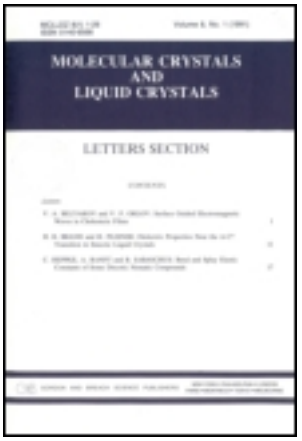

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A Novel 3D Coordination Polymer Based on Bridging Interactions of the Pyridine-2,3-dicarboxylic Acid

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A Novel 3D Coordination Polymer Based on Bridging Interactions of the Pyridine-2,3-dicarboxylic Acid

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*A novel three-dimensional (3D) coordination polymer $[Cd(pdc)Cl]_n$ (**1**) has been synthesized under hydrothermal conditions, containing pyridine-2,3-dicarboxylic acid (H_2pdc) as a bridging ligand. X-ray analysis shows an infinite 3D structure in which the cadmium(II) centers are bridged by multidentate H_2pdc ligand. The novel complex was characterized by IR spectrum, elemental analysis, fluorescent properties, thermogravimetric analysis, single-crystal X-ray diffraction, and powder X-ray diffraction (PXRD).*

[Supplemental materials are available for this article. Go to the publisher's online edition of *Molecular Crystals and Liquid Crystals* to view the free supplemental file: CCDC 935077 contains the supplementary crystallographic data for this article. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.]

Keywords Bridging interaction; pyridine-2,3-dicarboxylic acid; three-dimensional infinite structure

Introduction

During the past decades, the design and synthesis of novel metal-organic frameworks (MOFs) have provoked significant interest owing to their enormous variety of intriguing structural topologies as well as great potential applications as microporous, magnetic, nonlinear optical, and fluorescent materials [1–4]. Although the design and synthesis of such materials are highly influenced by many factors, such as the coordination trend of metal centers, the nature of ligands used, metal–ligand ratio, reaction conditions, etc., the judicious selection for multifunctional organic ligands is still an effective approach to construct MOFs with unique structures and properties [5–7]. Polydentate organic ligands can be selected for their diversity in the coordination modes. Many of these hybrid materials have been synthesized and characterized by rational selection of suitable ligands. Among the various ligands, multidentate N– or O–donor ligands, such as pyridine or imidazole (di)carboxylic acids, have drawn extensive attention in the construction of coordination polymer or MOF. For example, pyridine or imidazole dicarboxylic ligands, including pyridine-2,6-, 2,5-, or

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3,4-dicarboxylic and imidazole-3,4-dicarboxylic acids, have been extensively employed in the construction of such MOFs [8,9]. Compared with other pyridine-dicarboxylic acids, pyridine-2,3-dicarboxylic acid (H_2pdc) is rarely used as a linkage ligand [10–12]. It is probably due to the following reasons: First, it often behaves like picolinic acid, acting as a chelating bidentate ligand through the nitrogen atom and one oxygen atom of the carboxylic group in *ortho* position, and the second carboxyl group remains idle [13]. Second, it prefers decarboxylation of the carboxylic group in the ortho position and transforms to nicotinic acid [14].

Taking these into consideration, we believe that H_2pdc will be an ideal ligand for constructing novel metal-organic hybrid compounds. In this article, we report the hydrothermal syntheses, structure determinations, and properties of a three-dimensional (3D) coordination polymer of H_2pdc, formulated as $[Cd(pdc)Cl]_n$ (**1**). Single crystal X-ray diffractions show ligand H_2pdc in the compounds is singly deprotonated, and the singly deprotonated $Hpdc^-$ coordinate in the μ_1 or μ_2 mode to generate 3D MOFs. In addition, fluorescent properties, thermal decomposition process, and powder X-ray diffraction (PXRD) of compound **1** were studied.

Experimental

All chemicals were commercial materials of analytical grade and used without purification. Elemental analysis for C, H, and N was carried out on a Perkin–Elmer 2400 II elemental analyzer. The FT-IR spectrum was obtained on a PE Spectrum One FT-IR Spectrometer Fourier transform infrared spectroscopy in the 4000–400 cm^{-1} regions, using KBr pellets. Perkin–Elmer Diamond TG/DTA thermal analyzer was used to record simultaneous TG and DTG curves in the static air atmosphere at a heating rate of 10 K min^{-1} in the temperature range 25°C–1000°C using platinum crucibles. Fluorescence spectra were recorded with F-2500 FL Spectrophotometer analyzer. PXRD patterns were obtained using a pinhole camera (Anton Paar) operating with a point focused Ni-filtered Cu Kα radiation in the 2θ range from 5° to 50° with a scan rate of 0.08° s^{-1}.

Synthesis of Complex $[Cd(pdc)Cl]_n$ (1)

The reagents of $CdCl_2 \cdot 2/5H_2O$ (0.228 g, 1.00 mmol) and H_2pdc (0.167 g, 1.00 mmol) were dissolved in 15 mL mixed solvent of DMF/H_2O (volume ratio 1:2) and added eight drops of py and then stirred for 0.5 h. Then an aqueous solution of sodium hydroxide was added dropwise with stirring to adjust the pH value of the solution to 6. The resulting mixture was sealed in a 30 mL Teflon-lined stainless reactor, kept under autogenous pressure at 150°C for 72 h, and then slowly cooled to room temperature at a rate of 5°C h^{-1}. The block crystals suitable for X-ray diffraction were isolated directly (Yield: 65%, based on Cd). Anal. Calcd for $C_7H_3CdCl\,NO_4$ (%): C, 26.86; H, 0.97; Cl, 11.33; N, 4.48; Found: C, 26.73; H, 0.89; Cl, 11.25; N, 4.63. IR data (KBr pellets, cm^{-1}): 3084(w), 1667(w), 1610(s), 1580(s), 1450(s), 1389(vs), 1234(w), 1176(w), 1146(w), 1102(s), 871(m), 843(m), 826(m), 783(s), 658(s), 602(w), 500(w), 455(w).

X-Ray Data Collection and Structure Refinement

Suitable single crystal with approximate dimensions were mounted on a glass fiber and used for X-ray diffraction analyses. Data were collected at 293(2) K on a Bruker Apex CCD diffractometer using the ω scan technique with Mo Kα radiation ($\lambda = 0.71069$ Å).

Table 1. Experimental data for Complex **1**

Complexes	**1**
Empirical formula	$C_7H_3CdClNO_4$
Formula weight	312.95
Temperature	296 (2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2 (1)/c
a (Å)	6.552 (2)
b (Å)	11.054 (4)
c (Å)	10.763 (4)
α (°)	90.0000 (10)
β (°)	97.644 (4)
γ (°)	90.000 (2)
Volume (Å^3)	772.7 (4)
Z	4
$D_{calc.}$ (Mg·m^{-3})	2.690
Absorption coefficient (mm^{-1})	3.153
$F(000)$	596
Crystal size	0.27 × 0.25 × 0.24
θ range for data collection (°)	2.65–25.00
Reflections collected	3983
Unique reflections	1353 [R(int) = 0.0250]
Completeness to $\theta = 25.00$	99.1%
Absorption correction	Semi-empirical
Max. and min. transmission	0.5183 and 0.4832
Data/restraints/parameters	1353/0/127
Goodness of fit on F^2	1.179
R indices [$I > 2\sigma(I)$]	$R1 = 0.0491$, $wR2 = 0.1394$
R indices (all data)	$R1 = 0.0495$, $wR2 = 0.1397$
Largest diff. peak and hole (e.Å^{-3})	0.751 and −2.720

Absorption corrections were applied using the multi-scan technique [15]. The structure was solved by the Direct Method and refined by full-matrix least-square techniques on F^2 using SHELXL-97 [16]. All non-hydrogen atoms were refined anisotronically. The crystal data and structure refinement details for Complex **1** are shown in Table 1. Selected bond lengths and angles of the complex are listed in Table 2, and possible hydrogen bond geometries are given in Table 3.

Results and Discussion

Description of the Structure

Single-crystal X-ray diffraction analysis reveals that Complex **1** possesses a 3D infinite structure and its building unit is [Cd(pdc)Cl] (Fig. 1). The Cd(II) ion is six-coordinate with an NO_4Cl donor set in the distorted octahedron environment. One O atom (O4) and one N atom (N1) are from the same pdc group, the other three O atoms (O1, O2, O3) are from

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

Cd(1)-O(1)#1	2.252 (6)	Cd(1)-N(1)	2.318 (7)	O(1)-Cd(1)#4	2.252 (6)
Cd(1)-O(3)#2	2.252 (6)	Cd(1)-O(2)#3	2.326 (7)	O(2)-Cd(1)#5	2.326 (7)
Cd(1)-O(4)	2.313 (6)	Cd(1)-Cl(1)	2.357 (7)	O(3)-Cd(1)#6	2.252 (6)
O(1)#1-Cd(1)-O(3)#2	91.5 (2)	O(3)#2-Cd(1)-O(2)#3	88.9 (3)	O(2)#3-Cd(1)-Cl(1)	79.4 (2)
O(1)#1-Cd(1)-O(4)	97.2 (2)	O(4)-Cd(1)-O(2)#3	82.8 (3)	O(3)#2-Cd(1)-O(4)	171.3 (2)
N(1)-Cd(1)-O(2)#3	90.3 (2)	O(1)#1-Cd(1)-N(1)	105.4 (2)	O(1)#1-Cd(1)-Cl(1)	84.5 (2)
O(3)#2-Cd(1)-N(1)	105.2 (2)	O(3)#2-Cd(1)-Cl(1)	80.6 (2)	O(4)-Cd(1)-N(1)	72.1 (2)
O(4)-Cd(1)-Cl(1)	100.5 (2)	O(1)#1-Cd(1)-O(2)#3	163.6 (2)	N(1)-Cd(1)-Cl(1)	168.1 (2)

Symmetry transformation: #1 –x + 2, y–1/2, –z + 3/2; #2 x, –y + 1/2, z–1/2; #3 –x + 1, y–1/2, –z + 3/2; #4 –x + 2, y + 1/2, –z + 3/2; #5 –x + 1, y + 1/2, –z + 3/2; #6 x, –y + 1/2, z + 1/2.

Table 3. Hydrogen bond lengths (Å) and bond angles (°) of Complex **1**

D—H···A	Symmetry code	D—H	H···A	D···A	D—H···A
Complex **1**					
C(1)–H(1)···O(4)	*–x*, *–y* + 1, *–z*	0.93	2.30	3.124 (10)	147
C(3)–H(3)···Cl(1)	*–x* + 1/2, *–y* + 3/2, *–z*	0.93	2.78	3.698 (11)	170

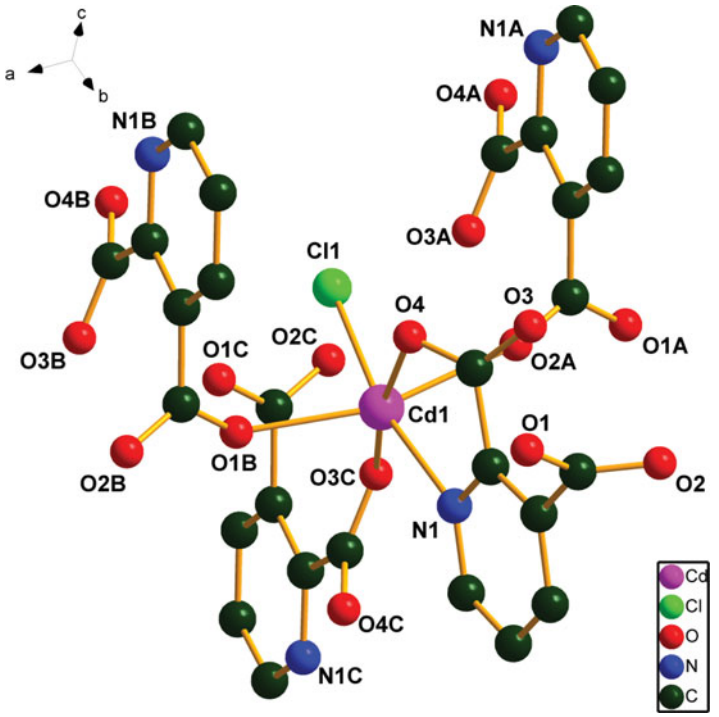

Figure 1. The coordination environment of the Cd(II) ion in Complex **1**. All the hydrogen atoms are omitted for clarity.

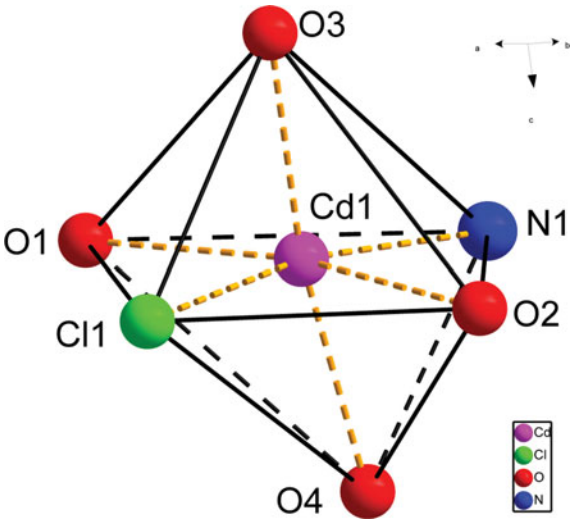

Figure 2. The coordination polyhedron of the Cd(II) ion of Complex **1**.

three different pdc ligands (Fig. 2). The equatorial plane is defined by the O1, O2, N1, and Cl1 atoms with the O3 and O4 atoms occupying the apical positions. The bond lengths of Cd–O range from 2.252(6) to 2.326(7) Å, the bond length of Cd–N is 2.318(7) Å, and the bond length of Cd–Cl is 2.357(7). In the crystal, the pdc group plays a bridging role. The two β-carboxylic O atoms (O1, O2) bridge equivalent Cd(II) ions and the Cd(II) ion is connected to a 1D infinite chain along the *a* axis. Along the *c* axis, the two α-carboxylic O atoms (O3, O4) separately coordinate to two equivalent Cd(II) ions. The Cd(II) ions are also connected to a 1D infinite structure. Then, Complex **1** is connected to a regular 2D structure in the *ac* plane (Fig. 3). Moreover, along the *b* axis, the α-carboxylic O atom (O4)

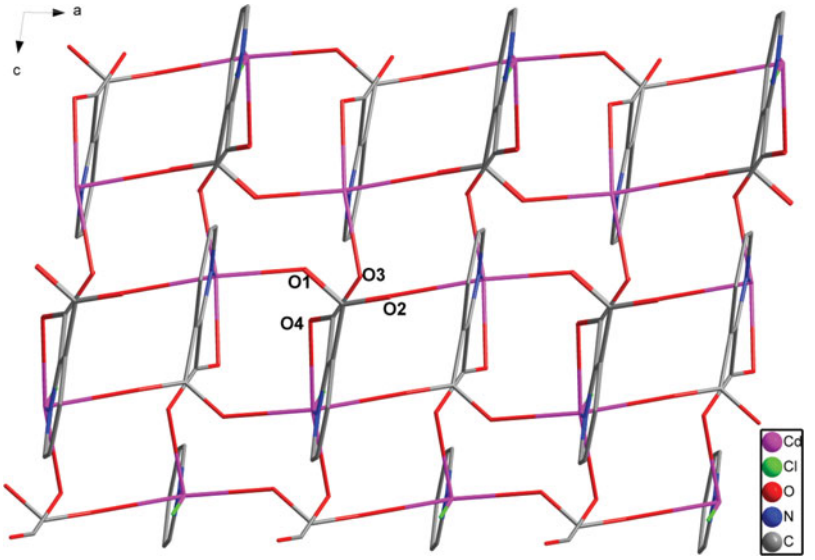

Figure 3. The 2D structure of the *ac* plane in Complex **1**. Unnecessary atoms are omitted for clarity.

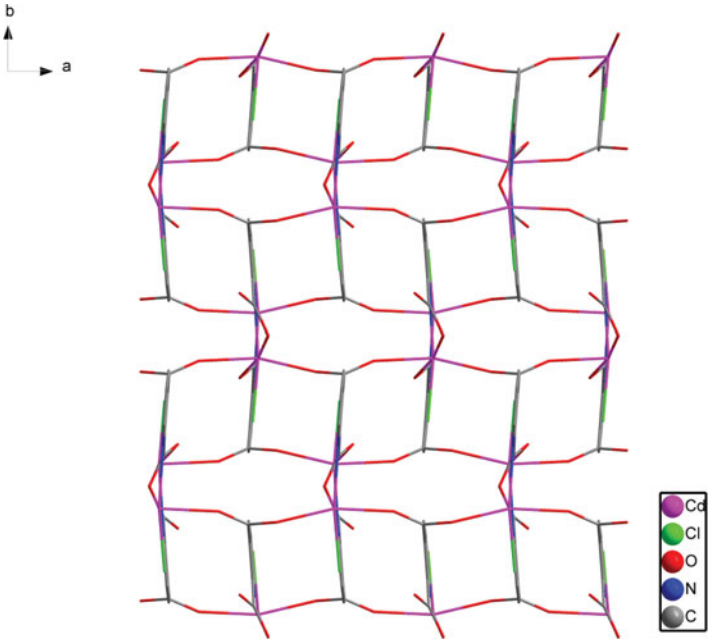

Figure 4. The 2D structure of the *ab* plane in Complex **1**. Unnecessary atoms are omitted for clarity.

together with the pyridine N atom chelate to one Cd(II) ion, the α-carboxylic O atom (O3) coordinates to the other equivalent Cd(II) ion, and then the Cd(II) ions are also linked to a 1D infinite chain. It can be seen that the *ab* plane is also a regular 2D web structure (Fig. 4). Complex **1** is therefore webbed to a 3D infinite structure (Fig. 5).

IR Spectrum

In the IR spectra of Complex **1**, υ_{as}COO appears as two peaks at 1667 cm^{-1} and 1610 cm^{-1} and υ_{s}COO appears as strong peak at 1389 cm^{-1}. For Complex **1**, the strong peak at

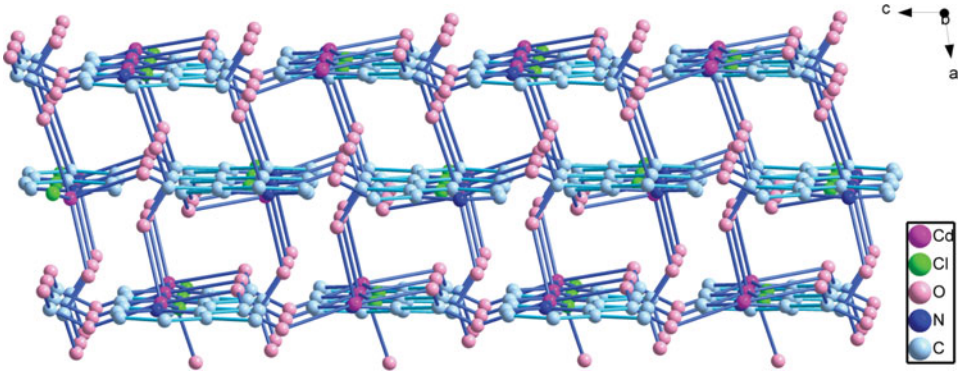

Figure 5. The 3D structure of Complex **1**. Unnecessary atoms are omitted for clarity.

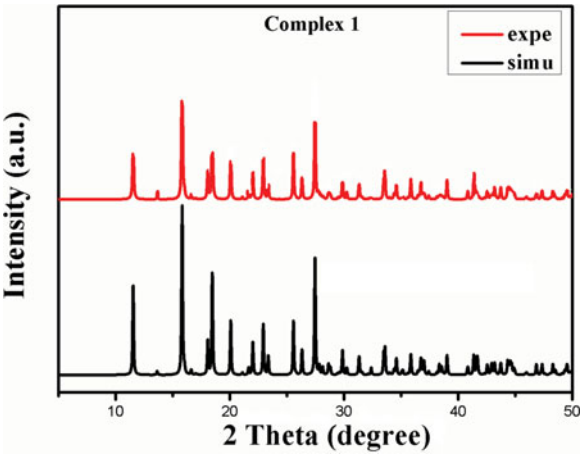

Figure S1. Simulated and experimental powder X-ray diffraction patterns of Complex **1**.

1450 cm^{-1} is attributed for υArC$\cdots$C, and additional peaks at 1234 cm^{-1} and 1102 cm^{-1} are attributed for υC—N and υC—O, respectively.

XRD Patterns

In order to confirm the phase purity of the polymers, simulated and experimental PXRD patterns of Complex **1** are shown in Figure S1 (available online). All the peaks in the recorded curves approximately match those in the simulated curves generated from single-crystal diffraction data, which confirms the phase purity of the as-prepared products.

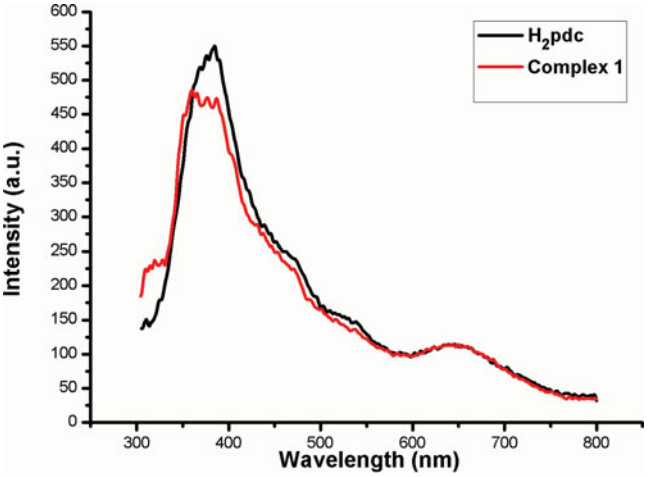

Figure 6. Solid-state fluorescent emission spectra of H_2pdc (black), Complex **1** (red) at room temperature.

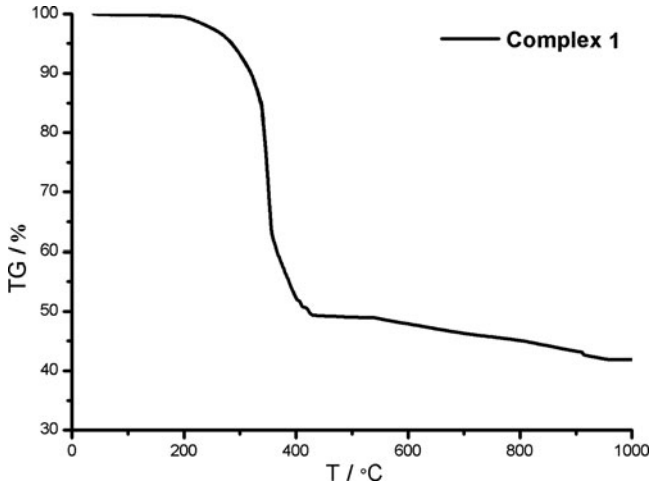

Figure 7. The TG curves of Complex **1**.

Fluorescence Properties

Recently, polymeric Zn(II) and Cd(II) complexes with their metal cations adopting d^{10} configuration have been intensively investigated for attractive fluorescence properties and potential applications as new luminescent materials [17]. For example, some zinc complexes have been used as organic light-emitting diodes (OLEDs) [18]. Hence, the solid state photoluminescence properties of H_2pdc ligand and Polymer **1** were investigated at room temperature (Fig. 6) under the same experimental conditions. In the solid state, the strongest emission peak for the free ligand H_2pdc is at 384 nm with the excitation peak at 246 nm, which is attributed to the π^*–n transitions [19]. The strongest excitation peak for **1** is at 249, and emission spectra mainly show strong peak at 360 nm. The ligand chelation to the metal center may effectively increase the rigidity of the ligand and reduce the loss of energy by radiationless decay, thus causing the blue shift in Complex **1**. Therefore, the luminescence behavior of complex is caused by metal ligand charge transfer (MLCT) [20].

Thermogravimetric (TG) Analyses

In order to study the framework stability of the title complex, the thermogravimetric (TG) analysis was performed in N_2 atmosphere on polycrystalline sample of complex, and the TG curve is shown in Fig. 7. The TG curve shows the weight loss begins at 200°C, and the first loss of 50.65% was in the temperature range of 200°C–400°C, which indicates the exclusion of pdc^{2-} (calcd, 52.75%). It also corresponds to the collapse of the compound into the mixture of CdO and $CdCl_2$ (the calculated residue weight is 20.52% for CdO, and that for $CdCl_2$ is 29.29%). The second stage occurs between 400°C and 950°C; the anhydrous complex loses 7.35% of total weight, which is because the $CdCl_2$ is completely oxidized into CdO (calcd, 8.78%).

Conclusion

In summary, a novel 3D coordination polymer $[Cd(pdc)Cl]_n$ (**1**) has been synthesized under hydrothermal conditions, containing H_2pdc as a bridging ligand. The new multidentate

ligand H_2pdc displays plentiful coordination modes and main control for MOF topologies through coordination orientation of dicarboxylate group, and a tunable modification for structures can result from the engrafted pyridyl group and the coordination geometry of the introduced metal centers. In addition, the luminescence measurements reveal that the complex exhibit good fluorescent emission in solid state at room temperature. Also, thermal decomposition process and PXRD of the complexes were investigated.

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