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Reactivity and solid-state photo-luminescence of cadmium compounds constructed from 4'-Ph-terpy and cadmium salts

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Three cadmium compounds, $[\text{Cd}_2\text{L}_2\text{Cl}(\text{C}_6\text{H}_5\text{O}_7)]_n$ (**1**), $[\text{CdLCl}_2]$ (**2**), and $[\text{CdL}_2(\text{NO}_3)](\text{NO}_3) \cdot 2\text{H}_2\text{O}$ (**3**) ($\text{L} = 4'\text{-Ph-terpy}$), were synthesized by hydrothermal methods from 4'-Ph-terpy and cadmium salts. The structure of **1** consists of a helical structure with cadmiums coordinated by 4'-Ph-terpy ligands and chloride and bridged by citrate, constructing a chiral 1-D polymeric compound. The cadmium in **2** is five-coordinate, bound to one tridentate terpyridine ligand and two chlorides, exhibiting a neutral mononuclear unit with an irregular CdN_3Cl_2 polyhedron. Compound **3** shows a seven-coordinate cadmium bound to two tridentate terpy ligands and one oxygen from nitrate in a *mer* configuration. The reactions producing these compounds are temperature dependent. The compounds show photo-luminescence in the solid state.

Keywords: Photo-luminescence; Cadmium; Compound; Hydrothermal synthesis

1. Introduction

Effort has been made on the studies of cadmium complexes [1] owing to their coordination and photo-luminescence with different ligands. The observation of luminescence from a number of semiconducting materials of cadmium(II) along with other d^{10} metals represents an important factor for the development of luminescent complexes. Several cadmium coordination polymers have been prepared [2, 3] by the self-assembly of cadmium ions and multidentate ligands with various sizes and geometrical preferences. Terpy coordinates with metal ions [4–9] present stable square-planar complexes, showing strong fluorescence, in particular, complexes of platinum and palladium. Combinations of different ligands may present novel structures and show the mechanism and function of these complexes in material and medicinal chemistry. Although many complexes of metal ions with terpy ligands have been reported, complexes of cadmium are scarce [10]. To better understand the effects of a flexible carboxylic acid as chain-bridge and aromatic planar terpy on the structure and

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properties of cadmium complexes, we synthesized a multi-pyridyl ligand, 4'-Ph-terpy, and obtained cadmium(II) compounds. Herein, we present syntheses, structures, and characterizations of three cadmium compounds, constructed from 4'-Ph-terpy and cadmium in the presence of citrate ligand; characterizations include the X-ray crystal structure, elemental analysis, X-ray powder diffraction (XRPD), Electrospray ionisation-mass spectrometry (ESI-MS), ^1H NMR, and photo-luminescence.

2. Experimental

Collection of X-ray single crystal data was performed on a Rigaku R-AXIS RAPID Weissenberg IP Diffractometer or a Rigaku Mercury-CCD Diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). ^1H NMR was performed on a Varian Unity 500 spectrometer. Elemental analyses were determined by an Elementar Vario EL III Elemental Analyser. Electrospray mass spectra (ES-MS) were recorded on a Finnigan LCQ Mass Spectrometer using DMF-methanol or methanol as mobile phase. Emission and excitation spectra were recorded on a Perkin-Elmer LS 55 luminescent spectrometer with a red-sensitive photomultiplier type R928. All reagents used in experiments were of analytical grade or purified by standard method.

2.1. Free ligand *L*

The multi-pyridyl ligand, 4'-Ph-terpy was condensed from 2-acetyl pyridine and benzaldehyde and refluxed in ethanol with ammonium acetate [11].

2.2. Synthesis of $[\text{Cd}_2\text{L}_2\text{Cl}(\text{C}_6\text{H}_5\text{O}_7)]_n$ (**1**)

A mixture of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (0.045 g, 0.20 mM), 4'-Ph-terpy (0.061 g, 0.20 mM), $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ (0.039 g, 0.13 mM) and distilled water (20 mL) was sealed in a 25 mL stainless reactor with a Teflon liner and heated at 165°C for 3 days. Yellow crystals of **1** were isolated by mechanical separation. The yield of **1** was 48% based on CdCl_2 . Anal. Calcd for $[\text{Cd}_2\text{C}_{48}\text{H}_{35}\text{N}_6\text{O}_7\text{Cl}]_n$ (%): C, 53.83; H, 3.30; N, 7.85. Found: C, 53.85; H, 3.25; N, 7.91.

2.3. Synthesis of $[\text{Cd}(4'\text{-Ph-terpy})\text{Cl}_2]$ (**2**)

A mixture of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (0.045 g, 0.20 mM), 4'-Ph-terpy (0.061 g, 0.20 mM), $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ (0.039 g, 0.13 mM), and distilled water (20 mL) was sealed in a 25 mL stainless reactor with a Teflon liner and heated at 120°C for 3 days. Colorless crystals of **2** were isolated in 36% based on CdCl_2 . $[\text{CdC}_{21}\text{H}_{15}\text{N}_3\text{Cl}_2]$ requires C 51.12, H 3.07, N 8.52; found C 51.03, H 3.30, and N 8.51. The ^1H NMR data: δ (500 MHz, DMSO- d_6): 7.64 (s, 2H), 7.66 (s, 1H), 7.85 (s, 2H), 8.21 (s, 2H), 8.32 (s, 2H), 8.78 (s, 2H), 8.97 (s, 2H), 9.01 (d, 2H). ESI-MS: $[\text{Cd}(4'\text{-Ph-terpy})\text{Cl}]^+$ (458.4, 100%).

2.4. Synthesis of $[Cd(4'-Ph-terpy)_2(NO_3)](NO_3) \cdot 2H_2O$ (**3**)

A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (0.040 g, 0.13 mM), 4'-Ph-terpy (0.040 g, 0.13 mM), $Na_3C_6H_5O_7 \cdot 2H_2O$ (0.039 g, 0.13 mM) and water (20 mL) was sealed in a 25 mL stainless reactor with a Teflon liner and heated at 180°C for 3 days. Orange crystals of **3** were isolated by mechanical separation from a mixture of **3** and unidentified yellow powder in 16% based on $Cd(NO_3)_2 \cdot [CdC_{42}H_{30}N_7O_3](NO_3) \cdot 2H_2O$ requires C 56.60, H 3.85, N 12.57; found C 56.23, H 4.04, N 12.28. The data of 1H NMR δ (500 MHz, DMSO- d_6): 7.68–7.69 (d, 10H), 8.24 (d, 8H), 8.54 (s, 4H), 8.99 (s, 4H), 9.07 (d, 4H). $[Cd(4'-Ph-terpy)_2]^{2+}$ (366.6, 100%), $[Cd(4'-Ph-terpy)_2](NO_3)^+$ (793.7, 15%).

2.5. Single-crystal X-ray structure determination

Crystals with dimensions $0.51 \times 0.29 \times 0.22$ mm³ for **1**, $0.72 \times 0.26 \times 0.25$ mm³ for **2** and $0.30 \times 0.27 \times 0.10$ mm³ for **3** were mounted on glass fibers. The data sets were collected at room temperature with ω scan mode and data reduction was carried out [12]. The intensity data were corrected for Lp factors for the three compounds and an ψ empirical absorption correction was done for **1** [13]. The structures of the three compounds were solved by direct methods (SHELXS-97) [14] and refined by full-matrix least squares on F^2 (SHELXL-97) [14] using $w = 1/[\sigma^2(F_o^2) + (P(F_o^2 + 2F_c^2)/3)^2]$. All non-hydrogen atoms were refined anisotropically and all hydrogens were added theoretically. All calculations were performed on a PC 586 computer using SHELXTL.

3. Results and discussion

The multi-pyridyl ligand, 4'-Ph-terpy, was condensed from 2-acetyl pyridine and benzaldehyde and refluxed in ethanol with ammonium acetate [11]. Compound **1** was synthesized hydrothermally by heating a mixture of $CdCl_2 \cdot 2.5H_2O$, 4'-Ph-terpy and $Na_3C_6H_5O_7 \cdot 2H_2O$ in a molar ratio of 3 : 3 : 2 at 165°C for 3 days. A perspective view of the molecular structure of $[Cd_2L_2Cl(C_6H_5O_7)]_n$ is shown in figure 1, crystal data in table 1 and selected bond lengths and angles in table 2. This compound is a chiral 1-D compound with an extended helical $CdL-[CdLCl(C_6H_5O_7)]-CdL$ subnetwork as shown in figures 2 and 3, although its overall structure is racemic. When cadmium(II) dichloride, 4'-Ph-terpy and $Na_3C_6H_5O_7 \cdot 2H_2O$ was reacted under hydrothermal conditions at 120°C for 3 days, **2** with formula of $[CdLCl_2]$ was isolated. The structure shows that no substitution reaction between chloride and carboxylate occurs. The hydrothermal reaction of cadmium(II) nitrate, 4'-Ph-terpy and $Na_3C_6H_5O_7 \cdot 2H_2O$ at 180°C produced **3** with formula $[CdL_2(NO_3)](NO_3) \cdot 2H_2O$.

The structure of **1** shows a 1-D zigzag chain architecture. There are two crystallographically independent Cd^{2+} ions, Cd(1) coordinated by one 4'-Ph-terpy and four oxygens from two citrates in a pentagonal bipyramidal geometry and Cd(2) coordinated by three nitrogens of one 4'-Ph-terpy, two oxygens from one citrate and one chloride in an octahedral CdN_3O_2Cl coordination. The distance of two independent cadmiums is 8.9817 Å via a $Cd1-O1-C01-C01-C05-C03-C04-O3-Cd2$ bridge. The distances between two central cadmium ions on the same adjacent position are 6.519 Å for $Cd(1)-Cd(1)$ and 16.788 Å for $Cd(2)-Cd(2)$. The 4'-Ph-terpy is tridentate as in many

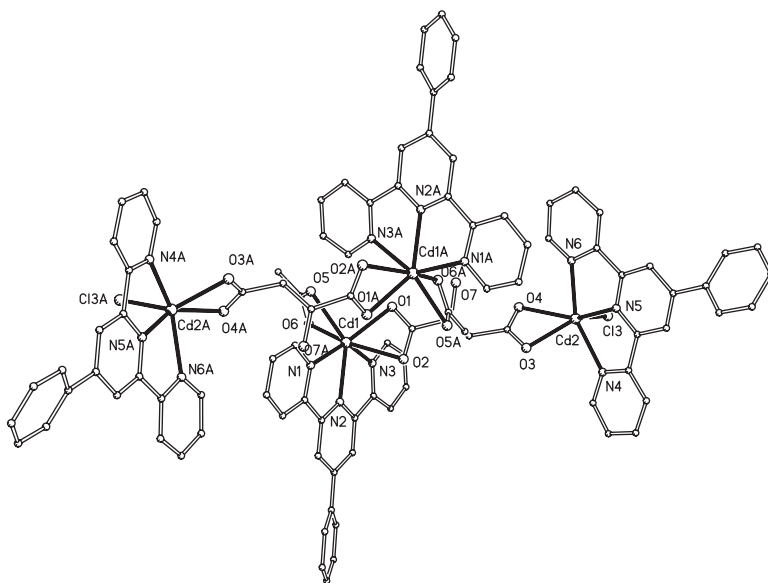


Figure 1. The molecular structure of 1.

Table 1. Crystallographic data of 1–3.

Empirical formula	$C_{48}H_{35}Cd_2ClN_6O_7$	$C_{21}H_{15}CdCl_2N_3$	$C_{42}H_{34}CdN_8O_8$
Formula weight	1068.07	493.67	891.17
Crystal system	Monoclinic	Monoclinic	Triclinic
Crystal size (mm ³)	$0.51 \times 0.29 \times 0.22$	$0.72 \times 0.26 \times 0.25$	$0.30 \times 0.27 \times 10$
Space group	$C2/c$	Cc	$P-1$
Unit cell dimensions (Å, °)			
<i>a</i>	36.355(2)	11.693(2)	10.091(3)
<i>b</i>	10.6824(4)	13.946(3)	12.769(3)
<i>c</i>	22.2270(9)	11.820(2)	17.000(4)
α	90	90	105.596(2)
β	99.336(1)	92.88(3)	95.1445(13)
γ	90	90	111.031(3)
Volume (Å ³), <i>Z</i>	8517.8(6), 8	1925.0(7), 4	1926.5(8), 2
Calculated density (mg m ⁻³)	1.666	1.700	1.536
Absorption coefficient (mm ⁻¹)	1.123	1.422	0.633
<i>F</i> (000)	4272	976	908
θ_{\max} , θ_{\min} (°)	27.49, 1.99	27.48, 2.27	25.00, 3.21
Index range	$0 \leq h \leq 47$ $0 \leq k \leq 13$ $-28 \leq l \leq 28$	$0 \leq h \leq 15$ $0 \leq k \leq 18$ $-15 \leq l \leq 15$	$-11 \leq h \leq 11$ $-15 \leq k \leq 11$ $-19 \leq l \leq 20$
Independent reflections	9583	2208	6705
Reflections collected	6947	2061	5917
No. of variables	595	244	577
<i>R</i>	0.0280	0.0233	0.0592
<i>wR</i>	0.0647	0.0606	0.1601
Goodness-of-fit	1.017	1.034	1.035
Largest difference peak ^a and hole (e Å ⁻³)	0.416 (−0.486)	0.300 (−0.551)	1.296 (−1.180)

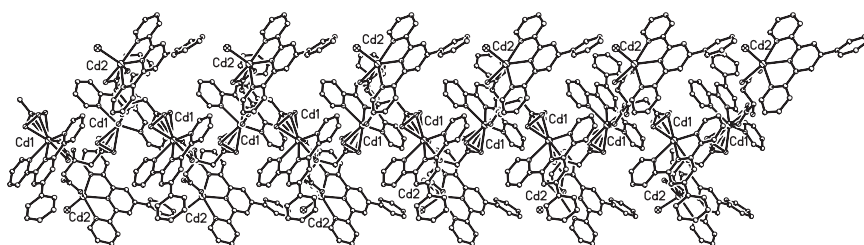
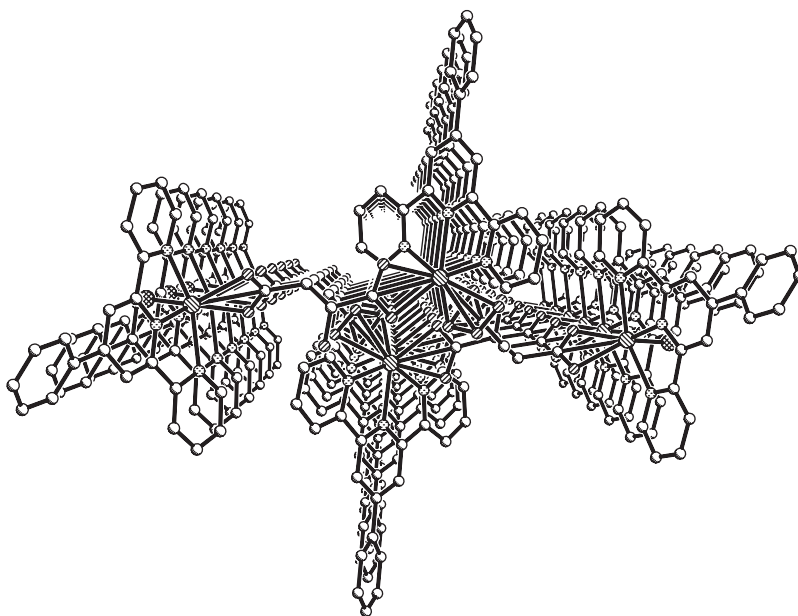
$$R = \sum \|F_o\| - |F_c| / \sum \|F_o\|; wR = \{\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)\}^{1/2}.$$

^aLargest peak (hole) in difference Fourier map.

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

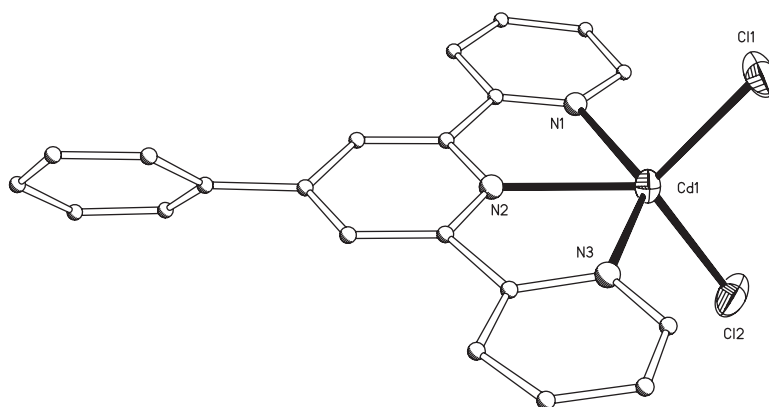
Cd(1)–O(1)	2.291(2)	Cd(1)–O(6)	2.298(3)	Cd(1)–N(2)	2.347(2)
Cd(1)–N(1)	2.383(2)	Cd(1)–N(3)	2.397(2)	Cd(1)–O(5)	2.427(3)
Cd(1)–O(5')	2.465(9)	Cd(1)–O(6')	2.466(8)	Cd(1)–O(2)	2.518(2)
Cd(2)–N(5)	2.349(2)	Cd(2)–N(6)	2.380(2)	Cd(2)–O(3)	2.268(2)
Cd(2)–Cl(3)	2.4512(7)	Cd(2)–O(4)	2.469(2)	Cd(2)–N(4)	2.428(2)
O(1)–Cd(1)–O(6)	115.1(1)	O(1)–Cd(1)–N(2)	134.17(7)		
O(6)–Cd(1)–N(2)	100.8(1)	O(1)–Cd(1)–N(1)	122.57(9)		
O(6)–Cd(1)–N(1)	105.1(1)	N(2)–Cd(1)–N(1)	69.33(7)		
O(1)–Cd(1)–N(3)	90.42(9)	O(6)–Cd(1)–N(3)	79.4(1)		
N(2)–Cd(1)–N(3)	68.33(7)	N(1)–Cd(1)–N(3)	137.50(7)		
O(1)–Cd(1)–O(5)	86.3(1)	O(6)–Cd(1)–O(5)	53.4(1)		
N(2)–Cd(1)–O(5)	139.4(1)	N(1)–Cd(1)–O(5)	86.6(1)		
N(3)–Cd(1)–O(5)	124.9(1)	O(1)–Cd(1)–O(5')	116.1(2)		
N(1)–Cd(1)–O(5')	73.9(2)	N(2)–Cd(1)–O(5')	109.7(2)		
N(1)–Cd(1)–O(6')	124.2(2)	N(3)–Cd(1)–O(5')	117.8(3)		
N(2)–Cd(1)–O(6')	137.4(3)	O(1)–Cd(1)–O(6')	76.8(2)		
N(3)–Cd(1)–O(6')	86.3(2)	O(6)–Cd(1)–O(2)	158.6(1)		
O(1)–Cd(1)–O(2)	53.44(8)	N(1)–Cd(1)–O(2)	95.96(7)		
N(2)–Cd(1)–O(2)	82.91(8)	O(5)–Cd(1)–O(2)	133.4(1)		
N(3)–Cd(1)–O(2)	82.45(9)	O(6')–Cd(1)–O(2)	128.6(2)		
O(5')–Cd(1)–O(2)	158.7(3)	O(3)–Cd(2)–N(5)	118.29(7)		
O(3)–Cd(2)–N(6)	109.87(9)	N(5)–Cd(2)–N(6)	68.85(7)		
O(3)–Cd(2)–N(4)	82.33(7)	N(5)–Cd(2)–N(4)	68.30(7)		
N(6)–Cd(2)–N(4)	135.99(7)	O(3)–Cd(2)–Cl(3)	130.48(7)		
N(5)–Cd(2)–Cl(3)	105.84(5)	N(6)–Cd(2)–Cl(3)	105.96(6)		
N(4)–Cd(2)–Cl(3)	94.86(5)	O(3)–Cd(2)–O(4)	54.55(7)		
N(5)–Cd(2)–O(4)	147.90(7)	N(6)–Cd(2)–O(4)	84.04(7)		
N(4)–Cd(2)–O(4)	131.67(7)	Cl(3)–Cd(2)–O(4)	97.71(5)		

complexes [4–9], binding one cadmium in its cavity and stopping the formation of a 2-D structure. The three pyridyl rings on two ligands are nearly planar and two phenyl groups on central pyridyls are twisted with planes of 32.0(1) and 23.8(1)°, respectively. The citrate functions as a hexadentate ligand links three Cd²⁺ ions into a helix as it binds three central ions by three carboxylates. By the effect of 4'-Ph-terpy and chloride, one arm of the citrate coordinated with Cd²⁺ was terminated. The other two arms of each citrate coordinate to two Cd²⁺ bridging along with other citrates into an infinite zigzag chain. The hydroxyl group of citrate is not coordinated. This conformation results in a 1-D structure in a helical conformation. The basic unit of the helix is 14-membered and right-handed with a 10.682 Å period of the helix. Only one type of intramolecular hydrogen bond is observed with uncoordinated hydroxyl of citrate bonding to neighboring coordinated carboxylate oxygen (O...O distances = 2.618(4) Å). The packing diagrams (figures 2 and 3) show that the 1-D zigzag chain is stabilized by π - π interactions, forming 1-D hydrophobic channels along the crystallographic *b* axis without guest water molecules, although the crystals were obtained in water. Bond lengths of Cd²⁺ to the central pyridyl ring [Cd–N 2.347(2)–2.349(2) Å] are shorter than those to the terminal pyridyl rings [Cd–N 2.380(2)–2.428(2) Å] as anticipated from the constrained *tpy* bite; all are longer than the respective reported bond lengths [10] in the range of 2.270(2)–2.290(3) Å for central and terminal pyridyl rings (Cd–N) 2.322(3)–2.355(3) Å. The distances between Cd²⁺ and oxygen from citrate ligands [Cd–O 2.291(2)–2.518(2) Å] are in the range, 2.216(3)–2.570(3) Å, of reported structures [2b].

Figure 2. A side view of **1**.Figure 3. A view of **1** along its helical axis.

Only one Cd–Cl bond length is in the range of a similar reported structure [Cd–Cl 2.4325(7)–2.4629(7) Å] [15].

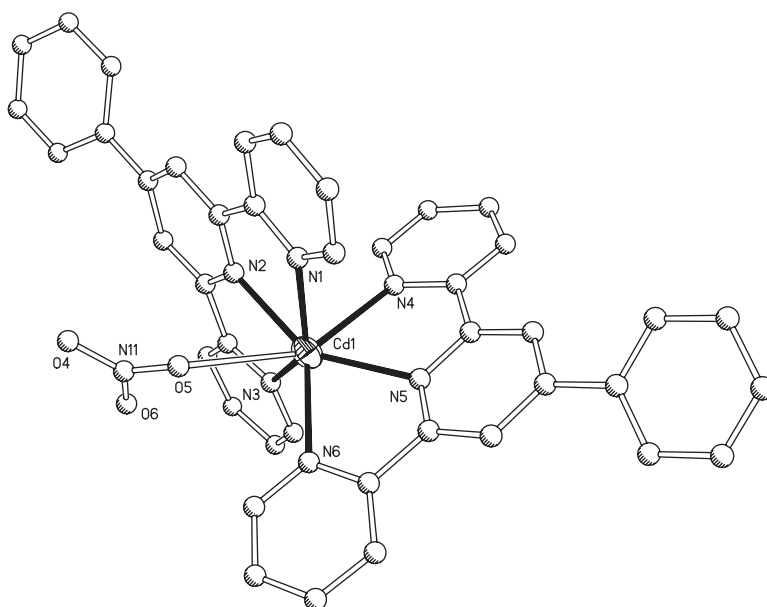
The structure of **2**, illustrated in figure 4, has four [CdC₂₁H₁₅N₃Cl₂] with *Cc* crystallographic symmetry in one unit cell. Selected bond distances and angles are listed in table 3. Each cadmium is coordinated by three nitrogens from one terpyridine and two chlorides in a neutral mononuclear unit. The cadmium forms a planar structure with terpy and gives an irregular CdN₃Cl₂ coordination structure as a distorted square pyramid. One chloride (Cl(2)) occupies the apical position and the four basal coordination positions are occupied by the three nitrogens and the other chloride (Cl(1)). This geometry is proved by the angles among the equatorial chloride (Cl(2)) and the three nitrogens (table 3). These angles indicate a distorted square pyramid with the three pyridyl rings nearly planar and the phenyl group at the central pyridyl twisted with an angle of 57.16(9)°. The average Cd–N bond length is 2.359 Å and that of Cd–Cl is 2.455 Å. A similar structure, constructed by cadmium dichloride and terpy ligand, has been reported [16a], as it has a similar irregular polyhedron CuN₃Br₂ [16b, c].

Figure 4. The molecular structure of **2**.Table 3. Selected bond lengths (Å) and angles (°) of **2**.

Cd(1)–N(3)	2.330(7)	Cd(1)–N(2)	2.336(2)	Cd(1)–N(1)	2.413(6)
Cd(1)–Cl(1)	2.444(3)	Cd(1)–Cl(2)	2.466(3)		
N(3)–Cd(1)–N(2)	69.7(3)	N(3)–Cd(1)–N(1)	138.08(9)		
N(2)–Cd(1)–N(1)	68.4(3)	N(3)–Cd(1)–Cl(1)	101.6(2)		
N(2)–Cd(1)–Cl(1)	126.9(2)	N(1)–Cd(1)–Cl(1)	102.3(2)		
N(3)–Cd(1)–Cl(2)	100.0(2)	N(2)–Cd(1)–Cl(2)	125.6(2)		
N(1)–Cd(1)–Cl(2)	104.9(2)	Cl(1)–Cd(1)–Cl(2)	107.41(4)		

The molecular structure of **3** is illustrated in figure 5 and bond lengths and angles in table 4. Each cadmium is seven-coordinate, bound to two *tpy*, *mer* configuration, and one oxygen from a nitrate. The NO_3^- has weak contact, 2.743(4) Å, with the central Cd^{2+} ion. The bond length between Cd^{2+} and the central pyridyl ring [Cd(1)–N(2) 2.301(4) Å] is shorter than the two terminal pyridyl rings [Cd–N 2.370(4)–2.336(3) Å] in one terpy. In the other terpy, the similar bond length [Cd(1)–N(5) 2.344(4) Å] is between the terminal pyridyl rings [Cd(1)–N(4) 2.472(4) Å, Cd(1)–N(6) 2.328(4) Å]. The two terpyridyl units are essentially planar with dihedral angles of the pyridyl being 0.88° and 7.78° for one terpyridyl and 12.61° and 16.05° for the other. The phenyl rings are twisted as the dihedral angles of phenyls and their pyridyl are 28° and 32°, respectively. In a reported structure [17], each cadmium is six-coordinate. The difference between this and the reported structure is coordination of nitrate, since the reported structure has uncoordinated PF_6^- . In the reported structure [17], the bond lengths between Cd^{2+} and the central pyridyl rings [Cd–N 2.270(2)–2.290(3) Å] are shorter in both ligands [Cd–N 2.322(3)–2.355(3) Å] and essentially planar (torsion angles 0.8–10.3).

The photo-luminescence of the compounds has been studied. Emission spectra in the solid state at room temperature are shown in figure 6. Compound **1** has two bands in its emission spectra, one with low intensity but with high energy at *ca* 434.5 nm and the other with high intensity but lower energy at *ca* 572.5 nm. In comparison with the photo-luminescence of the ligand [18], the higher energy of **1** is assigned to chloride or

Figure 5. The molecular structure of **3**.Table 4. Selected bond lengths (Å) and angles (°) of **3**.

Cd(1)–N(1)	2.370(4)	Cd(1)–N(2)	2.301(4)	Cd(1)–N(3)	2.336(4)
Cd(1)–N(4)	2.472(4)	Cd(1)–N(5)	2.344(4)	Cd(1)–N(6)	2.328(4)
Cd(1)–O(5)	2.743(4)				
N(2)–Cd(1)–N(6)	141.5(1)	N(2)–Cd(1)–N(3)	70.4(1)		
N(6)–Cd(1)–N(3)	100.3(2)	N(2)–Cd(1)–N(5)	147.8(1)		
N(6)–Cd(1)–N(5)	69.3(2)	N(3)–Cd(1)–N(5)	122.1(1)		
N(2)–Cd(1)–N(1)	70.3(2)	N(6)–Cd(1)–N(1)	112.0(2)		
N(3)–Cd(1)–N(1)	140.6(2)	N(5)–Cd(1)–N(1)	91.0(2)		
N(2)–Cd(1)–N(4)	85.2(1)	N(6)–Cd(1)–N(4)	132.7(2)		
N(3)–Cd(1)–N(4)	88.0(1)	N(5)–Cd(1)–N(4)	67.0(1)		
N(1)–Cd(1)–N(4)	86.2(2)				

carboxyl to terpy (LLCT) and the latter to ligand-based intramolecular charge transfer (ICT) [18], unlike reported results [1]. Figure 6 also shows the photo-luminescence of **2** with two bands at 408.0 nm, strong, and at 538.5 nm, weak. The former is assigned as intraligand (IL) and the latter as LMCT (ligand-to-metal charge transfer). The emission spectrum of **3** shows two weak bands at 399.5 and 545.5 nm. The former is assigned as IL and the latter as LMCT. The results illustrate the rich photo-luminescent properties of cadmium complexes with different ligands.

In summary, we have prepared three cadmium compounds with 4'-Ph-terpy in hydrothermal conditions. These compounds show special structures and photo-luminescence in the solid states.

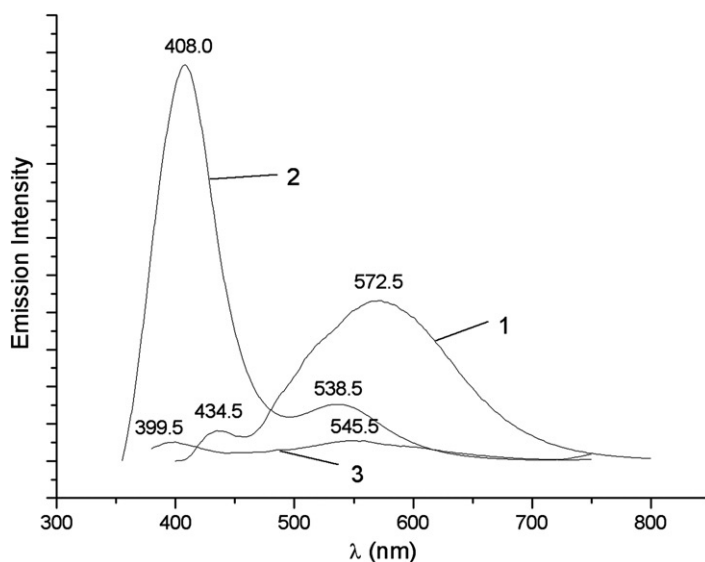


Figure 6. The emission spectra of **1** (excited at 360 nm), **2** (excited at 320 nm) and **3** (excited at 342 nm) in solid state at room temperature.

Supplementary material

The additional crystallographic details and complete listings have been deposited at the Cambridge Crystallographic Data Center (CCDC) as supplementary publication reference numbers 253226, 253228, and 714673.

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