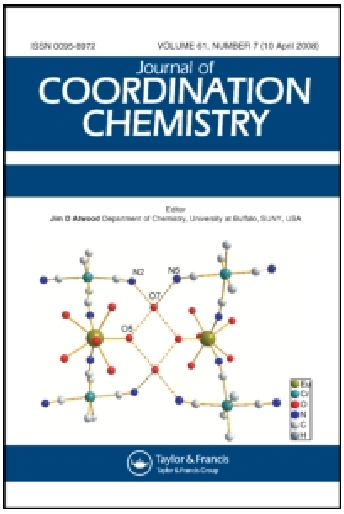

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Syntheses, structures, and luminescent properties of Zn(II) and Cd(II) complexes: 3-D supramolecules based on 2,6-bis(imino)pyridine ligands constructed by hydrogen bonding interactions

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Syntheses, structures, and luminescent properties of Zn(II) and Cd(II) complexes: 3-D supramolecules based on 2,6-bis(imino)pyridine ligands constructed by hydrogen bonding interactions

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Six 5-coordinate 2,6-bis(imino)pyridine metal complexes, [2,6-(ArN=CMe)$_2$C$_5$H$_3$NMCl$_2\cdot n$CH$_3$CN] (Ar = 4-MeC$_6$H$_4$, M = Zn, $n = 0.5$, **Zn1**, M = Cd, $n = 1$, **Cd1**; Ar = 2,6-Et$_2$C$_6$H$_3$, M = Zn, $n = 0.5$, **Zn2**, M = Cd, $n = 0.5$, **Cd2**; Ar = 2,4,6-Me$_3$C$_6$H$_2$, M = Zn, $n = 1$, **Zn3**, M = Cd, $n = 1$, **Cd3**), were synthesized in acetonitrile by the reactions of the corresponding bis(imino)pyridines with ZnCl$_2$ or CdCl$_2\cdot$2.5H$_2$O, respectively. The structures of **Zn1**–**Zn3** and **Cd1**–**Cd3** were determined by the single-crystal X-ray diffraction. In all complexes, the ligand is tridentate with further coordination by two chlorides, resulting in a distorted trigonal bipyramid. All complexes self-assemble through hydrogen bonding interactions to form a 3-D supramolecular structure. At 298 K in dichloromethane, all complexes have blue luminescent emissions at 405–465 nm, which can be attributed to ligand-centered $\pi^* \rightarrow \pi$ transitions. The zinc and cadmium centers play a key role in enhancing fluorescent emission of the ligands.

Keywords: Bis(imino)pyridine metal complexes; Crystal structures; Luminescent properties

1. Introduction

Luminescent coordination compounds with nitrogen-containing ligands have attracted the attention in sensor technologies and electroluminescent devices [1–12]. For example, luminescent noble metal complexes with bipyridine-containing ligands have high luminescent efficiency [10, 11]. However, low yields and higher costs of these complexes are the disadvantages for their use as optoelectronic materials. Low-cost d^{10} metal complexes with nitrogen-containing ligands have been synthesized and their luminescent behavior was studied [1–6]; zinc(II) and cadmium(II) complexes have been widely investigated as potential luminescent materials [1–5]. Self-assembly *via* intermolecular

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hydrogen bonding and/or aromatic π–π interactions provide an effective approach to functional coordination frameworks [13, 14]. The size of π-conjugated system of the ligand and the electronic effect of substituents on the ligand are important factors for modulating luminescent properties [3, 4]. Iron and cobalt complexes with bulky aryl substituted bis(imino)pyridine ligands, reported by Gibson *et al.* [15–17], exhibit high activity for olefin polymerization. In 2009, Jurca *et al.* [18] reported a 2,6-bis(imino)pyridyl indium complex as a monomeric In(I) species with a surprisingly long metal–ligand bond. We have devoted efforts toward the synthesis of bis(imino)pyridine complexes with luminescent properties [12]. To fulfill full-color electroluminescent displays, three color components, i.e. red, green, and blue, must be available. Stable blue luminescent compounds used for electroluminescent devices are rare and very challenging to prepare. In this work, we report the syntheses, structures, and blue luminescence of six new zinc(II) and cadmium(II) complexes with bis(imino)pyridine ligands.

2. Experimental

2.1. *Reagents and general techniques*

All manipulations were carried out under nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glove box. Elemental analyses were performed with a Perkin-Elmer 240c elemental analyzer. IR spectra were obtained with a Nicolet Impact 410 FTIR spectrometer using KBr pellets. NMR spectra were recorded with a Varian Mercury 400 MHz spectrometer. UV-Vis spectra were obtained with a Perkin-Elmer Lambda 20 spectrometer. Luminescence spectra were measured with a Perkin-Elmer LS55 Luminescence spectrometer at room temperature. 4-Methylaniline, 2,6-diethylaniline, and 2,4,6-trimethylaniline were purchased from Aldrich Chemical Co. and used as received. Solvents were refluxed in the presence of an appropriate drying agent, and distilled and degassed prior to use. For methanol, Mg ribbon was used as drying agent, whereas acetonitrile and dichloromethane were dried with calcium hydride. 2,6-Diacetylpyridine was prepared according to a published procedure [19].

2.2. *Syntheses of complexes*

2.2.1. 2,6-bis[1-(4-methylphenylimino)ethyl]pyridine $ZnCl_2 \cdot 0.5CH_3CN$ (Zn1). A mixture of L^1 (185 mg, 0.54 mmol) and $ZnCl_2$ (73 mg, 0.54 mmol) in CH_3CN (45 mL) was stirred under nitrogen at room temperature for 12 h. Evaporation of the solvent gave the crude product as yellowish powder. Pure **Zn1** was obtained in 74% yield (204 mg) by recrystallization from CH_3CN/CH_2Cl_2 (2 : 1). ^1H NMR (400 MHz, CD_3CN): $\delta = 8.40$ (d, 2H, $J = 8.0$ Hz, Py-H_m), 8.19 (t, 1H, $J = 8.0$ Hz, Py-H_p), 7.09–6.39 (m, 8H, Ar-H), 2.19 (s, 6H, $N=CMe$), 2.00 (s, 6H, Ar-Me) ppm. IR (KBr, cm^{-1}): 3074 (w), 3025 (w), 2915 (w), 1638 (m), 1589 (s), 1506 (s), 1372 (m), 1258 (s), 1230 (m), 1101 (w), 1023 (m), 845 (m), 819 (m), 548 (w), 515 (w), 466 (w). Calcd for $C_{23}H_{23}N_3ZnCl_2 \cdot 0.5CH_3CN$ (%): C, 57.86; H, 4.96; N, 9.84. Found (%): C, 57.89; H, 5.00; N, 9.64.

2.2.2. 2,6-bis[1-(2,6-diethylphenylimino)ethyl]pyridine $ZnCl_2 \cdot 0.5CH_3CN$ (Zn2). The procedure is similar to that described for the preparation of **Zn1**, except L^2 was used in the place of L^1 to obtain yellowish crystals of **Zn2**. Yield 76%. ^1H NMR (400 MHz, CD_3CN): $\delta = 8.51$ (d, 2H, $J = 7.8$ Hz, Py-H_m), 8.22 (t, 1H, $J = 7.8$ Hz, Py-H_p), 7.20–6.39 (m, 6H, Ar-*H*), 2.62 (q, 8H, $J = 7.6$ Hz, Ar-CH_2Me), 2.37 (s, 6H, N=C*Me*), 1.19 (t, 12H, $J = 7.6$ Hz, Ar-CH_2*Me*) ppm. IR (KBr, cm^{-1}): 3067 (w), 2970 (s), 2937 (m), 2879 (m), 1636 (s), 1590 (s), br 1455 (s), 1377 (s), 1247 (s), 1215 (s), 1104 (m), 1026 (m), 858 (m), 807 (s), 781 (s), 690 (w), 632 (w), 548 (w), 431 (w). Calcd for $C_{29}H_{35}N_3ZnCl_2 \cdot 0.5CH_3CN$ (%): C, 61.87; H, 6.32; N, 8.42. Found (%): C, 61.78; H, 6.26; N 8.68.

2.2.3. 2,6-bis[1-(2,4,6-trimethylphenylimino)ethyl]pyridine $ZnCl_2 \cdot CH_3CN$ (Zn3). The procedure is similar to that described for the preparation of **Zn1**, except L^3 was used in the place of L^1 to obtain yellowish crystals of **Zn3**. Yield 70%. ^1H NMR (400 MHz, CD_3CN): $\delta = 8.45$ (d, 2H, $J = 7.2$ Hz, Py-H_m), 8.20 (t, 1H, $J = 7.2$ Hz, Py-H_p), 6.91 (s, 4H, Ar-*H*), 2.51 (s, 6H, N=C*Me*), 2.24 s, 18H, Ar-*Me*). IR (KBr, cm^{-1}): 3106 (w), 3008 (w), 2911 (m), 2853 (w), 2730 (w), 1640 (s), 1590 (s), 1474 (s), 1364 (s), 1260 (s), 1221 (s), 1150 (w), 1021 (m), 852 (m), 813 (m), 736 (w), 645 (w), 567 (m), 438(w). Calcd for $C_{27}H_{31}N_3ZnCl_2 \cdot CH_3CN$ (%): C, 60.59; H, 5.96; N, 9.75. Found (%): C, 60.50; H, 5.66; N 9.88.

2.2.4. 2,6-bis[(4-methylphenylimino)ethyl]pyridine $CdCl_2 \cdot CH_3CN$ (Cd1). A mixture of L^1 (123 mg, 0.36 mmol) and $CdCl_2 \cdot 2.5H_2O$ (82 mg, 0.36 mmol) in acetonitrile (40 mL) was stirred under nitrogen at room temperature for 12 h. The volume of the reaction mixture was reduced to 15 mL and the mixture was left to stand at 0°C for several days. Yellowish crystals of **Cd1** were formed and separated from the solution. Yield: 147 mg (72%). ^1H NMR (400 MHz, CD_3CN): $\delta = 8.24$ (quint, $J = 7.0$ Hz, 3H, Py-*H*), 7.20–6.37 (m, 8H, Ar-*H*), 2.34 (s, 6H, N=C*Me*), 2.22 (s, 6H, Ar-*Me*) ppm. IR (KBr, cm^{-1}): 3079 (w), 3026 (w), 2921 (w), 1638 (m), 1585 (s), 1506 (s), 1459 (w), 1370 (m), 1253 (s), 1228 (s), 1188 (w), 1104 (w), 1018 (m), 844 (m), 815 (m), 767 (w), 740 (w), 707 (w), 635 (w), 542 (w), 515 (w). Calcd for $C_{23}H_{23}N_3CdCl_2 \cdot CH_3CN$ (%): C, 53.07; H, 4.63; N, 9.90. Found (%): C, 53.29; H, 4.72; N, 9.78.

2.2.5. 2,6-bis[1-(2,6-diethylphenylimino)ethyl]pyridine $CdCl_2 \cdot 0.5CH_3CN$ (Cd2). The procedure is similar to that described for the preparation of **Cd1**, except L^2 was used in the place of L^1 to obtain yellowish crystals of **Cd2**. Yield 70%. ^1H NMR (400 MHz, CD_3CN): $\delta = 8.27$ (quint, $J = 7.2$ Hz, 3H, Py-*H*), 7.18–7.24 (m, 6H, Ar-*H*), 2.65 (q, $J = 6.8$ Hz, 8H, Ar–CH_2Me), 2.33 (s, 6H, N=C*Me*), 1.11 (t, $J = 6.8$ Hz, 12H, Ar–CH_2*Me*) ppm. IR (KBr, cm^{-1}): 3068 (w), 2971 (s), 2932 (m), 2874 (m), 1634 (s), 1582 (s), 1452 (s), 1368 (s), 1251 (s), 1212 (s), 1115 (w), 1017 (m), 978 (w), 867 (w), 805 (s), 770 (s), 737 (w), 692 (w), 549 (w). Calcd for $C_{29}H_{35}N_3CdCl_2 \cdot 0.5CH_3CN$ (%): C, 57.25; H, 5.85; N, 7.79. Found (%): C, 57.11; H, 5.67; N, 7.68.

2.2.6. 2,6-bis[1-(2,4,6-trimethylphenylimino)ethyl]pyridine $CdCl_2 \cdot CH_3CN$ (Cd3). The procedure is similar to that described for the preparation of **Cd1**, except L^3 was used in the place of L^1 to obtain yellowish crystals of **Cd3** [20b]. Yield 72%. ^1H NMR

(400 MHz, CD_3CN): $\delta = 8.50$ (quint, $J = 6.8$ Hz, 3H, Py-*H*), 6.91–7.05 (m, 4H, Ar-*H*), 2.51 (s, 6H, N = C*Me*), 2.24 (s, 6H, Ar-*Me*), 2.17 (s, 12H, Ar-*Me*) ppm. IR (KBr, cm^{-1}): 3093 (w), 2950 (w), 2911 (m), 2853 (w), 2736 (w), 1636 (s), 1590 (s), 1474 (s), 1370 (m), 1260 (s), 1227 (s), 1150 (w), 1105 (w), 1020 (m), 852 (m), 807 (m), 742 (w), 638 (w), 574 (w). Calcd for $C_{27}H_{31}N_3CdCl_2 \cdot CH_3CN$ (%): C, 56.01; H, 5.51; N, 9.01. Found (%): C, 56.38; H, 5.31; N, 9.36.

2.3. *X-ray crystallograghy*

The data were collected with a Rigaku R-AXIS RAPID IP or a Siemens SMART 1000 CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 ± 2 K. The structure was determined by direct methods and refined by full-matrix least squares based on F^2 using the SHELXTL 5.1 software package [21]. All non-hydrogen atoms were refined anisotropically and the hydrogens were included in idealized position. Crystallographic data are given in table 1.

3. Results and discussion

3.1. *Synthesis and characterization*

2,6-bis[1-(4-methylphenylimino)ethyl]pyridine(L^1), 2,6-bis[1-(2,6diethylphenylimino) ethyl]pyridine(L^2), and 2,6-bis[1-(2,4,6trimethylphenylimino)ethyl]pyridine(L^3) were synthesized according to modified published procedures in good yields by the condensation of 2,6-diacetylpyridine with the corresponding aniline in refluxing absolute methanol in the presence of a catalytic amount of formic acid (scheme 1) [12, 13]. **Zn1**–**Zn3** and **Cd1**–**Cd3** were prepared in good yields (>70%) as yellow crystalline solids by the reaction of $ZnCl_2$ or $CdCl_2 \cdot 2.5H_2O$, respectively, with 2,6-bis(imino)pyridine in acetonitrile. Upon exposure to air, all complexes were stable in the solid state and in CH_2Cl_2, CH_3CN, DMSO, or DMF solutions. They were characterized by ^1H NMR, UV-Vis, and IR spectroscopy, elemental analysis, and single-crystal X-ray diffraction analysis.

3.2. *Description of structures*

The crystals of **Zn1**–**Zn3** and **Cd1**–**Cd3** suitable for X-ray structural determination were grown from acetonitrile/dichloromethane (2 : 1) solution (**Zn1**–**Zn3**), or from a concentrated acetonitrile solution (**Cd1**–**Cd3**). The molecular structures of complexes **Zn1**–**Zn3** and **Cd1**–**Cd3** are shown in figures 1–6 and selected bond lengths and angles are presented in table 2.

Zn1–**Zn3** (figures 1–3) and **Cd1**–**Cd3** (figures 4–6) possess the structures with approximate C_s symmetry about a plane bisecting the central pyridine ring and containing the metal and two chlorides. The central metal is coordinated to five groups in a distorted trigonal bipyramid, with the equatorial plane defined by N(2)(pyridine), Cl(1) and Cl(2), and N(1) and N(3)(imino) in axial positions. M–Cl (M = Zn or Cd) distances are significantly longer than M–N(2) and M–N(2) distances are appreciably

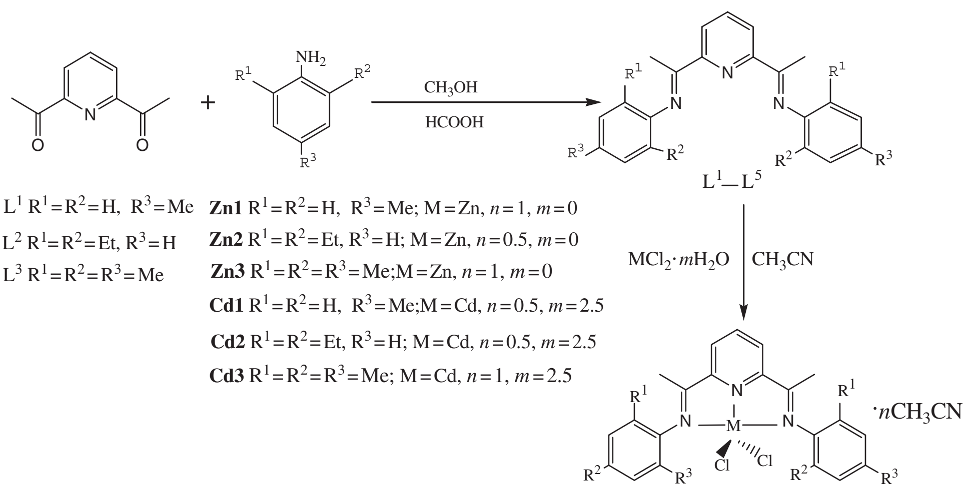
Table 1. Crystal data and structure refinement for **Zn1**–**Zn3** and **Cd1**–**Cd3**.

Data	**Zn1**	**Zn2**	**Zn3**	**Cd1**	**Cd2**	**Cd3**
Formula	$C_{24}H_{24.5}N_{3.5}Cl_2Zn$	$C_{30}H_{36.5}N_{3.5}Cl_2Zn$	$C_{29}H_{34}N_4Cl_2Zn$	$C_{25}H_{26}N_4Cl_2Cd$	$C_{30}H_{36.5}N_{3.5}Cl_2Cd$	$C_{29}H_{34}N_4Cl_2Cd$
Formal weight	498.24	582.40	574.87	565.8	629.43	621.90
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P2_1/n$
Unit cell dimensions (Å, °)						
a	8.095(3)	19.2465(15)	14.569(3)	13.248(13)	20.172(4)	14.545(3)
b	14.141(6)	25.347(2)	14.971(3)	13.248(13)	8.6139(18)	15.074(3)
c	22.857(9)	26.325(2)	14.708(3)	16.908(18)	17.986(4)	14.758(3)
α				81.016(15)		
β	95.360(8)	105.0340(10)	113.133(3)	81.016(15)	109.711(4)	111.516(2)
γ				69.01(2)		
Volume (Å^3), Z	2605.1(18),4	12402.9(17), 4^a	2950.0(9), 4	2720(5), 2^a	2942.1(11), 4	3010.3(9), 4
Calculated density (g cm^{-3})	1.270	0.624	1.294	1.381	1.421	1.372
Absorption coefficient (mm^{-1})	1.163	0.494	1.037	1.017	0.948	0.926
$F(000)$	1028	2440	1200	1144	1292	1272
θ range for data collection (°)	1.70–28.59	1.43–26.40	1.67–26.04	1.23–28.39	2.14–26.10	1.68–26.07
Limiting indices	$-10 \le h \le 10$	$-18 \le h \le 24$	$-13 \le h \le 17$	$-17 \le h \le 10$	$-24 \le h \le 14$	$-17 \le h \le 17$
	$-18 \le k \le 16$	$-27 \le k \le 31$	$-18 \le k \le 18$	$-17 \le k \le 16$	$-10 \le k \le 10$	$-16 \le k \le 18$
	$-29 \le l \le 21$	$-32 \le l \le 28$	$-18 \le l \le 17$	$-22 \le l \le 22$	$-21 \le l \le 22$	$-18 \le l \le 15$
Absorption correction	Semi-empirical					
Data/restraints/parameters	6152/18/289	12,228/54/650	5795/0/326	10,973/90/579	5388/36/340	5948/0/326
R_{int}	0.1092	0.1139	0.0932	0.7275	0.0973	0.0862
Goodness-of-fit on F^2	0.855	0.917	0.904	0.731	0.974	0.877
R_1^{b}	0.0696	0.0703	0.0501	0.0975	0.0726	0.0421
wR_2^{c}	0.2272	0.1726	0.0860	0.3040	0.1610	0.0909
Largest difference peak and hole (e Å^{-3})	0.953 and −0.322	1.136 and −0.458	0.538 and −0.256	0.830 and −0.781	0.723 and −0.683	0.681 and −0.393

[a] There are two crystallographically independent molecules in the asymmetric unit.

[b] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$.

[c] $wR_2 = [\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.



Scheme 1. The synthetic route of **Zn1**–**Zn3** and **Cd1**–**Cd3**.

shorter than that of M–N(1) and M–N(3). There are two independent complex molecules and one acetonitrile in the asymmetric unit of **Zn2**. **Zn3** and **Cd3** contain one independent molecule and one acetonitrile, whereas there are two independent molecules and two acetonitriles in the asymmetric unit of **Cd1**. **Zn1** and **Cd2** contain one independent molecule and 0.5 acetonitrile. Dihedral angles between the phenyl rings and plane formed by three coordinated nitrogens are in the range 74.98(26)–89.36(14)°. Dihedral angles between two phenyl rings are oriented essentially orthogonal in **Zn1**–**Zn3** and **Cd1**–**Cd3** [ranging between 79.93(16) and 87.32(23)°]. The mean deviation of the metals in **Zn1**–**Zn3** and **Cd1**–**Cd3** from the equatorial planes is 0.009, 0.023, 0.001, 0.019, 0.006, and 0.013 Å (0.016 and 0.030 Å for the other molecule in **Zn2** and **Cd1**, respectively), respectively, and the axial M–N(imino) bonds subtend angles of 148.15(13)°, 147.78(14)°, 147.20(13)°, 137.1(4)°, 150.56(17)°, and 138.27(11)° [147.06(15)° and 135.6(6)° for the other molecule in **Zn2** and **Cd1**, respectively], respectively. The metal atoms in **Zn1**–**Zn3** and **Cd1**–**Cd3** deviate by 0.023, 0.039, 0.100, 0.008, 0.359, and 0.094 Å (0.043 and 0.047 Å for the other molecule in **Zn2** and **Cd1**, respectively), respectively, from the coordinated plane. The M–N(pyridine) bonds in **Zn1**–**Zn3** and **Cd1**–**Cd3** range from 1.942(4) to 2.328(16) Å, while distances between metal and imino nitrogens in the six complexes are almost the same: 2.250(4) and 2.244(4) Å in **Zn1**; 2.311(5) and 2.295(4) Å in **Zn2** [2.330(4) and 2.292(4) Å for the other molecule in **Zn2**]; 2.301(3) and 2.302(3) Å in **Zn3**; 2.379(18) and 2.337(16) Å in **Cd1** [2.400(2) and 2.406(17) Å for the other molecule in **Cd1**]; 2.136(4) and 2.111(4) Å in **Cd2**; and 2.412(3) and 2.414(3) Å in **Cd3**. In each complex the M–N(pyridine) bond is significantly shorter than the M–N(imino) bonds, with the formal double-bond character of the imino linkages N(1)–C(1) and N(3)–C(7) being retained [C=N distances in the range 1.180(2)–1.390(18) Å].

There are no intermolecular packing features of interest in any of the six complexes. However, the structures of all complexes are stabilized by hydrogen bonds between Cl and C of adjacent molecules (figures 1–6 left), as indicated by the distances of Cl···C, 3.546–3.839 Å, and the bond angles of Cl···H···C, 137.52–177.08°, respectively,

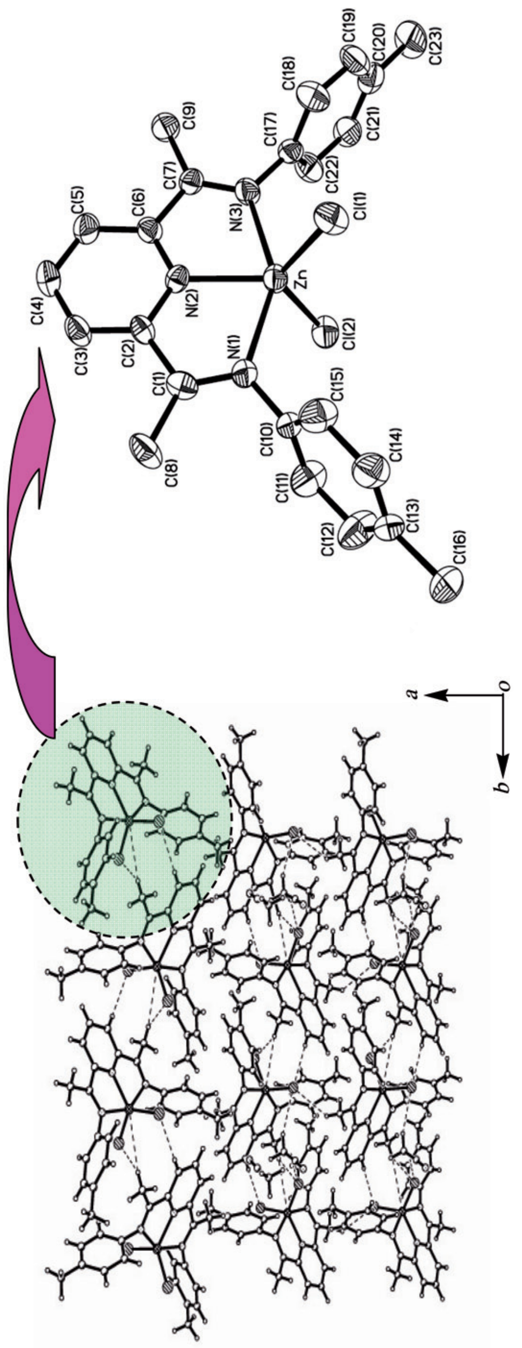


Figure 1. Right: Molecular structure of **Zn1** (0.5CH_3CN omitted for clarity). Left: Packing diagram of **Zn1** along the *c*-axis. Hydrogen bonds are indicated by dashed lines.

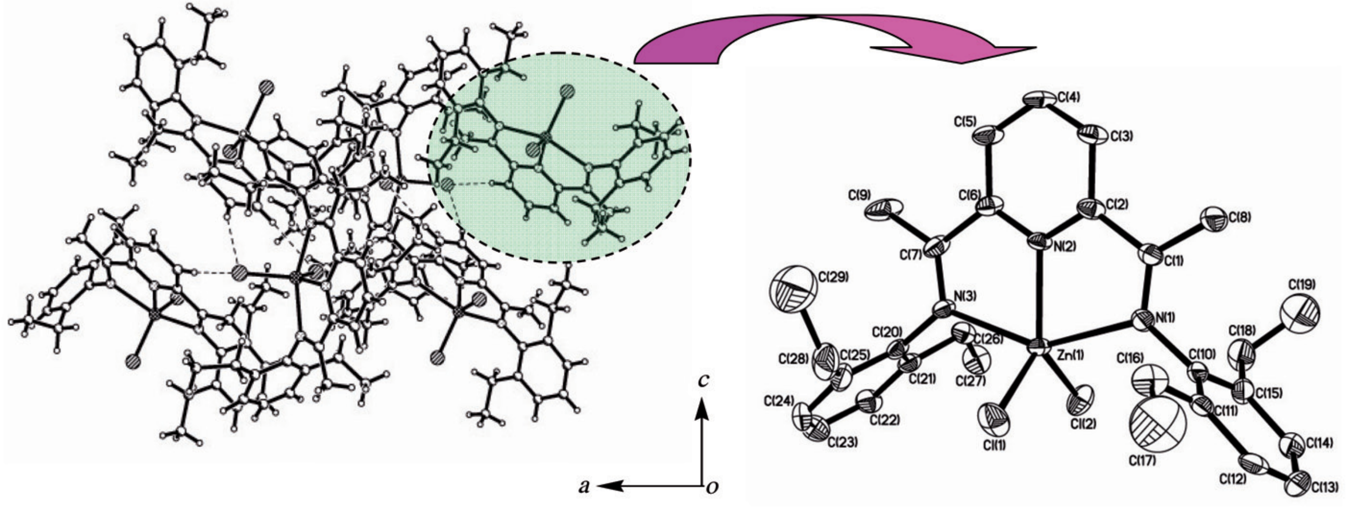


Figure 2. Right: Molecular structure of **Zn2** (the other molecule and CH_3CN have been omitted for clarity). Left: Packing diagram of **Zn2** along the *b*-axis. Hydrogen bonds are indicated by dashed line.

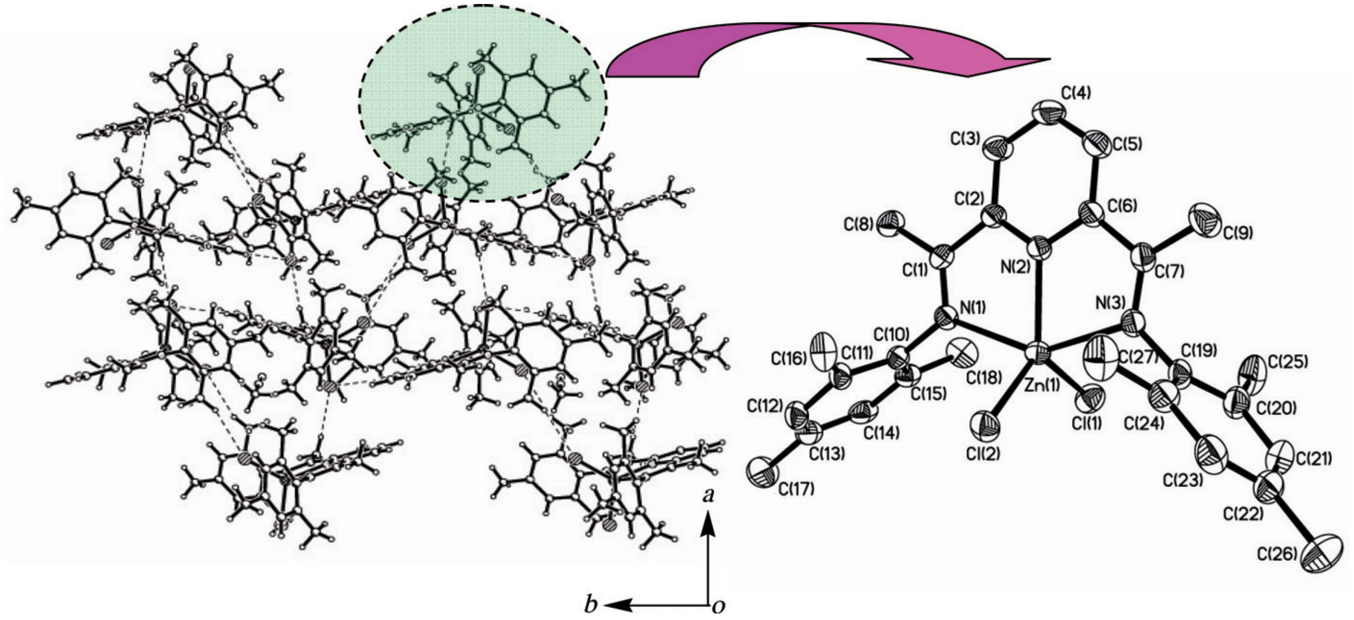


Figure 3. Right: Molecular structure of **Zn3** (CH_3CN omitted for clarity). Left: Packing diagram of **Zn3** along the *c*-axis. Hydrogen bonds are indicated by dashed lines.

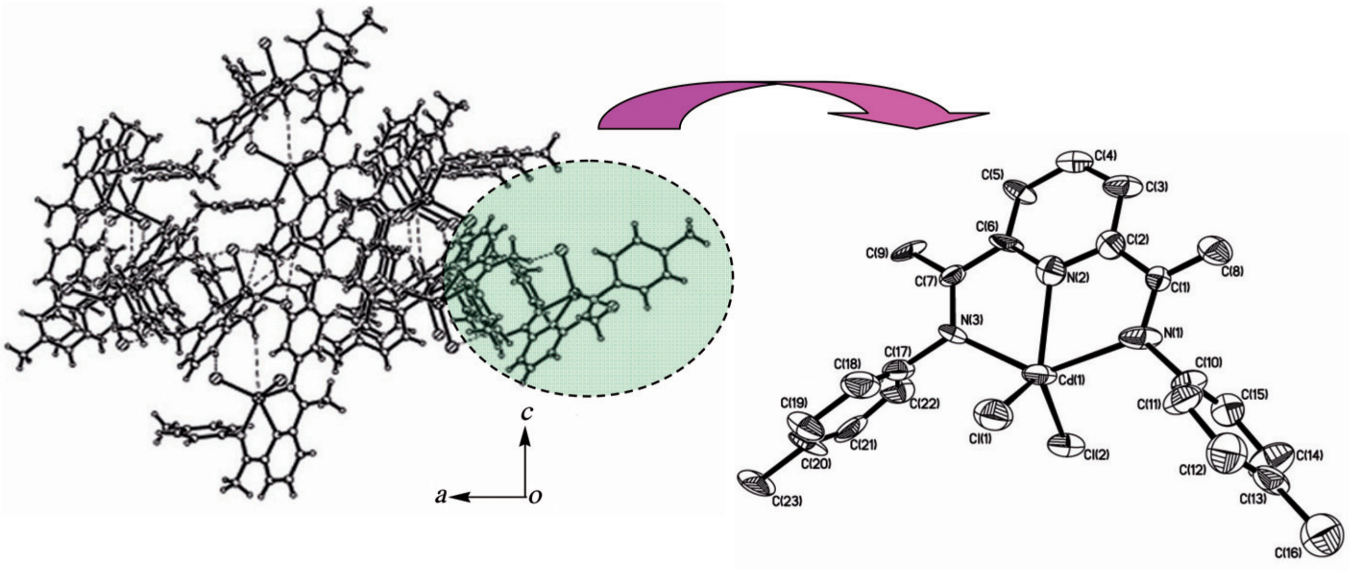


Figure 4. Right: Molecular structure of **Cd1** (the other molecule and CH_3CN have been omitted for clarity). Left: Packing diagram of **Cd1** along the *b*-axis. Hydrogen bonds are indicated by dashed lines.

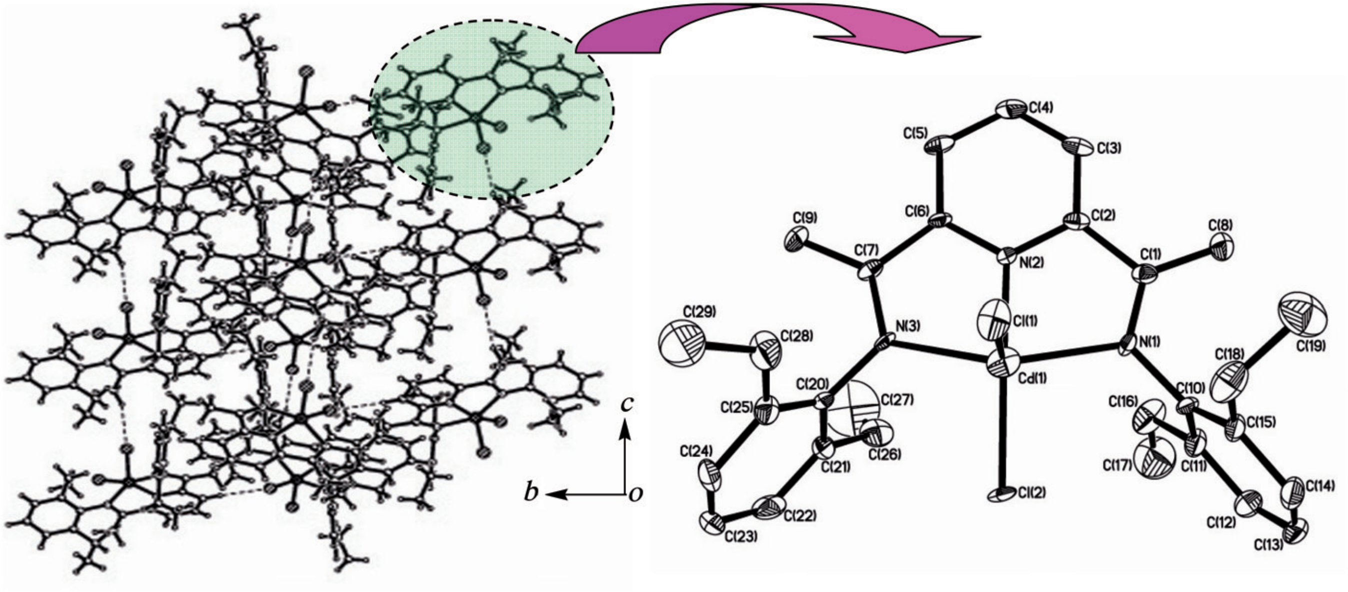


Figure 5. Right: Molecular structure of **Cd2** (0.5CH_3CN omitted for clarity). Left: Packing diagram of **Cd2** along the *a*-axis. Hydrogen bonds are indicated by dashed lines.

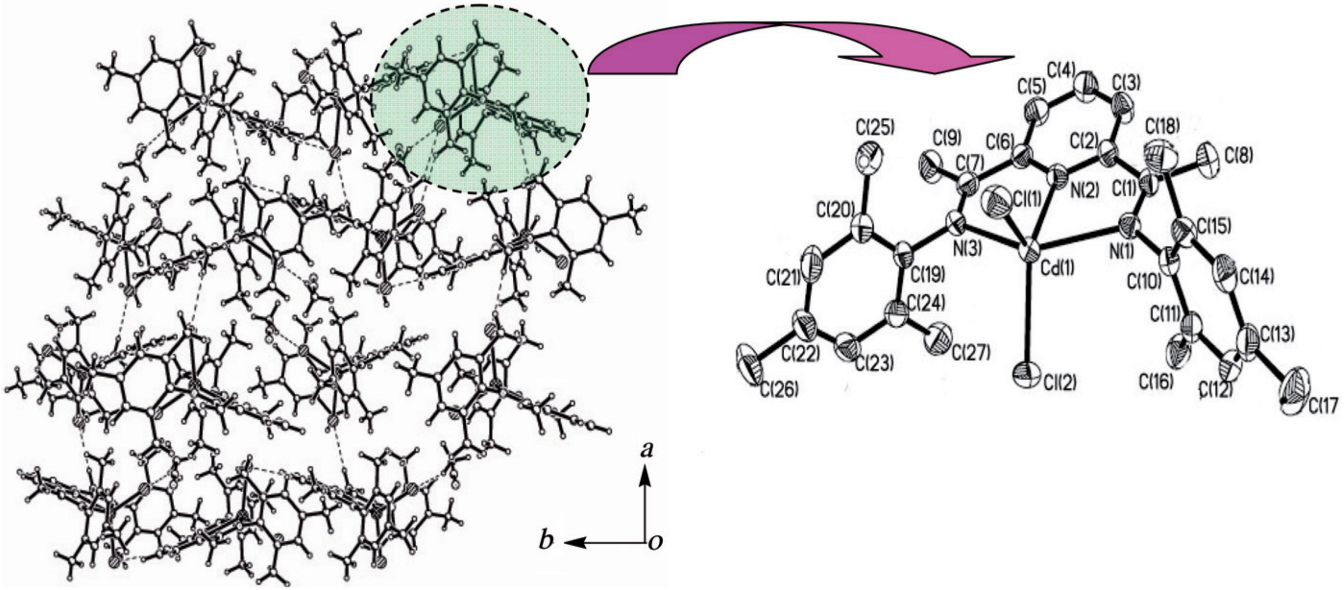


Figure 6. Right: Molecular structure of **Cd3** (CH_3CN omitted for clarity). Left: Packing diagram of **Cd3** along the *c*-axis. Hydrogen bonds are indicated by dashed lines.

Table 2. Selected bond lengths (Å) and angles (°) for **Zn1–Zn3** and **Cd1–Cd3**.

		Zn2[M = Zn]			**Cd1[M = Cd]**			
	Zn1[M = Zn]	Molecule 1	Molecule 1A	**Zn3[M = Zn]**	Molecule 1	Molecule 1A	**Cd2[M = Cd]**	**Cd3[M = Cd]**
M–N(2)	2.076(3)	2.072(4)	2.094(4)	2.078(3)	2.316(15)	2.328(16)	1.942(4)	2.307(3)
M–N(1)	2.250(4)	2.311(5)	2.330(4)	2.301(3)	2.379(18)	2.400(2)	2.136(4)	2.412(3)
M–Cl(1)	2.237(2)	2.221(2)	2.233(1)	2.244(1)	2.438(7)	2.431(6)	2.417(2)	2.437(1)
M–N(3)	2.244(4)	2.295(4)	2.292(4)	2.302(3)	2.337(16)	2.406(17)	2.111(4)	2.414(3)
M–Cl(2)	2.236(2)	2.225(2)	2.241(2)	2.228(1)	2.452(5)	2.436(5)	2.204(2)	2.411(1)
N(1)–C(1)	1.296(5)	1.274(6)	1.285(6)	1.275(5)	1.320(2)	1.180(2)	1.298(7)	1.283(4)
N(3)–C(7)	1.269(5)	1.268(6)	1.283(6)	1.274(5)	1.390(18)	1.230(2)	1.299(6)	1.283(5)
N(2)–M–N(1)	74.21(14)	73.67(16)	73.01(16)	73.85(13)	67.7(5)	66.2(7)	77.48(18)	69.47(11)
N(2)–M–Cl(1)	120.95(11)	121.45(13)	119.77(12)	117.61(9)	120.2(4)	117.3(3)	95.54(14)	118.83(8)
N(1)–M–Cl(1)	99.68(10)	96.98(11)	98.15(11)	96.98(9)	101.3(4)	100.0(4)	99.54(14)	97.87(7)
N(2)–M–N(3)	73.95(14)	74.14(16)	74.08(15)	73.53(12)	69.4(5)	69.4(6)	77.39(18)	68.90(11)
N(1)–M–N(3)	148.15(13)	147.78(14)	147.06(15)	147.20(13)	137.1(4)	135.6(6)	150.56(17)	138.27(11)
Cl(1)–M–N(3)	97.25(11)	100.83(12)	99.58(11)	101.04(9)	99.3(4)	101.2(4)	97.91(13)	104.38(8)
N(2)–M–Cl(2)	118.90(11)	125.93(12)	119.77(12)	127.10(10)	120.6(4)	123.0(3)	156.85(14)	126.51(8)
N(1)–M–Cl(2)	96.62(11)	99.12(13)	98.80(13)	100.10(9)	101.3(4)	101.4(4)	98.56(13)	102.90(7)
Cl(1)–M–Cl(2)	120.15(5)	112.59(7)	114.76(6)	115.29(5)	119.2(2)	119.7(2)	107.60(7)	114.65(4)
N(3)–M–Cl(2)	97.89(10)	98.50(11)	98.65(12)	96.66(9)	99.9(4)	101.2(3)	98.51(12)	99.23(8)

which are similar to those reported [20]. The Cl···C bond distances and Cl···H···C bond angles are listed in table 3. The 3-D supramolecular structures of all complexes are constructed by hydrogen bonding interactions. The Cl···H···C hydrogen bonding interactions are also observed in 3-D supramolecular network from $[CdCl_2(2,2'\text{-bipy})_2]_n$ 1-D coordination polymer chain by the Cl-bridged Cd atoms [20b]. These are different to classical N···H···O, O···H···N, O···H···O hydrogen bonding interactions in cadmium(II) complexes [20b, 22].

3.3. *Luminescence*

Table 4 presents the absorption and emission data for all the complexes in dichloromethane solution and in the solid state at room temperature. The Zn(II) and Cd(II) complexes show two main absorption bands, which are similar to ligands [12] in the UV region. The electronic absorption spectra of **Zn1**, **Zn2**, and **Zn3** show low-energy absorption bands at 380, 365, and 370 nm (361, 353, and 357 for **Cd1**, **Cd2**, and **Cd3**), respectively, and high-energy absorption bands at 307, 294, and 300 nm (320, 311, and 314 for **Cd1**, **Cd2**, and **Cd3**), respectively, which might be attributed to ligand-centered $\pi \rightarrow \pi^*$ transitions. The electronic absorption spectra of the Zn(II) and Cd(II) complexes compared with their ligands (347 and 300 nm for L^1, 338 and 287 nm for L^2, 342 and 296 nm for L^3) are red-shifted due to the metal-perturbed intra-ligand $\pi \rightarrow \pi^*$ transitions of the bis(imino)pyridyl unit. The energies of both absorption bands for **Zn2**, **Cd2**, and L^2 are larger than those for **Zn3**, **Cd3**, and L^3, in line with the electron-donating ability of the substituents on the aryl rings, where the electron-donating ability of Me in 2,4,6-dimethylphenyl for **Zn3**, **Cd3**, and L^3 is larger than that of Et in 2,6-diethylphenyl for **Zn2**, **Cd2**, and L^2 due to the better super-conjugated effect of Me.

Table 3. Hydrogen-bond geometry (A, °) for **Zn1–Zn3** and **Cd1–Cd3**.

	Cl–H···A	Cl···A	Cl–H···A
Zn1	Cl1–H···C9A	3.675	144.51
	Cl2–H···C5A	3.704	163.46
	Cl1–H···C25A	3.759	156.26
	Cl2–H···C25B	3.776	147.29
	Cl2–H···C8B	3.595	137.63
Zn2	Cl1–H···C8A	3.658	170.87
	Cl1–H···C5B	3.678	156.84
	Cl2–H···C29A	3.839	155.24
	Cl2–H···C16C	3.700	156.71
Zn3	Cl1–H···C9A	3.546	158.65
	Cl1A–H···C13B	3.683	137.52
	Cl1A–H···C3C	3.724	172.12
	Cl2A–H···C4C	3.707	157.00
	Cl2A–H···C19D	3.741	143.87
Cd1	Cl1–H···C8A	3.742	144.62
	Cl1–H···C8B	3.810	154.31
	Cl2–H···C3A	3.624	164.53
Cd2	Cl1–H···C8A	3.799	158.41
	Cl2–H···C5B	3.562	177.08
Cd3	Cl1–H···C5A	3.622	158.25
	Cl1–H···C8B	3.614	172.31
	Cl2–H···C16C	3.681	146.09
	Cl2–H···C29A	3.721	159.19

Zn1, **Cd1**, and $\mathbf{L^1}$ show the lowest absorption energy which is attributed to the lower steric hindrance on *p*-methyl-substituted phenyl ring of bis(imino)pyridine leading to emission energy red shift.

Six complexes have blue emission in CH_2Cl_2 solution (concentration: [M] $\approx 10^{-5}$) at room temperature, with $\lambda_{max} = 465$ (**Zn1**), 448 (**Zn2**), 456 (**Zn3**), 427 (**Cd1**), 405 (**Cd2**), and 420 (**Cd3**) nm, respectively. Similar to the electronic absorption data for **Zn1**–**Zn3** and **Cd1**–**Cd3**, emission energy trends **Zn1** < **Zn3** < **Zn2** and **Cd1** < **Cd3** < **Cd2** are observed. Their emission energies depend on the electron-donation by the alkyl substituents on the aryl rings of the bis(imino)pyridine ligand and steric effects. The quantum yields of all compounds have been determined in solution (table 3) and the Zn(II) and Cd(II) complexes are higher than free ligands [12]. The metal centers in **Zn1**–**Zn3** and **Cd1**–**Cd3** play a significant role in enhancing ligand-centered $\pi^* \rightarrow \pi$ fluorescent emission due to the chelation of the ligands, increasing rigidity of the ligands, and thus reducing the loss of energy by thermal vibrational decay. Quantum yields of **Zn1**–**Zn3** are higher than those of **Cd1**–**Cd3**, attributed to the heavy atom effect [5] from the coordination of the ligand to a heavy Cd(II) center. In the solid state at room temperature, zinc, and cadmium complexes exhibit bright greenish blue emission with maximum at $\underline{\lambda}_{max} = 502$ (**Zn1**), 488 (**Zn2**), 488 (**Zn3**), 495 (**Cd1**), 489 (**Cd2**), and 489 (**Cd3**) nm, respectively, red-shifted about 30–80 nm from emission in the solution. This dramatic red shift of emission energy from solution to solid is caused by the intermolecular hydrogen bonds in the solid state that effectively decrease the energy gap. The emission wavelengths of **Zn1**–**Zn3** and **Cd1**–**Cd3** are similar to those of zinc(II) coordination polymers $[Zn_2(FPDB)_2(pyridine)_2 \cdot 5H_2O]_n$ and $[Zn(H_2cit)(H_2O)]_n$ in the solid state at room temperature [5c, d].

4. Conclusions

A series of Zn(II) and Cd(II) complexes with 2,6-bis(imino)pyridine ligands have been synthesized and characterized. Six complexes have blue fluorescent emission

Table 4. Photoluminescent data for **Zn1–Zn3** and **Cd1–Cd3.**[a]

Compound	Absorption (nm) ε ($dm^3\,mol^{-1}\,cm^{-1}$)	Excitation (λ_{max}, nm)	Emission (λ_{max}, nm)	Quantum yields (ϕ)[b]	Conditions
Zn1	307 (19745), 380 (16121)		465	0.078	CH_2Cl_2, 298 K
		330	502		solid, 298 K
Zn2	294 (10582), 365 (9243)		448	0.064	CH_2Cl_2, 298 K
		330	488		solid, 298 K
Zn3	300 (17329), 370 (12620)		456	0.070	CH_2Cl_2, 298 K
		330	488		solid, 298 K
Cd1	320 (13923), 361 (6694)		427	0.066	CH_2Cl_2, 298 K
		330	495		solid, 298 K
Cd2	311 (16874), 353 (7404)		405	0.058	CH_2Cl_2, 298 K
		330	489		solid, 298 K
Cd3	314 (17328), 357 (7101)		420	0.058	CH_2Cl_2, 298 K
		330	489		solid, 298 K

[a] Concentration: $[M] = 1 \times 10^{-5}$ M.

[b] Determined using quinine sulfate in 0.1 M sulfuric acid as a standard.

at 405–465 nm in dichloromethane at room temperature and fluorescent emission bands in the solid state at room temperature, with $\lambda_{max} = 502$ (**Zn1**), 488 (**Zn2**), 488 (**Zn3**), 495 (**Cd1**), 489 (**Cd2**), and 489 (**Cd3**) nm, respectively. All complexes self-assemble through hydrogen bonding interactions to form a 3-D supramolecular structure. Their luminescent properties show that they are a new class of luminescent metal compounds with potential applications in luminescent materials.

Supplementary material

The crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 732515–732517 (**Zn1**–**Zn3**), 732513 (**Cd1**), 732514 (**Cd2**), and 663580 (**Cd3**). The copies of this information may be obtained free of charge from The Director, CCDC 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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