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# Effect of anions on cadmium(II) complexes with ligand 2-(pyrazin-2-yl)-1*H*-benzimidazole

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#### ABSTRACT

Three new supramolecular complexes based on a 2-(pyrazin-2-yl)-1*H*-benzimidazole (Hpbi) and a series of Cd(II) salts have been solvothermally synthesized and structurally characterized by single-crystal X-ray diffraction analysis. Reaction of CdCl<sub>2</sub>·2.5H<sub>2</sub>O with Hpbi afforded a one-dimensional chain [Cd(Hpbi)Cl<sub>2</sub>] (**1**), which exhibits a three-dimensional (3-D) supramolecular architecture through intermolecular X-H…Cl (X = N and C) hydrogen bonds and  $\pi$ - $\pi$  stacking interactions. When using CdBr<sub>2</sub>·4H<sub>2</sub>O instead of CdCl<sub>2</sub>·2.5H<sub>2</sub>O under similar reaction conditions, a bisnuclear complex [Cd(Hpbi)<sub>2</sub>Br<sub>2</sub>] (**2**) is obtained, which obviously exhibits intermolecular X-H…Br (X = N and C) hydrogen bonds and  $\pi$ - $\pi$  stacking interactions. When Cdl<sub>2</sub> take place of CdCl<sub>2</sub>·2.5H<sub>2</sub>O, a mononuclear complex, [Cd(Hpbi)<sub>2</sub>l<sub>2</sub>] (**3**), is isolated, which shows a 3D supramolecule framework formed by intermolecular hydrogen bonds and  $\pi$ - $\pi$  packing interactions. Interestingly, the Hpbi ligand exhibits the same coordination modes in complexes **1-3**. It is noteworthy that the radius of anions plays an important role in affecting the structures and luminescent intensity of the final products. The TGA for **1-3** have been investigated and discussed in detail.

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# 1. Introduction

The rational design and synthesis of metal complexes have attracted considerable attention not only due to their intriguing variety of architectures [1,2] but also owing to their useful properties, such as nonlinear optics [3], catalysis [4,5], ferroelectricity [6,7], luminescence [8], magnetism [9], gas adsorption [10-13], and molecular recognition [14,15]. Despite some significant advancement, the ability to rationally predict and prepare the final architectures remains still a great challenge. There exist several factors affecting the supramolecular assemblies, such as the coordination geometry of the central metal ions [16-20], ligand structure [21,22], metal-ligand ratio [23,24], reaction conditions (solvents [25,26], pH value [27-30], and temperature [31,32]), and counterions [33-36]. Among these factors, the anions play an important role in controlling synthesis of the molecular architecture. Additionally, the noncovalent forces, such as hydrogenbonding (X-H...Y) (X = C, N or O atoms; Y = N, O, Cl, Br or I ones), C–H··· $\pi$ ,  $\pi$ ··· $\pi$  stacking, and other interactions, obviously affect the supramolecular topology and dimensionality although they are weaker than the covalent force [37-39]. With this understanding, one key aim of this contribution is to investigate the influence of counterions on the structural self-assemblies, which may

provide further insights in developing new specified functional materials.

Recently, benzimidazole and its derivatives have exclusively been developed in areas of the coordination chemistry, materials and medicine [40–46]. So far, more studies on metal complexes based on ligands containing both pyridine and benzimidazole have been established, which exhibit beautiful structures and fascinating properties with luminescence [47–49]. However, little attention has been paid to metal complexes with rigid ligands possessing both pyrazine and benzimidazole, 2-(pyrazin-2-yl)-1*H*-benzimidazole (Hpbi) [50,51].

As a section of our program for constructing of intriguing and functional coordination polymers with the asymmetric rigid or flexible ligands, the design and control of the self-assemblies of coordination polymers and supramolecular complexes have been investigated [52–54]. In this contribution, we have chosen and synthesized a bridging ligand Hpbi, which probably results in the versatile structure of supramolecules with the desired properties. It has characteristics based on the following advantages: (i) it has four potential binding sites; (ii) it has a strong capability of forming hydrogen bonding and stacking interactions along aromatic rings (Scheme 1). To the best of our knowledge, these Cd(II)-based supramolecular complexes constructed by this ligand have not been reported. Herein, we report the synthesis, characterization and structures of three new Cd(II)-based coordination complexes containing rigid Hpbi ligand, [Cd(Hpbi)Cl<sub>2</sub>] (1), [Cd(Hpbi)<sub>2</sub>Br<sub>2</sub>] (2)



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Scheme 1. The ligand Hpbi.

and  $[Cd(Hpbi)_2I_2]$  (**3**), in which the effect of counter-anions on the luminescent intensity is observed, and the bridging character of halide deceases down the radius of counter anions. Additionally, the TGA for complexes **1**–**3** have also been presented and discussed in detail.

#### 2. Experimental

#### 2.1. Materials and physical measurements

The reagents and solvents employed were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm<sup>-1</sup> on a Bruker spectrometer. Thermogravimetric analysis (TGA) data were collected with a TA SDTQ600 analyzer in N<sub>2</sub> flow at a heating rate of 15 °C min<sup>-1</sup>. Powder X-ray diffraction (PXRD) patterns were recorded on a D8 ADVANCE diffractometer with Cu K $\alpha$  radiation ( $\lambda$  = 1.5409 Å) at a scanning rate of 4° min<sup>-1</sup> with 2 $\theta$  ranging from 5° to 60°. The emission/excitation spectra were recorded on an Edinburgh FLS920 spectrometer equipped with a continuous Xe900 Xenon lamp and an nF900 nanosecond flash lamp.

# 2.2. Synthesis of ligand 2-(pyrazin-2-yl)-1H-benzimidazole (Hpbi)

Ligand Hpbi was prepared by modifying a reported literature procedure [55]. The pyrazine-2-carboxylic acid (2.604 g, 21 mmol) and *o*-phenylenediamine (2.16 g, 20 mmol) were mixed. Then polyphosphate acid (20 ml) was added to the above mixture. The reaction mixture was irradiated in microwave oven. After 10 min, the reaction mixture was cooled to room temperature, poured in the iced water (100 ml), and neutralized by 10% NaOH. The solid compound obtained was filtered, washed with water, and recrystallized from aqueous ethanol. Yield: 62.63% (2.455 g). The spectra analysis of Hpbi is identical to that of the reported compound.

# 2.3. Synthesis of [Cd(Hpbi)Cl<sub>2</sub>] (1)

CdCl<sub>2</sub>·2.5H<sub>2</sub>O (22 mg, 0.1 mmol) and Hpbi (20 mg, 0.1 mmol) were mixed with a mixture solvents of methanol (3 mL) and water (3 mL). The mixture was sealed in a 25 mL Teflon-lined autoclave, heated at 160 °C for 2 days, and then slowly cooled to room temperature. Orange plate crystals suitable for X-ray diffraction were obtained in a yield of ca. 85%. *Anal.* calc. for C<sub>11</sub>H<sub>8</sub>CdCl<sub>2</sub>N<sub>4</sub>: C, 34.81; H, 2.12; N, 14.76. Found: C, 34.31; H, 2.14; N, 14.79%. IR (KBr, cm<sup>-1</sup>): 3217(br), 3151(w), 3093(w), 3062(w), 2922(w), 2852(w), 2638(w), 2507(w), 2331(w), 1964(w), 1917(w), 1805(w), 1616(w), 1593(m), 1531(m), 1483(m), 1431(s), 1392(m), 1314(m), 1305(m), 1240(m), 1171(m), 1149(m), 1122(w), 1028(m), 978(m), 943(w), 858(m), 821(w), 762(s), 725(m), 652(m), 503(m), 434(m), 410(w).

# 2.4. Synthesis of $[Cd(Hpbi)_2Br_2]$ (2)

Complex **2** was synthesized by a similar solvothermal procedure using CdBr<sub>2</sub>·4H<sub>2</sub>O in the place of CdCl<sub>2</sub>·2.5H<sub>2</sub>O. Orange plate crystals

suitable for X-ray diffraction were obtained in a yield of ca. 40%. Anal. calc. for  $C_{22}H_{16}Br_4Cd_2N_8$ : C, 28.20; H, 1.72; N, 11.96. Found: C, 28.37; H, 1.73; N, 11.91%. IR (KBr, cm<sup>-1</sup>): 3184(br), 3143(w), 3061(w), 2981(w), 2681(w), 2331(w), 1956(w), 1800(w), 1616(w), 1589(m), 1531(w), 1483(m), 1431(s), 1394(m), 1315(s), 1231(m), 1173(s), 1141(w), 1114(w), 1053(m), 1030(s), 978(m), 945(w), 853(m), 819(m), 760(s), 717(m), 656(m), 628(w), 570(w), 543(w), 505(w), 436(w), 410(w).

# 2.5. Synthesis of $[Cd(Hpbi)_2I_2]$ (3)

Complex **3** was synthesized by a similar solvothermal procedure using CdI<sub>2</sub> in the place of CdCl<sub>2</sub>·2.5H<sub>2</sub>O. Orange plate crystals suitable for X-ray diffraction were obtained in a yield of ca. 47%. *Anal.* calc. for  $C_{22}H_{16}CdI_2N_8$ : C, 34.83; H, 2.13; N, 14.77. Found: C, 34.73; H, 2.14; N, 14.81%. IR (KBr, cm<sup>-1</sup>): 3408(br), 3183(w), 3140(w), 3049(w), 3016(2), 2854(w), 2762(w), 1933(w), 1807(w), 1591(m), 1531(m), 1481(m), 1431(s), 1317(m), 1296(w), 1255(w), 1231(w), 1167(m), 1145(w), 1057(m), 1024(m), 978(m), 908(w), 835(m), 768(s), 754(w), 681(m), 570(w), 546(w), 505(w), 436(m), 413(w).

#### 2.6. X-ray crystallography

Single crystal X-ray diffraction measurements of 1-3 were carried out with a Bruker Smart APXII CCD diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection at 296(2) K. Data collections were performed with Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) by  $\omega$ -scan mode. No evidence was found for crystal decay during data collection of complexes 1–3. All the measured independent reflections were used in the structural analysis, and semi-empirical absorption corrections were applied using the sADABS program. The program SAINT [56] was used for integration of the diffraction profiles. All the structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined with SHELXL [57]. Metal atoms were located from the E-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full-matrix least-squares methods with anisotropic thermal parameters for all the nonhydrogen atoms on  $F^2$ . All the hydrogen atoms were first found in difference electron density maps, and then placed in the calculated sites and included in the final refinement in the riding model approximation with displacement parameters derived from the parent atoms to which they were bonded. A summary of the crystallographic data and structure refinements are listed in Table 1.

# 3. Results and discussion

#### 3.1. Preparation of Hpbi and complexes 1-3

The ligand Hpbi was synthesized as a pale-brown solid by the condensation reaction of pyrazine-2-carboxylic acid and *o*-phenylenediamine in polyphosophoric acid under microwave radiation. The ligand possesses four potential donor sites, two nitrogen donor atoms from the pyrazine rings, two nitrogen atoms from the imidazole (Scheme 1). The one-dimensional chain, binuclear and mononuclear complexes were readily isolated in moderate yield by the reaction of Hpbi with a series of Cd(II) with different halo anions in 1:1 mol ratio in methanol solution, respectively. The structures of these complexes were not obviously changed though the ligand/metal ratios changed from 2:1 to 1:2. The chelated complexes were always obtained, which were confirmed by their PXRD (Figs. S1–S3). The present results indicate that the final products are independent of the molar ration of ligand/metal salts.

Table	1
Table	

Crystal data and structure refinement parameters for **1–3**.

	1	2	3
Empirical formula	$C_{11}H_8CdCl_2N_4$	$C_{22}H_{16}Br_4Cd_2N_8$	C <sub>22</sub> H <sub>16</sub> CdI <sub>2</sub> N <sub>8</sub>
Formula weight	379.52	936.85	758.64
T (K)	296	296	296
λ (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	orthorhombic
Space group	<i>P</i> 2 <sub>1</sub> /c (No. 14)	<i>P</i> 1̄ (No. 2)	<i>P</i> ccn (No. 56)
a (Å)	7.0841(7)	8.1346(12)	16.9291(17)
b (Å)	18.7054(19)	8.8032(13)	9.8548(10)
<i>c</i> (Å)	9.5569(10)	9.6850(14)	14.5912(14)
α (°)	90	76.676(2)	90
β (°)	97.492(1)	78.926(2)	90
γ (°)	90	76.945(2)	90
V (Å <sup>3</sup> )	1255.6(2)	650.22(17)	2434.3(4)
Ζ	4	1	4
$\mu$ (mm <sup>-1</sup> )	2.149	7.810	3.461
Crystal size (mm)	$0.10 \times 0.10 \times 0.30$	$0.10 \times 0.10 \times 0.30$	$0.10 \times 0.10 \times 0.40$
$ ho (\text{g cm}^{-3})$	2.008	2.393	2.070
Reflections collected	10 747	5741	20 081
Independent reflections	2869	2930	2808
Reflections $[I > 2\sigma(I)]$	2608	2462	2291
R <sub>int</sub>	0.027	0.028	0.036
$\theta$ (°)	2.2/27.5	2.2/27.5	2.4/27.6
Goodness-of-fit (GOF) on F <sup>2</sup>	1.36	1.09	1.04
Largest hole and peak (e Å <sup>-3</sup> )	-0.57/0.54	-1.01/0.89	-0.85/0.97
$R_1^a \left[ I > 2\sigma(I) \right]$	0.0341	0.0312	0.0301
$wR_2^{\rm b}$ (all data)	0.0974	0.0927	0.0838

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

<sup>b</sup>  $wR_2 = \left[\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\right]^{1/2}$ .

These complexes give satisfactory microanalytical data, and the crystal structures show that the ligand Hpbi in complexes possesses the same chelated form. Complexes **1–3** are air stable and can retain their structural integrity at room temperature for a considerable length of time.

#### 3.2. Description of crystal structures

Reactions of  $CdX_2$  (X = Cl<sup>-</sup>, Br<sup>-</sup>, l<sup>-</sup>) and the ligand Hpbi yield the structures of  $[Cd(Hpbi)(\mu_2-Cl)_2]$  (1),  $[Cd(Hpbi)_2(\mu_2-Br)_2]$  (2), and  $[Cd(Hpbi)_2]$  (3), respectively. Chloride serves as a bridging ligand to generate one-dimensional complex 1. Bromide acts as both a simple coordinating ligand and a bridging ligand to form bromide-bridged dinuclear complex 2. Iodide only plays at a simple coordinating ligand to produce a mononuclear complex 3. From the present results, it is interestingly observed that bridging ability of halides decreases from chloride to iodide (Chart 1).

X-ray single-crystal determination indicates that complex **1** is one-dimensional chain. As shown in Fig. 1a, in compound **1**, the crystallographically unique Cd atom with a distorted octahedral geometry bonds to four Cl atoms and two N atoms from a Hpbi molecule. The Cd–N distance is normal 2.334(3)–2.455(4) Å, but the Cd–Cl distances spin a rather wider range from 2.552(1) to



Chart 1.

2.721(1) Å (Table 2), which are similar to those found in the reported complexes [58]. The adjacent Cd(II) centers are bridged by two  $\mu_2$ -Cl atoms into a 1-D zig-zag type chain with a dihedral angle of 78.9° between two adjacent Cd2Cl2 planes. In this plane unit, the interachain Cd–Cl–Cd angle is 96.41(4)°, and the interchain Cd-..Cd spearation is 3.972(1) Å, obviously larger than that found in complexes [59]. There exists the torsion angle of  $-5.96(5)^\circ$  between the benzimidazole ring and pyrazine one in Hpbi ligand, which is different from that found in the document [51].

The Hpbi molecules arrange alternately on both sides of the parent chain because the Hpbi rings of adjacent CdCl2 chains are inter-ditigated through the  $\pi$ - $\pi$  stacking interactions with a distance of 3.630(3) and 3.688(3)Å along the *b* axial direction (Fig. 1b). Additionally, along the *b* axis direction, the interchain hydrogen bonds are formed through the nitrogen atom and carbon one from each Hpbi ligand with the Cl atoms (N4-H4...Cl1<sup>i</sup> 3.364(4) Å, 164(5)°; C10-H10A···Cl2<sup>*i*</sup> 3.517(5) Å, 158°, i = x, y, 1 + z), which extends these 1-D chains into a 2-D grid-like supramolecular sheet (Fig. 1b). Meanwhile, there exist the intrachain weak hydrogen bonds (C7–H7A…Cl2 3.568(5) Å). The carbon atom from each Hpbi ligand is connected to uncoordinated nitrogen atom from pyrazine group on the neighboring layers via the hydrogen bonds (C4-H4A···N2<sup>*i*</sup> 3.319(8), 141°, i = x, 1/2 - y, -1/2 + z), which propagates finally the 2-D supramolecular layers into a 3-D supramolecular architecture along the *a* axial direction (Fig. 1c and Table 3).

Unlike **1**, complex **2** crystallizes in the orthorhombic space group *P*ccn and consists of a bisnuclear unit. As shown in Fig. 2a, an asymmetric unit contains a Cd atom, a Hpbi ligand, two bromides, and whole dinuclear molecule has been generated through the inversion center in the middle of the molecule. Each Cd(II) ion coordinates two nitrogen atoms of the chelating Hpbi ligand, two bridging bromides, and a simple coordinating bromide occupying an apical position, adopting an distorted square pyramid geometry (CdN2Br3). The Cd–N bond distances are 2.300(4) and 2.419(4) Å, similar to those found in the literature (Table 2) [59].



**Fig. 1.** (a) Local coordination environment around Cd atom for **1**. (b) 2-D supramolecular layer extended by hydrogen bonds along the *b* axis in **1**. Thin purple and red lines denote hydrogen bonds and stacking interactions, respectively. (c) 3-D packing diagram generated by hydrogen bonds along the *a* axis in **1**. Thin red lines stand for hydrogen bonds. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)

The Cd– $\mu_2$ -Br distances are 2.6842(8) and 2.7211(7) Å, respectively, which are much longer than the Cd–Br<sub>no bridge</sub> distances (2.5836(8) Å). This implies that the bridging capacity of the bromide is weaker than that of the chloride. In the dinuclear unit in **2**, the Cd–Br–Cd angle is 93.87(2)°, being much smaller than that of complex **1**. Though so, the Cd–Cd distance is 3.949(1) Å, which is comparable to that in the chloride-bridged complex **1**. Both benzimidazole and pyrazine ring little distorts with the torsion angle N1–C1–C5–N3 of  $-5.73(1)^\circ$ , being slightly equal to the corresponding value in **1**. Alike **1**, there exist two kinds of the weak

hydrogen-bonding interactions, including N4–H4…Br1<sup>*i*</sup> (3.475(4) Å, 160(5), *i* = 2 – *x*, –*y*, –*z*), between the nitrogen atom from imidazole group and a simple coordinated bromide from adjacent dimer unit, and C2–H2A…Br1<sup>*i*</sup> (3.724(6) Å, 156°, *i* = 2 – *x*, –*y*, –*z*) between the carbon atom from pyrazine ring and a simple coordinated bromide atom from adjacent dimer unit. In addition, the  $\pi$ … $\pi$  stacking interactions (3.614(3) Å) occur between the imidazole ring and pyrazine one from the adjacent dimer unit. These interactions give rise to a 1-D chain. Strong face-to-face  $\pi$ … $\pi$  stacking interactions (minimum centroid-to-centroid distances 3.599(3)

Table 2
Selected bond lengths (Å) and bond angles (°) for <b>1–3</b> .

1			
Cd1-Cl1	2.6058(11)	Cd1-N3	2.334(3)
Cd1-Cl2	2.5518(12)	Cd1-Cl2 <sup>a</sup>	2.6754(12)
Cd1-N1	2.455(4)	Cd1–Cl1 <sup>b</sup>	2.7210(12)
Cl1-Cd1-Cl2	101.41(3)	Cl1 <sup>b</sup> -Cd1-Cl2	98.59(4)
Cl1-Cd1-N1	96.57(9)	N1-Cd1-N3	69.93(12)
Cl1-Cd1-N3	161.71(9)	Cl2 <sup>a</sup> -Cd1-N1	81.98(9)
Cl1-Cd1-Cl2 <sup>a</sup>	92.83(3)	Cl1 <sup>b</sup> -Cd1-N1	94.04(9)
Cl1–Cd1–Cl1 <sup>b</sup>	83.59(3)	Cl2 <sup>a</sup> -Cd1-N3	97.23(9)
Cl2-Cd1-N1	159.02(9)	Cl1 <sup>b</sup> –Cd1–N3	85.10(9)
Cl2-Cd1-N3	94.45(9)	Cl1 <sup>b</sup> –Cd1–Cl2 <sup>a</sup>	174.34(4)
Cl2-Cd1-Cl2 <sup>a</sup>	86.41(3)		
2			
Cd1-Br1	2.5836(8)	Cd1-N3	2.300(4)
Cd1-Br2	2.6842(8)	Cd1-Br2 <sup>a</sup>	2.7211(7)
Cd1-N1	2.419(4)		
Br1-Cd1-Br2	105.98(2)	Br2-Cd1-N3	98.89(10)
Br1-Cd1-N1	100.96(10)	Br2-Cd1-Br2 <sup>a</sup>	86.13(2)
Br1-Cd1-N3	104.25(10)	N1-Cd1-N3	71.03(13)
Br1-Cd1-Br2 <sup>a</sup>	110.92(2)	Br2 <sup>a</sup> -Cd1-N1	87.23(9)
Br2-Cd1-N1	152.87(10)	Br2 <sup>a</sup> -Cd1-N3	141.57(9)
3			
I1-Cd1	2.8372(5)	Cd1-N3	2.312(3)
Cd1-N1	2.605(3)		
I1-Cd1-N1	88.60(7)	N1-Cd1-N3	67.28(10)
I1-Cd1-N3	98.69(7)	N1-Cd1-N1 <sup>a</sup>	83.06(9)
I1-Cd1-I1 <sup>a</sup>	99.83(1)	N1-Cd1-N3 <sup>a</sup>	80.45(10)
I1-Cd1-N1 <sup>a</sup>	171.29(7)	N3-Cd1-N3 <sup>a</sup>	136.72(10)
I1-Cd1-N3 <sup>a</sup>	108.90(7)		

Symmetry codes: for **1**:  ${}^{a}-x$ , 1 - y, -z;  ${}^{b}1 - x$ , 1 - y, -z;  ${}^{c}x$ , y, -1 + z for **2**:  ${}^{a}1 - x$ , -y, 1 - z;  ${}^{b}x$ , y, 1 + z for **3**:  ${}^{a}1/2 - x$ , 1/2 - y, z;  ${}^{b}x$ , -1 + y, z;  ${}^{c}1 - x$ , 1 - y, 1 - z.

Table 3Hydrogen bond geometries in the crystal structure of 1–3.

Complex	$D-H\cdots A^a$	H…A (Å)	D…A (Å)	D-H…A (°)
1				
	N4-H4…Cl1 <sup>a</sup>	2.64(6)	3.364(4)	164(5)
	C4-H4A…N2 <sup>b</sup>	2.5400	3.319(8)	141.00
	C7-H7ACl2	2.7800	3.568(5)	143.00
	C10-H10A…Cl2 <sup>a</sup>	2.6400	3.517(5)	158.00
2				
	N4-H4…Br1 <sup>a</sup>	2.53(6)	3.475(4)	160(5)
	C2-H2A…Br1 <sup>a</sup>	2.8600	3.724(6)	156.00
	C3–H3A…Br2 <sup>b</sup>	2.8800	3.768(6)	159.00
3				
	N4-H4…N2 <sup>a</sup>	2.27(6)	2.987(5)	139(4)
	C8–H8A…I1 <sup>b</sup>	3.0100	3.865(5)	153.00

Symmetry codes: for **1**:  ${}^{a}x, y, 1 + z$ ;  ${}^{b}x, 1/2 - y, -1/2 + z$ ; for **2**:  ${}^{a}2 - x, -y, -z$ ;  ${}^{b}1 + x, -1 + y, z$  for **3**:  ${}^{a}1 - x, 1/2 + y, 3/2 - z$ ;  ${}^{b}x, 1 + y, z$ .

and 3.642(3) Å, respectively) between 1-D chains form a 2-D supramolecular layer (Fig. 2b), which further extend to 3-D supramolecular networks through the weak C3–H3A…Br2<sup>*i*</sup> (3.768(6) Å, *i* = *x*, 1 + *y*, *z*) hydrogen bonds interactions (Fig. 2c and Table 3).

In contrast to the complexes **1** and **2**,  $[Cd(Hpbi)_2I_2](3)$  is a mononuclear complex (Fig. 3a). In the centrosymmetric mononuclear compound **3**, each Cd(II) ion, locating at the inversion center, coordinates to four nitrogen atoms from two distinct Hpbi molecues and two iodides, adopting a distorted octahedral geometry (CdN4I2). The Cd–N distances are 2.312(3) and 2.605(3) Å, respectively, which falls in normal range and are similar to those found in complexes published before [58,59]. The Cd–I length is 2.8372(5) Å, which is much shorter than those of Cd(II) complexes reported in the literature [59]. It indicates that the bridging capacity of the iodide is much weaker than that of the chloride and the bromide. The benzimidazole ring and the pyrazine one in the ligand is somewhat tilted with the torsion angle N1-C1-C5-N3 of  $-8.81(1)^\circ$ , which is different from the corresponding value in **1** and **2**.

Analysis of the crystal packing of **3** reveals the existence of intermolecular hydrogen bonds N4–H4···N2<sup>*i*</sup> (2.987(5) Å, *i* = 1 – *x*, 1/2 + *y*, 3/2 – *z*) between nitrogen atom from imidazole rings and nitrogen atom from pyrazine rings from adjacent complex molecules, which results in the formation of 2D supramolecular layers (Fig. 3b). Similar to **1** and **2**, the weak hydrogen-bonding (C8–H8A···11<sup>*i*</sup>, 3.865(5) Å, *i* = *x*, 1 + *y*, *z*) is also present, which is comparable to those of Cd(II) complexes documented previously [58,59]. Additionally, the  $\pi$ ··· $\pi$  stacking interactions (3.635(2) Å) occur at phenyl rings and imidazole rings from adjacent mononuclear complexes, arranging and stabilizing of the supramolecular networks **3** (Fig. 3c).

#### 3.3. Powder X-ray diffraction

To examine the phase purity of these complexes, the PXRD patterns of the compounds were investigated at room temperature. The peak positions of the simulated PXRD patterns are identical to that of experimental ones (Figs. S1–S3), which indicates that the purity of the products is single phase. The tiny discrepancy in intensity may be attributable to the preferred orientation of the microcrystalline powder samples.

#### 3.4. Thermogravimetric analysis

In order to estimate the thermal stability of complexes **1–3**, thermogravimetric analyses (TGA) were carried out. TGA of complexes **1–3** were performed under N<sub>2</sub> atmosphere with a heating rate of 20 °C min<sup>-1</sup>. TGA curves for **1–3** indicate complexes are stable up to 176, 350, and 330 °C, respectively (Figs. S4–S6). The weight loss occurs at the temperature range of 180–700 °C for **1**, 360–700 °C for **2**, and 332–580 °C for **3**, respectively, corresponding to the loss of Hpbi ligand, halide anion and the decomposition of the structure.

# 3.5. Luminescent properties

As illustrated Fig. 4, the solid-state room temperature photoluminescence of 1 exhibits the emission peak at 497 nm upon an excitation maximum at 280 nm. The solid-state photoluminescence spectrum of 2 at room temperature is observed with the main emission at 507 nm ( $\lambda_{ex}$  = 280 nm). Complex **3** also shows broad emission bands with  $\lambda_{max}$  at 517 nm upon 280 nm excitation. To further estimate the relative luminescence of between the free ligand and its complexes, the luminescent property of the free Hpbi ligand was also measured, indicating the maximum emission at ca. 548 nm ( $\lambda_{ex}$  = 280 nm) (Fig. S7). By comparison with the free ligand Hpbi, the emission maxima of complexes 1-**3** are obviously blue-shifted about 51, 41 and 31 nm, respectively, which may assign to the coordination effects of the ligand Hpbi to cadmium ions. It is difficult to oxidize or to reduce the Cd(II) ions. which is owing to their  $d^{10}$  configuration. For **1**–**3**, the similarity of luminescent profiles is probably attributable to the ligand-centred emission [60]. Notably, it is observed that the luminescent intensity for 1-3 increases because of effective increase of the rigidity of the ligand and reduction of the loss of energy by nonradiative decay [61]. Additionally, it is noteworthy that the photoluminescent intensity increase from 1 to 3, which may be assigned to their difference in polarization [60].



**Fig. 2.** (a) Local coordination environment around Cd atom for **2**. (b) 2-D supramolecular layer formed by hydrogen bonds and stacking interactions along the *b* axis in **2**. Thin purple and red lines represent intermolecular hydrogen bonds and stacking interactions, respectively. (c) The packing perspective along the *c* axis in **2**. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)

# 4. Conclusions

In summary, three new coordination supramolecular complexes have been generated from an *N*-heterocycle organic ligand 2-(pyrazin-2-yl)-1*H*-benzoimidazole (Hpbi) and a series of Cd<sup>II</sup> with different anions. The present results demonstrate that the structures and luminescent intensity of final product are affected by the radius and polarization of anions. It is noteworthy that the ligand Hpbi in these complexes is coordination unsaturated, which can be acted as "complex ligands" to



**Fig. 3.** (a) Local coordination environment around Cd atom for **3** (hydrogen atoms are omitted for clarity). (b) 2-D supramolecular layer constructed by hydrogen bonds along the *b* axis in **3**. Thin purple lines denote hydrogen bonds. (c) The packing perspective along the *b* axis in **3**. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)



Fig. 4. Solid-state fluorescent emission spectra of complexes  $1\mathchar`-3$  and ligand (Hpbi) at room temperature.

construct supramolecular compounds with other metal ions or complexes. It is anticipated that other new structures with different anions and fascinating properties may also be synthesized in future.

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

CCDC 795430, 795431 and 795432 contain the supplementary crystallographic data for complexes **1**, **2** and **3**, respectively. 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.2011.07.011.

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