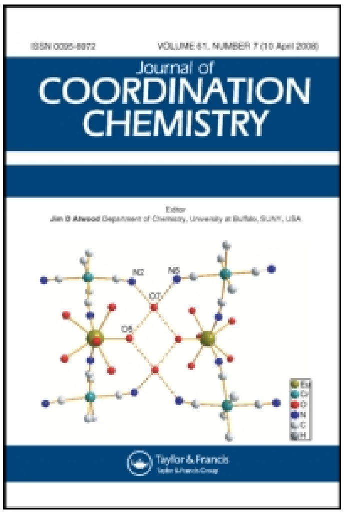

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Supramolecular structures of CdX_2-containing coordination compounds constructed by C-H ··· X synthons

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Supramolecular structures of CdX_2-containing coordination compounds constructed by C–H ··· X synthons

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Three CdX_2-containing $(X = Cl, Br)$ compounds $[CdBr_2(Him)_2]_n$ (Him = imidazole) (**1**), $[CdCl_2(2,2'\text{-bipy})]_n$ (2,2′-bipy = 2,2′-bipyridine) (**2**), and $[CdCl_2(phen)]$ (phen = phenanthroline) (**3**) have been synthesized through hydrothermal technique. Compound **1** adopts 1-D coordination chain, which is connected to form a 3-D supramolecular network by inter-chain N–H ··· Br and C–H ··· Br hydrogen bonds. Compound **2** also adopts 1-D coordination chain, which is connected to form 3-D supramolecular network by intra- and inter-chain C–H ··· Cl hydrogen bonds; **3** is discrete, linked to form 2-D supramolecular sheets by intra- and inter-molecular C–H ··· Cl hydrogen bonds. The different volume and coordination ability of organic ligands result in the different coordination structure and supramolecular synthons. All these compounds exhibit strong fluorescence emissions at room temperature.

Keywords: Crystal structure; C–H ··· X synthons; Supramolecular network; Fluorescence emission

1. Introduction

Intermolecular forces have importance in determining 3-D structures of proteins, DNA, and enzyme-substrate complexes, and in designing new materials [1]. These forces range from strong forces such as classical hydrogen bonds [2] to weaker ones such as halogen bonds [3], non-classical hydrogen bonds [4], halogen ··· halogen interactions [5] and π–π stacking [6]. Hydrogen bond is the most reliable design element in crystal engineering since it is directional.

Classical hydrogen bonds (O ··· H–O, N ··· H–O, and O ··· H–N) have been employed in supramolecular assemblies [7]; hydrogen bonds involving halogens have attracted less attention. Metal-bound chlorine and fluorine as well as halide ions are good hydrogen bond acceptors with O–H and N–H donors [8]. C–H ··· X interactions are even weaker than weak O–H ··· Cl and N–H ··· Cl hydrogen bonds because the donor is much less electronegative [9]. Nangia and coworkers statistically analyzed the crystallography databases and concluded that C–H ··· Cl and C–H ··· Cl–M often exist [10]. For example, some neutral $M^{II}Cl_2$-containing $[M = Co, Cu, \text{and } Zn]$ discrete

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coordination complexes of chelating organic ligands act as supramolecular synthons of variable metal coordination geometries to construct supramolecules with primarily weak C–H $\cdots$ Cl hydrogen bonds [11, 12]. Coordination polymer formation, imparted by a rigid coordination network, and ligand-based C–H $\cdots$ Cl interactions provided by softer hydrogen-bond interactions allows a combination of strength. Weaker C–H $\cdots$ X (X = Cl, Br) hydrogen bonds can also be structure-determining factors in inorganic–organic hybrid assemblies. In this work, we report two 1-D coordination polymers $[CdBr_2(Him)_2]_n$ (**1**), $[CdCl_2(2,2'\text{-bipy})]_n$ (**2**), and one discrete coordination compound $[CdCl_2(phen)]$ (**3**), which were all connected to high dimensional supramolecular networks by C–H $\cdots$ X (X = Cl, Br) or N–H $\cdots$ Br hydrogen-bonding interactions.

2. Experimental

2.1. *General*

Reagents were purchased commercially and used without purification. The elemental analyses were conducted on a Perkin–Elmer 2400 elemental analyzer. Infrared spectra were measured as KBr disks with a Perkin–Elmer spectrometer in the 4000–400 cm^{-1} region. Fluorescence data were collected on an Edinburgh FS900 instrument.

2.2. *Synthesis of $[CdBr_2(Him)_2]_n$ (1)*

Compound **1** was hydrothermally synthesized from a mixture of $3CdSO_4 \cdot 8H_2O$ (0.38 g, 0.67 mmol), NaBr (0.62 g, 6 mmol), imidazole (0.2 g, 3 mmol), and H_2O (15 mL) with pH about 5.0 (adjusted by 0.1 M HCl) at 170°C for 3 days. Then, the reactant mixture was cooled to room temperature to give a 78% yield (based on Cd) of **1** as colorless needles which were collected by mechanical isolation and washed with water. $C_6H_8Br_2CdN_4$ (408.38): Calcd C, 17.63; H, 1.96; N, 13.71; found C, 17.56; H, 2.01; N, 14.04%. IR (cm^{-1}, KBr pellet): 3130(m), 2959(m), 1614(m, br), 1537(s), 1502(m), 1486(s), 1433(s), 1325(s), 1258(s), 1170(m), 1132(s), 1101(s), 1064(s), 938(s), 918(m), 848(s), 761(s), 716(s), 648(s), 611(s).

2.3. *Synthesis of $[CdCl_2(2,2'\text{-bipy})]_n$ (2)*

Compound **2** was synthesized in the same way as **1** with $CdCl_2 \cdot 2.5H_2O$ (0.45 g, 2 mmol), malic acid (0.27 g, 2 mmol), 2,2′-bipy (0.32 g, 2 mmol), and H_2O (15 mL) with pH about 5.0. Colorless needles of **2** were obtained (about 80% yield based on Cd). $C_5H_4Cd_{0.5}ClN$ (169.74): Calcd C, 35.35; H, 2.36; N, 8.25; found C, 35.76; H, 2.29; N, 8.32%. IR (cm^{-1}, KBr pellet): 3050(w), 1627(m), 1592(s), 1476(m), 1440(s), 1316(w), 1247(w), 1170(m), 1054(w), 773(s), 735(m), 648(w).

2.4. *Synthesis of $CdCl_2(phen)_2$ (3)*

Compound **3** was synthesized in the same way as **1** with the reaction mixture of $CdCl_2 \cdot 2.5H_2O$ (0.45 g, 2 mmol), terephthalic acid (0.35 g, 2 mmol), phen

Table 1. Crystal data collection and structure refinement for **1**–**3**.

	1	**2**	**3**
Empirical formula	$C_6H_8Br_2CdN_4$	$C_5H_4Cd_{0.5}ClN$	$C_{24}H_{16}CdCl_2N_4$
Formula weight	408.38	169.74	543.71
Temperature (K)	239(2)	239(2)	239(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*P2(1)/n*	*C2/c*	*P2(1)/c*
Units cell dimensions (Å, °)			
a	8.4129(15)	17.5432(14)	9.6149(8)
b	13.712(2)	9.3054(7)	15.1556(10)
c	9.2099(16)	7.1653(6)	14.6453(9)
β	93.960(3)	110.9180(10)	99.502(5)
V (Å^3)	1059.9(3)	1092.62(15)	2104.8(3)
Z	4	8	4
ρ_{Calcd} (g cm^{-3})	2.559	2.064	1.716
$F(000)$	760	656	1081
Data/restraints/parameters	2581/0/118	1244/0/69	5325/0/344
Goodness-of-fit on F^2	1.125	1.329	1.044
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0652$ $wR_2 = 0.0931$	$R_1 = 0.0372$ $wR_2 = 0.919$	$R_1 = 0.0308$ $WR_2 = 0.0692$
Largest difference peak and hole (e Å^{-3})	0.766 and −4.557	0.551 and −1.673	0.650 and −0.705

(0.36 g, 2 mmol), and H_2O (15 mL) with pH about 5.0. Colorless needles of **3** were obtained (about 62% yield based on Cd). $C_{24}H_{16}CdCl_2N_4$ (543.71): Calcd C, 53.07; H, 2.95; N, 10.32; found C, 53.56; H, 2.83; N, 10.40%. IR (cm^{-1}, KBr pellet): 3053(m), 1620(s), 1580(s), 1509(s), 1420(s), 1341(m), 1133(w), 1094(w), 1007(w), 851(s), 782(m), 724(s), 631(m).

2.5. *X-ray crystallography*

X-ray single-crystal data collections for **1**–**3** were carried out at 293 K on a Siemens SMART system equipped with a CCD detector with Mo-Kα radiation at 0.71073 Å. The structures were solved by conventional methods and refined with full-matrix least-squares using SHELXS-97 and SHELXP-97 programs, respectively. Anisotropic thermal parameters were applied to all non-hydrogen atoms. Hydrogens for **1** and **2** were fixed geometrically and not refined. For **3**, hydrogen bonds were determined from Fourier maps. Further details of the X-ray structural analysis are given in table 1. Selected bond lengths and angles for **1**–**3** are given in table 2.

3. Results and discussion

3.1. *Crystal structure of [$CdBr_2(Him)_2]_n$ (1)*

A single crystal X-ray diffraction study reveals that **1** adopts a 3-D supramolecular structure. As shown in figure 1, each Cd center is six coordinate with four Br and two nitrogens from two Him ligands. Br1 bridges two Cd centers to form rhombic $CdBr_2$

Table 2. Selected bond lengths (Å) and angles (°) of **1**–**3**.

1			
Cd(1)–N(1)	2.253(5)	Cd(1)–N(3)	2.253(5)
Cd(1)–Br(2)	2.9216(9)	Cd(1)–Br(1)	2.9109(9)
Cd(1)–Br(1)#1	2.8288(9)	Cd(1)–Br(2)#2	2.8478(9)
N(3)–Cd(1)–N(1)	179.06(15)	N(3)–Cd(1)–Br(2)#1	90.31(12)
N(1)–Cd(1)–Br(2)#1	89.86(11)	N(3)–Cd(1)–Br(1)#2	91.16(12)
N(1)–Cd(1)–Br(1)#2	88.66(11)	Br(2)#1–Cd(1)–Br(1)#2	178.23(2)
N(3)–Cd(1)–Br(1)	90.97(11)	N(1)–Cd(1)–Br(1)	89.94(11)
Br(2)#1–Cd(1)–Br(1)	95.10(3)	Br(1)#2–Cd(1)–Br(1)	85.88(3)
N(3)–Cd(1)–Br(2)	89.87(11)	N(1)–Cd(1)–Br(2)	89.22(11)
Br(2)#1–Cd(1)–Br(2)	86.23(3)	Br(1)#2–Cd(1)–Br(2)	92.78(3)
Br(1)–Cd(1)–Br(2)	178.428(19)		
2			
Cd(1)–N(1)	2.352(2)	Cd(1)–Cl(1)	2.5497(8)
Cd(1)–Cl(1)#2	2.7513(9)		
N(1)–Cd(1)–N(1)#1	70.00(12)	N(1)–Cd(1)–Cl(1)	160.26(7)
N(1)#1–Cd(1)–Cl(1)	94.28(6)	N(1)–Cd(1)–Cl(1)#1	94.28(6)
N(1)#1–Cd(1)–Cl(1)#1	160.26(7)	Cl(1)–Cd(1)–Cl(1)#1	103.35(4)
N(1)–Cd(1)–Cl(1)#2	85.34(6)	N(1)#1–Cd(1)–Cl(1)#2	95.71(6)
Cl(1)–Cd(1)–Cl(1)#2	84.43(3)	Cl(1)#1–Cd(1)–Cl(1)#2	94.78(3)
N(1)–Cd(1)–Cl(1)#3	95.71(6)	N(1)#1–Cd(1)–Cl(1)#3	85.34(6)
Cl(1)–Cd(1)–Cl(1)#3	94.78(3)	Cl(1)#1–Cd(1)–Cl(1)#3	84.43(3)
Cl(1)#2–Cd(1)–Cl(1)#3	178.72(3)		
3			
Cd(1)–N(1)	2.397(2)	Cd(1)–N(3)	2.399(2)
Cd(1)–N(4)	2.445(2)	Cd(1)–N(2)	2.485(2)
Cd(1)–Cl(2)	2.5105(8)	Cd(1)–Cl(1)	2.5294(8)
N(1)–Cd(1)–N(3)	154.97(8)	N(1)–Cd(1)–N(4)	88.14(7)
N(3)–Cd(1)–N(4)	68.77(8)	N(1)–Cd(1)–N(2)	68.06(7)
N(3)–Cd(1)–N(2)	98.19(7)	N(4)–Cd(1)–N(2)	82.08(8)
N(1)–Cd(1)–Cl(2)	105.91(5)	N(3)–Cd(1)–Cl(2)	93.64(6)
N(4)–Cd(1)–Cl(2)	157.57(6)	N(2)–Cd(1)–Cl(2)	87.04(5)
N(1)–Cd(1)–Cl(1)	90.32(5)	N(3)–Cd(1)–Cl(1)	99.28(5)
N(4)–Cd(1)–Cl(1)	90.98(6)	N(2)–Cd(1)–Cl(1)	157.38(6)
Cl(2)–Cd(1)–Cl(1)	106.01(3)		

Symmetry codes: **1** #1 $-x, -y, -z+1$, #2 $-x+1, -y, -z+1$; **2** #1 $-x+1, y, -z+3/2$, #2 $-x+1, -y+1, -z+1$, #3 $x, -y+1, z+1/2$.

sub-structure, as does Br2. Thus, a 1-D coordination chain with Him extruding out of two sides is formed. There are no π–π stacking interactions between the intra-chain Him rings with dihedral angle 139.7°.

The 1-D coordination chains are self-assembled to 3-D supramolecular network through non-classical hydrogen bonds. As shown in figure 2(a), Br1 as acceptor hydrogen bonds to N4-H and C2-H, while Br2 hydrogen bonds to N2-H and C5-H. Thus, the adjacent chains are linked by two kinds of inter-chain hydrogen bonds N–H $\cdots$ Br and C–H $\cdots$ Br. Each Him ligand links two adjacent coordination chains through two kinds of inter-chain hydrogen bonds (N–H $\cdots$ Br and C–H $\cdots$ Br), and each chain possesses two kinds of Him ligands (N1–C3 and N3–C6) and hydrogen bonds to four adjacent ones. So, the 3-D supramolecular network (shown in figure 2b) is formed. In this network, each Br2 accepts hydrogen bonds and each Him ligand offers C–H and N–H groups to form two hydrogen bonds (N4–H $\cdots$ Br1, C2–H $\cdots$ Br1 or N2–H $\cdots$ Br2, C5–H $\cdots$ Br2). The parameters of the hydrogen bonds are listed in table 3.

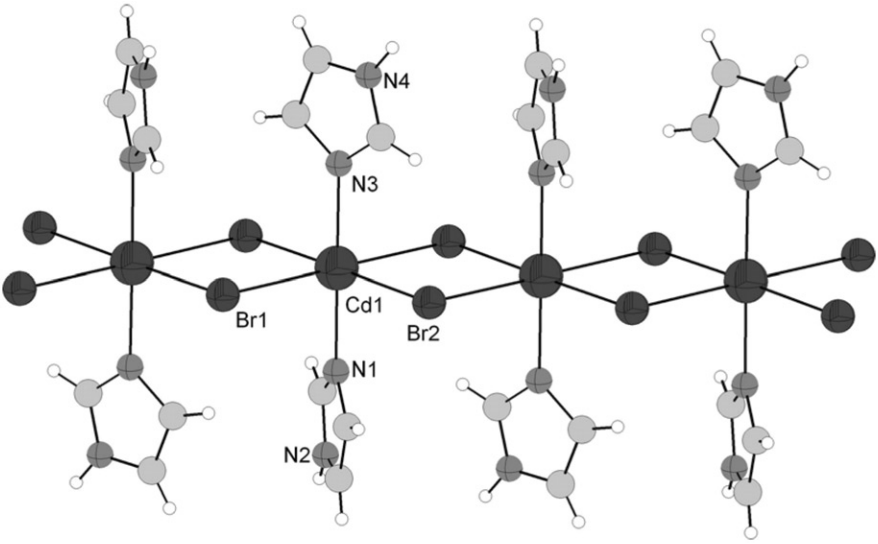

Figure 1. The 1-D coordination chain of **1**.

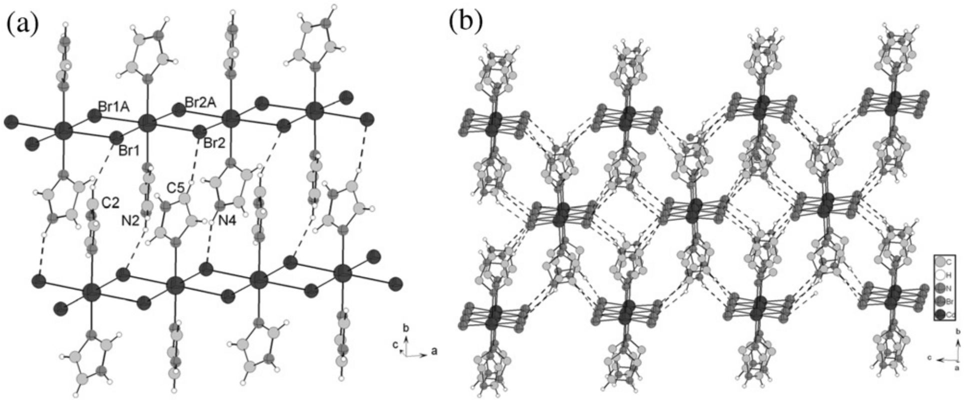

Figure 2. (a) The inter-chain hydrogen bonds existing in **1**; (b) the 3-D supramolecular structure of **1** (hydrogen atoms which do not form hydrogen bond are omitted for clarity).

3.2. *Crystal structure of [$CdCl_2$(2,2′-bipy)]$_n$ (2)*

A single X-ray diffraction study reveals that the structure of **2** is similar to that of **1**. Cd is in the center of a distorted octahedron, coordinated by four Cl's and two N atoms from one 2,2′-bipy. The Cl's bridge Cd centers to form a 1-D coordination chain along *c* with 2,2′-bipy alternately extruding out of its sides. The dihedral angle of the two phenyl rings from one 2,2′-bipy ligand is 7.7°, while the intra-chain 2,2′-bipy ligands are parallel.

Three kinds of C–H ··· Cl hydrogen bonds link the 1-D coordination chains of **2** to form a 3-D supramolecular network. As shown in figure 3(a), one is intra-chain hydrogen bond C1–H ··· Cl1, stabilizing the 1-D coordination chain. The second one is inter-chain hydrogen bond C4–H ··· Cl1, connecting adjacent coordination chains along *b*.

Table 3. The parameters of hydrogen-bonds for **1**–**3**.

D–H···A	d(H···A)	d(D···A)	∠DHA
1			
N4–H···Br1	2.572(2)	3.437(2)	154.82(1)
N2–H···Br2	2.578(2)	3.449(3)	156.12(1)
C2–H···Br1	3.047(3)	3.819(3)	150.42(1)
C5–H···Br2	3.079(3)	3.819(3)	145.48(1)
2			
C1–H···Cl1	2.872(2)	3.533(12)	129.09(74)
C4–H···Cl1	2.823(2)	3.536(12)	134.38(75)
C2–H···Cl2	2.766(3)	3.675(12)	165.98(87)
C7–H···Cl2	2.850(2)	3.532(11)	131.19(69)
3			
C1–H···Cl1	2.780(2)	3.438(2)	138.06(1)
C18–H···Cl1	2.745(1)	3.574(1)	172.88(1)
C3–H···Cl2	2.854(1)	3.695(2)	157.87(1)
C6–H···Cl2	2.754(2)	3.607(7)	178.64(1)

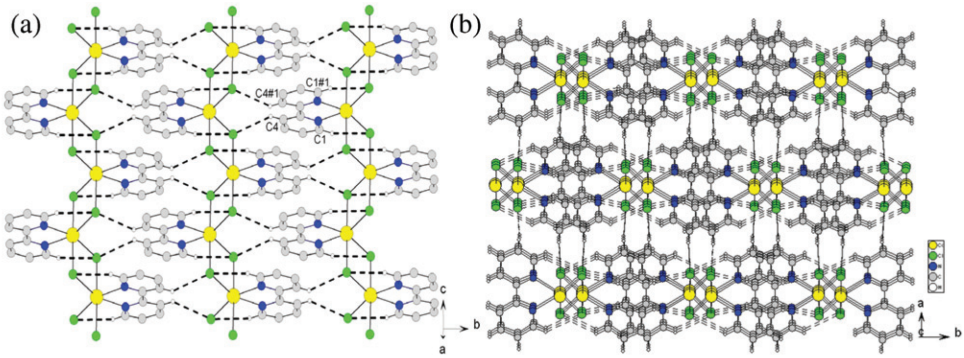

Figure 3. (a) The hydrogen-bond interactions along *b*-axis in **2** (hydrogen atoms which do not form hydrogen bond are omitted for clarity); (b) the 3-D supramolecular structure of **2**.

The distance between the adjacent bipy rings coming from different chains is 3.3529 Å with 0° dihedral angle. The third is C2–H···Cl1 (shown in figure 3b); four chlorides, coordinating to the same Cd, are hydrogen acceptors to four C2–H groups along *a* direction, coming from four adjacent coordination chains. Thus, each chain hydrogen bonds to six adjacent ones to form a 3-D supramolecular network. In **2**, each Cl^- accepts three hydrogens and each bipy ring offers six C–H groups to form intra- and inter-chain hydrogen bonds. The hydrogen bond parameters are listed in table 3. The C–H···Cl hydrogen bond in **2** is strong with mean distance of Cl–H 2.828 Å, agreeing with the reported range 2.474–3.300 Å and shorter than the average 2.974 Å [10].

3.3. *Crystal structure of [CdCl$_2$(phen)$_2$] (3)*

Unlike **1** and **2**, compound **3** is mononuclear. Cd is six coordinate with two chlorides and four nitrogens from two phen molecules. As shown in figure 4, Cl2 accepts two

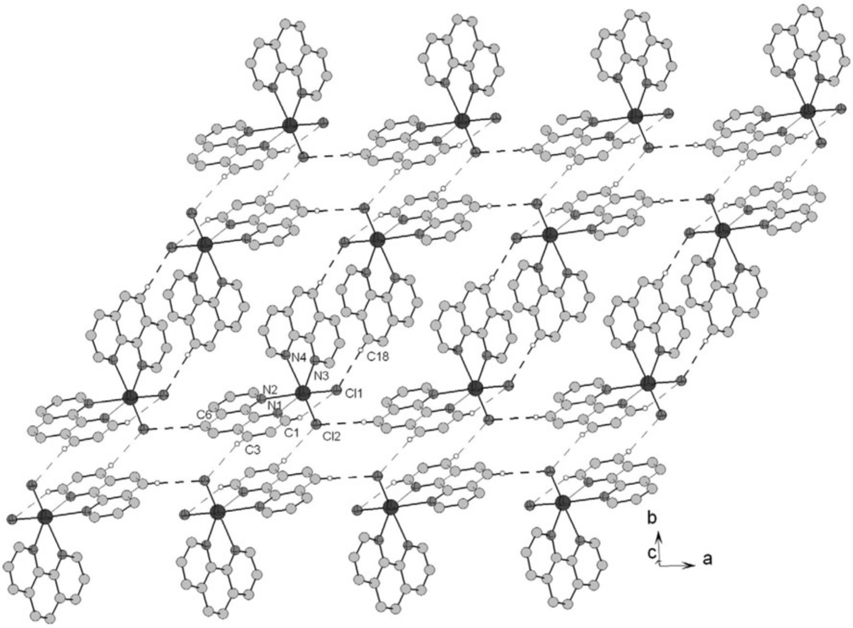

Figure 4. The 2-D supramolecular structure formed by C–H ··· Cl of **3** (hydrogen atoms which do not form hydrogen bond are omitted for clarity).

C–H groups of N1–N2 phen rings from two adjacent [$CdCl_2(phen)_2$] units. Each [$CdCl_2(phen)_2$] links three adjacent ones by inter-molecular hydrogen bonds C3–H ··· Cl2 and C6–H ··· Cl2 to form a 1-D double chain along *a*. The 1-D chains are further connected by inter-molecular hydrogen bonds C18–H ··· Cl1 to form a 2-D supramolecular sheet parallel to the *ab* plane. There also exist intra-molecular hydrogen bonds C1–H ··· Cl1, which stabilized the 2-D supramolecular sheet. Parameters of all hydrogen bonds are listed in table 3. The C–H ··· Cl hydrogen bonds in **3** are strong with mean distance of Cl–H 2.783 Å.

4. Discussion

For compounds **1**–**3**, Cd centers are six coordinate and linked to be high dimensional supramolecules by C–H ··· X. Compounds **1** and **2** exhibit 1-D coordination chains, while compound **3** is discrete, because of the strong coordination ability and the large volume of phen obstructs forming a 1-D coordination chain. There is no intra-molecular hydrogen bond in compound **1**, which is different from **2** and **3**. Because the volume of Him is less than that of 2,2′-bipy and phen, the distance between Br and Him is longer and the interaction should be ignored. The dihedral angle between adjacent Him rings in **1** is 139.7°, while the adjacent 2,2′-bipy rings in **2** are parallel, probably caused by the intra-chain hydrogen bonds. Thus, subtle differences in organic ligands strongly influence coordination and supramolecular structure; the secondary bond can also influence the structure of coordination host.

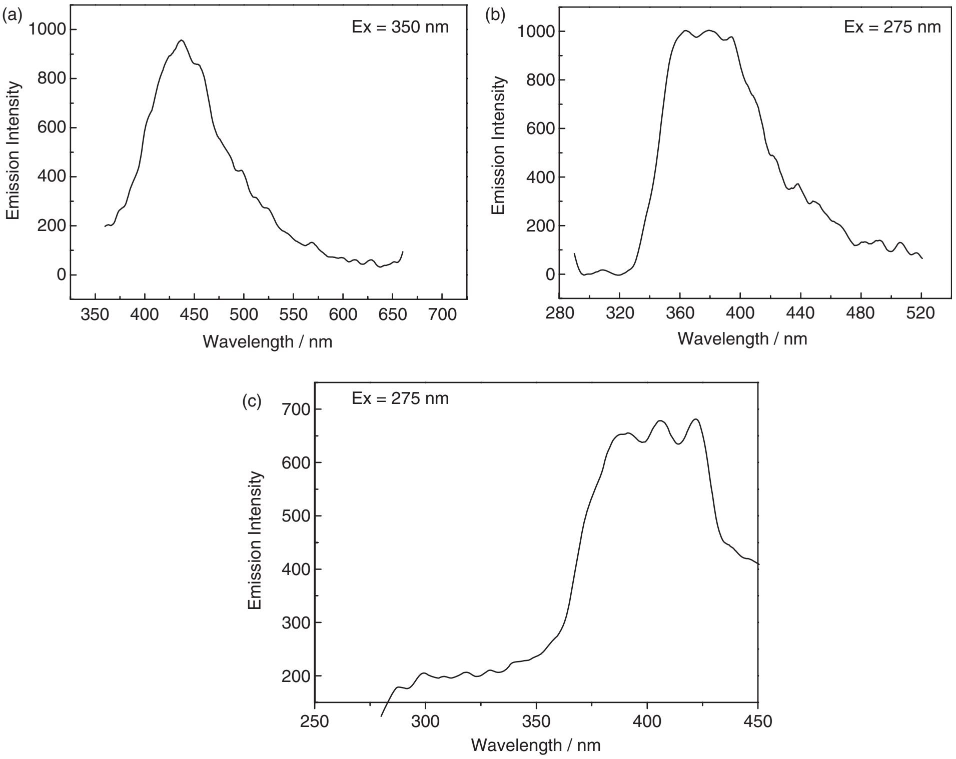

Figure 5. Fluorescence spectra of **1** (a), **2** (b), and **3** (c) measured at room temperature in solid state.

4.1. *Fluorescence properties*

The solid fluorescence of **1**–**3** and ligands were measured at room temperature. As shown in figure 5(a), the broad emission band of **1** at 437 nm ($\lambda_{ex} = 350$ nm) is slightly red shifted compared with that of free Him ($\lambda_{em} = 420$ nm, $\lambda_{ex} = 350$ nm). Thus, the emission of **1** may be attributed to the $\pi^* \rightarrow n$ transition of Him and undergoes a red shift because of Him hydrogen bonds. As shown in figure 5(b), the broad emission of **2** from 360 to 400 nm ($\lambda_{ex} = 275$ nm) should be assigned to the $\pi^* \rightarrow \pi$ transition of 2,2′-bipy ligand, although free 2,2′-bipy exhibits almost no fluorescence emission; coordinating with Cd atom, the rigidity of the 2,2′-bipy ligand increases and the non-radiative decay of the intra-ligand is reduced and fluorescence emission intensity of **2** is strong. Similar enhancements have also been found in polypyridyl cadmium(II) and polypyridyl zinc(II) polymers [13]. The emission band of **3** located from 385 to 422 nm (shown in figure 5c) is broader than that of **2**. The emission band of **3** is similar to that of the free phen with slight red shift; it is assigned to the $\pi^* \rightarrow \pi$ transition of phen.

5. Conclusion

Three low-dimensional or discrete coordination compounds are linked to form supramolecular networks by C–H$\cdots$Cl/Br hydrogen bonds which are important synthons during supramolecular assembly, although weaker than the classical O/N–H···O hydrogen bonds. There are subtle differences among **1**–**3**, probably caused by the different volume and coordination ability of supporting organic ligands.

Supplementary material

CCDC-651304 (for compound **1**), 651305 (for compound **2**), and 651306 (for compound **3**) contain the supplementary crystallographic data for this article. These data can be obtained free of charge from Cambridge Crystallographic Data Center via http://www.ccdc.cam.ac.uk/data_request/cif

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