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# Preparation and characterization of two supramolecular complexes with 5-amino-2,4,6-triiodoisophthalic acid under *N*-donor auxiliary ligand intervention

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### ABSTRACT

Assemblies of 5-amino-2,4,6-triiodoisophthalic acid (H<sub>2</sub>ATIBDC) with Cd(II) and Zn(II) in the presence of *N*-donor auxiliary ligand, 1,4-bis(1,2,4-triazol-1-yl)butane (btb), at ambient conditions yield two new supramolecular complexes, [Cd(ATIBDC)(btb)(H<sub>2</sub>O)<sub>2</sub>]·3H<sub>2</sub>O (**1**), and [Zn(ATIBDC)(btb)]·2H<sub>2</sub>O (**2**). Generally, these two complexes display 1D ATIBDC<sup>2–</sup>-bridged coordination arrays. Distinct extended 3D network architectures are further constructed with the help of weak secondary interactions especially aromatic stacking, halogen bonding, and hydrogen bonding as supramolecular driving forces. It is worthy to mention that halogen bonds (C–I···π and C–I···N/O) play important roles in the supramolecular assembly. The pentameric cluster (H<sub>2</sub>O)<sub>5</sub> in **1** assembles into highly ordered helical infinite chains. Complex **2** exhibits the fascinating single-walled tube-like chain structure. It loses crystallinity rapidly in the air and leads to the formation of [Zn(ATIBDC)(btb)]·H<sub>2</sub>O (**2A**). Thermal stabilities and solid state fluorescent properties of complexes **1** and **2A** have been studied.

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# 1. Introduction

The aim of contemporary supramolecular chemistry and crystal engineering is the development of new crystalline materials with various functions and possible applications such as molecular adsorption, magnetism, nonlinear optics, molecular sensing, heterogeneous catalysis, and photoactive materials although the rational design and synthesis of metal-organic frameworks (MOFs) with target structure and function still remains a long-term challenge [1-11]. The construction of supramolecular architectures depends on the combination of several factors, such as the coordination geometry of metal ions, the nature of organic ligands, the use of noncovalent interactions (hydrogen bonding, halogen bonding,  $\pi$ - $\pi$  interactions, or their combination in different ways) and sometimes the reagent ratio [12-15]. So, understanding how these considerations affect metal coordination and influence crystal packing is at the forefront of controlling coordination supramolecular arrays. It has been documented that the geometries of organic ligands play crucial roles in determining the resulted polymeric structures [16].

At present, we are focusing our attention on using iodinecontaining 5-amino-2,4,6-triiodoisophthalic acid (H<sub>2</sub>ATIBDC) as the organic moiety to assemble with transition metal ions in the presence of *N*-donor auxiliary ligand, which is based mostly upon the following considerations: (1) Three I atoms in H<sub>2</sub>ATIBDC are potential interaction sites for forming C-I···N/O, C-I···I, or C- $I \cdots \pi$  halogen bonds which may help to extend the linkage into high dimensional supramolecular network due to their specific directional nature and relatively high halogen bonding energy. (2)  $ATIBDC^{2-}$  is a rigid aromatic dicarboxylate ligand and thus can play the role of a bridging rod. Therefore, a structural prediction of the resulting polymeric complexes may be possible to some extent. Furthermore, due to the presence of aromatic/hetero rings of ATIBDC<sup>2-</sup> and *N*-donor auxiliary ligand in the assembled system, the delicate  $\pi \cdots \pi$  stacking interactions are available to play an significant role in regulating the resulting supramolecular networks. Several novel complexes with the ATIBDC<sup>2-</sup> ligand have been reported [17,18].

We had finished a systematic study focusing on the p-block metal Pb(II) with ATIBDC<sup>2–</sup> ligand [19]. In this paper, we will describe our recent research results of the synthesis, crystallography, and properties of two supramolecular complexes with H<sub>2</sub>ATIBDC in order to further understand the coordination chemistry of H<sub>2</sub>ATIBDC with d<sup>10</sup> metal ions, the roles of three I atoms in the supramolecular assembly. With the introduction of organonitrogen auxiliary





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ligand, 1,4-bis(1,2,4-triazol-1-yl)butane (btb), two interesting supramolecular complexes,  $[Cd(ATIBDC)(btb)(H_2O)_2]\cdot 3H_2O$  (1) and  $[Zn(ATIBDC)(btb)]\cdot 2H_2O$  (2), have been obtained. In this work, we attempt to demonstrate the roles of supramolecular interactions, such as hydrogen bonding and halogen bonding  $(C-I\cdots\pi, C-I\cdots N/O)$ , in engineering the resultant crystalline architectures. The pentameric water cluster  $(H_2O)_5$  in 1 assembles into highly ordered helical infinite chains. Complex 2 exhibits a fascinating single-walled tube-like chain structure and desolvates partly in the air forming  $[Zn(ATIBDC)(btb)]\cdot H_2O$  (2A). Solid state fluorescent properties of 1 and 2A have been investigated.

# 2. Experimental

#### 2.1. Materials and characterization

The nitrogenous auxiliary ligand, 1,4-bis(1,2,4-triazol-1-yl)butane (btb), was synthesized according to the literature method [20]. The other reagents were purchased commercially. Elemental analyses (C, H, and N) were carried out on a 240 C Elemental analyzer. FT-IR spectra (4000–400 cm<sup>-1</sup>) were recorded from KBr pellet in Magna 750 FT-IR spectrophotometer. Solid state emission spectra were recorded using an F 4500 fluorescence spectrometer. Both the excitation and emission pass width are 5.0 nm. Thermogravimetric analysis (TGA) was taken on NETZSCH STA 409 PG/ PC instrument from room temperature to 800 °C at a heating rate of 10 °C/min in N<sub>2</sub>. X-ray powder diffraction data were collected at room temperature on a computer-controlled Bruker D8 Advanced XRD diffractometer equipped with Cu K $\alpha$  monochromator ( $\lambda = 1.5418$  Å) at a scanning rate 0.04°/s from 5° to 50°.

#### 2.2. Crystal structure determination

Crystallographic data were collected at 293(2) K with a Siemens SMART CCD diffractometer using graphite-monochromated (Mo K $\alpha$ ) radiation ( $\lambda$  = 0.71073 Å),  $\psi$  and  $\omega$  scans mode. The structures were solved by direct methods and refined by Full-Matrix least-squares on  $F^2$  method. Intensity data were corrected for Lorenz and polarization effects and a multi-scan absorption correction was performed. All non-hydrogen atoms were refined anisotropically. The carbon-bound hydrogen atoms of all the complexes were added geometrically. The oxygen-bound hydrogen atoms of water molecules were located in the difference Fourier map and then kept fixed in that position. The contribution of these hydrogen atoms was included in the structure factor calculations. Two oxvgen atoms (O4W and O5W) of lattice water molecules in 1 were disordered over two positions. All calculations were carried out on a PC computer using SHELXL-97 program [21]. Details of crystal data, collection, and refinement are listed in Table 1.

# 2.3. Synthesis of $[Cd(ATIBDC)(btb)(H_2O)_2]$ ·3H<sub>2</sub>O (1)

A mixture of H<sub>2</sub>ATIBDC (0.056 g, 0.100 mmol) and NaOH (0.4 ml, 0.5 mol/l) was dissolved in water (5 ml) and then an aqueous solution of CdCl<sub>2</sub>·2.5H<sub>2</sub>O (0.046 g, 0.200 mmol) was added while stirring. To this solution btb (0.019 g, 0.100 mmol) in water (5 ml) was added and then filtered. Pale yellow polyhedral crystals were collected (61% based on H<sub>2</sub>ATIBDC). *Anal.* Calc. for C<sub>16</sub>H<sub>24</sub>CdI<sub>3-</sub>N<sub>7</sub>O<sub>9</sub>: C, 20.20; H, 2.54; N, 10.30. Found: C, 20.11; H, 2.47; N, 10.21%.

# 2.4. Synthesis of [Zn(ATIBDC)(btb)] 2H<sub>2</sub>O (2)

Complex **2** can be obtained following the same synthetic procedure as that for **1** except that  $Zn(NO_3)$ · $GH_2O$  (0.060 g, 0.200 mmol),

#### Table 1

Crystal data and structure refinement for the complexes 1-2.

	1	2
Empirical formula Formula weight	C <sub>16</sub> H <sub>24</sub> CdI <sub>3</sub> N <sub>7</sub> O <sub>9</sub> 951.52	C <sub>16</sub> H <sub>18</sub> I <sub>3</sub> N <sub>7</sub> O <sub>6</sub> Zn 850.44
Temperature (K)	293(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	Pna2 <sub>1</sub>
a (Å)	8.1689(4)	16.511(3)
b (Å)	20.2307(9)	14.854(2)
c (Å)	17.2518(8)	10.1159(15)
α (°)	90	90
β(°)	96.9830(10)	90
γ (°)	90	90
$V(Å^3)$	2829.9(2)	2480.9(6)
Ζ	4	4
$D_{\text{calc}} (\text{mg/m}^3)$	2.233	2.277
Absorption coefficient (mm <sup>-1</sup> )	4.099	4.769
F(000)	1792	1600
$\theta$ range for data collection (°)	1.56-27.50	1.84-27.42
Index ranges	$-10\leqslant h\leqslant 10$	$-21 \leqslant h \leqslant 21$
	$-26 \leqslant k \leqslant 23$	$-17 \leqslant k \leqslant 19$
	$-21 \leqslant l \leqslant 21$	$-12 \leqslant l \leqslant 13$
Reflections collected	17 765	20 561
Unique (R <sub>int</sub> )	6452	5466
	[R(int) = 0.0222]	[R(int) = 0.0466]
Completeness to $\theta$ = 27.5	99.40%	99.60%
Maximum and minimum transmission	0.406 and 0.226	0.424 and 0.249
Goodness-of-fit on $F^2$	1.047	1.066
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0285$	$R_1 = 0.0323$
	$wR_2 = 0.0775$	$wR_2 = 0.0723$
R indices (all data)	$R_1 = 0.0352$	$R_1 = 0.0420$
	$wR_2 = 0.0809$	$wR_2 = 0.0879$
Largest different peak and hole (e Å <sup>-3</sup> )	1.927 and -1.019	0.982 and -0.784

btb (0.019 g, 0.100 mmol), H<sub>2</sub>ATIBDC (0.112 g, 0.200 mmol), and NaOH (0.8 ml, 0.5 mol/l) were used. Pale yellow crystals were formed. Complex **2** loses crystallinity in the open air and turns into the pale yellow powder formulated as [Zn(ATIBDC)(btb)]·H<sub>2</sub>O (**2A**) (44% based on btb). *Anal.* Calc. for C<sub>16</sub>H<sub>16</sub>I<sub>3</sub>N<sub>7</sub>O<sub>5</sub>Zn: C, 23.09; H, 1.94; N, 11.78. Found: C, 22.89; H, 1.89; N, 11.69%.

#### 3. Results and discussion

#### 3.1. Synthesis of the complexes

The formation of the products is sensitive to synthetic conditions. The hydrothermal method is not suitable for the syntheses of these two complexes since the ATIBDC<sup>2–</sup> ligand decomposes under hydrothermal condition. Therefore, the complexes **1–2** have been obtained under soft ambient conditions. NaOH is used to neutralize the acid. Interestingly, the molar ratio of H<sub>2</sub>ATIBDC:NaOH is important for the formation of **1–2**. The molar ratio of H<sub>2</sub>ATI-BDC:NaOH = 1:2 was used to synthesize the complexes **1–2**. Otherwise the polycrystals or cotton-like solids were obtained.

Complex **2** loses crystallinity rapidly in the open air, resulting in the formation of the powder [Zn(ATIBDC)(btb)]-H<sub>2</sub>O (**2A**) supported by the elemental and thermogravimetric analysis.

### 3.2. Structure description of $[Cd(ATIBDC)(btb)(H_2O)_2]$ ·3H<sub>2</sub>O (**1**)

Complex **1** crystallizes in monoclinic system with space group  $P2_1/n$ . There are one Cd(II) atom, one ATIBDC<sup>2–</sup> anion, two coordinated water molecules, and three lattice water molecules in the asymmetric unit (Fig. 1A). The Cd(II) lies in a distorted pentagonal bipyramid environment, in which the equatorial plane contains O1, O2, and O3 atoms from two carboxylate groups of two different



**Fig. 1.** (A) View of the coordination environment of Cd(II) and the conformation of btb in **1**. Symmetry transformations #1 - x + 3/2, y + 1/2, -z + 3/2. (B) 1D loop-like chain, showing the conformation of btb ligand and the coordination mode of ATIBDC<sup>2-</sup>. (C) Hydrogen-bonded 2D layer. All the disordered positions of O4W and O5W are shown. (D) Halogen-bonded 2D layer. (E) 3D MOF along [0 1 0] through both the H-bonding and halogen bonding between the chains.

ATIBDC<sup>2-</sup> ligands and O1W and O2W from two coordinated water molecules. The two triazole nitrogen atoms N2 and N7 from two different btb ligands occupy the axial positions with N2–Cd1–N7 angle of 168.71(13)° (Table 2). The btb ligand exhibits the *trans*-*trans*-*gauche* conformation (Scheme 1). On the other hand, each ATIBDC<sup>2-</sup> ligand coordinates with two Cd(II) atoms. One carboxylate group adopts a  $k^2$ -chelating coordination mode, while the other carboxylate group adopts a  $k^1$  monodentate coordination mode. So, the ATIBDC<sup>2-</sup> ligand exhibits the  $k^1-k^2-\mu_2$  coordination mode (Scheme 2). As shown in Fig. 1B, both the btb and ATIBDC<sup>2-</sup> ligand

bridge the Cd1 and Cd2 atoms to form an infinite 1D loop-like chain with the nearest Cd  $\cdots$  Cd distance of 10.125 Å.

Interestingly, the acyclic pentameric water cluster (O1W, O2W, O3W, O4W, O5W) assembles into 1D helical water chain, which further acts as a glue to link the adjacent chains into 2D supramolecular hydrogen-bonded layer (Fig. 1C and Table 3). It is worthy to note that both O4W and O5W are disordered over two positions.

The 2D hydrogen-bonded supramolecular layers are further halogen-bonded to each other, which is verified by the C–I $\cdots$ N distance of 3.292 Å. Thus, 3D supramolecular MOF with 1D channels



Fig. 1 (continued)

is formed. So, the C–I $\cdots$ N halogen bonding plays a significant role in the 3D supramolecular assembly (Fig. 1D and E).

#### 3.3. Structure description of [Zn(ATIBDC)(btb)]·2H<sub>2</sub>O (**2**)

Complex **2** also crystallizes in monoclinic space group  $P2_1/n$ . Quite different from the structure of **1**, complex **2** has a novel single-walled tube-like chain structure. The asymmetric unit of **2** contains one zinc ion, one ATIBDC<sup>2–</sup> ligand, one btb ligand, and two uncoordinated H<sub>2</sub>O molecules. As shown in Fig. 2A, the central zinc ion is four-coordinated by two oxygen atoms from two different ATIBDC<sup>2–</sup> ligands and two triazole nitrogen atoms from two different btb ligands in a distorted tetrahedral geometry with the average Zn–O and Zn–N distances of 1.952 and 2.008 Å, respectively (Table 2). The btb molecule acts as a bidentate bridging ligand, linking the Zn(II) ions into a btb-bridged chain with the nearest intrachain Zn··Zn distance of 10.1159(20) Å. The btb ligand shows the *gauche-gauche-trans* conformation in complex **2** (Scheme 1).

The nearest two Zn(II)-btb-bridged chains are further connected by the bridging ATIBDC<sup>2–</sup> ligands in  $(k^1)-(k^1)-\mu_2$  coordination mode to generate a single-walled tube-like  $2_1$  helical chain (Scheme 2). The Zn…Zn separation by ATIBDC<sup>2–</sup> bridge is 7.1579(14) Å (Fig. 2B–D). Within the helical tube-like chain, there are  $\pi \cdots \pi$ stacking interactions between the imidazole ring N4N5N6C15C16 of btb and benzene ring of the ATIBDC<sup>2–</sup> ligand as evidenced by the centeroid…centeroid distance of 3.6019(5) Å. There are no residual solvent-accessible void in the "tube" calculated by PLATON [22].

It should be interesting to note that the halogen bonding C8– 11…N5 [3.1862(75)Å] also exists within the tube-like chain (Fig. 2C). It is really fascinating that the halogen bonding,  $\pi \cdots \pi$ stacking interactions as well as the tetrahedral configuration of Zn(II) ion act as the directing forces of the tube-like chain. Although various MOFs with tubular channels have been synthesized, it is difficult to prepare isolated coordination tubes owing to the interlocks or interpenetration [23–25]. Only a few isolated coordination tubes have been reported to date [26–34]. The work

Table 2	
Selcted bond lengths (Å) and angles (°) for the complexes	5.

$\begin{array}{c c} Complex \ 1 \\ \hline Cd(1)-N(2) & 2.250(4) & Cd(1)-O(2W) & 2.406(3) \\ Cd(1)-N(7)\#1 & 2.277(3) & Cd(1)-O(2) & 2.438(3) \\ Cd(1)-O(1W) & 2.342(3) & Cd(1)-O(1) & 2.612(4) \\ Cd(1)-O(3)\#1 & 2.388(3) \\ \hline N(2)-Cd(1)-N(7)\#1 & 168.71(13) & N(7)\#1-Cd(1)-O(2) & 87.63(12) \\ N(2)-Cd(1)-O(1W) & 100.83(14) & O(1W)-Cd(1)-O(2) & 122.19(11) \\ N(7)\#1-Cd(1)-O(1W) & 85.83(13) & O(3)\#1-Cd(1)-O(2) & 154.56(11) \\ N(2)-Cd(1)-O(3)\#1 & 84.65(11) & O(2W)-Cd(1)-O(2) & 77.60(12) \\ N(7)\#1-Cd(1)-O(3)\#1 & 87.26(11) & N(2)-Cd(1)-O(1) & 82.36(13) \\ O(1W)-Cd(1)-O(3)\#1 & 82.24(10) & N(7)\#1-Cd(1)-O(1) & 188.17(12) \\ N(7)\#1-Cd(1)-O(3)\#1 & 82.24(10) & N(7)\#1-Cd(1)-O(1) & 108.17(12) \\ N(2)-Cd(1)-O(2W) & 87.64(14) & O(1W)-Cd(1)-O(1) & 153.04(11) \\ O(1W)-Cd(1)-O(2W) & 156.79(12) & O(2W)-Cd(1)-O(1) & 153.04(11) \\ O(1W)-Cd(1)-O(2W) & 77.04(11) & O(2)-Cd(1)-O(1) & 153.04(11) \\ N(2)-Cd(1)-O(2W) & 77.04(11) & O(2)-Cd(1)-O(1) & 153.04(11) \\ N(2)-Cd(1)-O(2W) & 156.79(12) & O(2W)-Cd(1)-O(1) & 153.04(11) \\ N(2)-Cd(1)-O(2W) & 156.79(12) & O(2W)-Cd(1)-O(1) & 150.04(11) \\ N(2)-Cd(1)-O(2W) & 156.79(12) & O(2W)-Cd(1)-O(1) & 150.04(1) \\ N(2)-Cd(1)-O(2W) & 156.79(12) & O(2W)-Cd(1)-O(1) & 15$				
$\begin{array}{llllllllllllllllllllllllllllllllllll$	Complex 1 Cd(1)-N(2) Cd(1)-N(7)#1 Cd(1)-O(1W) Cd(1)-O(3)#1	2.250(4) 2.277(3) 2.342(3) 2.388(3)	Cd(1)-O(2W) Cd(1)-O(2) Cd(1)-O(1)	2.406(3) 2.438(3) 2.612(4)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$\begin{array}{l} N(2)-Cd(1)-N(7)\#1\\ N(2)-Cd(1)-O(1W)\\ N(7)\#1-Cd(1)-O(3)\#1\\ N(2)-Cd(1)-O(3)\#1\\ N(7)\#1-Cd(1)-O(3)\#1\\ O(1W)-Cd(1)-O(2W)\\ N(2)-Cd(1)-O(2W)\\ N(7)\#1-Cd(1)-O(2W)\\ O(1W)-Cd(1)-O(2W)\\ O(3)\#1-Cd(1)-O(2W)\\ N(2)-Cd(1)-O(2W)\\ N(2)-Cd(1)-O(2)\\ \end{array}$	168.71(13) 100.83(14) 85.83(13) 84.65(11) 87.26(11) 87.24(10) 87.64(14) 82.87(13) 156.79(12) 77.04(11) 96.32(12)	$\begin{array}{l} N(7)\#1-Cd(1)-O(2)\\ O(1W)-Cd(1)-O(2)\\ O(3)\#1-Cd(1)-O(2)\\ O(2W)-Cd(1)-O(2)\\ N(2)-Cd(1)-O(1)\\ N(7)\#1-Cd(1)-O(1)\\ O(1W)-Cd(1)-O(1)\\ O(3)\#1-Cd(1)-O(1)\\ O(2W)-Cd(1)-O(1)\\ O(2W)-Cd(1)-O(1)\\ O(2)-Cd(1)-O(1)\\ \end{array}$	87.63(12) 122.19(11) 154.56(11) 77.60(12) 82.36(13) 108.17(12) 77.17(11) 153.04(11) 125.69(12) 51.05(11)
	Complex <b>2</b> Zn(1)-N(1) Zn(1)-O(1) O(1)-Zn(1)-O(3)#3 O(1)-Zn(1)-N(6)#4 O(3)#3-Zn(1)-N(6)#4	2.017(6) 1.941(5) 106.9(2) 115.6(2) 113.2(2)	Zn(1)-O(3)#3 Zn(1)-N(6)#4 O(1)-Zn(1)-N(1) O(3)#3-Zn(1)-N(1) N(6)#4-Zn(1)-N(1)	1.963(4) 1.999(6) 115.2(2) 99.7(2) 105.2(2)

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

presented here reports a convenient one-pot synthesis of a new isolated infinite tube-like single-walled chain by using two kinds of bidentate ligands, which may provide an efficient way to synthesize isolated tube.

Both the lattice water molecules O1W and O2W act as double hydrogen bond donor (Table 3). The interchain hydrogen bonds [O1W-H1WA $\cdots$ O4 2.790(9), O1W-H1WB $\cdots$ N2 3.010(11), O2W-H2WA $\cdots$ O2 2.891(7), O2W-H2WB $\cdots$ O3 3.007(8)Å] further extends single-walled tube-like chain into 3D supramolecular network (Fig. 2E).

#### 3.4. Discussion of the structures

From the above-mentioned structural descriptions, it can be seen that the metal centers have great influence on the crystalline architectures of these two compounds. Both Zn(II) and Cd(II) have no crystal field stabilization energy due to their closed d<sup>10</sup> electronic shells when their complexes are formed. The coordination numbers of Zn(II) and Cd(II) are mainly determined by the steric repulsion between different ligands. Since the radius of Cd(II) is larger than that of Zn(II), the coordination number of Cd(II) in **1** is seven, which is larger than that of Zn(II) in **2** (four). Thus, the structural discrepancies between **1** and **2** may mainly be attributed to the differences in the coordination numbers of Zn(II) and Cd(II) because the auxiliary ligand in these two complexes is the same



Scheme 2. Schematic representation of the coordination modes of the ATIBDC<sup>2-</sup> ligand in 1-2.

Table 3	
The details of the hydrogen bonds for the title complex	es.

$\begin{array}{c ccc} Complex \ 1 \\ \text{N1-H1N1\cdots I3} \\ \text{N1-H1N2\cdots I2} \\ \text{N1-H1N2\cdots I2} \\ \text{N1-H1N2\cdots O3W} \\ \text{N1-H1N2\cdots O3W} \\ \text{N2-P} \\ \text{N1-H1N2\cdots O3W} \\ \text{N2-P} \\ \text{N2-P} \\ \text{N1-H1N2\cdots O3W} \\ \text{N2-P} \\ N2-$	D−H···A	d(D-H)	$d(H{\cdot}{\cdot}{\cdot}A)$	$d(D{\cdots}A)$	<dha< th=""><th>Symmetry of A</th></dha<>	Symmetry of A
$\begin{array}{ccccc} N1-H1N1\cdots I3 & 0.8600 & 2.7200 & 3.196(4) & 117.00 \\ N1-H1N2\cdots I2 & 0.8600 & 2.7100 & 3.191(4) & 117.00 \\ N1-H1N2\cdots O3W & 0.8600 & 2.4200 & 3.125(5) & 140.00 & 1/2 + x, \\ & & & & & & & & & & & & & & & & & & $	Complex <b>1</b>					
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N1-H1N1···I3	0.8600	2.7200	3.196(4)	117.00	
$\begin{array}{ccccc} \mathrm{N1-H1N2\cdots03W} & 0.8600 & 2.4200 & 3.125(5) & 140.00 & 1/2 + x, \\ 3/2 - y, \\ 1/2 + z & & & & & & & & \\ 01W-H1W1\cdots03W & 0.8500 & 2.0500 & 2.869(5) & 162.00 & 1 + x, y, z & & \\ 02W-H2W1\cdots04W & 0.8500 & 2.0900 & 2.995(7) & 162.00 & x, 1 + y, z & & \\ 02W-H2W2\cdots03W & 0.8500 & 2.1900 & 2.937(5) & 147.00 & & & & & & & \\ 03W-H3W2\cdots02 & 0.8600 & 2.0000 & 2.814(5) & 157.00 & & & & & & & \\ 03W-H3W1\cdots05W & 0.8500 & 1.9200 & 2.770(7) & 179.00 & 1/2 - x, & & & & & & \\ 1/2 + y, & & & & & & & & & & \\ 03W-H3W1\cdots05W & 0.8500 & 1.9200 & 2.770(7) & 179.00 & 1/2 - x, & & & & & \\ 1/2 + y, & & & & & & & & & \\ 03W-H3W1\cdots05W & 0.9300 & 2.5800 & 3.114(6) & 117.00 & 3/2 - x, & & & & & \\ -1/2 + y, & & & & & & & & \\ 01W-H1W8\cdots04 & 0.8600 & 1.9400 & 2.790(9) & 174.00 & 1 - x, 1 - y, & & & \\ 01W-H1W8\cdots04 & 0.8600 & 1.9400 & 2.790(9) & 174.00 & 1 - x, 1 - y, & & & & \\ 01W-H1W8\cdots04 & 0.8600 & 2.3600 & 3.010(11) & 133.00 & 1/2 - x, & & & & \\ -1/2 + y, & & & & & & & & & \\ 02W-H2W8\cdots02 & 0.8500 & 2.2600 & 2.891(7) & 131.00 & 3/2 - x, & & & & \\ 02W-H2W8\cdots03 & 0.8500 & 2.4500 & 3.007(8) & 124.00 & & & & & \\ 02W-H2W8\cdots04 & 0.8500 & 2.3800 & 3.220(8) & 174.00 & & & & & & \\ N7-H7A\cdots12 & 0.8600 & 2.7400 & 3.211(6) & 116.00 & & & \\ N7-H7A\cdots02W & 0.8600 & 2.3600 & 3.078(9) & 141.00 & x, y, -1 + z & & \\ N7-H7B\cdots13 & 0.8600 & 2.7300 & 3.217(7) & 117.00 & & & & & & & & & & \\ C10-H10\cdots02 & 0.9300 & 2.4200 & 3.265(8) & 151.00 & 1 - x, 1 - y, & & & & & & & & & & & & & & & & & & $	N1-H1N2···I2	0.8600	2.7100	3.191(4)	117.00	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N1-H1N203W	0.8600	2.4200	3.125(5)	140.00	1/2 + x,
$\begin{array}{c} 1/2 + z \\ 1/2 + z \\ 01W-H1W1\cdots 03W \\ 0.8500 \\ 2.0900 \\ 2.905(7) \\ 162.00 \\ 2.905(7) \\ 162.00 \\ x, 1 + y, z \\ 02W-H2W2\cdots 03W \\ 0.8500 \\ 2.0900 \\ 2.937(5) \\ 147.00 \\ 03W-H3W2\cdots 02 \\ 0.8600 \\ 2.0000 \\ 2.814(5) \\ 157.00 \\ 03W-H3W2\cdots 02 \\ 0.8600 \\ 2.0000 \\ 2.814(5) \\ 157.00 \\ 03W-H3W1\cdots 05W \\ 0.8500 \\ 2.0000 \\ 2.814(5) \\ 157.00 \\ 1/2 - x, \\ 1/2 + y, \\ 3/2 - z \\ 03W-H3W1\cdots 05W \\ 0.8500 \\ 2.5800 \\ 3.114(6) \\ 117.00 \\ 3/2 - x, \\ -1/2 + y, \\ 3/2 - z \\ 01W-H1WA\cdots 04 \\ 0.8600 \\ 1.9400 \\ 2.790(9) \\ 174.00 \\ 1 - x, 1 - y, \\ 1/2 + z \\ 01W-H1WB\cdots N2 \\ 0.8600 \\ 2.3600 \\ 3.010(11) \\ 133.00 \\ 1/2 - x, \\ -1/2 + y, \\ 1/2 + z \\ 02W-H2WA\cdots 02 \\ 0.8500 \\ 2.2600 \\ 2.891(7) \\ 131.00 \\ 3/2 - x, \\ -1/2 + y, \\ 1/2 + z \\ 02W-H2WB\cdots 03 \\ 0.8500 \\ 2.3600 \\ 3.007(8) \\ 124.00 \\ 3.220(8) \\ 174.00 \\ N7-H7A\cdots 12 \\ 0.8600 \\ 2.3800 \\ 3.208(8) \\ 174.00 \\ N7-H7A\cdots 02W \\ 0.8600 \\ 2.3600 \\ 3.078(9) \\ 141.00 \\ x, y, -1 + z \\ N7-H7B\cdots 13 \\ 0.8600 \\ 2.7300 \\ 3.217(7) \\ 117.00 \\ (9-H9\cdots 02W \\ 0.9300 \\ 2.4200 \\ 3.265(8) \\ 151.00 \\ 1 - x, 1 - y, \\ -1/2 + z \\ (10-H10\cdots 02 \\ (0.9300 \\ 2.4500 \\ 3.178(8) \\ 128.00 \\ (15 - H15\cdots 01W \\ 0.9300 \\ 2.4500 \\ 3.189(12) \\ 136.00 \\ 1/2 + x, \\ 3/2 - y, z \\ \end{array}$						3/2 - y,
$\begin{array}{cccccccccccccccccccccccccccccccccccc$						1/2 + z
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	01W-H1W103W	0.8500	2.0500	2.869(5)	162.00	1 + x, y, z
$\begin{array}{ccccc} 02W-H2W2\cdots03W & 0.8500 & 2.1900 & 2.937(5) & 147.00 \\ 03W-H3W2\cdots02 & 0.8600 & 2.0000 & 2.814(5) & 157.00 \\ 03W-H3W1\cdots05W & 0.8500 & 1.9200 & 2.770(7) & 179.00 & 1/2 - x, \\ & & & & & & & & & & & \\ 1/2 + y, & & & & & & & & \\ 3/2 - z \\ C15-H15\cdots02W & 0.9300 & 2.5800 & 3.114(6) & 117.00 & 3/2 - x, \\ & & & & & & & & & & & \\ -1/2 + y, & & & & & & & \\ 3/2 - z \\ \hline C01W-H1WA\cdots04 & 0.8600 & 1.9400 & 2.790(9) & 174.00 & 1 - x, 1 - y, \\ & & & & & & & & & \\ 1/2 + z \\ O1W-H1WB\cdotsN2 & 0.8600 & 2.3600 & 3.010(11) & 133.00 & 1/2 - x, \\ & & & & & & & & & \\ -1/2 + y, & & & & & & \\ 1/2 + z \\ O2W-H2WA\cdots02 & 0.8500 & 2.2600 & 2.891(7) & 131.00 & 3/2 - x, \\ & & & & & & & & & & \\ 02W-H2WB\cdots03 & 0.8500 & 2.4500 & 3.007(8) & 124.00 \\ 02W-H2WB\cdots04 & 0.8500 & 2.3800 & 3.220(8) & 174.00 \\ N7-H7A\cdots12 & 0.8600 & 2.7300 & 3.217(7) & 117.00 \\ O2W-H2WB\cdots04 & 0.8500 & 2.3600 & 3.078(9) & 141.00 \\ N7-H7A\cdots02W & 0.8600 & 2.7300 & 3.217(7) & 117.00 \\ C9-H9\cdots02W & 0.9300 & 2.4200 & 3.265(8) & 151.00 & 1 - x, 1 - y, \\ & & & & & & & & & & & \\ -1/2 + z \\ C10-H10\cdots02 & 0.9300 & 2.4200 & 3.178(8) & 128.00 \\ C15-H15\cdots01W & 0.9300 & 2.4500 & 3.178(8) & 128.00 \\ C15-H15\cdots01W & 0.9300 & 2.4500 & 3.178(8) & 128.00 \\ C15-H15\cdots01W & 0.9300 & 2.4500 & 3.178(8) & 128.00 \\ C15-H15\cdots01W & 0.9300 & 2.4500 & 3.178(8) & 128.00 \\ C15-H15\cdots01W & 0.9300 & 2.4500 & 3.178(8) & 128.00 \\ C15-H15\cdots01W & 0.9300 & 2.4500 & 3.189(12) & 136.00 & 1/2 + x, \\ 3/2 - y, z \end{array}$	02W-H2W104W	0.8500	2.0900	2.905(7)	162.00	x, 1 + y, z
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	02W-H2W203W	0.8500	2.1900	2.937(5)	147.00	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	03W-H3W202	0.8600	2.0000	2.814(5)	157.00	
$\begin{array}{ccccc} 1/2 + y, & 3/2 - z \\ -1/2 + y, & 3/2 - z \\ -1/2 + y, & 3/2 - z \\ 01W-H1WA - 04 & 0.8600 & 1.9400 & 2.790(9) & 174.00 & 1 - x, 1 - y, \\ 1/2 + z \\ 01W-H1WB - N2 & 0.8600 & 2.3600 & 3.010(11) & 133.00 & 1/2 - x, \\ -1/2 + y, & 1/2 + z \\ 02W-H2WA - 02 & 0.8500 & 2.2600 & 2.891(7) & 131.00 & 3/2 - x, \\ -1/2 + y, & 1/2 + z \\ 02W-H2WB - 03 & 0.8500 & 2.4500 & 3.007(8) & 124.00 \\ 02W-H2WB - 04 & 0.8500 & 2.3800 & 3.220(8) & 174.00 \\ N7-H7A - 02W & 0.8600 & 2.7400 & 3.211(6) & 116.00 \\ N7-H7A - 02W & 0.8600 & 2.7300 & 3.217(7) & 117.00 \\ N7-H7A - 02W & 0.9300 & 2.4200 & 3.265(8) & 151.00 & 1 - x, 1 - y, \\ -1/2 + z \\ C10-H10 - 02 & 0.9300 & 2.5200 & 3.178(8) & 128.00 \\ C15-H15 - 01W & 0.9300 & 2.4500 & 3.189(12) & 136.00 & 1/2 + x, \\ 3/2 - y, z \end{array}$	03W-H3W105W	0.8500	1.9200	2.770(7)	179.00	1/2 - x,
$\begin{array}{cccccccccccccccccccccccccccccccccccc$						1/2 + y,
$\begin{array}{cccccccccccccccccccccccccccccccccccc$						3/2 - z
$\begin{array}{c} -1/2 + y, \\ 3/2 - z \end{array}$	C15-H15···O2W	0.9300	2.5800	3.114(6)	117.00	3/2 - x,
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$						-1/2 + y,
$\begin{array}{c ccc} Complex \ \textbf{2} \\ O1W-H1WA\cdots O4 \\ O1W-H1WB\cdots N2 \\ O2W-H2WA\cdots O2 \\ O2W-H2WA\cdots O2 \\ O2W-H2WB\cdots O3 \\ O2W-H2WB\cdots O3 \\ O2W-H2WB\cdots O4 \\ O2W-H2WB\cdots O4 \\ O2W-H2WB\cdots O4 \\ O2W-H2WB\cdots O4 \\ O3L02 \\ O3L02 \\ O2W-H2WB\cdots O4 \\ O3L02 \\ O$						3/2 - z
Complex 2OTW-H1WA···O40.86001.94002.790(9)174.00 $1 - x, 1 - y, 1/2 + z$ O1W-H1WB···N20.86002.36003.010(11)133.00 $1/2 - x, -1/2 + y, 1/2 + z$ O2W-H2WA···O20.85002.26002.891(7)131.00 $3/2 - x, -1/2 + y, 1/2 + z$ O2W-H2WB···O30.85002.45003.007(8)124.00O2W-H2WB···O40.85002.38003.220(8)174.00N7-H7A···120.86002.74003.211(6)116.00N7-H7A···130.86002.73003.217(7)117.00C9-H9···O2W0.93002.42003.265(8)151.00 $1 - x, 1 - y, -1/2 + z$ C10-H10···O20.93002.45003.178(8)128.001/2 + x, 3/2 - y, z	Complex 2					
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	01W - H1WA = 04	0.8600	1 9/00	2 700(0)	174.00	1 v 1 v
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0100-11100/1004	0.0000	1.5400	2.750(5)	174.00	1 - x, 1 - y, 1/2 + z
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	01W_H1WBN2	0.8600	2 3600	3 010(11)	133.00	1/2 - x
$\begin{array}{c} & 1/2 + y, \\ 1/2 + z \\ 02W - H2WA \cdots 02 \\ 02W - H2WB \cdots 03 \\ 02W - H2WB \cdots 03 \\ 02W - H2WB \cdots 04 \\ 08500 \\ 2.3800 \\ 2.4500 \\ 2.3800 \\ 3.220(8) \\ 174.00 \\ 02W - H2WB \cdots 04 \\ 0.8500 \\ 2.3800 \\ 3.220(8) \\ 174.00 \\ 0.8500 \\ 2.3800 \\ 3.220(8) \\ 174.00 \\ 174.00 \\ 0.8500 \\ 2.3800 \\ 3.220(8) \\ 174.00 \\ 174.00 \\ 0.9 \\ 141.00 \\ x, y, -1 + z \\ 0.9 \\ 141.00 \\ x, y, -1 + z \\ 0.9 \\ 141.00 \\ x, y, -1 + z \\ 0.9 \\ 141.00 \\ 1 - x, 1 - y, \\ -1/2 + z \\ 0.9 \\ 100 \\ 1 - x, 1 - y, \\ -1/2 + z \\ 0.9 \\ 100 \\ 1 - x, 1 - y, \\ -1/2 + z \\ 0.9 \\ 100 \\ 1 - x, 1 - y, \\ -1/2 + z \\ 0.9 \\ 100 \\ 1 - x, 1 - y, \\ -1/2 + z \\ 0.9 \\ 100 \\ 1 - x, 1 - y, \\ -1/2 + z \\ 0.9 \\ 100 \\ 1 - x, 1 - y, \\ -1/2 + z \\ 0.9 \\ 100 \\ 1 - x, 1 - y, \\ -1/2 + z \\ 0.9 \\ 100 \\ 1 - x, 1 - y, \\ -1/2 + z \\ 0.9 \\ 100 \\ 1 - x, 1 - y, \\ -1/2 + z \\ 0.9 \\ 100 \\ 1 - x, 1 - y, \\ -1/2 + z \\ 0.9 \\ 100 \\ 1 - x, 1 - y, \\ -1/2 + z \\ 0.9 \\ 100 \\ 1 - x, 1 - y, \\ -1/2 + z \\ 0.9 \\ 100 \\ 1 - x, 1 - y, \\ -1/2 + z \\ 0.9 \\ 100 \\ 1 - x, 1 - y, \\ -1/2 + z \\ 0.9 \\ 100 \\ 1 - x, 1 - y, \\ -1/2 + z \\ 0.9 \\ 100 \\ 1 - x, 1 - y, \\ -1/2 + z \\ 0.9 \\ 1 - x, 1 - y, \\ -1/2 + z \\ 0.9 \\ 1 - x, 1 - y, \\ -1/2 + z \\ 0.9 \\ 1 - x, 1 - y, \\ -1/2 \\ 1 - y, \\$	0100-111000-1112	0.8000	2.3000	5.010(11)	155.00	$\frac{1}{2} - \chi$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$						$\frac{1}{2} + y$ , $\frac{1}{2} + z$
02W H2WE $\cdot 03$ 0.8500         2.2500         2.051(7)         15130 $-1/2 + y, 1/2 + z$ 02W-H2WE $\cdot 03$ 0.8500         2.4500         3.007(8)         124.00           02W-H2WE $\cdot 04$ 0.8500         2.3800         3.220(8)         174.00           N7-H7A $\cdot 12$ 0.8600         2.7400         3.211(6)         116.00           N7-H7A $\cdot 02W$ 0.8600         2.7300         3.217(7)         117.00           C9-H9 $\cdot 02W$ 0.9300         2.4200         3.265(8)         151.00 $1 - x, 1 - y, -1/2 + z$ C10-H10 $\cdot \cdot 02$ 0.9300         2.4500         3.178(8)         128.00           C15-H15 $\cdot \cdot 01W$ 0.9300         2.4500         3.189(12)         136.00         1/2 + x, 3/2 - y, z	02W_H2WA02	0.8500	2 2600	2 891(7)	131.00	$\frac{1}{2} \cdot \frac{2}{2}$ $\frac{3}{2} - \frac{y}{2}$
$\begin{array}{c} 1/2 - y, \\ 1/2 + z \end{array}$ $02W - H2WB \cdots 03  0.8500  2.4500  3.007(8)  124.00 \\ 02W - H2WB \cdots 04  0.8500  2.3800  3.220(8)  174.00 \\ N7 - H7A \cdots 12  0.8600  2.7400  3.211(6)  116.00 \\ N7 - H7A \cdots 02W  0.8600  2.3600  3.078(9)  141.00  x, y, -1 + z \\ N7 - H7B \cdots 13  0.8600  2.7300  3.217(7)  117.00 \\ C9 - H9 \cdots 02W  0.9300  2.4200  3.265(8)  151.00  1 - x, 1 - y, \\ -1/2 + z \\ C10 - H10 \cdots 02  0.9300  2.5200  3.178(8)  128.00 \\ C15 - H15 \cdots 01W  0.9300  2.4500  3.189(12)  136.00  1/2 + x, \\ 3/2 - y, z \end{array}$	0210-1121011-02	0.0500	2,2000	2.031(7)	151.00	-1/2 + y
O2W-H2WBO3         0.8500         2.4500         3.007(8)         124.00           O2W-H2WBO4         0.8500         2.3800         3.220(8)         174.00           N7-H7A12         0.8600         2.7400         3.211(6)         116.00           N7-H7A02W         0.8600         2.3600         3.078(9)         141.00         x, y, $-1+z$ N7-H7B13         0.8600         2.7300         3.217(7)         117.00           C9-H902W         0.9300         2.4200         3.265(8)         151.00 $1-x, 1-y, -1/2+z$ C10-H1002         0.9300         2.5200         3.178(8)         128.00           C15-H1501W         0.9300         2.4500         3.189(12)         136.00         1/2 + x, 3/2 - y, z						$\frac{1}{2} + y$ , $\frac{1}{2} + z$
O2W-H2WBO4         0.8500         2.3800         3.220(8)         174.00           N7-H7AI2         0.8600         2.7400         3.211(6)         116.00           N7-H7AI2         0.8600         2.3600         3.078(9)         141.00         x, y, $-1+z$ N7-H7BI3         0.8600         2.7300         3.217(7)         117.00           C9-H9O2W         0.9300         2.4200         3.265(8)         151.00 $1-x, 1-y, -1/2+z$ C10-H10O2         0.9300         2.4500         3.178(8)         128.00           C15-H15O1W         0.9300         2.4500         3.189(12)         136.00         1/2 + x, 3/2 - y, z	02W-H2WB03	0 8500	2,4500	3 007(8)	124 00	1/2 . 2
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	02W-H2WB04	0.8500	2,3800	3 220(8)	174.00	
N7-H7A02W       0.8600       2.3600       3.078(9)       141.00 $x, y, -1 + z$ N7-H7B13       0.8600       2.7300       3.217(7)       117.00         C9-H902W       0.9300       2.4200       3.265(8)       151.00 $1 - x, 1 - y, -1/2 + z$ C10-H1002       0.9300       2.5200       3.178(8)       128.00         C15-H1501W       0.9300       2.4500       3.189(12)       136.00 $1/2 + x, 3/2 - y, z$	N7-H7A12	0.8600	2,7400	3 211(6)	116.00	
N7-H7B···I3       0.8600       2.7300       3.217(7)       117.00         C9-H9···02W       0.9300       2.4200       3.265(8)       151.00 $1-x, 1-y, -1/2+z$ C10-H10···02       0.9300       2.5200       3.178(8)       128.00         C15-H15···01W       0.9300       2.4500       3.189(12)       136.00 $1/2+x, -3/2-y, z$	N7-H7A02W	0.8600	2,3600	3.078(9)	141.00	x v - 1 + 7
C9-H902W         0.9300         2.4200         3.265(8)         151.00 $1 - x, 1 - y, -1/2 + z$ C10-H1002         0.9300         2.5200         3.178(8)         128.00           C15-H1501W         0.9300         2.4500         3.189(12)         136.00 $1/2 + x, 3/2 - y, z$	N7-H7B···I3	0.8600	2.7300	3.217(7)	117.00	,,,,
$\begin{array}{c} -1/2 + z \\ C10-H10\cdots 02 \\ C15-H15\cdots 01W \\ 0.9300 \\ 2.4500 \\ 3.189(12) \\ 136.00 \\ 1/2 + x, \\ 3/2 - y, z \end{array}$	C9-H902W	0.9300	2.4200	3.265(8)	151.00	1 - x, $1 - y$ .
C10-H1002 0.9300 2.5200 3.178(8) 128.00 C15-H1501W 0.9300 2.4500 3.189(12) 136.00 1/2 + x, 3/2 - y, z						-1/2 + z
C15-H15O1W 0.9300 2.4500 3.189(12) 136.00 1/2 + x, 3/2 - y, z	C10-H10···O2	0.9300	2.5200	3.178(8)	128.00	,
3/2 - y, z	C15-H1501W	0.9300	2.4500	3.189(12)	136.00	1/2 + x,
						3/2 - y, z

(btb). So, the coordination behavior of the metal nodes plays a significant role in the case.



Scheme 1. The conformations of the auxiliary ligand, btb, in complexes 1–2.



**Fig. 2.** (A) The coordination environment of Zn(II) and the conformation of btb in **2**. (B) Side view of 1D helical chain, where the dashed red and green lines represent  $\pi \cdots \pi$  stacking interactions and the halogen bonding (C8–I1…N5), respectively. (C) Schematic view of the 1D helical tube-like chain. The solid yellow line represents 2<sub>1</sub> helice. (D) Top view of 1D helical chain. (E) 3D supramolecular MOF formed by interchain hydrogen bonding (yellow dashed lines). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

# 3.5. FT-IR spectra and thermal stability

The FT-IR spectral data show features attributable to the carboxylate stretching vibrations of **1** and **2A**. The absence of bands

in the range of 1680–1760 cm<sup>-1</sup> indicates the complete deprotonation of H<sub>2</sub>ATIBDC in the two complexes. The characteristic bands of the carboxylate groups appear in the range 1552–1598 cm<sup>-1</sup> for the asymmetric stretching and 1384–1490 cm<sup>-1</sup> for the symmetric





stretching. The broad band at ca.  $3300 \text{ cm}^{-1}$  corresponds to the vibration of the  $-NH_2$  group in the ATIBDC<sup>2-</sup> ligand, and water molecules in the corresponding complexes **1** and **2A** [35].

To study the thermal stability of the compounds, the thermogravimetric analysis (TGA) was performed on all samples under a nitrogen atmosphere in flowing N<sub>2</sub> with a heating rate of 10 °C min<sup>-1</sup> (Fig. 3). Complex **1** exhibits a weight loss of 10.31% in the temperature range 30–140 °C, corresponding to the removal of both the coordinated and lattice water molecules (Calc. 9.64%). The second step begins at 248 °C and then followed by a long tail.

The weight loss of 1.96% from 85 to 148 °C corresponds to the release of one lattice water molecule, which further reveals that  $[Zn(ATIBDC)(btb)]\cdot 2H_2O$  (**2**) loses one lattice water molecule rapidly in the open air and changes into  $[Zn(ATIBDC)(btb)]\cdot H_2O$  (**2**A) (Calc. 2.16%). The second step begins from 295 °C and the whole decomposition process does not finish at 800 °C.

X-ray powder diffraction measurement further shows that the structure of **2A** is slightly different from that of **2** (Fig. 4).

#### 3.6. Fluorescent properties

The solid state fluorescent properties of the polymeric Zn(II) and Cd(II) complexes have been investigated at room temperature. To well-compare the fluorescent intensity of these compounds, we determined all the emission spectra with the same excitation wavelength. Excitation of the complexes at 290 nm leads to the generation of similar fluorescent emissions in **1** and **2A** (Fig. 5), with the same peaks occurring at 473 and 453 nm, although the intensities are different. To further understand the origin of these emission bands, the fluorescent spectrum of H<sub>2</sub>ATIBDC has also been measured. The free H<sub>2</sub>ATIBDC acid exhibits the nearly same emission ( $\lambda_{ex}$  = 290 nm) peaks as those in **1** and **2A**. These observa-



**Fig. 3.** The TG curves of complexes **1** (black) and **2** (red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 4**. PXRD patterns of **2** (black) simulated from the single-crystal data, (red) for the powder sample **2A**. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 5.** The emission spectra of H<sub>2</sub>ATIBDC (black), **1** (red), **2** (green) in the solid state at 298 K. The corresponding excitation wavelengths,  $\lambda_{ex}$ , is 290 nm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

tions suggest that the coordination of the ATIBDC<sup>2–</sup> ligand with Zn(II) and Cd(II) ions in the presence of btb auxiliary ligand has no influence on the emission mechanism of the metal–organic coordination polymers [36]. So, the emissions of the complexes **1** and **2A** may be assigned to an intraligand  $\pi \cdots \pi \ast$  transition [37]. The small differences of the peak intensities in **1** and **2A** are considered to be a result of the dissimilar coordination environments of the metal centers with the incorporation of co-ligands, which may also participate in the process of energy transfer involved in the fluorescence.

# 4. Conclusion

In summary, two d<sup>10</sup> metal–organic supramolecular complexes **1–2** with the ATIBDC<sup>2–</sup> ligand have been prepared and structurally characterized. These two complexes showed polymeric chain structures and possess extended 3D supramolecular architectures with the aid of supramolecular driving forces. The features of the ATIBDC<sup>2-</sup> ligand, strong ability of hydrogen/halogen bonding, have been embodied in these two complexes. Complex 2 gives an interesting example of an infinite single-walled tube-like chain constructed by using two kinds of polydentate ligands. The interesting characteristic embodied in **2** may provide a new means of constructing discrete 1D single-walled coordination tube through combination of appropriate polydentate ligands and metal ions. Three I atoms in H<sub>2</sub>ATIBDC play important roles in constructing the supramolecular architectures of 1-2. The studies further reveal that the halogen bonds  $(C-I \cdots \pi \text{ and } C-I \cdots O/N)$  are useful tools to construct supramolecular networks. The use of halogen bonding as supramolecular driving force opens up new insights to supramolecular synthesis. Initially, it is likely that the interest can be stimulated to develop a novel family of iodine-substituted aromatic polycarboxylate ligands as supporting spacers. Further synthesis of the related supramolecular complexes with the series of I-substituted aromatic polycarboxylate ligands are underway.

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

CCDC 743506 and 740001 for (1) and (2), respectively, contains 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.2010.12.038.

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