformation used to generate equivalent atoms: #1 x,y-1,z; #2 -x,y-1/2,-z+1/2; #3 -x+1,-y+1,-z; #4 -x,y+1/2,-z+1/2; #5 -x,-y,-z+1; #6 x,y+1,z for 1; #1 -x+2,y,-z+1/2; #2 -x+1,-y+1,-z+1; #3 -x+2,-y+1,-z+1; #4 -x+1,y,-z-1/2 for 2; #1 x,-y+1,z-1/2; #2 x,-y+3,z-1/2; #3 -x+1/2,-y-1/22,-z+1; #4 -x,-y+3,-z; #5 x,-y+1,z+1/2; #6 x,-y+3,z+1/2 for 3; #1 -x+1,y,-z+1/2; #2 -x-1/2,-y+1/2,-z+1 for 4; #1 -x+1,-y+3,-z+2; #2 -x,y,-z+3/2; #3 -x,-y+2,-z+2 for 5.

## 3.2. Crystal structures of 1 and 2

The X-ray crystallographic analysis reveals that **1** is a 3D architecture. As depicted in Fig. 1a, the Zn1 center lies in tetrahedral coordination geometry defined by two oxygen atoms from two different  $btc^{3-}$  and two nitrogen atoms from two different btc. The Zn2 center is in an octahedral coordination sphere, in which the

equatorial positions are furnished by two carboxylate oxygen atoms from two different btc<sup>3–</sup>, and two nitrogen atoms from two different btx. The axial sites are occupied by two water molecules. The btc<sup>3–</sup> in **1** acts as  $\mu_3$ -bridge, in which all the carboxylate groups adopt monodentate mode to connect two Zn1 and one Zn2 centers. The separations of the Zn…Zn bridged by btc<sup>3–</sup> anion are 10.125 Å for Zn1…Zn1a, and 10.114 or 8.302 Å for Zn1…Zn2.

The btc<sup>3-</sup> anion, acting as a triconnector links the Zn<sup>2+</sup> centers to form a 1D chain running along the *b*-axis. It is noticeable that the Zn<sup>2+</sup> centers are arranged in coplanar parallel lines. All btx spacers assume trans conformation. For the btx to which N1 belongs, the dihedral angles between the two triazole ring planes and the least-squares plane of phenyl group are 88.6° and 68.6°, respectively, with the two triazole groups twisted by 47.2°. The bidentate btx establishes a physical bridge between two chains generating an infinite corrugated 2D layer motif (Fig. 1b). The btx containing N7, possessing C<sub>i</sub> symmetry, have the planes steeply tilted 77° with respect to the average plane of phenyl ring. The 2D layers are further pillared by btx, leading to the formation of 3D framework with the void space occupied by uncoordinated water molecules. From the topology viewpoint, if the bidentate btx is simplified to be linear connector, the 3D framework can be reduced to a (3,4)-connected  $(6^3)(6^4 \cdot 7 \cdot 8)(6 \cdot 7^3 \cdot 8^2)$  net, where the btc<sup>3–</sup>, Zn1, and Zn2 are assigned as three-, four- and four-connected nodes, respectively (Fig. 1c).

The replacement of the H<sub>3</sub>btc molecule in **1** by H<sub>2</sub>bdc results in a 2D complex **2**. The asymmetric unit of complex **2** consists of one Zn<sup>2+</sup> center, two halves of bdc<sup>2–</sup> anions and two halves btx ligands. Complex **2** crystallizes in the monoclinic with space group C2/c, rather than in monoclinic with space group P2(1)/c as observed in **1**. Each Zn<sup>2+</sup> center in **2** is coordinated to two carboxylate oxygen atoms [Zn–O = 1.948–1.975 Å] and two btx nitrogen atoms (Zn– N = 1.996–2.060 Å), completing a distorted tetrahedral coordination geometry (Fig. 2a). The Zn–O/N distances fall in the normal range found in other Zn complexes [28]. It is interesting that two different types of *cis* and *trans* conformations of btx simultaneously coexist in **2**.

Both  $bdc^{2-}$  and btx act as bidentate ligands bridging  $Zn^{2+}$  centers, resulting in two kinds of chains, namely single chain 1 (Fig. 2b) and composite chain 2 (Fig. 2c), respectively. In single chain 1, the  $Zn^{2+}$  centers are in turn connected by  $bdc^{2-}$  and btx to form a single chain running along the *c*-axis, in which the flexible btx ligands adopt trans conformation. The triple-stranded



Fig. 1. (a) Two types of zinc coordination environments in the structure of polymer 1, one of which involves two terminal aqua molecules, all the hydrogen atoms, solvent molecules and part atom labels are omitted for clarity. (b) The 1D chains bridged by bidentate btx containing N1 to form 2D layer motif. (c) Schematic drawing of the topology for the 3D porous framework in 1.

composite chain 2 contains three "S" like interpenetrated single chains running along the *c*-axis, in which the  $bdc^{2-}$  and btx alternately bond to different  $Zn^{2+}$  centers. In the composite chain, all btx adopt *cis* conformation. Both sets of btx ligands possess  $C_i$  symmetry. For the btx adopting cis conformation, the triazole ring and phenyl group are twisted by 120°, while the corresponding angle is decreased to 80° for the btx in *trans* form. The single chain 1 resembles a flexible ribbon, connecting three chains of composite chain 2 to extend into layers (Fig. 2d). The chain 1 and composite chain 2 are edge-sharing and both chains are arranged in the –ABAB– arranging order. The 2D sheets are connected by H-bonded interactions to form a 3D supramolecular framework. It is noteworthy that btx ligands have different conformations in **1** and **2**, although they bind with the same  $Zn^{2+}$  center. All carboxyl groups of btc<sup>3-</sup> and bdc<sup>2-</sup> adopt monodentate mode in **1** and **2**, although they have diverse binding modes. The primary difference between **1** and **2** is the shape of organic anions. In **1**, the tri(monodentate) btc<sup>3-</sup> anion serves as a trigonal connector and possesses a rigid disk-like conformation, which connects  $Zn^{2+}$  centers oriented in three different directions, thus contributing to forming structures of higher dimensions. While bis(monodentate) bdc<sup>2-</sup> functions as a linear linker in **2**, each bdc<sup>2-</sup> can only bind two  $Zn^{2+}$  centers concurrently. In the presence of bdc<sup>2-</sup>, the main ligand btx shows two distinct types of conformation, which is different from complex **1**. These re-



**Fig. 2.** (a) The crystal structure of polymer **2**, the hydrogen atoms and part labels are omitted for clarity. (b) The zigzag-like chain 1 running along *c*-axis. (c) Composite chain 2 constructed from three interpenetrating chains running along *c*-axis. (d) The 2D layer motif of complex **2** parallel to *a*,*c*-plane.

sults indicated that the structurally different polycarboxylates have profound impact on the conformation of btx and on the structure of resulted complexes [29,30].

#### 3.3. Crystal structures of complexes 3 and 4

Complex **3** also crystallizes in the space group C2/c. The Ag1 adopts trigonal coordination geometry, which is defined by one btx nitrogen atom, one nitrogen atom from 3,5-pydc<sup>2–</sup> anion and one carboxylate oxygen atom from another 3,5-pydc<sup>2–</sup> (Fig. 3a). Whereas the Ag2 is in a planar quadrilateral coordination sphere surrounded by two nitrogen atoms from two different btx and two oxygen atoms from one chelating carboxylate group. The values of Ag–N are 2.235–2.346 Å, and the slightly long Ag–O bond lengths range from 2.432 to 2.581 Å, and the similar bond lengths are observed in the reported complexes [31,32].

In the complex **3**, each 3,5-pydc<sup>2–</sup> acts as a triconnector by one monodentate carboxylate, one chelating carboxylate, and pyridyl N moiety linking three silver centers. Both types of btx with bi- and tetradentate coordination modes have  $C_i$  symmetry and adopt

trans conformations. For the bidentate btx, the dihedral angle between the triazole ring and the phenyl plane is 72.8°, which is larger than that in the tetradentate btx  $(66.6^{\circ})$ . It is noticeable that each tetradentate btx binds four Ag2 centers to form 1D ladder-like motif propagating along c-axis (Fig. 3b). The 1D chains are further cross-linked by 3,5-pydc<sup>2-</sup> bridges and Ag1 centers, resulting in an infinite 2D bilayer motif extending parallel to the *b,c*-plane, in which each Ag1 center ligates two 3,5-pydc<sup>2-</sup> molecules via coordinating to one carboxylate and one pyridyl nitrogen atom (Fig. 3c). Each bilayer contains many parallel 1D channels running along *c*-axis. As shown in Fig. 3d, these bilayers are strongly puckered allowing for an interpenetration of two such parallel bilayers to form a composite layer. Such composite layers are further pillared via the bidentate trans btx running along the a-axis in AA sequence. The crystalline water molecules are located in the voids of the 3D framework. The single network **3** is a rare example with parallel interpenetrated bilayers as building block. If the bidentate btx is simplified as a line connecting the metal centers, the framework of 3 can be symbolized as four-nodal (3,4)-connected net. The network can best be described as a  $(4 \cdot 10^2)(10^3)(10^3)(4^2 \cdot 10^4)$ 



**Fig. 3.** (a) Perspective view of the coordination environment of the metal centers, all the hydrogen atoms and solvent molecules are omitted for clarity. (b) The 1D ladder-like chain running along *c*-axis based on btx and Ag ions. (c) The 2D bilayer viewed along the *a*-axis. (d) The composite layer is constructed from two parallel interpnetrated 2D bilayers viewed along the *c*-axis. (e) The schematic representation of 3D framework.

topology if we define the Ag2, 3,5-pydc<sup>2–</sup> anion, Ag1 and tetradentate btx as three-, three-, three- and four-connected nodes, respectively (Fig. 3e).

When 2,6-H<sub>2</sub>pydc was incorporated into the reaction system instead of  $3,5-H_2$  pydc in complex **3**, an infinite 1D zigzag chain complex 4 was obtained. Crystallographic analysis reveals that complex **4** crystallized in the monoclinic with space group  $C_2/c$ as well. The fundamental building unit of **4** is composed of one Ag(I) center, half 2,6-Hpydc<sup>1-</sup> anion and half btx. As shown in Fig. 4, each Ag center is coordinated by two nitrogen atoms from two different btx and one nitrogen atom from 2,6-Hpydc<sup>1-</sup> to furnish the triangular coordination geometry. The btx serves as bismonodentate linker and bridges the adjacent Ag(I) centers. The btx has *C<sub>i</sub>* symmetry and adopts *trans* conformation, in which triazole ring and phenyl group are twist by 86.8°. The 2,6-pydc<sup>1-</sup> possesses a twofold axis through N1 as well as Ag1 atoms, and serves as monodentate ligand using the pyridyl N group. The Ag-N bond lengths range from 2.259 to 2.336 Å, within the normal range. In addition, the strong Ag-O contact (Ag-O 2.649 Å) exists, little beyond the values reported for other silver(I) complexes (Ag-O 2.33–2.62 Å) [33,34]. The 1D chain structure is further stacked into 3D supramolecular architecture via strong intermolecular interaction with O1...O1' 2.445 Å and hydrogen bonds (C...O 3.129 Å for C8-H...O1 and C...O 3.34 Å for C10-H...O2). A comparison between 3 and 4 indicates that the structural features and coordination modes of the organic anions can clearly affect the coordination sphere of metal center and hence framework connectivity. The 3,5-pydc<sup>2-</sup> and 2,6-pydc<sup>1-</sup> are isomers with different positions of carboxylate moieties on the pyridyl ring. In complexes **3**, the tetradentate 3,5-pydc<sup>2–</sup> acting as a three-connected nodes of trigonal geometry connects silver centers, which is conducive to the formation of multidimensional coordination architecture. Whereas the 2,6-pydc<sup>1–</sup> has a rigid 120° angle between the central pyridyl ring and two carboxylate groups and therefore prefer to form stable chelate. In 4, the pyridyl nitrogen atom and two carboxylate groups of chelate 2,6-pydc<sup>1-</sup> are on the same side of the coordination sphere Ag(I) center and two btx reside on the opposite side, thus the space hindrance prevents other carboxylate groups further linking to other Ag(I) centers. Herein, the 2,6pydc<sup>1–</sup> only coordinated to one silver center, thus a 1D structure was attained through bidentate btx bridging silver centers.

# 3.4. Crystal structure of complex 5

The X-ray crystallographic analysis shows that the asymmetric unit of complex **5** contains one  $Cd^{2+}$  center, one 2,6-pydc<sup>2-</sup> anion, half btx and one water molecule. The  $Cd^{2+}$  center is in a distorted pentagonal bipyramidal coordination sphere, which is defined by one nitrogen atom from btx and one carboxylate oxygen atom occupying the apical positions, while the basal plane is completed by three oxygen atoms (Cd–O = 2.303–2.511 Å) and one nitrogen atom (Cd–N = 2.280–2.331 Å) from two different 2,6-pydc<sup>2-</sup>, as well as one aqua molecule (Fig. 5a).

The 2,6-H<sub>2</sub>pydc can potentially provide various coordination modes to form both discrete and consecutive metal complexes under appropriate conditions [35,36]. In structure **5**, the 2,6-pydc<sup>2–</sup> acts as a triconnector through the bismonodentate carboxylate and pyridyl N group linking three cadmium centers. Two Cd1 centers are bridged by three  $\mu_2$ -O bridges from two separate carboxylate moieties and one aqua molecule to form dimer units, in which the Cd…Cd separations is 3.453 Å. The dimer units are further interconnected by another two carboxylate oxygen bridges to lead to a 1D chain running along the *c*-axis (Fig. 5b). It should be noted that the two 2,6-pydc<sup>2–</sup> of one dimer unit locate at the same side of the chain with the dihedral angle of 21.553°, whereas the 2,6-pydc<sup>2–</sup> of the adjacent dimer moieties lie on the opposite sides. All btx possess *C<sub>i</sub>* symmetry and hold *trans* conformation. The dihedral angle between triazole ring and the phenyl group is 102.5°.



Fig. 4. The zigzag chain fragment of complex 4, all hydrogen atoms and part labels are omitted for clarity.



**Fig. 5.** (a) View of the coordination environment of  $Cd^{2+}$  ions in complex **5** with part atom label schemes. (b) The 1D chain running along the *c*-axis based on 2,6-pydc<sup>2-</sup> anions and  $Cd^{2+}$  ions. (c) The 3D framework of complex **5**.



Fig. 6. The figure of TGA curves.

The 1D chain is further pillared along the *a*- and *b*-axes with bidentate btx resulting in the formation of a 3D framework (Fig. 5c).

#### 3.5. Thermal properties

Complexes **1–5** are air-stable and can retain their crystalline integrity at ambient temperature. The TGA curve (Fig. 6) shows that the weight loss of 7.84% for **1** from 52 to 185 °C (calc. 7.52%) corresponds to the loss of three water molecules per formula. The dehydrated complex is stable up to 285 °C. For complex **3**, the weight loss takes place between 60 and 140 °C, and the total weight loss in this temperature range is 4.93%, which is attributed to the uncoordinated water molecules (calc. 5.51%), and then it is stable up to 240 °C. For complex **5**, it is stable up to 220 °C, which shows that the H<sub>2</sub>O molecules are tightly held in the 3D framework. The first weight loss of 4.43% is assigned to the liberation of one water molecule (calc. 4.44%). The burning of the organic groups starts from 330 °C. The anhydrous complexes **2** and **4** are stable up to 300 and 225 °C, respectively.

## 3.6. Luminescence properties

The photoluminescence properties of complexes **1–5** were investigated and the results were provided in Fig. 7. In the solid state, strong emissions were found at 429 nm ( $\lambda_{ex}$  = 371 nm), 438 nm ( $\lambda_{ex}$  = 381 nm), and 437 nm ( $\lambda_{ex}$  = 379 nm) for complexes **1**, **2** and **5**, respectively. For excitation wavelength between 298



**Fig. 7.** Solid-state photoluminescence spectra of 1 ( $\lambda_{ex}$  = 371 nm), **2** ( $\lambda_{ex}$  = 381 nm), **3** ( $\lambda_{ex}$  = 399 nm), **4** ( $\lambda_{ex}$  = 398 nm) and **5** ( $\lambda_{ex}$  = 379 nm) at room temperature.

and 396 nm, free H<sub>2</sub>bdc shows fluorescence emission band at 393 nm ( $\lambda_{ex}$  = 347 nm), whereas free H<sub>3</sub>btc, 2,6-H<sub>2</sub>pydc, 3,5-H<sub>2</sub>pydc and btx ligands present very weak photoluminescence emission under the same experimental conditions. The results agree with previous studies that coordination polymers containing cadmium and zinc ions exhibit photoluminescent properties [37]. Unfortunately, only weak emissions of complexes **3** ( $\lambda_{em}$  = 436 nm) and **4** ( $\lambda_{em}$  = 449 nm) were observed. Taking the strong emission of 5 into consideration, the result imparts that the silver ion does negatively impact the fluorescence of 3 and 4. In contrast to the free ligands, the emission maximums of complexes 1-5 have changed, which may be attributed to the changes of HOMO-LUMO energy gap caused by the deprotonated polycarboxylate acid and neutral ligand coordinating to metal centers. A charge-transfer may be attributed to the joint contribution of intra-ligand transitions or between the coordinated ligands and the metal centers [38,39].

## 4. Conclusions

In summary, five new d<sup>10</sup> metal coordination complexes were synthesized and structurally characterized. Single crystal structure analysis shows that **1**, **3** and **5** possess 3D structures, **2** takes a 2D layer motif, and **4** exhibits a 1D chain structure. These results demonstrate the difference in coordination modes of the aromatic polycarboxylic acids has a significant influence on the formation and structures of the resultant complexes. The flexible btx has the ability to adjust its configuration and coordination mode to meet the coordination requirements of metal centers. The joint contribution of the polycarboxylate acids and the flexible btx results in a variety of fascinating coordination polymers.

# Acknowledgment

We gratefully acknowledge the financial support by the National Natural Science Foundation of China (No. 20671082), NCET and the Outstanding Talents Foundation by the He'nan province.

#### **Appendix A. Supplementary material**

CCDC 723809, 723810, 723811, 723812 and 723813 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2009.08.009.

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