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Synthesis, Crystal Structure, and Luminescent Property of a New Two-Dimensional Cd(II) Coordination Polymer Based on 1,10-Phenanthroline and Dicarboxylate[1]

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Abstract—A novel Cd(II) coordination polymers based on 2-(2-fluorophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline (L) and 1,4-naphthalenedicarboxylate (1,4-NDC), namely, $[Cd_2(L)_2(1,4\text{-NDC})_2] \cdot H_2O$ (**I**), has been successfully synthesized under hydrothermal conditions. Its structure has been determined by single crystal X-ray diffraction analysis. Complex **I** crystallizes in monoclinic system, space group $P2_1/n$, with lattice parameters $a = 12.474(2)$, $b = 15.002(3)$, $c = 13.766(3)$ Å, $\beta = 98.45(4)°$, $V = 2548.1(8)$ Å^3, $Z = 2$, and $\rho_{calcd} = 1.694$ mg m^{-3}. Compound **I** shows a two-dimensional (2D) layer structure. The neighboring layers are linked by π–π interactions to form a 3D supramolecular architecture. In addition, the luminescent property of the compound has also been investigated in solid state at room temperature.

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INTRODUCTION

Supramolecular chemistry and crystal engineering based on metal and organic building blocks have been rapidly expanding due to structural topologies, potential applications in host-guest chemistry, catalysis, and electrical conductivity [1–5]. Consequently, a number of coordination polymers with various topological architectures have been constructed and reported [6–12]. Generally, extended high-dimensional networks can be obtained by assembly of low dimensional coordination polymers via noncovalent intermolecular forces such as hydrogen-bonding and π–π interactions [13]. In this regard, versatile functional organic ligands (such as N- or O-containing ligands) which have strong coordination ability as well as providing the π-conjugated systems and hydrogen bond acceptors/donors are often employed in construction of novel supramolecular framework [14].

1,10-Phenanthroline (Phen) ligand is particularly interesting because of its excellent coordinating ability and large conjugated system that can easily form π–π interactions. Its derivative 2-(2-fluorophenyl)-1H-imidazo[4,5-f] [1,10]phenanthroline (L), as a good candidate for construction of supramolecular architectures, has not been well studied in coordination chemistry [15]. In this work, we selected L as a N-donor chelating ligand and 1,4-naphthalenedicarboxylate (1,4-NDC) as an organic linker, generating a new 2D coordination polymer, namely $[Cd_2(L)_2(1,4\text{-NDC})_2] \cdot H_2O$ (**I**). Its structure has been determined by single crystal X-ray diffraction analysis. In addition, the luminescent properties of the compound have also been investigated in solid state at room temperature.

EXPERIMENTAL

Measurements and reagents. All reagents and solvents were of reagent grade. Elemental analyses (C, H, and N) were carried out on a PerkinElmer 240C elemental analyzer. The excitation and emission spectra were measured on a PerkinElmer LS55 spectrometer.

Synthesis of I. A mixture of $CdCl_2 \cdot 2H_2O$ (0.5 mmol), 1,4-H_2NDC (0.5 mmol) and L (0.5 mmol) was dissolved in 10 mL distilled water, followed by addition of triethylamine until the pH value of the system was adjusted to between 5 and 6. The resulting solution was sealed in a 23 mL Teflon-lined stainless-steel autoclave and heated at 443 K for 6 days under autogeneous pressure. Then, the reaction system was slowly cooled to room temperature. Pale-yellow crystals of **I** suitable for single-crystal X-ray diffraction analysis were collected by filtration, washed several times with distilled water and dried in air at ambient temperature. The yield was 31%.

For $C_{62}H_{36}Cd_2F_2N_8O_9$

anal. calcd., %:	C, 57.29;	H, 2.79;	N, 8.62.
Found, %:	C, 57.38;	H, 2.86;	N, 8.39.

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[1] The article is published in the original.

Table 1. Crystallographic parameters and summary of data collection for **I**

Parameter	Value
Empirical formula	$C_{62}H_{36}Cd_2F_2N_8O_9$
Fw	1299.79
Crystal system	Monoclinic
Space group	$P2_1/n$
a, Å	12.474(2)
b, Å	15.002(3)
c, Å	13.766(3)
α, deg	90
β, deg	98.45(4)
γ, deg	90
Volume, Å^3	2548.1(8)
Z	2
ρ_{calcd}, g/cm^3	1.694
Crystal size, mm	0.17 × 0.15 × 0.12
μ, mm^{-1}	0.914
F(000)	1300
Scan mode	ω scan
θ Range, deg	3.10–27.48
Limiting indices h, k, l	$-16 \le h \le 13$, $-19 \le k \le 19$, $-17 \le l \le 17$
Reflections collected/unique, R_{int}	24117/5747 (0.0205)
Reflections with $I > 2\sigma(I)$	5206
GOOF	1.085
Number of parameters	379
R_1, wR_2 ($I > 2\sigma(I)$)	0.0254, 0.0690
R_1, wR_2 (all data)	0.0287, 0.0701
$\Delta\rho_{min}/\Delta\rho_{max}$, e Å^{-3}	−0.251/0.768

X-ray crystallography. Single-crystal X-ray diffraction data for **I** was recorded on a Rigaku RAXIS-RAPID image plate diffractometer with graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å) at 293 K. The structure was solved with the direct method of SHELXS-97 and refined with full-matrix least-squares techniques using the SHELXL-97 program [16, 17]. The non-hydrogen atoms of the complexes were refined with anisotropic temperature parameters. The hydrogen atoms attached to carbons were generated geometrically. Water H atom was not located in a difference Fourier map. Crystallographic parameters and the data collection statistics for structure **I** are given in Table 1. Selected bond lengths and bond angles are listed in Table 2. Further crystallographic parameters have been deposited with the Cambridge Crystallographic Data Centre (no. 844903; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

As shown in Fig. 1a, the asymmetric unit of **I** contains one unique Cd(II) atom, one L ligand, one 1,4-NDC ligand, and one free water molecule. Each Cd(II) atom is six-coordinated by four carboxylate oxygen atoms from three different 1,4-NDC ligands, and two nitrogen atom from one L ligand. Three carboxylate oxygen atoms (O(1), O(3*A*) and O(4*A*)) and one nitrogen atom (N(2)) make up the basal plane, and the axial positions are occupied by one nitrogen atom (N(1)) and one carboxylate oxygen atom (O(2*A*)). The Cd–O distances vary from 2.2581(15) to 2.3565(18) Å. Notably, two carboxylates of 1,4-NDC ligand show different coordination modes: one carboxylate connects one Cd(II) atom in a chelating mode, while the other bridges two Cd(II) atoms in a bridging mode. In this way, a dinuclear Cd(II) unit is formed, which are

Table 2. Selected bond lengths (Å) and bond angles (deg) for **I***

Bond	d, Å	Bond	d, Å
Cd(1)–N(1)	2.3651(17)	Cd(1)–N(2)	2.3076(19)
Cd(1)–O(1)	2.2581(15)	Cd(1)–O(2)$^{\#1}$	2.3248(15)
Cd(1)–O(3)$^{\#3}$	2.3263(17)	Cd(1)–O(4)$^{\#2}$	2.3565(18)
Angle	**ω, deg**	**Angle**	**ω, deg**
O(1)Cd(1)N(2)	125.95(6)	O(1)Cd(1)O(2)$^{\#1}$	88.18(5)
N(2)Cd(1)O(2)$^{\#1}$	94.68(6)	O(1)Cd(1)O(3)$^{\#2}$	88.49(6)
N(2)Cd(1)O(3)$^{\#2}$	143.44(6)	O(2)$^{\#1}$Cd(1)O(3)$^{\#2}$	98.73(7)
O(1)Cd(1)O(4)$^{\#2}$	141.33(6)	N(2)Cd(1)O(4)$^{\#2}$	92.52(7)
O(2)$^{\#1}$Cd(1)O(4)$^{\#2}$	84.42(7)	O(3)$^{\#2}$Cd(1)O(4)$^{\#2}$	55.52(7)
O(1)Cd(1)N(1)	97.99(6)	N(2)Cd(1)N(1)	71.36(6)
O(2)$^{\#1}$Cd(1)N(1)	165.83(6)	O(3)$^{\#2}$Cd(1)N(1)	94.19(7)
O(4)$^{\#2}$Cd(1)N(1)	98.27(7)		

* Symmetry codes: $^{\#1}$ $-x + 1$, $-y$, $-z + 2$; $^{\#2}$ $x - 1/2$, $-y + 1/2$, $z - 1/2$.

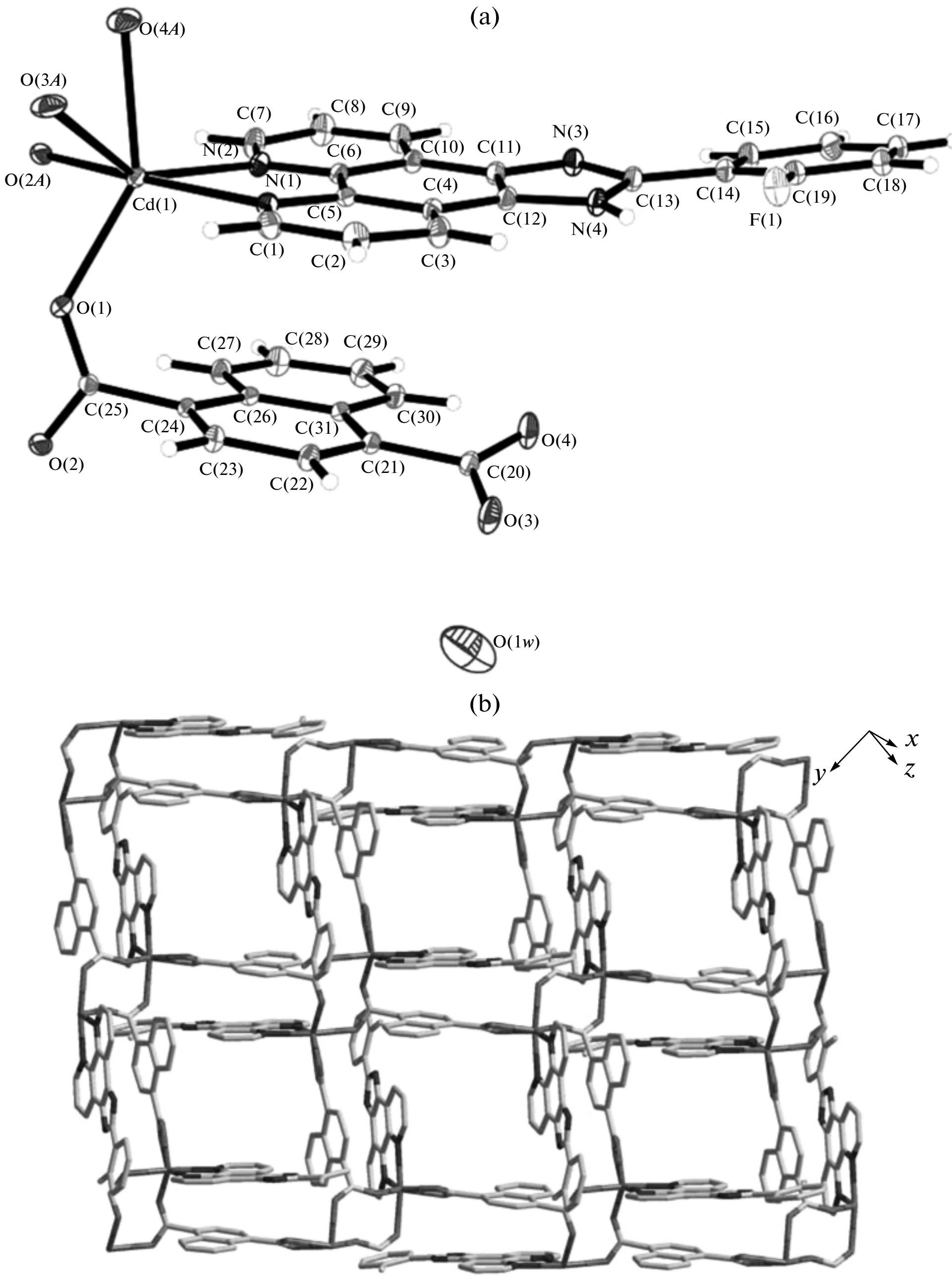

Fig. 1. The coordination environment (at 30% probability level) of the Cd(II) center of **I** (a); view of the 2D layer structure of **I** (b); view of the 3D supramolecular architecture of **I** formed by π–π stacking interactions (c).

further bridged by the backbones of the 1,4-NDC ligands to yield a 2D layer structure (Fig. 1b). There exist strong π–π stacking interactions between the L ligands of neighboring layers (centroid-to-centroid distance of ~3.64 Å and face-to-face distance of ca. 3.52 Å), yielding a 3D supramolecular architecture (Fig 1c). In addition, there exists N–H···O hydrogen bond among neighboring layers, which further consolidates the 3D supramolecular architecture of **I**.

The photoluminescence of d^{10} metal complexes has been attracting intensive research interest, owing to their potential applications in chemical sensors and photochemistry. The solid-state photoluminescent spectrum of **I** is depicted in Fig. 2. The emission and excitation peaks of 1,4-NDC and related L are at 472 and 475 nm, respectively [12]. The emission bands for these free ligands are attributable to $\pi^* \to n$ or $\pi^* \to \pi$ transitions. It should be pointed out that the emission of compound **I** is neither metal-to-ligand charge transfer nor ligand-to-metal charge transfer in nature since the Cd^{2+} ions is difficult to oxidize or to reduce due to their d^{10} configuration, which are mainly based on the luminescence of ligands. Upon complexation with Cd(II), strong luminescences was observable in

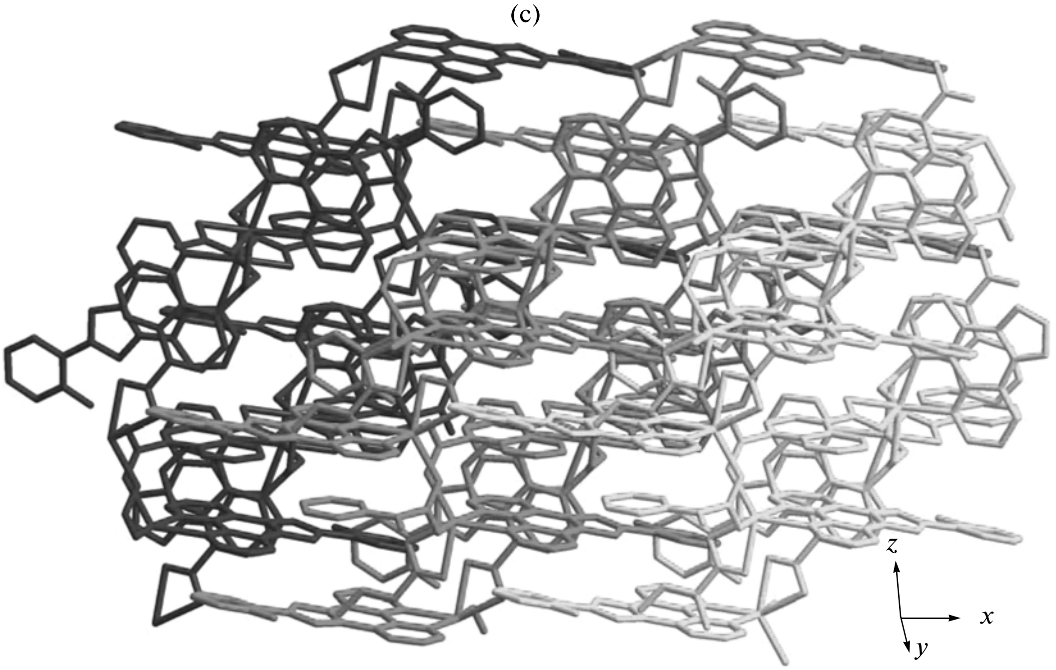

Fig. 1. (Contd.)

the solid state at ambient temperature. The emission peak of **I** is at 542 nm ($\lambda_{ex} = 340$ nm). The photoluminescence of **I** may be assigned to intra-ligand fluorescent emission.

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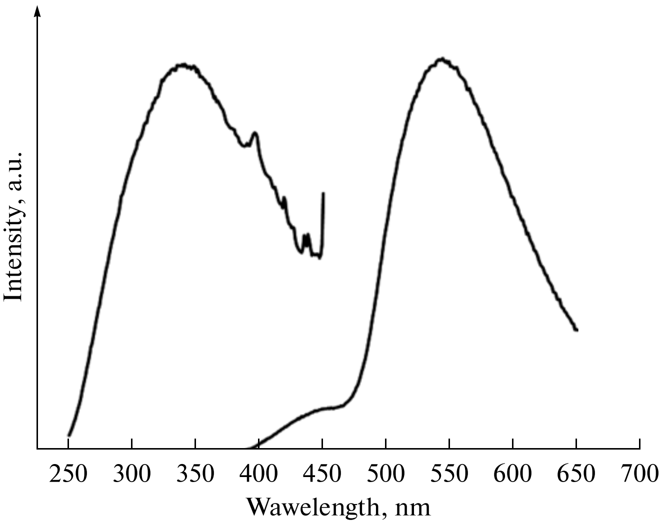

Fig. 2. Photoluminescent excitation and emission spectra of **I** in solid state at room temperature.

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