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Halide/pseudohalide complexes of cadmium(II) with benzimidazole: Synthesis, crystal structures and fluorescence properties

Hai-Yan Zhao<sup>1\*</sup>, Fu-Li Yang<sup>2</sup>, Na Li<sup>1</sup>, Xiao-Jing Wang<sup>1</sup>

<sup>1</sup> College of Science, Hebei University of Science and Technology, Shijiazhuang 050018, China

<sup>2</sup>Department of Chemical and Environmental Engineering, Hebei Chemical & Pharmaceutical College, Shijiazhuang, Hebei 050026, China

\*Corresponding author:

Hai-Yan Zhao. Tel: +86-0312-88168532. E-mail: hbhaiyanzh@163.com

### ABSTRACT

Cd(II) complexes,  $[CdL^1Cl_2]_2 \cdot H_2O$ Two new dinuclear (1)and [CdL<sup>1</sup>(N<sub>3</sub>)<sub>2</sub>]<sub>2</sub>·CH<sub>3</sub>OH (2) and one dicyanamide bridged one-dimensional polynuclear network  $[CdL^{1}(\mu_{1.5}-dca)dca]_{n}$  (3) of the potentially tridentate NNN-donor Schiff base 2-((1H-benzimidazol-2-yl-ethylimino)-methyl)pyridine ( $L^1$ ) and another dinucler Cd(II) complex [CdL<sup>2</sup>Cl(dca)]<sub>2</sub> (4) of a similar NNN-donor Schiff base ligand 2-((1H-benzimidazol-2-yl-propylimino)-methyl)pyridine  $(L^2)$ , have been synthesized and characterized by elemental analyses, IR and single crystal X-ray crystallography. The ligands  $L^1$  and  $L^2$  are [1+1] condensation products of pyridine-2-carbaldehyde 2-aminoethyl-1H-benzimidazole 2-aminopropyl-1H-benzimidazole, with and respectively. In the complexes 1 and 4 the two Cd(II) centers are held together by the bridged chloride ligands, while in 2 the two Cd(II) centers are bridged by  $\mu_{1,1}$ -azide ions. Complex 3 has a one-dimensional infinite chain structure in which Cd(II) ions are bridged by single dicyanamide groups in end-to-end fashion. All the metal centers have a distorted octahedral geometry and H-bonding or  $\pi \cdots \pi$  interactions are operative to bind the complex units in the solid state. Furthermore, these complexes have been investigated by thermogravimetric analyses and fluorescence spectra.

## Keywords:

Benzimidazole-based-Schiff base, Cadmium(II) complexes, Crystal structures, Fluorescence

# Graphical abstract



Three new dinuclear Cd(II) complexes,  $[CdL^1Cl_2]_2 \cdot H_2O$ ,  $[CdL^1(N_3)_2]_2 \cdot CH_3OH$ and  $[CdL^2Cl(dca)]_2$  and one polynuclear network  $[CdL^1(\mu_{1,5}-dca)dca]_n$  have been prepared and characterized by single-crystal X-ray crystallography using the benzimidazole derived primary Schiff base ligands  $L^1$  and  $L^2$ . The fluorescent properties of two ligands as well as four compounds were also studied.

### 1. Introduction

Recently, complexes of Cd(II) with tridentate and tetradentate Schiff base ligands have growing interest, not only because of their fascinating structures, but also adsorption. their antibacterial, antitumor activities, photocatalytic activity, electrochemical luminescence and fluorescent properties, as well as other potential applications [1-33]. In these complexes Cd(II) ions can exhibit a wide variety of geometries and coordination numbers along with mono-, di-, polynuclear coordination molecules and 1D, 2D and 3D supramolecular frameworks due to its larger radius and d<sup>10</sup> electronic configuration [8]. The coordination geometry of these complexes also depends upon the coordination behaviors of Schiff bases, the coordination ability and size of counteranions, as well as the reaction temperature and pH [1-4, 34-35]. In additions, multiple weak non-covalent forces like hydrogen bonding,  $\pi \cdots \pi$  and C-H... $\pi$  interactions play an important role in construction of these architectures [3–5, 11–14, 36–39]. Halides and pseudohalides such as thiocyanate (SCN<sup>-</sup>), dicyanamide (dca), and azide  $(N_3)$  are suitable inorganic building blocks which can link one or more metal ions in versatile coordination modes for creating different mono-, di-, polynuclear coordination molecules and supramolecular entities. Many different cadmium(II) compounds with interesting molecular or supramolecular structures using organic ligands in combination with halides/pseudohalides are well-studied in the literatures [8–12, 38–46].

For the present work, we chose two tridentate N-donor Schiff bases,  $L^1(2-((1H-benzimidazol-2-yl-ethylimino)-methyl)pyridine) and <math>L^2$  (2-((1H-benzimidazol-2-yl-propylimino)-methyl)pyridine )(Scheme 1), which differ by only one  $-CH_2-$  group in their ligating backbone to construct Cd(II) complexes in combination with various anion co-ligands including chloride (Cl<sup>-</sup>), azide (N<sub>3</sub><sup>-</sup>) and dicyanamide (dca): (i) Due

to presence of NH group and large aromatic system of the two Schiff bases, they can act as hydrogen bonds donors and provide potential supramolecular recognition sites for  $\pi \cdots \pi$  stacking interactions leading to supramolecular architecture. Furthermore, Cd(II) complexes of the two Schiff bases which contain conjugated  $\pi$  systems may have fluorescent properties; (ii) The anion co-ligands chloride (Cl<sup>-</sup>), azide (N<sub>3</sub><sup>-</sup>) and dicyanamide (dca) can tune the coordination numbers and geometry of the Cd(II) centers through coordinate to the Cd(II) centers, which may influence the properties of these resulting complexes. In addition, these anions can also act as the hydrogenbonded acceptor to extend the complexes into high-dimension networks.

Based on the above considerations, we report herein the synthesis, structures, supramolecular architectures, thermal stability and fluorescent properties of four distinct Cd(II) Schiff base complexes. All the Cd(II) ions in the four complexes are six coordinate, however, very interesting structural diversities occurred on varying the anion co-ligands. Complexes **1** [CdL<sup>1</sup>Cl<sub>2</sub>]<sub>2</sub>·H<sub>2</sub>O and **2** [CdL<sup>1</sup>(N<sub>3</sub>)<sub>2</sub>]<sub>2</sub>·CH<sub>3</sub>OH are binuclear complexes, which are bridged by chloride and azide groups, respectively. Complex **3** [CdL<sup>1</sup>( $\mu_{1,5}$ -dca)dca]<sub>n</sub> is a one dimensional chain through the  $\mu_{1,5}$ -bridged dca anions. Dca and chloro anions produce complex **4** [Cd(L<sup>2</sup>)( $\mu^2$ -Cl)(dca)]<sub>2</sub>, which is also a chroride bridged binuclear complex and one of the axial positions is occupied by the dca anions. All the complexes reported here exhibit 3D supramolecular frameworks in **1**, **3**, and **4** and 2D supramolecular frameworks in **2** via hydrogen bonding and  $\pi$ ··· $\pi$  interactions.

### 2. Experimental

2-Aminoethyl-1H-benzimidazole dihydrochloride and 2-aminopropyl-1Hbenzimidazole dihydrochloride were prepared by the method reported by Cescon et al [47]. A solution of 10.8 g (0.1 mol) of *o*-phenylenediamine and 13.4g (0.15 mol) of  $\beta$ -

alanine in 100 mL of 5.5 mol·L<sup>-1</sup> hydrochloric acid was refluxed for 24 h. The solution was cooled overnight and the hydrochloride removed by filtration. It was recrystallized from 90% ethyl alcohol with the aid of decolorizing carbon. 2-Aminopropyl-1H-benzimidazole dihydrochloride was prepared by the same procedure as that of 2-Aminoethyl-1H-benzimidazole dihydrochloride, but using  $\gamma$ -aminobutyric acid 10.3 g (0.1 mol) in place of *p*-alanine. All of the other reagents were of AR grade and were obtained from commercial sources and used without further purification.

## 2.1. Preparations

### 2.1.1. Preparation of ligands

# 2.1.1.1. Synthesis of $L^1$ (2-((1H-benzimidazol-2-yl-ethylimino)-methyl)pyridine).

The ligand L<sup>1</sup> was synthesized by a condensation reaction between 2-aminoethyl-1H-benzimidazole dihydrochloride (1.170g, 5mmol), previously neutralized with K<sub>2</sub>CO<sub>3</sub> (0.828g, 6mmol), and pyridine-2-carbaldehyde (0.535g, 5mmol) in 25 mL of methanol. The reaction mixture was stirred at room temperature for approximately 2h. The resulting brown solution was removed on a rotatory evaporator and the light brown product was then filtered and recrystallized from EtOH for two times. Yield: 1.06 g (85%). m.p.: 155-156 °C IR (KBr pellet, cm<sup>-1</sup>): 1635(v<sub>C=N</sub>), 1437(v<sub>C=C-C=N</sub>). <sup>1</sup>H NMR (500MHz, *d*<sub>6</sub>-DMSO, ppm)  $\delta$ : 3.22–3.25(t, 2H, –CH<sub>2</sub>–), 4.05–4.08 (t, 2H, – CH<sub>2</sub>–), 7.42–8.97(m, 8H, Ar–H), 8.98(s, 1H, –CH=N–), 12.61(br s, 1H, NH). UV-Vis (methanol,  $\lambda_{max}$ , nm): 204, 248, 276, 281. *Anal*. Calc. for C<sub>15</sub>H<sub>14</sub>N<sub>4</sub>: C, 71.98; H, 5.64; N, 22.38. Found: C, 71.86; H, 5.57; N, 22.29%.

# 2.1.1.2. Synthesis of $L^2$ (2-((1H-benzimidazol-2-yl-propylimino)-methyl)pyridine).

The ligand  $L^2$  was prepared following the same procedure as that of  $L^1$ , but using 2-aminopropyl-1H-benzimidazole dihydrochloride (1.24 g, 5 mmol) in place of 2-

aminoethyl-1H-benzimidazole dihydrochloride. Yield: 1.08 g (82%). m.p.: 118-119 °C IR (KBr pellet, cm<sup>-1</sup>): 1635( $v_{C=N}$ ), 1437( $v_{C=C-C=N}$ ). <sup>1</sup>H NMR (500MHz, *d*<sub>6</sub>-DMSO, ppm)  $\delta$ : 2.26–2.32(m, 2H, –CH<sub>2</sub>–), 2.99–3.02(t, 2H, –CH<sub>2</sub>–), 3.69–3.71 (t, 2H, –CH<sub>2</sub>–), 7.43–8.97(m, 8H, Ar–H), 8.98(s, 1H, –CH=N–), 12.64(br s, 1H, NH). UV-Vis (methanol,  $\lambda_{max}$ , nm): 204, 239, 273, 280. *Anal*. Calc. for C<sub>16</sub>H<sub>16</sub>N<sub>4</sub>: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.52; H, 6.05; N, 21.08%.

### 2.1.2. Synthesis of the complexes

# 2.1.2.1. Synthesis of $[CdL^{1}Cl_{2}]_{2} \cdot H_{2}O(1)$

To a methanol solution (10 mL) of L<sup>1</sup> (0.025g, 0.1 mmol), a solution of CdCl<sub>2</sub>·2.5H<sub>2</sub>O (0.023g, 0.1mmol) in the same solvent was slowly added. The stirring was continued for addition 2 h and filtered. The light yellow solution was kept at room temperature, which produced yellow crystals suitable for X-ray diffraction after 7 days. The crystals were isolated by filtration and air-dried. Yield: (0.055g, 61%). IR (KBr pellet, cm<sup>-1</sup>): 3416(v<sub>OH</sub>), 3200-2700(v<sub>NH</sub>), 1624(v<sub>C=N</sub>), 1451(v<sub>C=C-C=N</sub>). UV-Vis (methanol,  $\lambda_{max}$ , nm): 201, 203, 232, 273, 279. *Anal.* Calc. for C<sub>30</sub>H<sub>32</sub>Cd<sub>2</sub>Cl<sub>4</sub>N<sub>8</sub>O<sub>2</sub>: C, 39.89; H, 3.57; N, 12.41%. Found: C, 39.84; H, 3.49; N, 12.30%.

# 2.1.2.2. Synthesis of the $[CdL^{1}(N_{3})_{2}]_{2}$ ·CH<sub>3</sub>OH (2)

To a methanol solution (10 mL) of L<sup>1</sup> (0.025g, 0.1 mmol), a solution of Cd(ClO<sub>4</sub>)·6H<sub>2</sub>O (0.042g, 0.1 mmol) in the same solvent was slowly added, followed by drop addition of a 1 mL aqueous solution of NaN<sub>3</sub> (0.013g, 0.2 mmol). The stirring was continued for addition 2 h and filtered. The light yellow solution was kept at room temperature, which produced yellow crystals suitable for X-ray diffraction after 7 days. The crystals were isolated by filtration and air-dried. Yield: (0.062, 65%). IR (KBr pellet, cm<sup>-1</sup>): 3587(v<sub>OH</sub>), 3400-2800(v<sub>NH</sub>), 1629(v<sub>C=N</sub>), 1453(v<sub>C=C-C=N</sub>),

2076( $v_{N3}$ ). UV-Vis (methanol,  $\lambda_{max}$ , nm): 201, 203, 233, 273, 279. *Anal.* Calc. for C<sub>32</sub>H<sub>36</sub>Cd<sub>2</sub>N<sub>20</sub>O<sub>2</sub>: C, 40.14; H, 3.79; N, 29.25. Found: C, 40.05; H, 3.76; N, 29.05%.

# 2.1.2.3. Synthesis of the $[CdL^{1}(\mu_{1,5}-dca)dca]_{n}(3)$

Complex 3 was prepared by the same procedure as that of complex 2, but using NaN(CN)<sub>2</sub> (0.018 g, 0.2 mmol) in place of NaN<sub>3</sub> .Yield: (0.033g, 67%). IR (KBr pellet, cm<sup>-1</sup>): 3230-2825(v<sub>NH</sub>), 1628(v<sub>C=N</sub>), 1450(v<sub>C=C-C=N</sub>), 2301, 2208, 2250, 2237, 2164, 2146(v<sub>dca</sub>). UV-Vis (methanol,  $\lambda_{max}$ , nm): 201, 204, 235, 273, 279. *Anal.* Calc. for C<sub>19</sub>H<sub>14</sub>Cd N<sub>10</sub>: C, 46.12; H, 2.85; N, 28.31. Found: C, 46.08; H, 2.80; N, 28.25%.

### 2.1.2.4. Synthesis of $[CdL^2Cl(dca)]_2(4)$

To a methanol solution (10 mL) of L<sup>2</sup> (0.026g, 0.1 mmol), a solution of CdCl<sub>2</sub>·2.5H<sub>2</sub>O (0.023g, 0.1mmol) in the same solvent was slowly added, followed by drop addition of a 1 mL aqueous solution of NaN(CN)<sub>2</sub> (0.018 g, 0.2 mmol). The stirring was continued for addition 2 h and filtered. The light yellow solution was kept at room temperature, which produced yellow crystals suitable for X-ray diffraction after 7 days. The crystals were isolated by filtration and air-dried. Yield: (0.060g, 63%). IR (KBr pellet, cm<sup>-1</sup>): 3260-2740(v<sub>NH</sub>), 1624(v<sub>C=N</sub>), 1450(v<sub>C=C-C=N</sub>), 2276, 2215, 2159(v<sub>dca</sub>). UV-Vis (methanol,  $\lambda_{max}$ , nm): 202, 204, 237, 272, 279. *Anal.* Calc. for C<sub>36</sub>H<sub>32</sub>Cd<sub>2</sub>Cl<sub>2</sub>N<sub>14</sub>: C, 45.21; H, 3.37; N, 20.50. Found: C, 45.17; H, 3.34; N, 20.38%.

### 2.2. Physical measurements

Elemental analyses were taken using a Perkin-Elmer 240C analyzer. <sup>1</sup>H NMR spectra were recorded on a Bruker Avance500MHz spectrometer at 25 °C in DMSO with tetramethylsilane as the internal reference. The infrared spectra in KBr pellets were obtained on a ThermoFisher Nicolet 6700 spectrometer in the 4000–400 cm<sup>-1</sup>

region. A Shimadzu UV-2550 spectrophotometer was used to record the electronic spectra. Fluorescent spectra were measured with a Hitachi F-4600 spectrophotometer. The powder XRD data was collected in a  $2\theta$  range of 5–50° using a Rigaku D/MAX-2500 X-ray diffractomete at ambient conditions.

### 2.3. X-ray crystallography

Diffraction intensities for complexes **1**, **3** and **4** were collected on a Bruker Smart 1000 CCD area detector using graphite-monochromatized Mo- $K\alpha^{\bullet}$  radiation ( $\lambda =$ 0.71073 Å) with  $\omega$  scan mode at 298(2) K for **1** and **3** and 293(2) K for **4**, repectively. Diffraction intensities for complex **2** was collected on a Bruker FRAMBO CCD area detector using graphite-monochromatized Cu- $K\alpha^{\bullet}$  radiation ( $\lambda = 1.54178$  Å) with  $\omega$ scan mode at 298(2) K. Unit cell dimensions were obtained with least-squares refinements and semi-empirical absorption corrections were applied using SADABS program [48]. All the structures were solved by direct method and non-hydrogen atoms were obtained in successive difference Fourier syntheses. The final refinements were performed by full-matrix least-squares methods on  $F^2$  by SHELXL-97 program package [49]. Hydrogen atoms were included in calculated positions and refined with fixed thermal parameters riding on their parent atoms. Further crystallographic data and experimental details for structural analyses are summarized in Table 1.

#### (Insert Table 1 here)

#### 3. Results and discussion

### 3.1. Synthesis

Two unsymmetrical Schiff base ligands  $L^1$  and  $L^2$  were respectively synthesized by the condensation of pyridine-2-carbaldehyde with 2-aminoethyl-1H-benzimidazole

and 2-aminopropyl-1H-benzimidazole in MeOH, in which both  $L^1$  and  $L^2$  are light brown crystalline solid. Complex **1** was obtained by mixing CdCl<sub>2</sub>·2.5H<sub>2</sub>O and  $L^1$  in a 1:1 ratio in methanol. Complexes **2**, **3** and **4** were obtained by the reaction of the ligands L and the respective Cd(II) salts and different pseudohalids taken in a 1:1:2 ratio (where  $L = L^1$  (2 and 3) or  $L^2$  (4)). X-ray quality crystals of **1-4** were obtained upon slow evaporation of the suitable reaction mixtures at room temperature. The complexes are soluble in common organic solvents such as EtOH, MeOH, DMSO and DMF. The analytical and spectral data are completely consistent with the proposed formulation.

### 3.2. Crystal structures of the complexes

The molecular structures of the complexes **1-4** are displayed in Fig.1-8. The selected bond lengths and bond angles relevant to the coordination sphere are listed in Table 2.

## (Insert Table 2 here)

# 3.2.1. Molecular and supramolecular structures of $[CdL^{1}Cl_{2}]_{2}$ ·H<sub>2</sub>O (1)

A perspective view of complex 1, with the atomic numbering scheme, is shown in Fig. 1. Complex 1 crystallizes in the space group *Pbca*. The structure of 1 consists of one water molecule and one centrosymmetric  $[Cd(L^1)(\mu^2-Cl)Cl]_2$  dimer containing two cadmium ions bridged by two chloride ligands. Each Cd(II) cation shows a distorted octahedral geometry. The equatorial plane is formed by N1 from azomethine, N2 from benzimidazole, N4 from pyridine and the bridging Cl1 atom, while the axial positions are occupied by Cl1A atom and the terminal Cl2 atom. The Cd atoms are shifted by a distance of 0.2338 Å downward from the equatorial plane towards the terminal Cl2 atom. The Cd–N distances fall within the range 2.267(4)–2.363(5) Å,

while the two Cd–Cl (bridging) bond lengths are 2.4907(13) and 2.9345(15) Å and the Cd–Cl (non-bridging) bond length is 2.5833(15) Å, as were observed in other reported complex [15]. The *cisoid* and *transoid* angles in the equatorial plane are in the range of 70.26(17)–107.95(12)° and 152.98(16)–162.26(12)°, respectively, indicating the distortion from an ideal octahedral geometry. In this dimeric unit, the Cd…Cd separation is 2.935 Å. Furthermore, through the inter- and intramolecular hydrogen bonds N3–H3…O1, O1–H1E…Cl2 and O1–H1F…Cl2, the dinuclear unit is assembled into a 3D supramolecular network (Table 3, Fig. 2). The lattice water molecules act as both donors and acceptors, together with the NH of the benzimidazole ring and the terminal Cl<sup>-</sup>, all of which play an important role in constructing those hydrogen bonds.

# (Insert Fig.1 and Fig.2 here)

# 3.2.2. Molecular and supramolecular structures of $[Cd(L^1)(N_3)_2]_2 \cdot CH_3OH(2)$

A perspective view of complex **2**, with the atomic numbering schemes, is shown in Fig 3. Complex **2** crystallizes in the space group  $P2_1/c$ . The structure of **2** consists of a methanolic molecule and a centrosymmetric  $[Cd(L^1)(\mu_{1,1}-N_3)(N_3)]_2$  dimer, bridged by two end-on bridging azide groups. Here the ligand L<sup>1</sup> acts as a neutral tridentate NNN donor. Each Cd atom has a distorted octahedral geometry. Three nitrogen atoms, N3 from azomethine, N1 from benzimidazole, N4 from pyridine and N5A from the bridging azide group form the equatorial plane, while N5 from the other bridging azide ligand and N8 of the terminal azide ligand are situated in the axial positions. The Cd atom is shifted by a distance of 0.2829Å downward from the equatorial plane towards the dangling azide unit. The Cd–N bond distances are ranging from 2.236(10) to 2.545(11) Å, as were comparable to other similar

systems[12, 39]. The bridging azide is asymmetric [N5–N6 = 1.199(11) and N6–N7 = 1.141(12) Å], while two N–N bond distances of the dangling zaide are almost the same [N8–N9 = 1.161(14) and N9–N10 = 1.162(14) Å]. In this dimeric unit, the Cd…Cd separation is 3.697 Å. In addition, there are intermolecular  $\pi \cdots \pi$  interactions in which each pyridine ring Cg1 is offset-stacked with the phenyl ring Cg2 within the dimer with the centroid-to-centroid separation of 3.972 Å. The complex units are further connected by the inter- and intramolecular hydrogen bonds N–H…O, O–H…N and C–H…N between the methanolic molecule and the dimer to form a 2D supramolecular sheets parallel to *ab*-plane (Tables 3 and 4, Fig. 4).

(Insert Fig.3 and Fig.4 here)

# 3.2.3. Molecular and supramolecular structures of $[Cd(L^1)(\mu_{1,5}-dca)dca]_n(3)$

A perspective view of a short segment of the polynuclear architecture of complex **3**, with the atomic numbering schemes, is shown in Fig 5. Complex **3** crystallizes in the space group  $P\overline{1}$ . The coordination polyhedron around each Cd center in **3** is best described as a distorted octahedron with a CdN<sub>6</sub> chromophore. Three nitrogen atoms (N1, N2 and N4) of the tridentate ligand L<sup>1</sup> and one nitrile N atom (N5) of the terminal dca occupy the equatorial plane. The axial positions are occupied by one nitrile nitrogen N8 and a symmetry related (x - 1, y, z) nitrile nitrogen N10A of the  $\mu_{1,5}$ -bridged dca connects two neighboring Cd(II) centers in a non-ending fashion and produces the 1D chain structure. The Cd–N distances fall within the range 2.243(3)–2.454(4) Å. The intrachain Cd···Cd separation is 7.740 Å. The C=N–Cd bond angles are 161.0(3)°, 156.7(3)° and 135.6(3)°, which deviate from linearity, indicating that both the terminal and the  $\mu_{1,5}$ -bridged dca anions coordinate to Cd(II) in a bending fashion. The N7–C17 distance (1.141(6) Å) is some longer than

N5–C16 distance (1.136(5) Å), indicating coordination of N6 to Cd(II) for the terminal dca. The larger dca anions are non-linearity as reflected in the skeletal bond angles N–C–N (173.7(5)°, 175.1(6)°, 173.5(4)°, 173.9(5)°) and C–N–C(119.5(4)° and 123.8(4)°)

The 1D chains in **3** are further connected by two symmetry-independent  $\pi \cdots \pi$  stacking interactions between the pyridine rings C3g of one unit and the phenyl rings C4g of the other with centroid-to-centroid distance of 3.612 and 4.168 Å, respectively, to give rise to a 2D supramolecular network parallel to *ab*-plane(Table 4 and Fig. 6a). These 2D supramolecular sheets are further connected by N–H…N and C–H…N hydrogen bonding interactions to give rise to a 3D suparmolecular network (Table 3 and Fig. 6b).

### (Insert Fig.5 and Fig.6 here)

# 3.2.4. Molecular and supramolecular structures of $[Cd(L^2)(\mu^2-Cl)(dca)]_2(4)$

A perspective view of complex **4**, with the atomic numbering schemes, is shown in Fig 7. Complex **4** crystallizes in the space group  $P\overline{1}$ . Similar to the structure of **1**, the structure of **4** consists of a centrosymmetric  $[Cd(L^2)(\mu^2-Cl)(dca)]_2$  dimer containing two cadmium ions bridged by two chloride ligands. Each cadmium(II) cation shows a distorted octahedral geometry. The equatorial plane is formed by N1 from azomethine, N2 from benzimidazole, N4 from pyridine and the bridging Cl1 atom, while the axial positions are occupied by Cl1A atom and the nitrile nitrogen N5 of the terminal dca. The Cd atoms are nearly in the mean basal plane (0.0020 Å). The Cd–N distances fall within the range 2.277(5)–2.411(6) Å. The equatorial Cd–Cl bond length is 2.5653(19) Å and the axial atoms are less tightly bound with bond lengths of 2.7407(19) Å. In this dimeric unit, the Cd···Cd separation is 2.741 Å.

The discrete molecules of complex **4** are further connected by  $\pi \cdots \pi$  stacking interactions between the pyridine rings C5g of one molecule and the pyridine rings of the other, to give rise to a 1D supramolecular chain along the crystallographic *a*-axis (Table 4 and Fig. 8a). These 1D supramolecular chains are further connected by N–H…N and C–H…N hydrogen bonding interactions to give rise to a 3D suparmolecular network (Table 3 and Fig. 8b).

(Insert Fig.7 and Fig.8 here)

(Insert Talbe 3 and Table 4 here)

### 3.3. Powder X-ray diffraction and thermal analysis

To confirm whether the crystal structures are truly representative of the assynthesized materials, the powder XRD patterns for complexes **1–4** have been investigated at room temperature. The simulative powder diffraction patterns were based on the single crystal structural data (cif file) using CCDC Mercury software. As shown in Fig.9, the main peaks of experimental spectra of **1–4** are basically consistent with their simulated ones except for the relative intensity variation because of preferred orientations of the crystals. This suggests that all the complexes are single phase.

# (Insert Fig.9 here)

To characterize the thermal stabilities of compounds **1**–**4**, their thermal behaviors were studied by thermogravimetric analyses (TGA) under N<sub>2</sub> atmosphere(Fig.9). Complex **1** undergoes dehydration in the temperature range of 249-309 °C (obsd 3.42%, calcd 3.98%). Decomposition of one Schiff base occurs from 309 to 506 °C (obsd 28.92%, calcd 27.68%). The weight loss of 41.39% from 506 to 783 °C is attributed to departure of the four chlorides and the other Schiff base (calcd 43.40%). The remaining weight is 26.27%, which may correspond to the formation of CdO

(calcd 28.42%). For complex **2**, the first weight loss from 157 to 222 °C is assigned to the loss of one methanol molecule (obsd 1.95%, calcd 1.67%). The second weight loss in the temperature range of 222-508 °C is due to the loss of the other methanol molecule and four coordinated azido anions (obsd 23.96%, calcd 19.53%). The third weight loss is associated with the decomposition of one Schiff base between 508-784 °C (obsd 24.32%, calcd 26.32%). Complex **3** shows thermal stability up to 316 °C and from this temperature decomposition of the coordinated dca anions and Schiff base occurs up to 785 °C, followed by a drastic weight loss of 61.71%. However, it is difficult to identify the released fragments, which may be due to the unstability of the intermediate products. For complex **4**, the weight loss corresponding to the release of two bridging chlorides and two dca anions is observed from 192 to 508 °C (obsd 19.17%, calcd 21.22%). Decomposition of one Schiff base occurs from 508 to 735 °C (obsd 31.36%, calcd 27.60%). The thermogravimetric analyses of the complexes show that the complex **3** with 1D-polymeric structure is more stable than the other three dinuclear complexes.

## (Insert Fig.10 here)

## 3.4. IR, electronic and fluorescence spectra

In both of the two free Schiff bases, two bands at 1635 and 1437 cm<sup>-1</sup> are assigned as the v(C=N) of the imine and the  $v_a(-C=N-C=C-)$  of the benzimidazole ring stretching vibrations, respectively [50]. However, in all the four complexes the 1635 cm<sup>-1</sup> band shifts to lower frequencies by 6-11 cm<sup>-1</sup> whereas the 1437 cm<sup>-1</sup> band shifts to higher frequencies by 13-16 cm<sup>-1</sup>, indicating the coordination of the nitrogen atoms to Cd(II) ions. This is further supported by the band around 485 cm<sup>-1</sup> corresponding to the v(Cd–N) vibration. Several medium intensity bands spreading between 3200 and 2700 cm<sup>-1</sup> in all the four complexes indicate that the NH groups of

the benzimidazole rings are involved in hydrogen bonding with other electronegative atoms [51].

Broad bands at 3416 and 3587cm<sup>-1</sup> are assigned as v(O–H) stretching vibrations of the hydrate water molecules in complex **1** and methanol molecules in complex **2**, respectively, which are involved in hydrogen bonding in the crystals of the two complexes. A distinct band at 2076 cm<sup>-1</sup> is indicative of the presence of coordinated azide in complex **2**. The free dca shows three characteristic IR bands at 2287, 2229 and 2181 cm<sup>-1</sup>, which are assigned to  $v_{as}+v_s(C=N)$ ,  $v_{as}(C=N)$  and  $v_s(C=N)$  modes [52]. In complex **3** three bands at 2237, 2208, 2146 cm<sup>-1</sup> indicate the presence of terminal coordination mode of dca. In complex **4** these bands are split into two parts of which one part (2301, 2250, 2164 cm<sup>-1</sup>) indicates 1, 5 bridging coordination mode of dca, whereas the other part (2276, 2216 cm<sup>-1</sup>, 2146cm<sup>-1</sup>) indicates terminal dca coordination [53]. This is confirmed by X-ray structure determinations of **3** and **4**.

The electronic absorption spectra of the free Schiff base ligands and the four complexes in methanol were recorded at room temperature. UV bands around 275 and 283 nm are observed for the free Schiff bases, which are characteristic of the benzimidazole group and arise from a  $\pi$ - $\pi$ \* transition. These are blue-shifted upon coordination, showing clear evidence of C=N coordination to Cd(II) atoms [54]. Similarly, the ligand chromophore (C=N) (azomethine) absorbs at 248 nm for L<sup>1</sup> and 239 nm for L<sup>2</sup>, respectively, and shifts to a shorter wavelength by 2-12 nm upon complexation indicating the coordination of azomethine (C=N).

The fluorescent behaviors of complexes 1-4 and free Schiff bases  $L^1$  and  $L^2$  are investigated in the solid state at room temperature (Fig.11). The free Schiff bases  $L^1$  and  $L^2$  show a similar green emission band at 567 and 569 nm upon excitation at 280nm, respectively. The complexes 1-4, also upon excitation at 280nm, exhibit the

green emissions at 573, 571, 575 and 577nm, respectively. The emission bands for complexes 1, 2 and 4 are similar to those of the dinuclear Cd-Schiff base complexes  $[Cd(L^{1})Cl]_{2}, [Cd(L^{1})(NO_{3})]_{2}, [Cd(L^{2})(NO_{3})](CH_{3}OH)_{2} \text{ and } [Cd(L^{2})(NO_{3})](H_{2}O)_{2},$ where the maximum emission wavelength is at 564, 561, 549 and 548 nm. The emission band for complex 3 is similar to those of 1D polymer Cd-Schiff base complexes  $[Cd_2(L^1)_2](SCN)_2]_n$  and  $[Cd(L^2(SCN)_2]_n)$ , where the maximum emission wavelength is at 562 and 551nm ( $HL^1 = 2$ -((2-(dimethylamino-)ethylimino)) methyl)phenol,  $HL^2$  = methyl-2-pyridylmethylidenehy-drazinecarbodithioate). It is apparent that the emission spectra of 1-4 resemble those of the corresponding Schiff bases, which may be assigned to the intraligand  $\pi^* \rightarrow \pi$  transition. Compared with the emission spectra of the free corresponding Schiff bases, slightly red shifts of 6 nm in 1, 4 nm in 2, 8nm in both 3 and 4 can be observed, which may be mainly caused by the coordination of metal atom to ligand [3]. Moreover, we can find that the emission intensity of the four complexes is weaker than that of the corresponding Schiff bases, which are comparable to other Cd-organic complexes [41-42, 55]. This may be attributed to the heavy metal effect of Cd(II) ions and the quenching by the pseudohalide and halogens [42, 55]. In addition, the emission intensity of 1-4 were found to be  $1\approx3>4\approx2$ . It is possibly explained that 1 and 3 have bigger conformational rigidity for their 3D supramolecular network constructed by the cooperative association of coordination bonds as well as hydrogen bonds and  $\pi \cdots \pi$  packing interactions than 2 which has a 2D supramolecular network. Complex 4, though also having 3D supramolecular network, has the weaker emission intensity than 1 and 3 and compared to 2, which may be caused by the weaker non-covalent interactions and the appearance of both the pseudohalide (dca) and halogens (chloride).

## (Insert Fig.11 here)

### 4. Conclusion

The benzimidazole derived NNN donor Schiff bases  $L^1$  and  $L^2$  form four new Cd(II) complexes in the same reaction conditions, which are two dinuclear complexes and one 1D polymer with  $L^1$ , and one dinuclear complex with  $L^2$ . Compared the structures of the four complexes, we can find that the counter anions (Cl<sup>-</sup>,  $N_3^-$  and dca) play an important role in determining the resulting structures. The anions Cl<sup>-</sup>, N<sub>3</sub><sup>-</sup> and dca have strong coordination ability and can present both terminal and bridging coordination mode. In complexes 1 and 2, both Cl<sup>-</sup> and N<sub>3</sub><sup>-</sup> adopt terminal and  $\mu_{1,1}$ bridging coordination mode, resulting in the formation of dinuclear complexes 1 and 2. In complex 3, the counter anion dca with larger size and steric hindrance adopts terminal and  $\mu_{1, 5}$  bridging coordination mode and extends the SBUs, namely  $[CdL^{1}dca]^{+}$  to one direction. So a 1D chain structure is formed in 3. It is surprising that complex 4 is also a dinuclear structure containing dca and Cl<sup>-</sup>. In 4, the dca is coordinated to Cd(II) ions in the terminal mode, and Cl<sup>-</sup> is coordinated to the Cd(II) ion as a bridging ligand, which can be contributed to the competition and compromise between the two anions in the system, though both of them can act as bridging ligands. The crystal structures of these complexes have 3D networks in 1, 3 and 4, and 2D network in 2 due to the existence of hydrogen bonds and  $\pi \cdots \pi$  interactions. Thermal analysis reveals that the complex 3 with 1D polymeric chains is more stable than complexes 1, 2 and 4, which are dinuclear structures. The fluorescent spectra of all the four complexes are near to their corresponding Schiff bases excluding the slightly red shifts and weaker emission intensity.

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

CCDC 1507280–83 contain the supplementary crystallographic data for complexes **1–4**. These data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: <u>deposit@ccdc.cam.ac.uk</u>.

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	1	2	3	4
Formula	$C_{30}H_{32}Cd_2Cl_4N_8O_2$	$C_{32}H_{36}Cd_2N_{20}O_2$	C <sub>19</sub> H <sub>14</sub> Cd N <sub>10</sub>	$C_{36}H_{32}Cd_2Cl_2N_{14}$
$M(\text{g mol}^{-1})$	903.24	957.61	494.80	956.46
Temperature (K)	298(2)	298(2)	298(2)	293(2)
$\lambda$ (Å)	0.71073	1.54178	0.71073	0.71073
Crystal System	Orthorhombic	Monoclinic	Triclinic	Triclinic
Space group	Pbca	$P2_{1}/c$	$P\overline{1}$	Pī
Unit cell dimensions				
<i>a</i> (Å)	9.3942(6)	8.4191(9)	7.7400(6)	8.6625(4)
<i>b</i> (Å)	18.0449(14)	10.9282(11)	9.1690(8)	8.9921(5)
<i>c</i> (Å)	20.2242(16)	22.441(2)	15.4790(13)	13.6146(12)
α (°)	90	90	77.1490(10)	71.7030(10)
β (°)	90	105.912(2)	89.614(2)	89.019(2)
γ (°)	90	90	66.7310(10)	70.6300(10)
Volume (Å <sup>3</sup> )	3428.4(4)	1985.6(3)	979.84(14)	945.40(11)
Ζ	4	2	2	1
$\mu(\text{mm}^{-1})$	1.594	9.062	1.144	1.314
<i>F</i> (000)	1792	960	492	476
Crystal size (mm)	0.47 x 0.21 x 0.10	0.25 x 0.23 x 0.16	0.42 x 0.26 x 0.20	0.22 x 0.17 x 0.10
Theta range (°)	2.47 - 25.02	4.10 - 66.19	2.53 - 25.02	2.50 - 25.02
Index ranges	-11/10,-21/20, -22/24	±9, -12/11, -9/26	±9, -6/10, -17/18	$-10/9, -9/10, \pm 16$
$D_{\rm calc}$ (g cm <sup>-3</sup> )	1.750	1.602	1.677	1.680
Reflections collected	16040	6476	4901	4822
Independent reflections	3030	3434	3363	3276
$R_1$ , $_{\rm w}R_2(I>2\sigma(I))$	0.0372, 0.0786	0.0788, 0.0995	0.0333, 0.0729	0.0622, 0.1351
$R_1$ , $_{\rm w}R_2$ (for all $F_0^2$ )	0.0872, 0.0959	0.1631, 0.1331	0.0422, 0.0775	0.0832, 0.1429
Goodness-of-fit on $F^2$	1.014	0.964	1.058	1.045

### Table1 Crystallographic data and refinement parameters for 1-4.

Bond	Lengths	Bond	Lenghs	Bond	Lengths
1					
Cd1–N1	2.356(4)	Cd1–N2	2.267(4)	Cd1–N4	2.363(5)
Cd1–Cl1	2.4907(13)	Cd1Cl2	2.5833(15)	Cd1–Cl1A	2.9345(15)
Bond	Angles	Bond	Angles	Bond	Angles
N1-Cd1-N2	84.02(16)	N2Cd1N4	152.98(16)	N1-Cd1-N4	70.26(17)
N1-Cd1-Cl1	162.26(12)	N2-Cd1-Cl1	107.95(12)	N4Cd1Cl1	95.50(12)
N1-Cd1-Cl2	90.80(11)	N2-Cd1-Cl2	91.25(11)	N4Cd1Cl2	97.07(11)
Cl1-Cd1-Cl2	101.72(5)	N1-Cd1-Cl1A	81.55(10)	N2-Cd1-Cl1A	80.36(11)
N4–Cd1–Cl1A	87.62(11)	Cl1-Cd1-Cl1A	87.50(5)	Cl2–Cd1–Cl1A	169.15(5)
2					
Bond	Lengths	Bond	Lenghs	Bond	Lengths
Cd1–N1	2.258(10)	Cd1–N3	2.359(10)	Cd1–N4	2.376(10)
Cd1–N5	2.545(11)	Cd1–N5A	2.236(10)	Cd1–N8	2.284(13)
Bond	Angles	Bond	Angles	Bond	Angles
N5A-Cd1-N1	107.8(4)	N5A-Cd1-N8	99.5(4)	N1-Cd1-N8	96.3(4)
N5A-Cd1-N3	154.6(4)	N1-Cd1-N3	85.8(4)	N8-Cd1-N3	100.2(4)
N5A-Cd1-N4	94.0(4)	N1-Cd1-N4	154.9(4)	N8-Cd1-N4	92.1(4)
N3-Cd1-N4	69.4(4)	N5A-Cd1-N5	78.8(4)	N1-Cd1-N5	89.0(4)
N8-Cd1-N5	174.8(4)	N3-Cd1-N5	80.1(3)	N4-Cd1-N5	83.1(3)
3					
Bond	Lengths	Bond	Lenghs	Bond	Lengths
Cd1–N1	2.353(3)	Cd1–N2	2.282(3)	Cd1–N4	2.371(3)
Cd1–N5	2.454(4)	Cd1–N8	2.337(4)	Cd1-N10A	2.243(3)
Bond	Angles	Bond	Angles	Bond	Angles
N10A-Cd1-N2	111.64(12)	N10A-Cd1-N8	94.65(13)	N2-Cd1-N8	90.20(13)
N10A-Cd1-N1	162.7012	N2-Cd1-N1	83.11(11)	N8-Cd1-N1	94.27(13)
N10A-Cd1-N4	94.27(12)	N2-Cd1-N4	153.35(11)	N8-Cd1-N4	93.94(13)
N1-Cd1-N4	70.34(11)	N10A-Cd1-N5	85.90(14)	N2-Cd1-N5	82.49(12)
N8-Cd1-N5	172.31(13)	N1–Cd1–N5	87.24(14)	N4-Cd1-N5	93.67(12)
4					
Bond	Lengths	Bond	Lenghs	Bond	Lengths
Cd1–N2	2.277(5)	Cd1–N4	2.367(6)	Cd1–N1	2.398(6)
Cd1–N5	2.411(6)	Cd1-Cl1	2.5653(19)	Cd1–Cl1A	2.7407(19)
Bond	Angles	Bond	Angles	Bond	Angles
N2Cd1N4	156.0(2)	N2-Cd1-N1	85.6(2)	N4Cd1N1	70.9(2)
N2-Cd1-N5	91.6(2)	N4-Cd1-N5	90.8(2)	N1-Cd1-N5	84.3(2)
N2Cd1Cl1	101.41(15)	N4-Cd1-Cl1	102.36(17)	N1-Cd1-Cl1	172.34(16)
N5-Cd1-Cl1	92.23(15)	N2-Cd1-l1A	93.41(15)	N4–Cd1–Cl1A	84.88(15)
N1–Cd1–Cl1A	96.61(15)	N5–Cd1–Cl1A	174.97(14)	Cl1–Cd1–Cl1A	86.22(6)

# Table 2 Selected bond lengths [Å] and bond angles [°] for $1\!-\!\!4$

Symmetry codes: A -x+1,-y+1,-z+1 for 1; A -x+1,-y+1,-z for 2; A x-1, y, z B x+1,y,z

D–H	d (D–H)	d (H•••A)	∠DHA	d (D…A)	А	Symmetry
1						
N3-H3	0.860	1.938	161.70	2.767	01	- <i>x</i> +0.5, <i>y</i> -0.5, <i>z</i>
O1–H1E	0.850	2.256	175.77	3.104	Cl2	
O1–H1F	0.850	2.356	175.67	3.204	Cl2	<i>x</i> -0.5, <i>y</i> , - <i>z</i> +1.5
2						
N2-H2	0.860	1.862	163.54	2.698	01	<i>x</i> -1, <i>y</i> , <i>z</i>
O1-H1	0.820	1.940	157.75	2.716	N8	
O1–H1	0.820	2.551	160.62	3.335	N9	
C10-H10	0.930	2.575	150.21	3.414	N10	-x+1, -y+2, -z
C8–H8A	0.970	2.613	157.86	3.530	N9	x - 1, y, z
C8–H8A	0.970	2.8036	133.449	3.5417	N10	x - 1, y, z
3						
N3-H3	0.860	2.025	162.49	2.857	N7	-x+2, -y, -z
C6–H6	0.930	2.717	130.92	3.399	N9	-x+2, -y, -z+1
C9–H9	0.930	2.599	133.88	3.312	N5	x+1, -y+1, z
4						·
C8–H8	0.860	2.375	135.60	3.402	N7	-x+2, -y, -z+2
C15-H15	0.850	2.738	160.09	3.626	N5	-x+1, -y+2, -z+1
N3-H3	0.850	2.039	160.77	2.855	N7	-x+1, -y, -z+2

Table 3 Hydrogen bond distances [Å] and bond angles [°] of 1-4.

Cgi⋯Cgj	Rc <sup>a</sup>	α	R1v <sup>b</sup>	R2v <sup>c</sup>	Symmetry
$\pi \cdots \pi$ interactions					
2					
Cg1····Cg2	3.972	11.0	3.7066	3.4178	-x+1, -y+1, -z
3					
Cg3····Cg4	3.612	2.5	3.3352	3.2785	<i>x</i> −1, <i>y</i> +1, <i>z</i>
Cg4····Cg3	4.168	2.7	3.3620	3.4691	x, y–1, z
4					
Cg5····Cg5	4.047	0.0	3.3322	3.3322	-x, -y+2, -z+1
<i>a</i> = Dihedral angle between ring i and ring i (°) [Cg1: N4–C11–C12–C13–C14–C15, Cg2: C2–C3–C4–					

**Table 4** Geometrical parameters [Å, °] for  $\pi \cdots \pi$  interactions for **2-4**.

C5-C6-C7 for **2**; Cg3: N4-C11-C12-C13-C14-C15, Cg4: C4-C5-C6-C7-C8-C9 for **3**; Cg5: N4-

C11-C12-C13-C14-C15 for 4]

<sup>a</sup> Distance between the centroids of ring i and ring j.

<sup>b</sup> Perpendicular distance from the centroid of ring i to ring j.

<sup>c</sup> Perpendicular distance from the centroid of ring j to ring i.

Scheme 1





Fig.1 Molecular structure of dinuclear compound  $[CdL^1Cl_2]_2 \cdot H_2O(1)$  with atom labels. Symmetry code A:-x+1,-y+1,-z+1



Fig. 2 A view of the 3D molecular network fabricated by N-H…O and O-H…Cl hydrogen interactions in compound 1.



Fig. 3. Molecular structure of dinuclear compound  $[CdL^{1}(N_{3})_{2}]_{2} \cdot CH_{3}OH(2)$  with  $\pi \cdots \pi$  stacking between benzene and pyridine rings indicated by dashed lines. Symmetry code A: -x + 1, -y + 1, -z.



Fig. 4 A view of the 2D supramolecular layer assembled by  $\pi \cdots \pi$  stacking and N-H $\cdots$ O, O-H $\cdots$ N and C-H $\cdots$ N hydrogen interactions in the *ab* plane in compound 2.



Fig. 5 View of a 1D zigzag chain structure of  $[CdL^{1}(\mu_{1,5}-dca)dca]_{n}$  (3) formed through single  $\mu_{1,5}$ -dca bridges.

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Fig.6 2D supramolecular network parallel to *ab*-plane (a); 3D network assembled by  $\pi \cdots \pi$  stacking and N-H $\cdots$ N and C-H $\cdots$ N hydrogen interactions(b) in compound 3.



Fig. 7 Molecular structure of dinuclear compound  $[CdL^2Cl(dca)]_2$  (4) with atom labels. Symmetry code A:-x+1,-y+1,-z+1



Fig.8 1D supramolecular chain along the crystallographic a-axis (a); 3D network constructed by  $\pi \cdots \pi$  stacking and N-H $\cdots$ N and C-H $\cdots$ N hydrogen interactions (b) in compound 4.



Fig.9 PXRD patterns for simulated and experimental of compounds 1-4.



Fig.10 TG curve of compounds 1-4



Fig.11 The photoluminescent behaviors of complexes 1-4 and free Schiff bases L1-2.

# Highlights

► Four Cd(II) halides/pseudohalides complexes based on benzimidazole based Schiff bases ligand were prepared.

► X-ray structures reveal that 1-2 and 4 are dinuclear complexes and 3 is a dicyanamide bridged one-dimensional polymer.

► All the four complexes exhibit intraligand  ${}^{1}(\pi \rightarrow \pi^{*})$  fluorescence in the solid state at room temperature.