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Syntheses, crystal structures and luminescence of zinc(II) and cadmium(II) complexes with 4′-substituted 2,2′:6′,2″-terpyridines

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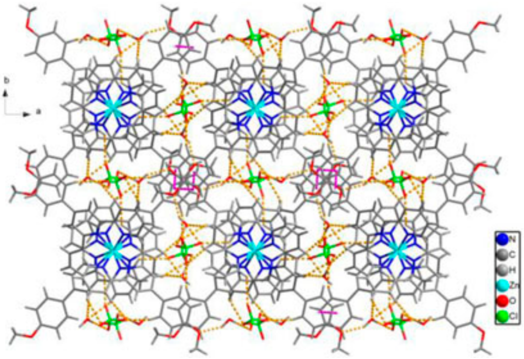

Four Zn(II) and Cd(II) complexes with two kinds of terpyridines have been synthesized and characterized. All these complexes are six N coordinated with two terpyridines. 3-D networks have been formed with hydrogen bonds and π–π interactions. The luminescence properties have been studied and all these ligands and complexes can be used as luminescence materials.

Four terpyridine coordination complexes, $[Zn(meophtpy)_2]\cdot(ClO_4)_2\cdot(H_2O)$ (**1**), $[Cd(meophtpy)_2]\cdot(ClO_4)_2$ (**2**), $[Zn(nh2phtpy)_2]\cdot(ClO_4)_2$ (**3**), and $[Cd(nh2phtpy)_2]\cdot(ClO_4)_2$ (**4**) (meophtpy = 4′-(p-methoxylphenyl)-2,2′:6′,2″-terpyridine, nh2phtpy = 4′-aminophenyl-2,2′:6′,2″-terpyridine), were synthesized using the solvothermal method. These complexes have been characterized by IR spectra, elemental analyses, and X-ray diffraction. In all these complexes, the metal ions are coordinated by six nitrogens from two terpyridines. 3-D networks have been constructed by hydrogen bonds and π–π interactions. The luminescence of these four complexes has been investigated in the solid state at room temperature.

Keywords: Zinc(II); Cadmium(II); Terpyridine; Crystal structure; Luminescence

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1. Introduction

Research on terpyridine coordination complexes has flourished in terms of diverse properties when terpyridine coordinates to different metal ions [1–4]. Zn(II) and Cd(II) are d^{10} metal ions with the complexes researched for luminescence properties. Different donor/acceptor substituents, especially at the 4′ position [5–11], have played important roles on luminescence. Alcock *et al.* studied the crystal structures and luminescence properties of 4′-biphenyl-2,2′:6′,2″-terpyridine (biphtpy) Zn(II) and Cd(II) complexes, where they found that the origin of the luminescence is LLCT [12]. Lee *et al.* researched 4′-terphenyl-2,2′:6′,2″-terpyridine Zn(II) and Cd(II) complexes with emission spectra of the Zn(II) and Cd(II) complexes very similar and all red-shifted compared to free ligand [13]. Kubota *et al.* examined 4′-(4′-pyridin-4-ylbiphenyl-4-yl)-2,2′:6′,2″-terpyridine Zn(II) and Cd(II) complexes, and blue emission was attributed to an intramolecular charge transfer (ICT) transition [14]. Chen *et al.* researched five Zn(II) terpyridine complexes with different substituents at the 4′ position. Zn(II)-terpyridine complexes have the potential to be efficient emitters for OLEDs [15]. Qiu *et al.* researched two Zn(II) terpyridine complexes, one is emissive, while the other is not, which may indicate an additional non-radiative decay pathway in the form of photo-induced electron transfer [16]. Two-photon absorption cross-sections of 4′-(4-[4-(1H-[1,2,4[-triazole)styryl]phenyl)-2,2′:6′,2″-terpyridine Zn(II) and Cd(II) complexes were evaluated by Zhou *et al.* [17]. Zhang *et al.* found that the emission of 2,2′:6′,2″-terpyridine-4′-carboxylic acid Zn(II) complex would be attributed to LLCT [6]. In addition to investigation of luminescence properties, many other properties of terpyridine Zn(II) complexes were reported recently. Wang *et al.* synthesized a 4′-4-(1,2,4-triazol-1-yl)-phenyl2,2′:6′,2″-terpyridine Zn(II) complex. They found that the complex is a probe for Co(II) and Ni(II) ions [18]. Ferrocenyl terpyridine Zn(II) complexes have been researched for DNA cleavage properties [19]. Mehrani *et al.* found that different terpyridine Zn(II) complexes are suitable precusors for oxide nanoparticles with different morphologies [20]. Methoxy and amino groups are among the most used substituents. In order to test substituent effect on supramolecular structures and luminescence properties, four homoleptic Zn(II) and Cd(II) complexes with 4′-(p-methoxylphenyl)-2,2′:6′,2″-terpyridine (meophtpy) and 4′-aminophenyl-2,2′:6′,2″-terpyridine (nh2phtpy) have been synthesized and luminescence properties have been investigated [21–30].

2. Experimental

2.1. *Materials and physical measurements*

4′-(p-methoxylphenyl)-2,2′:6′,2″-terpyridine and 4′-aminophenyl-2,2′:6′,2″-terpyridine were synthesized according to the literature [31]. All other reagents and solvents were commercially available and used as received. Fourier transform infrared spectra (FT-IR) were recorded on a Shimadzu Prestige-21 FT-IR spectrometer using dry KBr pellets from 400 to 4000 cm^{-1}. Elemental analyses were carried out on an EA1110 CHNS-0 CE elementalanalyzer. Photoluminescent analyses were performed on an Edinburgh EI920 fluorescence spectrometer with 450 W xenon light.

2.2. *Synthesis*

2.2.1. Synthesis of [Zn(meophtpy)$_2$]·(ClO$_4$)$_2$·(H$_2$O) (1). Meophtpy (0.034 g, 0.1 mmol), Zn(CH$_3$COO)$_2$·2H$_2$O (0.011 g, 0.05 mmol), and NaClO$_4$ (0.012 g, 0.1 mmol) were mixed in water (5 mL) and ethanol (5 mL) and sealed in a 16 mL Teflon-lined stainless steel vessel. After heating at 160 °C for 72 h, the temperature was gradually decreased to room temperature. Yellow block crystals were obtained and washed with water several times. Elemental Anal. Calcd (%) for $ZnC_{44}H_{38}Cl_2N_6O_{12}$: C, 53.97; H, 3.91; N, 8.58. Found: C, 56.06; H, 3.87; N, 9.14. IR (KBr, cm^{-1}): 3549(b), 1601(vs), 1574(s), 1549(s), 1518(s), 1475(s), 1433(s), 1408(m), 1365(w), 1305(w), 1280(w), 1244 (s), 1182(s), 1163(w), 1089 (vs), 1016(s), 881(w), 831(m), 793(s), 748(w), 731(w), 657(w), 638(w), 621(s), 577(m), 521(m), and 411(m).

2.2.2. Synthesis of [Cd(meophtpy)$_2$]·(ClO$_4$)$_2$ (2). The preparation of **2** was similar to that of **1** except that Cd(CH$_3$COO)$_2$·2H$_2$O (0.013 g, 0.05 mmol) was used instead of Zn (CH$_3$COO)$_2$·2H$_2$O. Elemental Anal. Calcd (%) for $CdC_{44}H_{34}Cl_2N_6O_{10}$: C, 53.38; H, 3.46; N, 8.49. Found: C, 53.50; H, 3.87; N, 8.58. IR (KBr, cm^{-1}): 3545(b), 1599(vs), 1572(s), 1547 (s), 1520(s), 1475(s), 1433(s), 1406(m), 1360(w), 1310(w), 1283(w), 1267(m), 1246 (s), 1188(s), 1091(vs), 1014(s), 903(vw), 881(w), 831(m), 797(s), 746(w), 727(w), 686(vw), 658(m), 640(m), 623(s), 577(m), 517(m), and 407(m).

Table 1. Crystallographic data and structure refinement parameters for **1–4**[1†].

Complexes	**1**	**2**	**3**	**4**
Empirical formula	$ZnC_{44}H_{38}Cl_2N_6O_{12}$	$CdC_{44}H_{34}Cl_2N_6O_{10}$	$ZnC_{42}H_{30}Cl_2N_8O_8$	$CdC_{42}H_{32}Cl_2N_8O_8$
Formula mass	979.07	990.07	911.01	960.06
Crystal system	Tetragonal	Triclinic	Orthorhombic	Monoclinic
Space group	*I4(1)/a*	*P-1*	$P2_12_12_1$	$P2_1/c$
a (Å)	24.899(2)	8.928(6)	8.9150(7)	9.6211(9)
b (Å)	24.899(2)	12.500(8)	13.7149(10)	12.7279(12)
c (Å)	13.805(2)	18.947(13)	33.045(2)	32.949(3)
α (°)	90	89.968(13)	90	90
β (°)	90	86.004(11)	90	98.1650(10)
γ (°)	90	83.013(12)	90	90
V (Å^3)	8558.3(17)	2094(2)	4040.3(5)	3993.9(6)
Z	8	2	4	4
D_{Calcd} (g/cm^3)	1.520	1.571	1.498	1.597
μ (mm^{-1})	0.771	0.717	0.805	0.747
F(000)	4032	1004	1864	1944
θ (°)	1.69–25.00	2.16–25.01	1.23–25.01	1.72–27.56
Reflections	30,587/3745	14,894/7210	29,946/7135	35,586/9189
R_{int}	0.0667	0.0840	0.0572	0.0308
GOF on F^2	1.068	0.941	1.022	1.032
Data/parameters	3745/314	7210/570	7135/513	9189/559
R_1, wR_2 [$(I > 2\sigma(I)$]	0.0456, 0.1401	0.0611, 0.1524	0.0728, 0.1780	0.0421, 0.1220
R_1, wR_2 (all data)	0.0557, 0.1655	0.0948, 0.2040	0.0774, 0.1811	0.0524, 0.1298
Largest diff. peak and hole (e/Å^3)	0.587 and −0.432	1.449 and −2.090	1.201 and −0.712	0.855 and −0.478

$^aR = \sum(||F_0| - F_c||)/\sum|F_0|$, $wR = [\sum w(|F_0|^2 - |F_c|^2)^2/\sum w(F_0{}^2)]^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (°) for **1–4**.

1			
Zn(1)–N(1)	2.049(2)	Zn(1)–N(2)	2.201(3)
Zn(1)–N(3)	2.165(2)		
N(1)–Zn(1)–N(1)#1	173.18(13)	N(1)–Zn(1)–N(3)	76.65(9)
N(1)–Zn(1)–N(3)#1	107.93(9)	N(3)–Zn(1)–N(3)#1	99.47(13)
N(1)–Zn(1)–N(2)	75.79(9)	N(1)#1–Zn(1)–N(2)	99.76(9)
N(3)–Zn(1)–N(2)	152.31(9)	N(3)#1–Zn(1)–N(2)	86.58(10)
N(2)–Zn(1)–N(2)#1	100.58(14)		
Symmetry code: #1 $-x+0$, $-y+3/2$, $z+0$			
2			
Cd(1)–N(4)	2.305(6)	Cd(1)–N(1)	2.313(7)
Cd(1)–N(6)	2.320(7)	Cd(1)–N(2)	2.342(6)
Cd(1)–N(3)	2.365(7)	Cd(1)–N(5)	2.397(7)
N(4)–Cd(1)–N(1)	165.9(2)	N(4)–Cd(1)–N(6)	70.5(2)
N(1)–Cd(1)–N(6)	121.8(2)	N(4)–Cd(1)–N(2)	119.9(2)
N(1)–Cd(1)–N(2)	70.2(2)	N(6)–Cd(1)–N(2)	87.4(2)
N(4)–Cd(1)–N(3)	101.4(2)	N(1)–Cd(1)–N(3)	68.6(2)
N(6)–Cd(1)–N(3)	110.6(2)	N(2)–Cd(1)–N(3)	138.6(3)
N(4)–Cd(1)–N(5)	69.8(2)	N(1)–Cd(1)–N(5)	98.2(2)
N(6)–Cd(1)–N(5)	140.0(3)	N(2)–Cd(1)–N(5)	108.6(2)
N(3)–Cd(1)–N(5)	81.8(2)		
3			
Zn(1)–N(1)	2.282(2)	Zn(1)–N(4)	2.287(2)
Zn(1)–N(2)	2.305(3)	Zn(1)–N(5)	2.332(3)
Zn(1)–N(3)	2.336(3)	Zn(1)–N(6)	2.403(2)
N(1)–Zn(1)–N(4)	164.21(8)	N(1)–Zn(1)–N(2)	70.37(8)
N(4)–Zn(1)–N(2)	110.03(9)	N(1)–Zn(1)–N(5)	124.95(8)
N(4)–Zn(1)–N(5)	70.77(9)	N(2)–Zn(1)–N(5)	102.46(9)
N(1)–Zn(1)–N(3)	70.15(8)	N(4)–Zn(1)–N(3)	107.66(8)
N(2)–Zn(1)–N(3)	140.51(9)	N(5)–Zn(1)–N(3)	100.59(10)
N(1)–Zn(1)–N(6)	94.47(8)	N(4)–Zn(1)–N(6)	69.84(8)
N(2)–Zn(1)–N(6)	89.40(9)	N(5)–Zn(1)–N(6)	140.57(9)
N(3)–Zn(1)–N(6)	92.74(9)		
4			
Cd(1)–N(2)	2.280(2)	Cd(1)–N(5)	2.286(2)
Cd(1)–N(4)	2.328(2)	Cd(1)–N(1)	2.349(3)
Cd(1)–N(3)	2.352(3)	Cd(1)–N(6)	2.354(3)
N(2)–Cd(1)–N(5)	175.12(8)	N(2)–Cd(1)–N(4)	114.25(8)
N(5)–Cd(1)–N(4)	70.60(8)	N(2)–Cd(1)–N(1)	70.50(8)
N(5)–Cd(1)–N(1)	110.88(8)	N(4)–Cd(1)–N(1)	88.64(9)
N(2)–Cd(1)–N(3)	70.68(8)	N(5)–Cd(1)–N(3)	108.14(8)
N(4)–Cd(1)–N(3)	103.62(9)	N(1)–Cd(1)–N(3)	140.97(8)
N(2)–Cd(1)–N(6)	105.09(8)	N(5)–Cd(1)–N(6)	70.09(8)
N(4)–Cd(1)–N(6)	140.60(9)	N(1)–Cd(1)–N(6)	102.80(9)
N(3)–Cd(1)–N(6)	90.95(9)		

2.2.3. Synthesis of [Zn(nh2phtpy)$_2$]·(ClO$_4$)$_2$ (3). Nh2phtpy (0.032 g, 0.1 mmol), Zn (CH$_3$COO)$_2$·2H$_2$O (0.011 g, 0.05 mmol), and NaClO$_4$ (0.012 g, 0.1 mmol) were mixed in water (10 mL) and sealed in a 16 mL Teflon-lined stainless steel vessel. After heating at 160 °C for 72 h, the temperature was gradually decreased to room temperature. Yellow block crystals were obtained and washed with water several times. Elemental Anal. Calcd (%) for ZnC$_{42}$H$_{30}$Cl$_2$N$_8$O$_8$: C, 55.37; H, 3.32; N, 12.30. Found: C, 55.11; H, 3.76; N, 12.51. IR (KBr, cm^{-1}): 3448(m), 3356(s), 1593(vs), 1545(s), 1522(s), 1474(s), 1439(m), 1414(s), 1362(w), 1308(w), 1277(vw), 1248(m), 1184(m), 1165(m), 1090(vs), 1014(s), 930 (vw), 879(vw), 831(m), 793(s), 746(w), 731(w), 690(vw), 658(m), 621(s), 577(m), 519(m), and 409(m).

2.2.4. Synthesis of [Cd(nh2phtpy)$_2$]·(ClO$_4$)$_2$ (4).

The preparation of **4** was similar to that of **3** except that Cd(CH$_3$COO)$_2$·2H$_2$O (0.013 g, 0.05 mmol) was used instead of Zn (CH$_3$COO)$_2$·2H$_2$O. Elemental Anal. Calcd (%) for CdC$_{42}$H$_{32}$Cl$_2$N$_8$O$_8$: C, 52.54; H, 3.36; N, 11.67. Found: C, 52.09; H, 3.60; N, 11.83. IR (KBr, cm^{-1}): 3545(m), 3422(m), 3360(s), 1593(vs), 1541(s), 1522(s), 1474(s), 1437(m), 1410(s), 1358(m), 1308(m), 1248(m), 1182 (m), 1165(m), 1088(vs), 1014(s), 927(w), 881(w), 849(w), 829(m), 791(s), 746(w), 729(m), 690(w), 658(m), 621(s), 575(m), and 517(m).

2.3. *X-ray crystallography*

Crystals of **1–4** were mounted on a Bruker SMART APEX II CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.071073 nm) at 123(2) K for **1** and **2** and 296(2) K for **3** and **4**. Empirical absorption corrections were applied by using SADABS. The structures were solved by direct methods and refined by full-matrix least squares on F^2 via SHELXL-97 [32]. All non-hydrogen atoms were refined anisotropically and hydrogens were generated geometrically. Crystallographic data and structural refinement parameters for **1–4** are listed in table 1. Selected bond lengths and angles are presented in table 2.

3. Results and discussion

3.1. *Crystal structure*

3.1.1. Crystal structure of [Zn(meophtpy)$_2$]·(ClO$_4$)$_2$·(H$_2$O) (1).

The asymmetric unit of **1** is comprised of half a Zn(II), one meophtpy, perchlorate, and a water molecule. In the crystal, shown in figure 1(a), Zn(II) is coordinated by six nitrogens from two meophtpy ligands. The distance between Zn(II) and central N (Zn(1)–N(1) = 2.049(2) Å) is shorter than that between Zn and outer nitrogens (Zn(1)–N(2) = 2.201(3) Å, Zn(1)–N(3) = 2.165 (2) Å). Bond angles around Zn(II) include three (N(1)–Zn(1)–N(1)#1 = 173.18(13)°, N(3)–Zn(1)–N(2) = 152.31(9)° and N(3)#1–Zn(1)–N(2)#1 = 152.31(9)) that are *transoid*, and the remaining that are *cisoid* and range from 75.79(9)° to 107.93(9)°. Differences in bond lengths and angles are indicative of a distortion of the octahedral coordination environment around Zn(II), common for [M(tpy)$_2$]$^{2+}$ cations [33, 34]. The angle between the phenyl and terpyridine ring is 36.1°. The angle between two terpyridine rings around Zn(II) is 76.5° which deviates from a right angle. The dications are overlapped along the c-direction adopting a pseudo S$_4$ symmetry, which is rare in terpyridine compounds. Six hydrogen bonds (table 3), two of O–H···O type and four of C–H···O type, as well as a face-to-face π–π interaction between phenyl rings with a centroid-to-centroid distance of 3.822 Å link the [M(tpy)$_2$]$^{2+}$ cations and perchlorates into a 3-D network as shown in figure 1(b).

3.1.2. Crystal structure of [Cd(meophtpy)$_2$]·(ClO$_4$)$_2$ (2).

The asymmetric unit of **2** is comprised of one Cd(II), two meophtpy, and two perchlorates. As shown in figure 2, Cd(II)

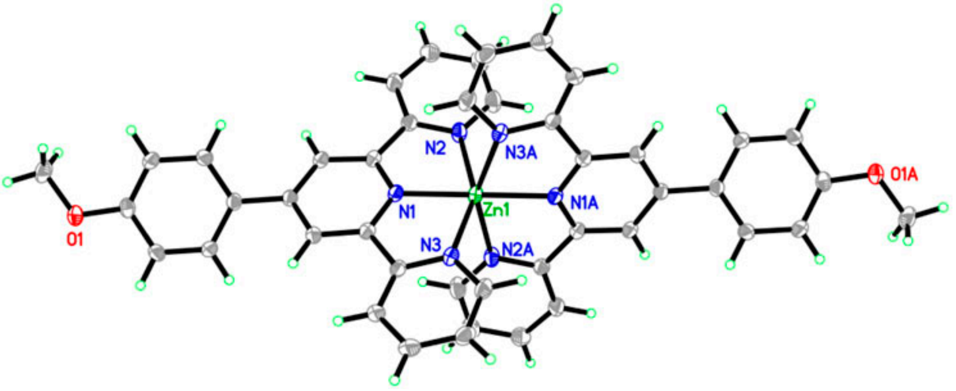

Figure 1(a). ORTEP view of **1** (30% thermal ellipsoids) showing the coordination environment of Zn(II) (symmetry codes for A = $-x$, $-y + 3/2$, z).

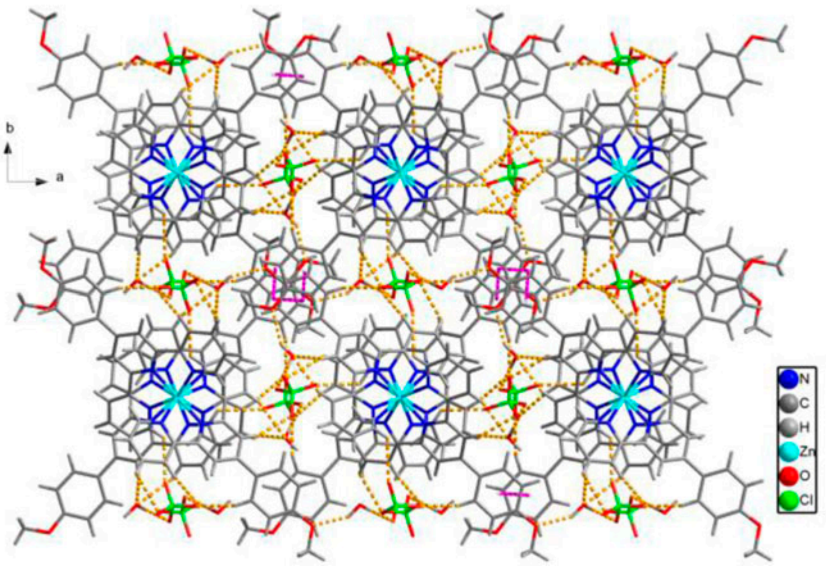

Figure 1(b). 3-D packing diagram of **1** showing hydrogen bonds (orange broken lines) and the aromatic stacking interactions (purple broken lines) (see http://dx.doi.org/10.1080/00958972.2015.1019486 for color version).

is coordinated by six nitrogens from two meophtpy ligands. The distances between Cd(II) and central N (Cd1–N4 = 2.305(6) Å, Cd(1)–N(1) = 2.313(7) Å) are shorter than that between Cd(II) and outer N (Cd(1)–N(6) = 2.320(7) Å, Cd(1)–N(2) = 2.342(6) Å, Cd(1)–N (3) = 2.365(7) Å, and Cd(1)–N(5) = 2.397(7) Å), common for $[M(tpy)_2]^{2+}$ cations. Bond angles around Cd(II) can be divided into (N(4)–Cd(1)–N(1) = 165.9(2)°, N(2)–Cd(1)–N(3) = 138.6(3)°, and N(6)–Cd(1)–N(5) = 140.0(3)°) *trans*, and *cis* angles that range from 68.6 (2)° to 121.8(2)°. Differences in the bond lengths and angles are also indicative of a distorted octahedral coordination environment. The angles between phenyl ring and the

Table 3. Hydrogen bonds for **1–4**.

D–H⋯A	d(D–H)/Å	d(H⋯A) /Å	d(D⋯A) /Å	∠DHA/°
1				
O1W–H1WB⋯O3^{i}	0.94	2.01	2.936(6)	169
O1W–H1WA⋯O1	0.91	2.05	2.874(4)	149
C2–H2⋯O1W^{i}	0.95	2.34	3.239(4)	157
C7–H7⋯O2^{ii}	0.95	2.37	3.235(6)	152
C12–H12⋯O1W^{i}	0.95	2.48	3.377(4)	157
C15–H15⋯O5^{iii}	0.95	2.57	3.191(4)	123
Symmetry code: $^{i}-x, -y, -z$; $^{i}-x - 1/2, -y + 1/2, -z - 1/2$; $^{iii}-y - 3/4, x + 1/4, -z - ¾$				
2				
C7–H7⋯O5^{i}	0.95	2.51	3.431(12)	164
C9–H9⋯O6	0.95	2.51	3.456(12)	172
C10–H10⋯O2^{ii}	0.95	2.59	3.061(12)	111
C15–H15⋯O12^{iii}	0.95	2.42	3.219(15)	141
C16–H16⋯O8^{iv}	0.95	2.49	3.392(12)	158
C20–H20⋯O5^{i}	0.95	2.48	3.382(11)	159
C30–H30⋯O7^{v}	0.95	2.47	3.271(11)	142
C35–H35⋯O7^{iii}	0.95	2.48	3.164(13)	129
Symmetry code: $^{i}-x + 1, -y + 1, -z$; $^{ii}-x + 1, -y + 1, -z + 1$; $^{iii}x + 1, y, z$; $^{iv}x + 1, y + 1, z$; $^{v}x, y + 1, z$				
3				
N8–H8E⋯O8^{i}	0.89	2.16	2.997(11)	156
C2–H2⋯N8^{ii}	0.93	2.52	3.169(5)	127
C5–H5⋯O2	0.93	2.49	3.190(8)	133
C12–H12⋯O5^{iii}	0.93	2.51	3.316(11)	144
C26–H26⋯O6^{iv}	0.93	2.41	3.317(5)	166
Symmetry code: $^{i}x + 1/2, -y + 1/2, -z$; $^{ii}-x + 1/2, -y + 1, z + 1/2$; $^{iii}x + 1, y, z$; $^{iv}-x + 1, y + 1/2, -z + 1/2$				
4				
N7–H7A⋯O2^{i}	0.97	2.32	3.132(6)	141
N7–H7B⋯O4^{ii}	1.03	2.22	3.174(5)	152
N8–H8A⋯O7^{iii}	0.97	2.34	3.281(6)	166
N8–H8B⋯O5^{iv}	0.92	2.23	3.144(9)	174
C2–H2⋯O7^{v}	0.93	2.53	3.294(7)	139
C13–H13⋯O8^{vi}	0.93	2.57	3.445(11)	158
C15–H15⋯O4	0.93	2.39	3.312(5)	173
C23–H23⋯N7^{vii}	0.93	2.57	3.338(5)	141
C26–H26⋯O6^{ii}	0.93	2.56	3.411(5)	153
C34–H34⋯O2^{viii}	0.93	2.54	3.455(6)	168
Symmetry code: $^{i}x + 1, -y + 3/2, z + 1/2$; $^{ii}-x + 1, -y, -z$; $^{iii}x, -y + 1/2, z - 1/2$; $^{iv}-x, y + 3/2, -z + 1/2$; $^{v}x + 1, y + 1, z$; $^{vi}-x, -y, -z$; $^{vii}x, -y + 3/2, z - 1/2$; $^{viii}-x, y + 5/2, -z + 1/2$				

terpyridine ring are 1.7° and 27.1°, respectively. The almost coplanar angle between one phenyl ring and the terpyridine rings is unusual for hydrogen repulsion [33, 34]. The angle between two terpyridine rings around Cd(II) is 71.6°, which deviates from a right angle. Six hydrogen bonds, all of C–H⋯O type, and two kinds of π–π interactions with distances of 3.597 and 3.757 Å link the $[Cd(meophtpy)_2]^{2+}$ cations and perchlorates into 2-D layers. Other hydrogen bonds of C35–H35⋯O7 (symmetry code: $x + 1, y, z$) and C9–H9⋯O6 link the 2-D layers to a 3-D network.

3.1.3. Crystal structure of $[Zn(nh2phtpy)_2]\cdot(ClO_4)_2$ (3).

The asymmetric unit of **3** is comprised of one Zn(II), two nh2phtpy ligands, and two perchlorates. As shown in figure 3(a), Zn(II) is coordinated by six nitrogens from two nh2phtpy ligands. The

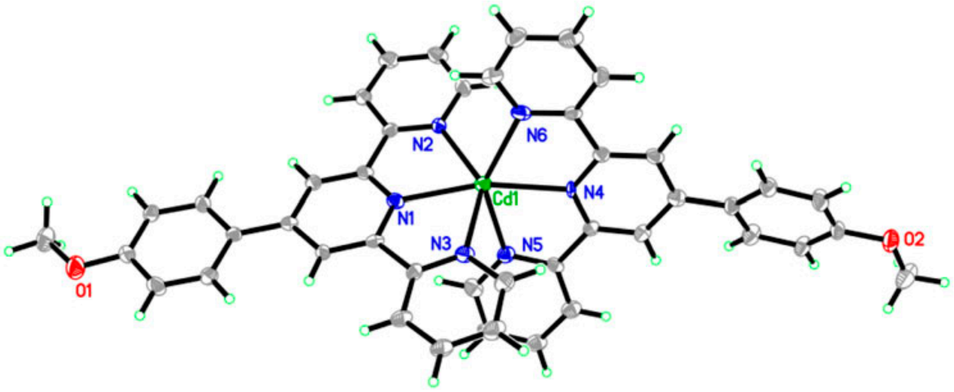

Figure 2(a). ORTEP view of **2** (30% thermal ellipsoids) showing the coordination environment of Cd(II).

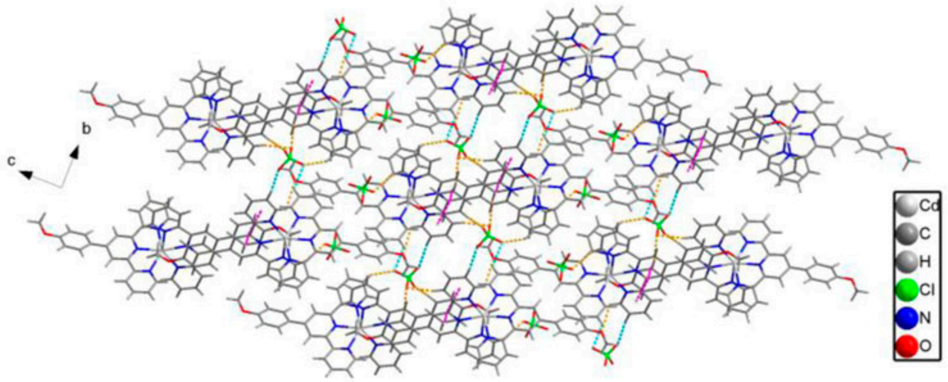

Figure 2(b). 3-D packing diagram of **2** showing hydrogen bonds (orange or sky-blue broken lines) and the aromatic stacking interactions (purple broken lines) (see http://dx.doi.org/10.1080/00958972.2015.1019486 for color version).

distances between Zn(II) and central N (Zn(1)–N(1) = 2.282(2) Å, Zn(1)–N(4) = 2.287(2) Å) are shorter than that between Zn(II) and outer N (Zn(1)–N(2) = 2.305(3) Å, Zn(1)–N(5) = 2.332(3) Å, Zn(1)–N(3) = 2.336(3) Å, and Zn(1)–N(6) = 2.403(2) Å), common for $[M(tpy)_2]^{2+}$ cations. Bond angles around Zn(II) involve (N(1)–Zn(1)–N(4) = 164.21(8)°, N(2)–Zn(1)–N(3) = 140.51(9)°, and N(5)–Zn(1)–N(6) = 140.57(9)°) *trans* and *cis* angles that range from 69.84(8)° to 124.95(8)°. The differences in bond lengths and angles are indicative of a distorted octahedral coordination environment. The angles between phenyl ring and the terpyridine ring are 23.3° and 40.1°, respectively. The mean deviation of terpyridine plane formed by N1, N2, and N3 and C1 to C15 is 0.2016 Å, which is consistent with a rare twist for a terpyridine compound. The angle between two terpyridine rings around Cd(II) is 89.2°, close to a right angle. Hydrogen bonds of N–H···O type, C–H···N type, and C–H···O type link the $[M(tpy)_2]^{2+}$ cations to a 3-D network as shown in figure 3(b).

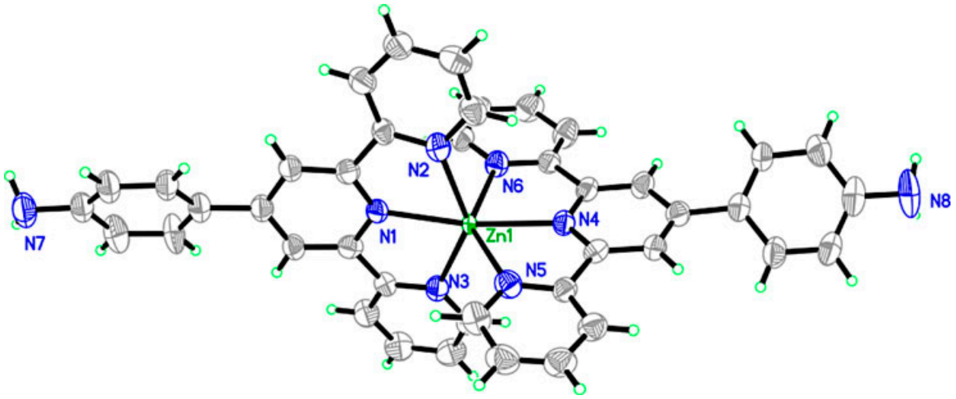

Figure 3(a). ORTEP view of **3** (30% thermal ellipsoids) showing the coordination environment of Zn(II).

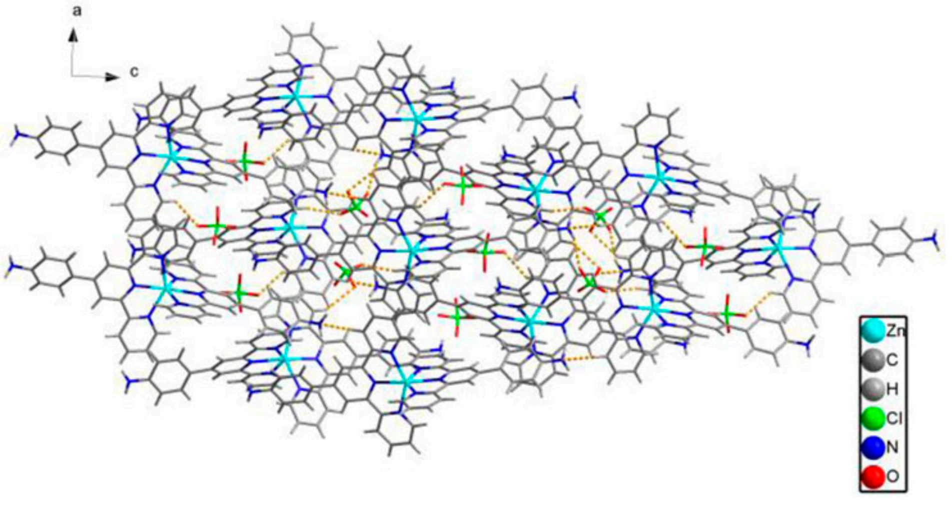

Figure 3(b). 3-D packing diagram of **3** showing hydrogen bonds (orange broken lines) (see http://dx.doi.org/10.1080/00958972.2015.1019486 for color version).

3.1.4. Crystal structure of [Cd(nh2phtpy)$_2$]·(ClO$_4$)$_2$ (4). The asymmetric unit of **4** is comprised of one Cd(II), two nh2phtpy ligands, and two perchlorates. As shown in figure 4(a), Cd(II) is coordinated by six nitrogens from two nh2phtpy ligands. The distance between Cd(II) and central N (Cd(1)–N(2) = 2.280(2) Å, Cd(1)–N(5) = 2.286(2) Å) is shorter than that between Cd(II) and outer N (Cd(1)–N(4) = 2.328(2) Å, Cd(1)–N(1) = 2.349(3) Å, Cd(1)–N(3) = 2.352(3) Å, and Cd(1)–N(6) = 2.354(3) Å), common for [M(tpy)$_2$]$^{2+}$ cations. Bond angles around Cd(II) are (N(2)–Cd(1)–N(5) = 175.12(8)°, N(1)–Cd(1)–N(3) = 140.97(8)°, and N(4)–Cd(1)–N(6) = 140.60(9)°) for *trans* and *cis* angles that range from 70.09(8)° to 114.25(8)°. Differences in bond lengths and angles are indicative of a distorted octahedral coordination environment around Cd(II). The angles between phenyl ring and the terpyridine ring are 50.0° and 25.5°, respectively. The mean

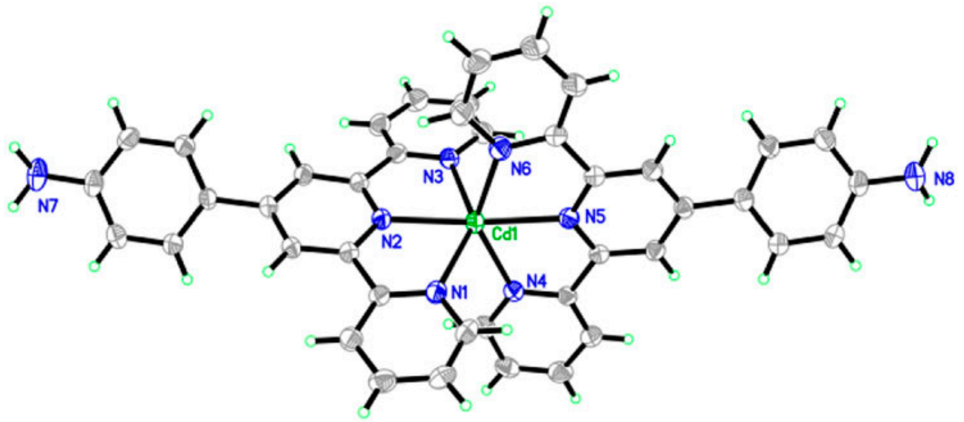

Figure 4(a). ORTEP view of **4** (30% thermal ellipsoids) showing the coordination environment of Cd(II).

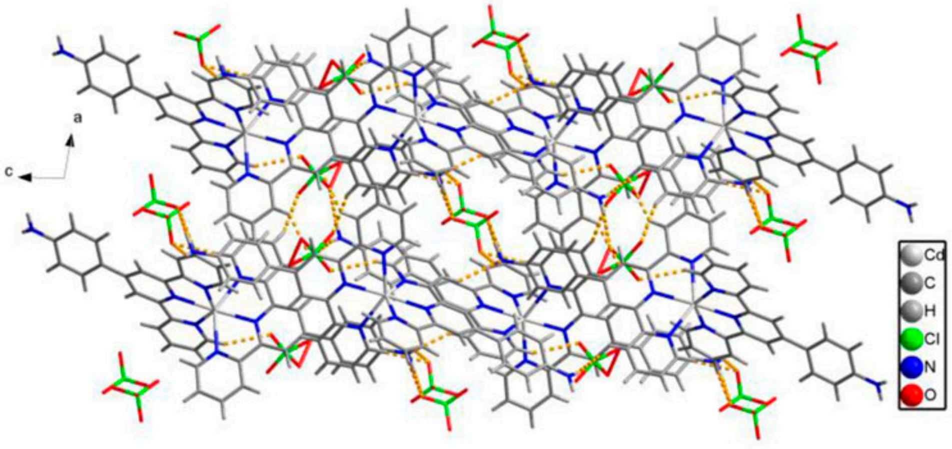

Figure 4(b). 3-D packing diagram of **4** showing hydrogen bonds (orange or sky-blue broken lines) and the aromatic stacking interactions (purple broken lines) (see http://dx.doi.org/10.1080/00958972.2015.1019486 for color version).

deviation of terpyridine plane formed by N1, N2, and N3 and C1–C15 is 0.1641 Å, which suggests a twist similar to **3**. The angle between two terpyridine rings around Cd(II) of 79.2° deviates from a right angle. Hydrogen bonds of N–H···O type, C–H···N type, and C–H···O type link the [M(tpy)$_2$]$^{2+}$ cations and perchlorates into a 3-D network as shown in figure 4(b). Hydrogen bonds and π–π interactions are common in terpyridine complexes [35].

3.2. *Luminescence properties of L1, L2, and 1–4*

The solid-state luminescence of meophtpy (L1), nh2phtpy (L2), and **1–4** were measured at room temperature (figure 5). In comparison to the emission of meophtpy (406 nm, excited at 332 nm), **1** and **2** shows almost the same fluorescence peaks at 405 nm (excited at

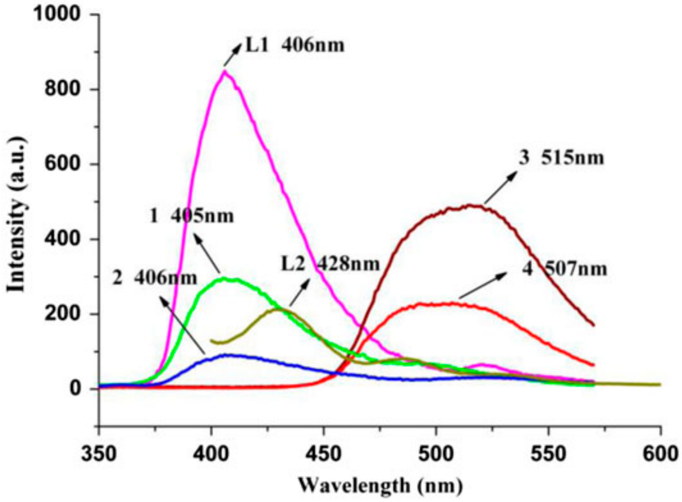

Figure 5. Emission spectra of **1**–**4** and free meophtpy (L1) and nh2phtpy (L2).

335 nm) and 406 nm (excited at 335 nm) with low intensity, which can be attributed to ICT. In comparison to the emission of nh2phtpy (428 nm, excited at 360 nm), **3** and **4** show different fluorescence peaks at 515 nm (excited at 360 nm) and 507 nm (excited at 360 nm) with a red-shift of 87 and 79 nm, respectively, and the intensities were also increased, which could be attributed to LLCT. L1, L2, **1** and **2** may be used as violet luminescence materials and **3** and **4** may be used as green luminescence materials.

4. Conclusion

Homoleptic Zn(II) and Cd(II) complexes with two kinds of terpyridines have been synthesized and characterized. Different substitutions at the 4′ position play roles in the resulting supramolecular structures. The luminescence properties of **1**–**4** and L1 and L2 have been studied. In comparison to L1, nearly the same emission peaks of **1** and **2** with low intensities are observed. Conversely, two red-shift emission peaks of **3** and **4** with strong intensities in comparison to L2 are observed. All complexes show potential applications as luminescent materials in optoelectronic devices such as OLEDs, photovoltaics, and sensors.

Supplementary material

CCDC 956276-956279 contain the supplementary crystallographic data for **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 Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax:+44 1223 336 033; or Email: deposit@ccdc.cam.ac.uk.

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References

[1] U.S. Schubert, H. Hofmeier, G.R. Newkome. *Modern Terpyridine Chemistry*, Wiley-VCH, Weinheim (2006).
[2] E.C. Constable. *Chem. Soc. Rev.*, **36**, 246 (2007).
[3] H. Hofmeier, U.S. Schubert. *Chem. Soc. Rev.*, **33**, 373 (2004).
[4] S.C. Yuan, H.B. Chen, H.C. Wang. *Prog. Chem.*, **21**, 2132 (2009).
[5] E.C. Constable, N. Hostettler, C.E. Housecroft, P. Kopecky, M. Neuburger, J.A. Zampese. *Dalton Trans.*, **41**, 2890 (2012).
[6] N. Zhang, J. Yang, R.-X. Hu, M.-B. Zhang. *Z. Anorg. Allg. Chem.*, **639**, 197 (2013).
[7] H. Yamazaki, S. Igarashi, T. Nagata, M. Yagi. *Inorg. Chem.*, **51**, 1530 (2012).
[8] J. Granifo, R. Gaviño, E. Freire, R. Baggio. *Acta Cryst. C*, **69**, 822 (2013).
[9] H. Zhou, F. Zhou, P. Wu, Z. Zheng, Z. Yu, Y. Chen, Y. Tu, L. Kong, J. Wu, Y. Tian. *Dyes Pigm.*, **91**, 237 (2011).
[10] G. Zhang, Q. Li, W. Fu, D. Wang. *Acta Cryst. E*, **66**, m681 (2010).
[11] E. Belhadj, A. El-Ghayoury, E. Ripaud, L. Zorina, M. Allain, P. Batail, M. Mazari, M. Sallé. *New J. Chem.*, **37**, 1427 (2013).
[12] N.W. Alcock, P.R. Barker, J.M. Haider, M.J. Hannon, C.L. Painting, Z. Pikramenou, E.A. Plummer, K. Rissanen, P. Saarenketo. *J. Chem. Soc., Dalton Trans.*, 1447 (2000).
[13] Y.H. Lee, E. Kubota, A. Fuyuhiro, S. Kawata, J.M. Harrowfield, Y. Kim, S. Hayami. *Dalton Trans.*, **41**, 10825 (2012).
[14] E. Kubota, Y.H. Lee, A. Fuyuhiro, S. Kawata, J.M. Harrowfield, Y. Kim, S. Hayami. *Polyhedron*, **52**, 435 (2013).
[15] X. Chen, Q. Zhou, Y. Cheng, Y. Geng, D. Ma, Z. Xie, L. Wang. *J. Lumin.*, **126**, 81 (2007).
[16] D.F. Qiu, Q. Zhao, K.C. Liu, Y.C. Guo, Y.Q. Feng. *Chinese J. Struct. Chem.*, **29**, 1513 (2010).
[17] F.-X. Zhou, Z. Zheng, H.-P. Zhou, W.-Z. Ke, J.-Q. Wang, Z.-P. Yu, F. Jin, J.-X. Yang, J.-Y. Wu, Y.-P. Tian. *CrystEngComm*, **14**, 5613 (2012).
[18] P. Wang, Z. Li, G.-C. Lv, H.-P. Zhou, C. Hou, W.-Y. Sun, Y.-P. Tian. *Inorg. Chem. Commun.*, **18**, 87 (2012).
[19] B. Maity, S. Gadadhar, T.K. Goswami, A.A. Karande, A.R. Chakravarty. *Dalton Trans.*, **40**, 11904 (2011).
[20] A. Mehrani, A. Morsali, P. Ebrahimpour. *J. Coord. Chem.*, **66**, 856 (2013).
[21] H.-Q. Liu, T.-C. Cheung, S.-M. Peng, C.-M. Che. *J. Chem. Soc., Chem. Commun.*, **31**, 1787 (1995).
[22] J.-L. Wang, X. Li, C.D. Shreiner, X. Lu, C.N. Moorefield, S.R. Tummalapalli, D.A. Medvetz, M.J. Panzner, F.R. Fronczek, C. Wesdemiotis, G.R. Newkome. *New J. Chem.*, **36**, 484 (2012).
[23] S. Rajalakshmi, T. Weyhermüller, M. Dinesh, B.U. Nair. *J. Inorg. Biochem.*, **117**, 48 (2012).
[24] T.T. Liu, X. Xia, F. Yue, G. Liu, J.D. Wang. *J. Xinjiang Univ.*, **27**, 214 (2010).
[25] W. Yang, Y. Zhong. *Chin. J. Chem.*, **31**, 329 (2013).
[26] W.-W. Fu, D.-Z. Kuang, F.-X. Zhang, Y. Liu, W. Li, Y.-F. Kuang. *Chin. J. Inorg. Chem.*, **29**, 654 (2013).
[27] G.D. Storrier, S.B. Colbran, D.C. Craig. *J. Chem. Soc., Dalton Trans.*, 3011, (1997).
[28] D. Hvasanov, A.F. Mason, D.C. Goldstein, M. Bhadbhade, P. Thordarson. *Org. Biomol. Chem.*, **11**, 4602 (2013).
[29] D.C. Goldstein, Y.Y. Cheng, T.W. Schmidt, M. Bhadbhade, P. Thordarson. *Dalton Trans.*, **40**, 2053 (2011).
[30] L. Li, J.L. Li, X.L. Wu. *J. Northwest Univ.*, **40**, 451 (2010).
[31] J. Wang, G.S. Hanan. *Synlett*, **16**, 1251, (2005).
[32] G.M. Sheldrick. *SHELXS-97 AND SHELXTL-97*, University of Göttingen, Germany (1997).
[33] J. McMurtrie, I. Dance. *CrystEngComm*, **11**, 1141 (2009).
[34] J. McMurtrie, I. Dance. *CrystEngComm*, **12**, 3207 (2010).
[35] L. Saghatforoush, E. Sahin, S. Babaei, A. Bakhtiari, A. Nasimian, Ö. Çelik, Z. Zabihollahi. *J. Coord. Chem.*, **67**, 1463 (2014).