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Hydrothermal Synthesis, Crystal Structure, and Photoluminescence of a New 2D Cadmium(II) Complex: $\{Cd(C_8H_5O_3Cl_2)_2(C_{10}H_8N_2)\}_n$[1]

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One new cadmium coordination polymer, $[Cd(2,4\text{-}Dcp)_2(4,4\text{-}Bipy)]_n$ (**I**) (2,4-HDcp = 2,4-dichlorophenoxyacetic acid, 4,4'-Bipy = 4,4'-bipyridine) with 2D layer structure, has been prepared by the hydrothermal synthesis and characterized by elemental analysis, IR, TGA and single-crystal X-ray diffraction. Complex **I** crystallizes belong to monoclinic system and has *C*2/*c* space group. Each Cd^{2+} ion is six-coordinated and located at an octahedral geometry. The Cd^{2+} ions are linked by bidentate 2,4-Dcp groups into a linear chain in which the benzene rings of 2,4-Dcp ligands point alternately up and down. These chains are further connected into a sandwich-like layer though 4,4'-Bipy ligands. Furthermore, the photoluminescence and lifetime of **I** in the solid state have been studied.

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INTRODUCTION

New organic-inorganic hybrid materials are receiving growing attention due to their potential applications in magnetism, ion exchange, catalysis, gas separation, sensor, and many other areas [1–5]. The rational selection of organic ligands is crucial to design and synthesize the target coordination polymers, which not only determine their structure and dimensionality, but also influence their potential properties and applications [6, 7]. Many of the reported works are based on the use of mixed functional organic ligands containing N- and/or O-donor atoms to bind to *d*-block transition metal ions [8, 9]. As is well known, 4,4'-bipyridine (4,4'-Bipy) ligands may act in bidentate bridging or monodentate terminal modes, leading to the formation of a variety of 1D chain, 2D layer and 3D network motifs [10]. The 2,4-dichlorophenoxyacetate (2,4-HDcp) ligand has versatile binding and coordination modes, and can also be used to construct multinuclear structures [11]. On the basis of these considerations, we chose 2,4-HDcp, 4,4'-Bipy, and Cd^{2+} as our building block. A new two-dimensional coordination framework, $[Cd(2,4\text{-}Dcp)_2(4,4\text{-}Bipy)]_n$ (**I**), resulted from the hydrothermal conditions, which has been characterized by IR spectroscopy, elemental analysis, single-crystal X-ray diffraction, TGA, photoluminescence, and lifetime measurements.

EXPERIMENTAL

Materials and measurements. All chemicals purchased were of reagent grade and used without further purification. All syntheses were carried out in 23 mL Teflon-lined autoclaves under autogenous pressure. Elemental analyses (C, H, and N) were performed on a PerkinElmer 240 CHN elemental analyzer. The IR spectra were acquired using Nicolet Avatar 360 FT-IR spectrophotometer. Luminescence spectra and lifetime for crystal solid samples were recorded at room temperature on an Edinburgh FLS920 phosphorimeter. Thermogravimetry analyses (TGA) were performed on a simultaneous SDT thermal analyzer (STA449C, Netzsch) under a flow of N_2 at a heating rate of 10°C/min between ambient temperature and 800°C.

Synthese of I. A mixture of $Cd(NO_3)_2 \cdot 6H_2O$ (0.154 g, 0.5 mmol), 4,4'-Bipy (0.78 g, 0.5 mmol), 2,4-HDcp (0.12 g, 0.5 mmol), NaOH (0.08 g, 0.2 mmol) and water (10 mL) was heated at 150°C for 72 h. Colorless crystals were obtained when cooling to room temperature at 5°C h^{-1}. The yield was 55% (based on Cd). The FT-IR main absorption bands are centered mainly at 1643 s, 1481 m, 1425 w, 1288 m, 1234 m, 1071 m, 1042 w, 817 m, 717 m, 646 m, 608 w.

For $C_{26}H_{18}N_2O_6Cl_4Cd$

anal. calcd., %:	C, 44.03;	H, 2.54;	N, 3.95.
Found, %:	C, 44.05;	H, 2.50;	N, 3.97.

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[1] The article is published in the original.

X-ray crystal determination. Single crystal X-ray diffraction data collections for **I** was performed on a Bruker Smart II CCD diffractometer operating at 50 kV and 30 mA using MoK_a radiation ($\lambda = 0.071073$ nm) at 293 K, and the intensity data were obtained in a range of $1.75° \le \theta \le 25.20°$ at 293(2) K by using an ω scan technique. Data collection and reduction were performed using the SMART and SAINT software [12]. A multi-scan absorption correction was applied using the SADABS program [12]. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXTL program package [13, 14]. All of the non-hydrogen atoms were refined anisotropically [14]. Crystal parameters and details of the data collection and refinement are given in Table 1. Selected bond lengths and angles are given in Table 2. Supplementary material for structure **I** has been deposited with the Cambridge Crystallographic Data Centre (no. 822091; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The asymmetric unit of the compound **I** consists of one Cd^{2+} ion, one 2,4-Dcp^- anion, and half a 4,4'-Bipy ligand. The Cd(II) centre is six-coordinated by four carboxylate O atoms from four different 2,4-Dcp ligands, two nitrogen atoms from two 4,4'-Bipy ligands, and displays an octahedral coordination geometry (Fig. 1). The Cd—O, Cd—N bond lengths and OCdO, OCdN bond angles range from 2.277(2) to 2.376(3) Å and 81.14(7)° to 98.10(9)°, respectively, which is within the reasonable range of observed values for other seven-coordinated Cd(II) complexes [15, 16]. The 2,4-Dcp ligands exhibit bidentate coordination mode to link Cd^{2+} ions to form an infinite chain along to the y axis of the cell in which the benzene rings of the 2,4-Dcp ligands point alternately up and down (Fig. 2a). The Cd···Cd distance is 4.916(2) Å. Finally, these Cd-carboxylate chains are further connected into a 2D sandwich-like layer by 4,4'-Bipy ligands which act as pillars (Fig. 2b).

The IR spectra of **I** reveals three strong bonds of the carboxylate groups at 1643 and 1481, 1423 cm^{-1} for the asymmetric (COO) and symmetric (COO) stretching vibrations. The features at 1288, 1234 and 1070, 1041 cm^{-1} are associated with the asymmetric (C—O—C) and symmetric (C—O—C) stretching vibrations [17].

The thermogravimetric (TG) analyses of compound **I** were performed in a N_2 atmosphere when the sample was heated to 800°C at a constant rate of 10°C/min. The TG curve is depicted in Fig. 3, which shows that compound **I** has thermal stability as no

Table 1. Crystalographic data and structure refinement information for compound **I**

Parameter	Value
Formula weight	708.62
Crystal system	Monoclinic
a, Å	23.384(4)
b, Å	11.8151(19)
c, Å	9.7842(15)
β, deg	96.960(2)
V, Å^3	2683.3(8)
Z	4
ρ_{calcd}, g/cm^3	1.754
Crystal size, mm	0.33 × 0.28 × 0.22
μ, mm^{-1}	1.258
F(000)	1408
Scan mode	φ and ω scan
θ Range, deg	1.75–25.20
Limiting indices (h, k, l)	$-27 \le h \le 27$, $-14 \le k \le 14$, $-11 \le l \le 11$
Reflection collected	9587
Independent reflections	2411
Reflections with $I > 2\sigma(I)$	2205
Number of parameters	179
Goodness-of-fit	1.012
R_1 ($I > 2\sigma(I)$)*	0.0230
wR_2 (all data)**	0.0699
$\Delta\rho_{min}/\Delta\rho_{max}$, e Å^{-3}	–0.465/0.465

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

Table 2. Selected bond distances (Å) and angles (deg) in structure **I***

Bond	*d*, Å	Bond	*d*, Å
Cd(1)–O(2)	2.276(2)	Cd(1)–O(1)	2.316(2)
Cd(1)–N(2)$^{\rm ii}$	2.377(3)	Cd(1)–N(1)	2.358(3)
Angle	**ω, deg**	**Angle**	**ω, deg**
O(2)$^{\rm iii}$Cd(1)O(2)$^{\rm iv}$	179.53(11)	O(2)$^{\rm iii}$Cd(1)N(1)	89.77(6)
O(1)Cd(1)O(1)	162.27(14)	O(2)$^{\rm iv}$Cd(1)O(1)	81.83(9)
O(2)$^{\rm iv}$Cd(1)O(1)$^{\rm i}$	98.10(9)	O(1)Cd(1)N(1)	81.14(7)

* Symmetry codes: $^{\rm i}$ $-x, y, 1.5 - z$; $^{\rm ii}$ $x, 1 + y, z$; $^{\rm iii}$ $-x, -y, 2 - z$; $^{\rm iv}$ $x, -y, -0.5 + z$.

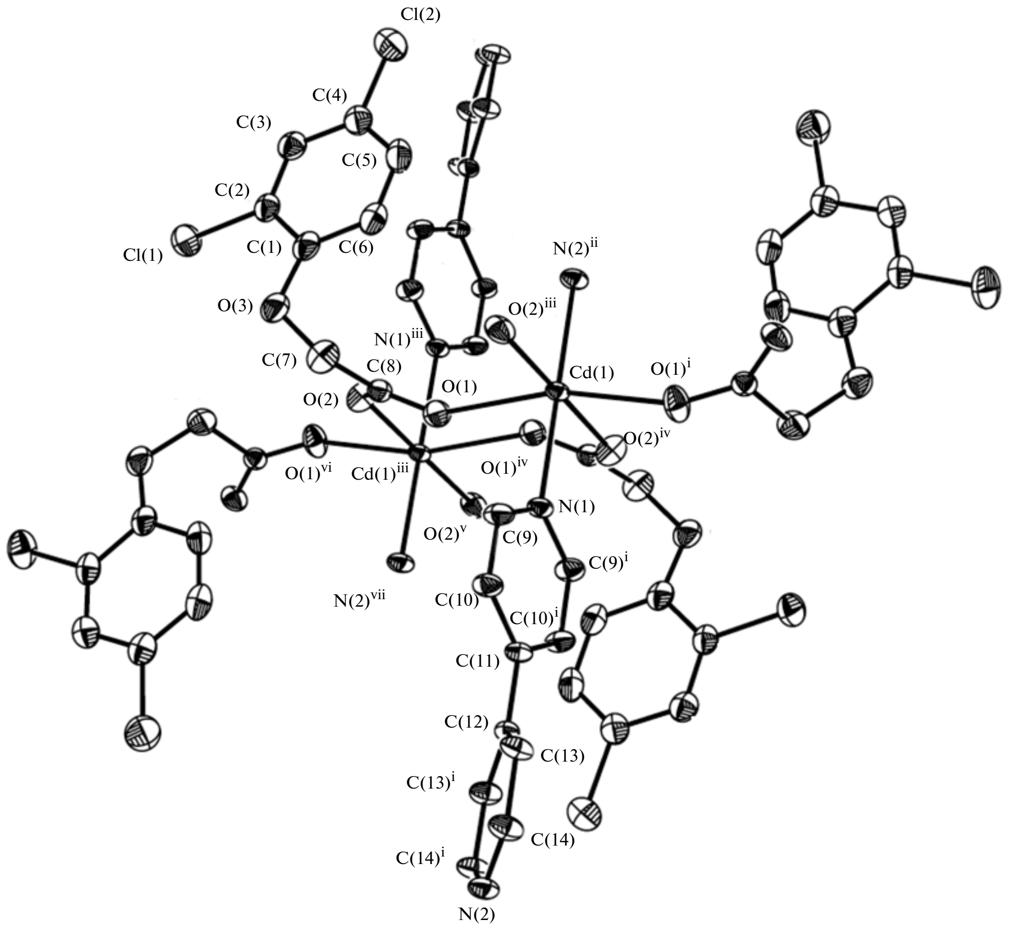

Fig. 1. Molecular structure of complex **I** with the ellipsoids presented at 30% probability level. All H atoms were omitted for clarity (symmetry codes: see Table 2).

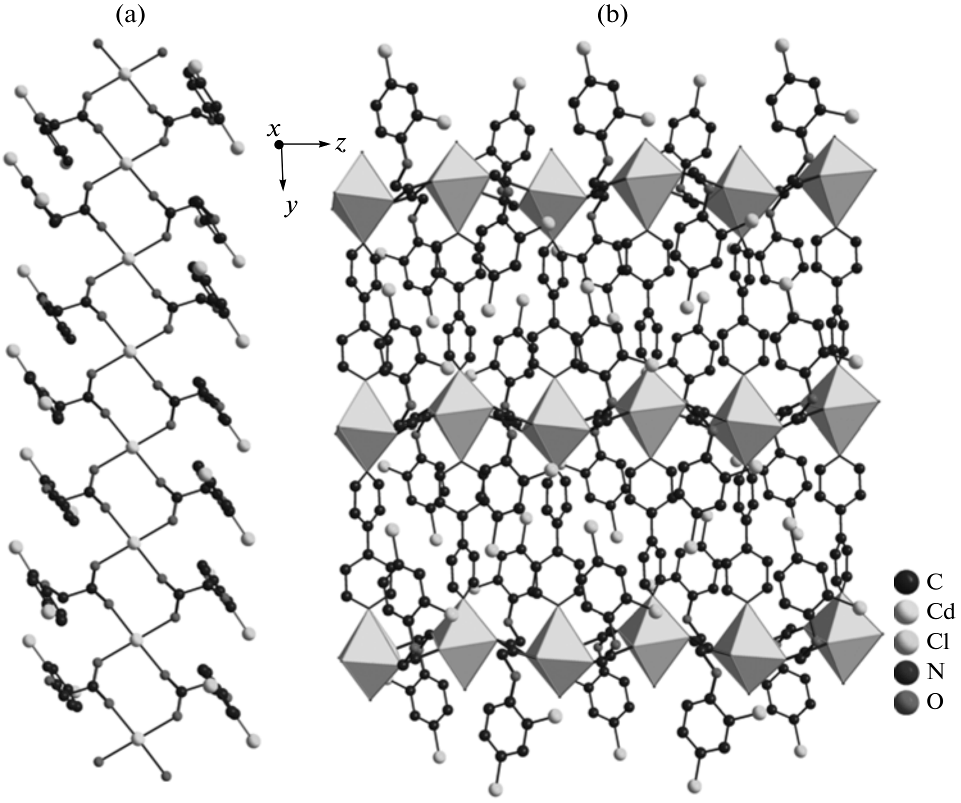

Fig. 2. View of Cd-carboxylate infinite chain of **I** along to the *y* axis (a); view of 2D sandwich-like layed network of **I** in the *yz* plane (b).

strictly clean weight loss step occurs below 210°C. The weight-loss step occurred above 210°C which corresponds to the decomposition of framework structure.

It is universally acknowledge that metal coordination frameworks with a d^{10} configuration possess excellent luminescence property [18, 19]. Herein, the luminescence property measurement of complex **I** was carried out in the solid state at room temperature. It can be observed that compound **I** exhibits indigotin photoluminescence with an emission maximum at ~454 nm upon excitation at 355 nm (Fig. 4a). As we know, it is usually believed that the energy transition of

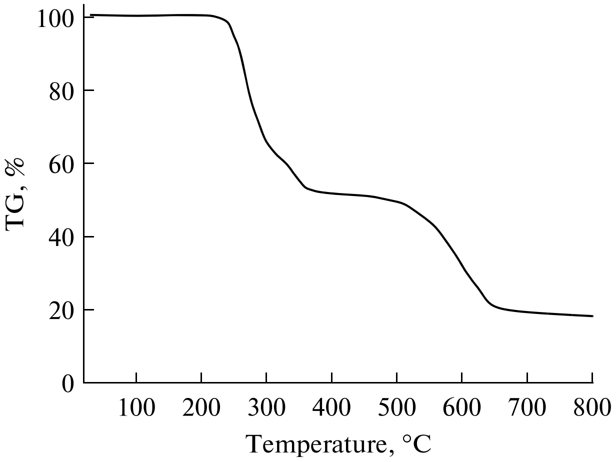

Fig. 3. TGA trace of compound **I**.

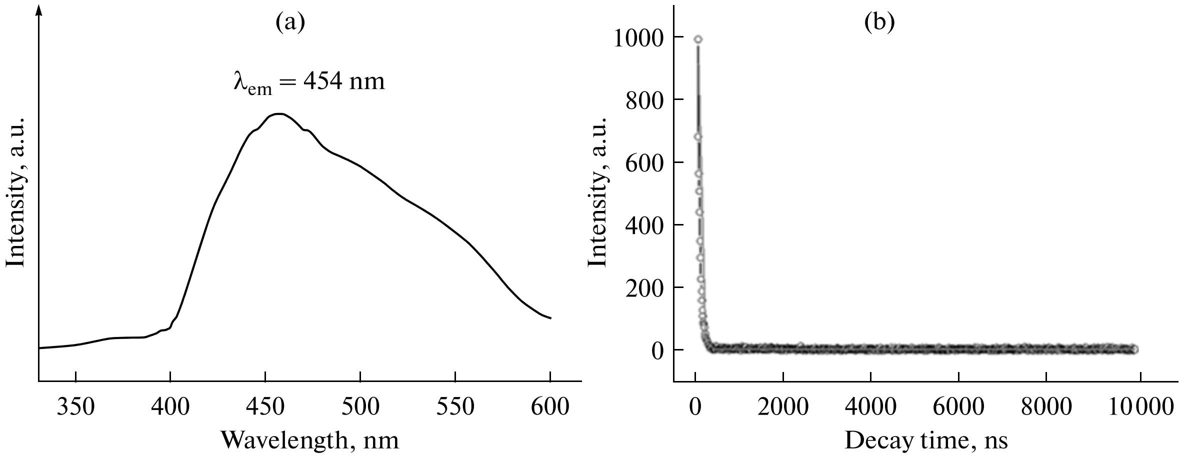

Fig. 4. Solid-state emission spectrum of **I** at room temperature, excited at 355 nm (a); luminescent lifetime of **I** (b).

d^{10} complexes can be assigned as metal-to-ligand charge transfer, intraligand emission and ligand-to-metal charge transfer. As previous reported [20], the photoluminescence mechanism of title compound is tentatively attributed to the ligation of the ligand to the metal center. Moreover, as shown in Fig. 4b, the luminescent lifetime of solid **I** using an Edinburgh FLS920 phosphorimeter with a 450 W xenon lamp as excitation source show lifetime for **I** of 49.6 ns.

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