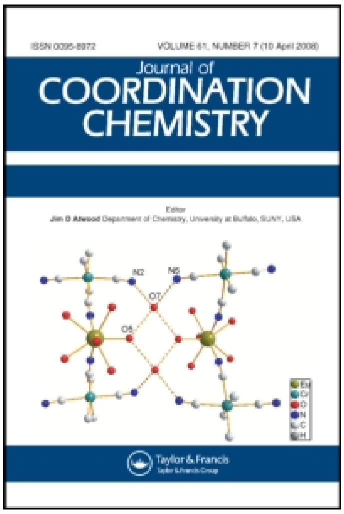

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Synthesis, structure and characterization of two Cd(II) coordination polymers with helical structures

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Synthesis, structure and characterization of two Cd(II) coordination polymers with helical structures

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Two coordination polymers, [Cd_2Cl_2(1,3-BDC)(TTBT)(H_2O)] (**1**) and [CdCl(1,4-HBDC)(TTBT)] (**2**) (1,3-BDC = 1,3-benzenedicarboxylate, 1,4-BDC = 1,4-benzenedicarboxylate, and TTBT = 10,11,12,13-tetrahydro-4,5,9,14-tetraaza-benzo[b]triphenylene), have been prepared under hydrothermal conditions and characterized by elemental analyses, IR spectra, thermal gravimetry (TG), fluorescence emission and single crystal X-ray diffraction analyses. The crystal structures were determined by X-ray diffraction and refined by full-matrix least-squares methods to $R = 0.0621$ and $wR = 0.1543$ using 4937 reflections with $I > 2\sigma(I)$ for **1**; and $R = 0.0525$ and $wR = 0.1427$ using 3386 reflections with $I > 2\sigma(I)$ for **2**. Compound **1** possesses a chiral chain structure. Adjacent chiral chains are further linked through π–π interactions between TTBT ligands to give a three-dimensional supramolecular architecture. Compound **2** displays a helical chain structure, with neighboring chains stacked by π–π interactions, generating an unusual three-dimensional supramolecular structure.

Keywords: Helical coordination polymers; Crystal structure; IR spectrum; Photoluminescence; TG

1. Introduction

Crystal engineering of metal-organic frameworks (MOFs) is of interest for potential applications in gas storage, chemical separations, microelectronics, nonlinear optics, and heterogeneous catalysis, and because of its intriguing structural diversity, new topologies and intricate entangled motifs [1–4]. Helical structures have received much attention in coordination chemistry and materials chemistry because helicity is an essence of life and also important in advanced materials such as optical devices, enantiomer separation, chiral synthesis, ligand exchange and selective catalysis [5]; many single-, double- and higher-order stranded helical complexes have been generated by self assembly [5]. Bridging ligands containing O-donors, for example multidentate aromatic

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polycarboxylate systems including 1,3-benzenedicarboxylate (1,3-BDC) and 1,4-benzenedicarboxylate (1,4-BDC), can connect metal ions in various modes [6]. Hence, 1,3-H_2BDC and 1,4-H_2BDC may be a good candidate for construction of helical coordination polymers. 1,10-Phenanthroline (phen) and its derivatives have numerous uses in construction of metal-organic complexes [7]. However, 10,11,12,13–tetrahydro-4,5,9,14-tetraaza-benzo[b]triphenylene (TTBT) as an important phen derivative has not been utilized in the construction of metal-organic coordination polymers. Two nitrogen atoms from a chelating TTBT ligand may occupy two coordination positions of central metals. The rest of the coordination positions are available for other carboxylate ligands to allow formation of a helix. Based on the above strategy, we selected 1,3-H_2BDC and 1,4-H_2BDC as bridging ligands and TTBT as a secondary chelating ligand to generate two new helical chain coordination polymers, [Cd_2Cl_2(1,3-BDC)(TTBT)H_2O] (**1**) and [CdCl(1,4-HBDC)(TTBT)] (**2**). The elemental analyses, IR, TG and photoluminescence of the two complexes were also studied.

2. Experimental

2.1. *Materials*

The TTBT ligand was synthesized by the literature method [7]. $CdCl_2 \cdot 2H_2O$, 1,3-H_2BDC, 1,4-H_2BDC and NaOH were purchased commercially and used without further purification.

2.2. *Syntheses*

2.2.1. Synthesis of [Cd_2Cl_2(1,3-BDC)(TTBT)(H_2O)] (1). A mixture of $CdCl_2 \cdot 2H_2O$ (0.114 g, 0.5 mmol), 1,3-H_2BDC (0.084 g, 0.5 mmol), TTBT (0.141 g, 0.5 mmol), NaOH (0.008 g, 0.2 mmol) and deionized water (15 mL) was heated to 180°C for 72 h in a 25 mL Teflon-lined stainless steel vessel under autogenous pressure. Subsequently, it was cooled to room temperature at a rate of $10^{\circ}C\,h^{-1}$. Yellow crystals of **1** were isolated by filtration and washed with water and dried at ambient temperature (36% yield based on Cd(II)). Anal. Calcd for $C_{44}H_{34}Cd_2Cl_2N_8O_5$ (%): C, 50.26; H, 3.24; N, 10.66. Found (%): C, 50.77; H, 2.98; N, 10.10.

2.2.2. Synthesis of [CdCl(1,4-HBDC)(TTBT)] (2). Compound **2** was synthesized by a method similar to that of **1** using 1,4-H_2BDC (0.084 g, 0.5 mmol) instead of 1,3-H_2BDC as the bridging ligand. Yellow crystals of **2** were collected in 44% yield based on Cd(II). Anal. Calcd for $C_{26}H_{19}CdClN_4O_4$: C, 52.06; H, 3.17; N, 9.35. Found: C, 52.81; H, 3.03; N, 9.96.

2.3. *General characterization and physical measurements*

Elemental analysis was carried out with a Perkin-Elmer 240°C analyzer; IR spectra were obtained on a Perkin-Elmer 2400LSII spectrometer; thermal gravimetric measurements

Table 1. Crystal data and structure refinements for **1** and **2**.

Compound	**1**	**2**
Formula	$C_{44}H_{34}Cd_2Cl_2N_8O_5$	$C_{26}H_{19}CdClN_4O_4$
Formula weight	1050.49	599.30
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/n$
a (Å)	13.9224(18)	10.772(4)
b (Å)	16.178(2)	14.381(5)
c (Å)	20.989(3)	14.801(6)
β (°)	90	93.416(5)
V (Å^3)	4727.6(10)	2288.9(15)
Z	4	4
$R1$ ($I>2\sigma(I)$)	0.0621	0.0525
$wR2$ ($I>2\sigma(I)$)	0.1543	0.1427
D_c (g cm^{-3})	1.476	1.739
F(000)	2096	1200
μ (Mo-Kα, mm^{-1})	1.063	1.114
Reflections collected	40756	19463
Unique reflections	9279	4544
Observed reflections [$I>2\sigma(I)$]	4937	3386

(TG) were performed on a NETZSCH STA 449°C analyzer; visible luminescence properties of the ligands and complexes were measured on a Perkin-Elmer LS55 spectrometer. Crystallographic data of **1** and **2** were collected at room temperature on a Bruker-AXS Smart CCD diffractometer equipped with a normal-focus, 2.4 kW X-ray source (graphite-monochromated Mo-Kα radiation with $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA with increasing ω (width of 0.3° and exposure time 30 s per frame). Both structures were solved by direct methods using SHELXS-97 [8] and refined by full-matrix least-squares techniques against F^2 using the SHELXTL-97 [9] crystallographic software package. All non-hydrogen atoms were easily found from the difference Fourier map and refined anisotropically; hydrogen atoms of the organic molecules were placed by geometrical considerations and added to the structure factor calculation. The detailed crystallographic data and structure refinement parameters for **1** and **2** are summarized in table 1.

3. Results and discussion

3.1. *Description of crystal structures*

3.1.1. [Cd_2Cl_2(1,3-BDC)(TTBT)(H_2O)] (1). Selected bond distances and angles for compounds **1** and **2** are listed in table 2. Compound **1** possesses a 1-D chiral chain structure with the asymmetric unit consisting of two Cd(II) atoms, two TTBT molecules, one 1,3-BDC and two coordinated μ_2 chlorides. As shown in figure 1a, the Cd1 is coordinated to two μ_2 chlorides (Cd1–Cl1 = 2.635(3) and Cd1–Cl2 = 2.586(3) Å), two TTBT nitrogens (Cd1–N1 = 2.380(9) and Cd1–N2 = 2.352(8) Å), and two oxygens from one carboxylate group of 1,3-BDC ligand (Cd1–O4A = 2.231(7) and Cd1–O1W = 2.391(7) Å) and one water in a distorted octahedron. Cd2 has a similar coordination environment, also bound to two μ_2 chlorides (Cd2–Cl1 = 2.550(3) and

Table 2. Selected bond distances (Å) and angles (°) for **1** and **2**.

$[Cd_2Cl_2(1,3\text{-BDC})(TTBT)(H_2O)]$ (**1**)			
N(1)–Cd(1)	2.380(9)	N(2)–Cd(1)	2.352(8)
N(5)–Cd(2)	2.324(8)	N(6)–Cd(2)	2.346(8)
O(1)–Cd(2)	2.350(8)	O(2)–Cd(2)	2.351(7)
O(1W)–Cd(1)	2.391(7)	Cd(1)–O(4)#1	2.231(7)
Cd(1)–Cl(2)	2.586(3)	Cd(1)–Cl(1)	2.635(3)
Cd(2)–Cl(1)	2.550(3)	Cd(2)–Cl(2)	2.557(4)
O(4)#1–Cd(1)–N(2)	160.2(3)	O(4)#1–Cd(1)–N(1)	90.6(3)
N(2)–Cd(1)–N(1)	70.3(3)	O(4)#1–Cd(1)–O(1W)	91.1(3)
N(2)–Cd(1)–O(1W)	85.6(3)	N(1)–Cd(1)–O(1W)	94.7(3)
O(4)#1–Cd(1)–Cl(2)	103.7(3)	N(2)–Cd(1)–Cl(2)	95.5(2)
N(1)–Cd(1)–Cl(2)	165.7(2)	O(1W)–Cd(1)–Cl(2)	85.3(2)
O(4)#1–Cd(1)–Cl(1)	89.8(2)	N(2)–Cd(1)–Cl(1)	96.0(2)
N(1)–Cd(1)–Cl(1)	92.6(2)	O(1W)–Cd(1)–Cl(1)	172.6(2)
Cl(2)–Cd(1)–Cl(1)	87.29(11)	N(5)–Cd(2)–N(6)	71.3(3)
N(5)–Cd(2)–O(1)	98.8(3)	N(6)–Cd(2)–O(1)	85.9(3)
N(5)–Cd(2)–O(2)	150.1(3)	N(6)–Cd(2)–O(2)	91.2(3)
O(1)–Cd(2)–O(2)	54.8(3)	N(5)–Cd(2)–Cl(1)	98.1(2)
N(6)–Cd(2)–Cl(1)	169.4(2)	O(1)–Cd(2)–Cl(1)	95.6(2)
O(2)–Cd(2)–Cl(1)	98.2(2)	N(5)–Cd(2)–Cl(2)	99.8(3)
N(6)–Cd(2)–Cl(2)	92.3(3)	O(1)–Cd(2)–Cl(2)	159.7(2)
O(2)–Cd(2)–Cl(2)	105.1(2)	Cl(1)–Cd(2)–Cl(2)	89.77(10)
$[CdCl(1,4\text{-HBDC})(TTBT)]$ (**2**)			
N(1)–Cd(1)	2.326(5)	N(2)–Cd(1)	2.370(5)
O(1)–Cd(1)	2.405(4)	O(2)–Cd(1)	2.345(4)
Cl(1)–Cd(1)	2.319(5)	O(3)–Cd(1)	2.182(4)
O(3)–Cd(1)–Cl(1)	90.27(18)	O(3)–Cd(1)–N(1)	158.81(17)
Cl(1)–Cd(1)–N(1)	90.52(18)	O(3)–Cd(1)–O(2)	105.24(17)
Cl(1)–Cd(1)–O(2)	144.52(17)	N(1)–Cd(1)–O(2)	86.00(17)
O(3)–Cd(1)–N(2)	90.85(17)	Cl(1)–Cd(1)–N(2)	122.83(17)
N(1)–Cd(1)–N(2)	71.06(16)	O(2)–Cd(1)–N(2)	89.26(17)
O(3)–Cd(1)–O(1)	111.99(16)	Cl(1)–Cd(1)–O(1)	89.13(16)
N(1)–Cd(1)–O(1)	89.20(16)	O(2)–Cd(1)–O(1)	55.56(15)
N(2)–Cd(1)–O(1)	141.32(16)		

Symmetry codes for (**1**): #1 $-x+1$, $y-1/2$, $-z+1/2$.

Cd2–Cl2 = 2.557(4) Å) and two nitrogens from one TTBT (Cd2–N5 = 2.324(8) and Cd2–N6 = 2.346(8) Å). The remaining two coordination sites of the octahedron are filled by two carboxylate oxygens (Cd2–O1 = 2.350(8) and Cd2–O2 = 2.351(7) Å) from 1,3-BDC [figure 1(a)]. As depicted in figure 1(b) and (c), two μ_2 chlorides bridge two adjacent Cd(II) centers to form a $[Cd_2Cl_2]^{2-}$ unit. The 1,3-BDC ligands further link neighboring $[Cd_2Cl_2]^{2-}$ units to result in an interesting chiral chain, where the Cd–Cd–Cd angle, defined by the orientations of the 1,3-BDC ligand and chloride in the chain, is 98.5°. The TTBT ligands are extended on both sides of the chiral chains. In addition, there exist π–π interactions between the TTBT ligands of neighboring chains (centroid-to-centroid distance of 3.72 Å, face-to-face distance of 3.52 Å, and dihedral angle of 8.01°). As a result, the chiral chains are connected by the π–π interactions to form 3-D supramolecular structures [figure 1(d)]. It should be noted that chiral coordination compounds have been widely reported, however, metal-organic coordination polymers with a chiral chain are relatively rare [5].

3.1.2. [CdCl(1,4-HBDC)(TTBT)] (2). X-ray single crystal diffraction analysis shows that **2** features a helical chain structure. The asymmetric unit of **2** consists of one

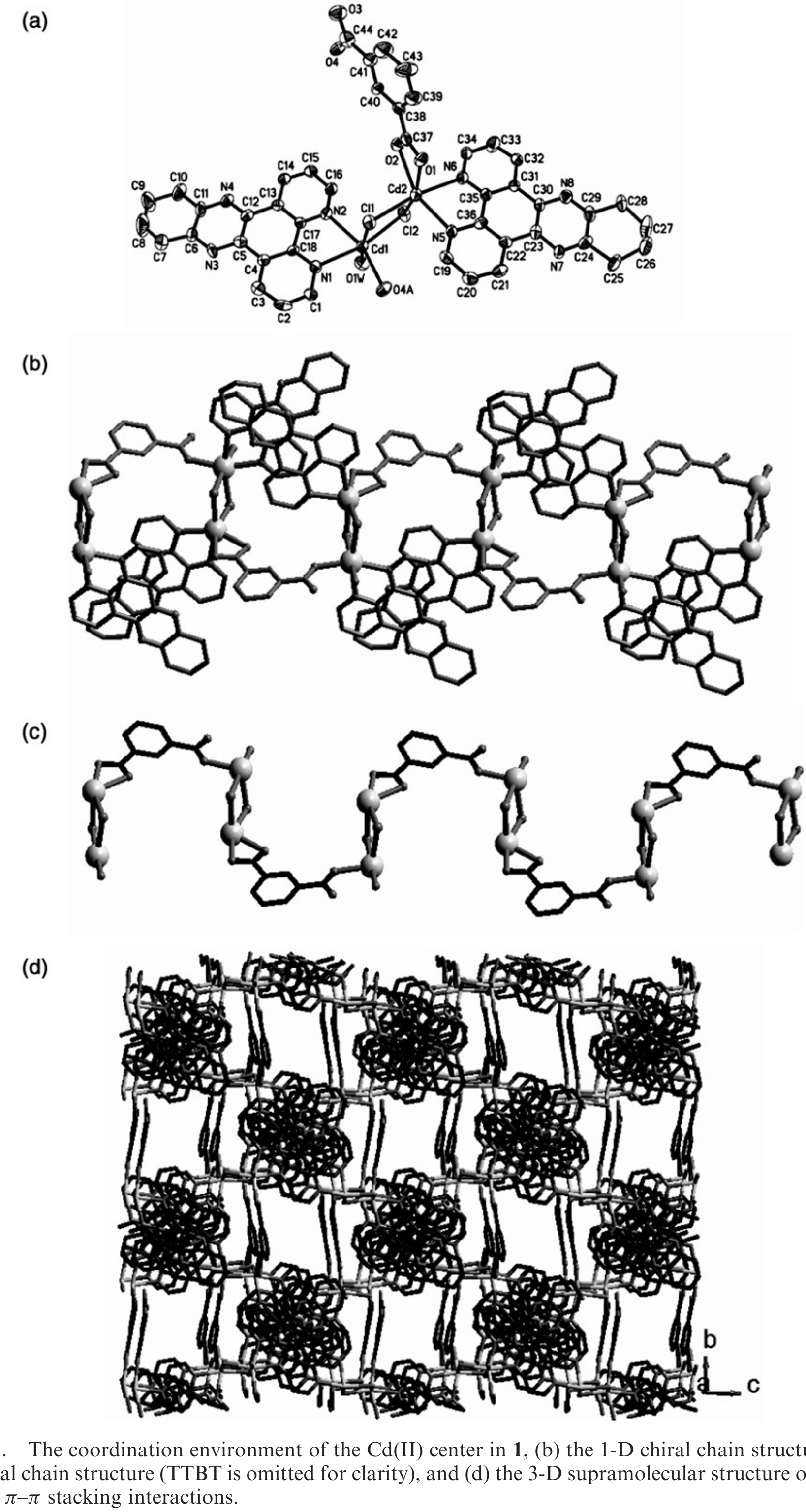

Figure 1. The coordination environment of the Cd(II) center in **1**, (b) the 1-D chiral chain structure, (c) the 1-D chiral chain structure (TTBT is omitted for clarity), and (d) the 3-D supramolecular structure of **1** formed through π–π stacking interactions.

Cd(II), one TTBT molecule, two 1,4-HBDC ligands, and one coordinated μ_2 chloride [figure 2(a)]. Each cadmium is six-coodinate with two nitrogens (Cd1–N1 = 2.326(5) and Cd1–N2 = 2.370(5) Å) from one TTBT ligand, one chloride (Cd1–Cl1 = 2.319(5) Å) and three carboxylate oxygens (Cd1–O1 = 2.405(4), Cd1–O2 = 2.345(4) and Cd1–O3 = 2.182(4) Å) from two 1,4-HBDC ligands in a distorted octahedral coordination [figure 2(a)]. Adjacent Cd(II) atoms are bridged by 1,4-HBDC ligands to form a helical chain with the Cd–Cd distance of 11.50 Å. The TTBT ligands are attached on both sides of the helical chain [figure 2(b)]. There are two types of π–π interactions: one exists between two TTBT ligands (centroid separation = 3.47 Å), while the other exists between the TTBT and 1,4-HBDC ligands (centroid separation = 3.52 Å). Consequently, neighboring helical chains are linked by π–π interactions to generate a three-dimensional supramolecular structure (centroid-to-centroid distance of 3.61 Å, face-to-face distance of 3.42 Å, and dihedral angle of 4.11°) [figure 2(c)]. Compounds **1** and **2** were synthesized under the same conditions, but two different structures with chiral and helical chains were formed. The result reveals that the carboxylate positions play an important role on complex constructions. From the structures of **1** and **2**, we also see that the π–π stacking not only stabilizes the 3-D supramolecular architectures, but also leads to formation of the helical structures.

3.2. *IR spectra of 1 and 2*

The IR spectra of the two compounds are provided in Supplementary Material. The peak at 3415 $\mathrm{cm^{-1}}$ can be attributed to O–H stretching of the coordinated water molecule in the polymer **1**. The peak at 1368 $\mathrm{cm^{-1}}$ for **1** and 1381 $\mathrm{cm^{-1}}$ for **2** are ascribed to ν(C=N) vibrations of the azine aromatic ring. For **1** and **2**, **t**he C–H stretching mode for the phenyl ring is relatively weak at 3020 $\mathrm{cm^{-1}}$. Peaks at about 1630 and 1560 $\mathrm{cm^{-1}}$ could be attributed to ν(C=C) vibration of aromatic ring [10]. The signals of 1414 and 1395 $\mathrm{cm^{-1}}$ can be assigned to ν(C=O).

3.3. *Thermal stability analysis*

TG curves have been obtained in air for crystalline samples of these two complexes in the temperature range 35 to 900°C (Supplementary Material); the TG curves of **1** and **2** exhibit similar weight loss stages. The first weight loss of 1.83% corresponding to removal of coordinated water molecule was observed over the wide temperature range 35–227°C for **1** (Calcd 1.72%). The second weight loss of 15.94% in the range 227–495°C was assigned to decomposition of 1,3-BDC (Calcd 16.21%). The third weight loss of 27.97% is ascribable to loss of TTBT (Calcd 27.23%) from 495 to 630°C. For **2**, the first weight loss is 28.23% in the temperature range 245–510°C, assigned to decomposition of 1,4-HBDC (Calcd 27.72%). The second weight loss of 48.33% is ascribable to loss of TTBT (Calcd 47.75%) from 510 to 660°C. Although the structures of **1** and **2** are very similar, the TGA of **1** and **2** are different. We believe that π–π stacking modes are the main reasons that lead to the difference in their TGA.

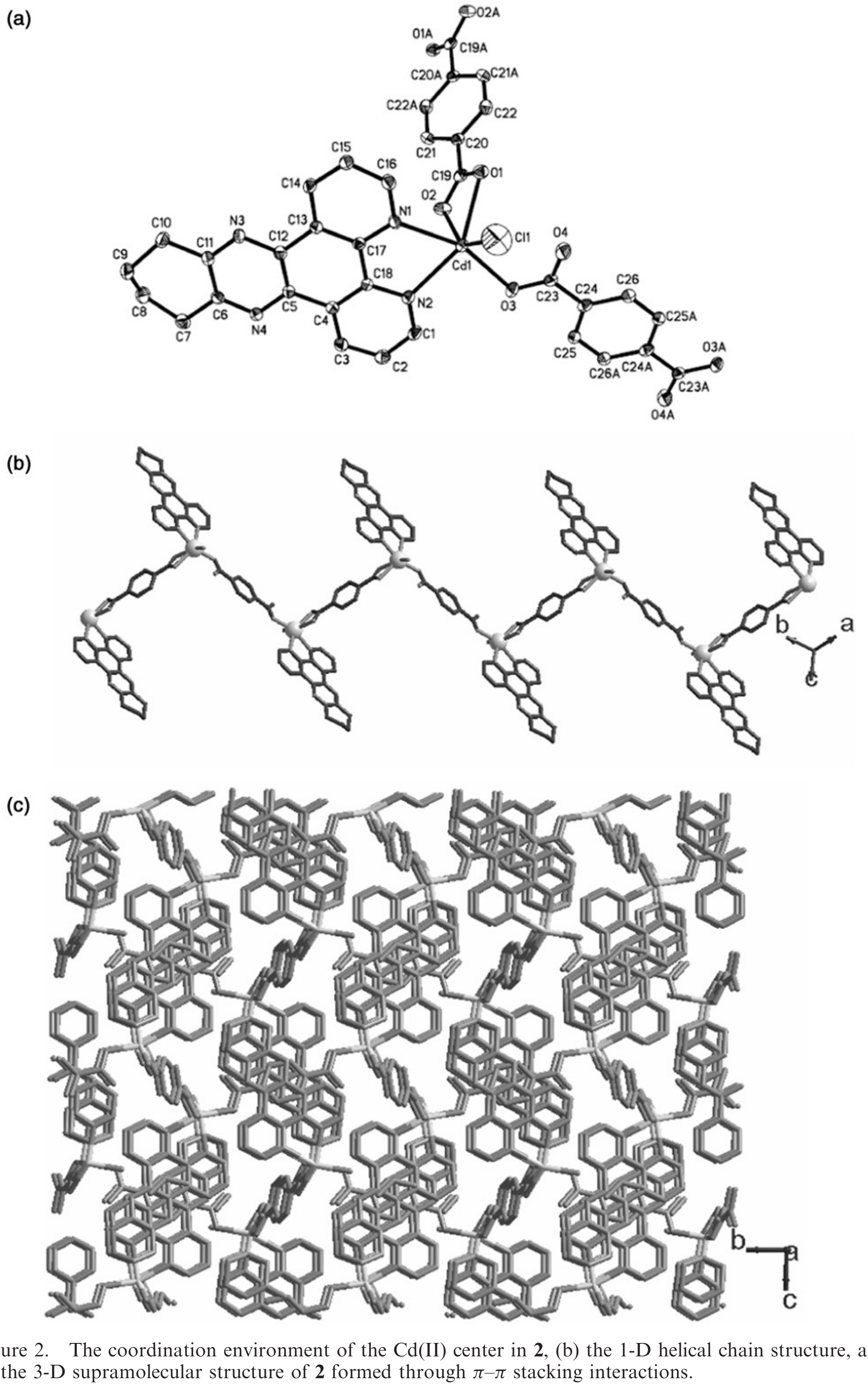

Figure 2. The coordination environment of the Cd(II) center in **2**, (b) the 1-D helical chain structure, and (c) the 3-D supramolecular structure of **2** formed through π–π stacking interactions.

3.4. *Fluorescent properties*

Coordination polymers containing Cd(II) exhibit photoluminescent properties [6]. The photoluminescent emission properties of **1** and **2** were investigated in the solid state at room temperature. The solid-state excitation-emission spectra of the free 1,3-H_2BDC and 1,4-H_2BDC ligands show the strongest emission peaks at about 382 and 378 nm, respectively [6]. The emission peaks for these free ligands may be attributable to the $\pi^* \rightarrow n$ or π–π transitions. Compared to the free ligands, the strongest emission peaks for **1** and **2** are at 525 and 531 nm (excitation at 367 nm, Supplementary Material), respectively, and the emissions arising from the free ligands are not observable for these two compounds. The absence of ligand-based emission suggests energy transfer from the ligands to the Cd(II) centers during photoluminescence [11]. Thus, the photoluminescence can be attributed to the ligand-to-metal charge-transfer (LMCT) transitions [12]. Compounds **1** and **2** may be good candidates for photoactive materials due to their strong fluorescent emissions.

The fluorescence quantum yields (Φ_F) of **1** (0.05) and **2** (0.06) [13] were determined using quinine sulfate ($\Phi_{ST} = 0.54$) as a standard according to the reported measurement method [13], according to the following equation:

$$\Phi_X = \Phi_{ST}\left(\frac{\mathrm{Grad}_X}{\mathrm{Grad}_{ST}}\right)\left(\frac{\eta_X^2}{\eta_{ST}^2}\right)\Bigg|$$

where the subscripts ST and X denote standard and test, respectively, Φ is the fluorescence quantum yield, Grad the gradient from the plot of integrated fluorescence intensity *vs* absorbance, and η the refractive index of the solvent. $\Phi_{ST} = 0.54$; $\eta_X = 1.478$ (DMSO); $\eta_{ST} = 1.337$ (0.2 mol L^{-1} H_2SO_4); X = 1, $\lambda_{ex} = 360$ nm, $\mathrm{Grad}_1/\mathrm{Grad}_{ST} = 0.0758$; X = 2, $\lambda_{ex} = 363$ nm, $\mathrm{Grad}_2/\mathrm{Grad}_{ST} = 0.0910$.

4. Conclusions

Two Cd(II) coordination polymers have been synthesized under hydrothermal conditions. Compound **1** possesses an interesting chiral chain structure, whereas **2** displays a helical chain structure. The structure variation of **1** and **2** depends primarily on the difference of carboxylate ligands. Also, the TTBT ligand played an important role in the formation of 3-D supramolecular architectures of **1** and **2**. The photoluminescence spectroscopy analyses indicate that the two compounds are good candidates for photoactive materials.

Supplementary material

The crystallographic data have been deposited at the Cambridge Crystallographic Data Centre, CCDC Nos 657291 for **1** and 657292 for **2**. Copies of this information may be obtained free of charge from the director, CCDC, 12 Union Road, Cambridge, CB2

IEZ, UK (E-mail: deposit@ccdc.cam.ac.uk; Fax: 44-1223-336-033; http://www.ccdc.cam.ac.uk).

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