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Syntheses, Crystal Structures, and Thermal Properties of Two Complexes Built by Imidazole-Based Multi-Carboxylate Ligands[1]

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Abstract—Based on two promising *p*-$CPhH_4IDC$ and *o*-$CPhH_4IDC$ ligands, one 2D coordination polymer, $[Ca(p\text{-}CPhH_2IDC)(H_2O)]_n$ (*p*-$CPhH_4IDC$ = 2-(4-carboxylphenyl)-1*H*-imidazole-4,5-dicarboxylic acid) (**I**) and one novel dimeric complex, $[Cd_2(o\text{-}CPhH_2IDC)_2(H_2O)_6] \cdot 4H_2O$ (*o*-$CPhH_4IDC$ = 2-(2-carboxylphenyl)-1*H*-imidazole-4,5-dicarboxylic acid) (**II**) have been hydrothermally synthesized and structurally characterized by elemental analyses, IR spectroscopy, and single crystal X-ray diffraction (CIF files CCDC nos. 929826 (**I**), 959841 (**II**)). Polymer **I** exhibits a graceful 2D grid sheet structure. Polymer **II** is a binuclear complex in which two Cd^{2+} ions are bridged by two carboxyates from two *o*-$CPhH_2IDC^{2-}$ ligands. Four and two types of coordination environments around the Ca and Cd atoms, respectively can be observed. Furthermore, the solid-state photoluminescence and thermal properties of the two complexes have been investigated.

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INTRODUCTION

In recent years, the design of functional complexes via metal ions and various organic ligands has become a hot research field. However, it is still a far-reaching challenge to predict the assembly of complexes owing to various influence factors such as pH values, molar ratios of raw materials, reaction solvents and temperatures [1–3]. As one might expect, the key is to select a powerful multifunctional organic ligand to build up useful complexes. For example, the types of organic linkers with N- or O-donors have led to a wide range of complexes with numerous interesting bridging modes [4–6]. That is to say, one of the best building bricks that can be used to attain such complexes is the imidazole-based dicarboxylate ligand, which can adopt different bonding modes to metals. Our laboratory has introduced 2-carboxyphenyl and 4-carboxyphenyl groups into the 2-position of the imidazole-4,5-dicarboxylic acid (H_3IDC) system respectively so as to synthesize two promising ligands, 2-(2-carboxylphenyl)-1*H*-imidazole-4,5-dicarboxylic acid (*o*-$CPhH_4IDC$), and 2-(4-carboxylphenyl)-1*H*-imidazole-4,5-dicarboxylic acid (*p*-$CPhH_4IDC$). More importantly, a series of fascinating structures bearing *o*-$CPhH_4IDC$ or *p*-$CPhH_4IDC$ have been obtained [7, 8].

This prompted us to prepare more similar complexes to explore their properties. To us excitement, two complexes: polymer $[Ca(p\text{-}CPhH_2IDC)(H_2O)]_n$ (**I**) and dimer $[Cd_2(o\text{-}CPhH_2IDC)_2(H_2O)_6] \cdot 4H_2O$ (**II**) have been synthesized successfully (Scheme 1). In this paper, single-crystal X-ray diffractions reveal that the *p*-$CPhH_4IDC$ and *o*-$CPhH_4IDC$ ligands show a variety of coordination modes severally (Fig. 1). The structural analyses of the complexes have been discussed in detail. Moreover, the thermal and solid-state photoluminescence properties of the complexes have also been investigated. The syntheses of complexes **I** and **II** are given below:

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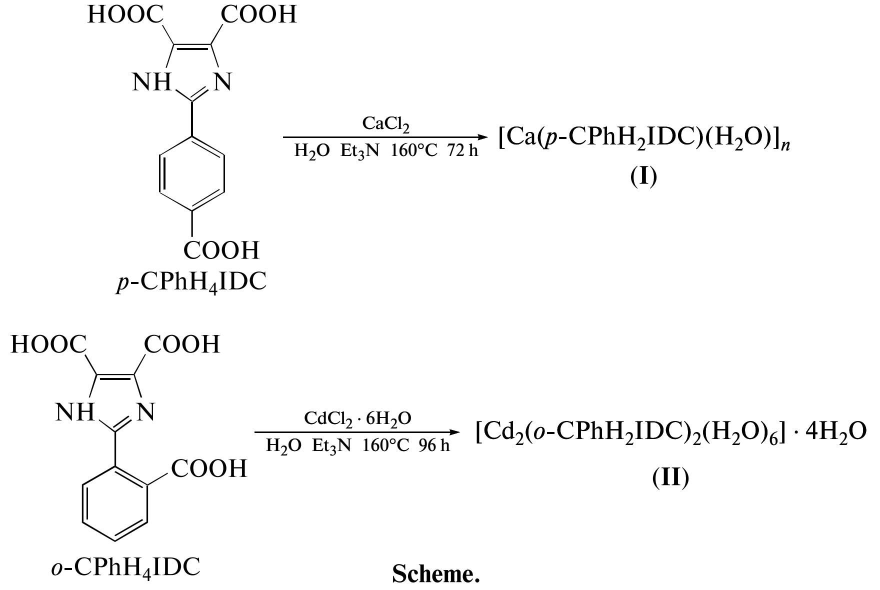


Scheme.

EXPERIMENTAL

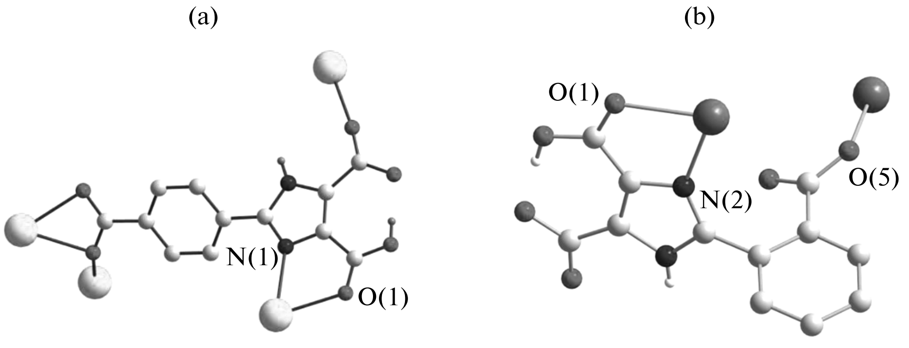
Materials and methods. All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. The organic ligands o-CPhH$_4$IDC and p-CPhH$_4$IDC were prepared according to the literature procedure [9]. Elemental analyses (C, H, and N) were performed on a FLASH EA 1112 analyzer. IR spectra were recorded on a BRUKER TENSOR 27 spectrophotometer as KBr pellets in the 400–4000 cm^{-1} region. TG measurements were performed by heating the crystalline sample from 20 to 1100°C at a rate of 10°C min^{-1} in the air on a Netzsch STA 409PC differential thermal analyzer. Fluorescence spectra were characterized at room temperature by a F-7000 fluorescence spectrophotometer (240 nm/min).

Synthesis of I. A mixture of p-CPhH$_4$IDC (27.4 mg, 0.1 mmol), CaCl$_2$ (11.1 mg, 0.1 mmol), H$_2$O (7 mL), triethylamine (Et$_3$N) (0.028 mL, 0.2 mmol) was sealed in a 25 mL Teflon-lined stainless steel autoclave, heated at 160°C for 72 h, and then cooled to room temperature at a rate of 10°C/h. The colorless long-strip crystals of **I** were isolated, washed with distilled water, and dried in air (51% yield based on Ca).

IR (KBr; ν, cm^{-1}): 3438 s, 3106 m, 2944 w, 1589 s, 1568 s, 1525 s, 1402 s, 1269 m, 1116 w, 1017 w, 973 m, 856 m, 796 m, 733 m, 663 w, 568 w, 453 w.

For C$_{12}$H$_8$N$_2$O$_7$Ca

anal. calcd., %:	C, 43.34;	H, 2.41;	N, 8.43.
Found, %:	C, 43.62;	H, 2.75;	N, 8.72.



μ$_4$-p-CPhH$_2$IDC^{2-} μ$_2$-o-CPhH$_2$IDC^{2-}

Fig. 1. Coordination modes of p-CPhH$_2$IDC^{2-} and o-CPhH$_2$IDC^{2-} anions in polymers **I** (a) and **II** (b).

Table 1. Crystallographic data and structure refinement information for compounds **I** and **II**

Parameter	Value	
	I	**II**
Temperature, K	296(2)	296(2)
Fw	332.28	953.34
Crystal system	Monoclinic	Monoclinic
Crystal size, mm	0.21 × 0.20 × 0.19	0.21 × 0.19 × 0.18
Space group	$P2(1)/c$	$C2/c$
a, Å	8.801(5)	23.29(3)
b, Å	16.932(10)	11.190(13)
c, Å	9.013(5)	17.10(4)
β	100.480(7)	128.951(10)
V, Å^3	1320.8(13)	3466(10)
ρ_{calcd}, mg m^{-3}	1.671	1.321
Z	4	4
μ, mm^{-1}	0.515	1.321
θ Range, deg	2.35–28.48	2.14–27.10
Reflections mesured/unique (R_{int})	7274/2318 (0.0285)	11056/3810 (0.0293)
Reflections with $I > 2\sigma(I)$	8828	11056
Data/restraints/parameters	2318/0/212	3810/12/271
GOOF on F^2	1.037	1.086
R, wR ($I > 2\sigma(I)$)	0.0373, 0.0936	0.0269, 0.0620
R, wR (all data)	0.0512, 0.1030	0.0367, 0.0663
$\Delta\rho_{max}$ and $\Delta\rho_{min}$, e Å^{-3}	0.262 and –0.257	0.636 and –0.480

Synthesis of II. A mixture of *o*-$CPhH_4IDC$ (27.6 mg, 0.1 mmol), $CdCl_2 \cdot 6H_2O$ (10.9 mg, 0.1 mmol), Et_3N (0.028 mL, 0.2 mmol) and H_2O (7 mL), was sealed in a 25 mL Teflon-lined autoclave and heated at 160°C for 96 h. Then the reaction mixture was allowed to cool to room temperature at a rate of 10°C/h. The colorless crystals of **II** were collected in 43% yield (based on Cd), washed with distilled water and dried in air.

IR (KBr; ν, cm^{-1}): 3357 m, 1715 m, 1551 s, 1450 m, 1401 s, 1292 m, 1228 w, 1146 m, 979 m, 849 s, 801 m, 765 m, 729 w, 677 w, 544 m, 424 w.

For $C_{24}H_{32}N_4O_{22}Cd_2$

anal. calcd., %:	C, 30.21;	H, 3.36;	N, 5.87.
Found, %:	C, 30.57;	H, 3.64;	N, 6.15.

X-ray crystallography. Measurements of compounds **I** and **II** were made on a Bruker smart APEXII CCD diffractometer with a graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å). Single crystals of **I** and **II** were selected and mounted on a glass fiber. All data were collected at room temperature 296(2) K using the ω–2θ scan technique and corrected for Lorenz-polarization effects. A correction for secondary extinction was applied. The two structures were solved by direct methods and expanded using the Fourier technique. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included but not refined. All calculations were performed using the SHELX-97 crystallographic software package [10]. Crystal data and experimental details for compounds **I** and **II** are contained in Table 1. Selected bond lengths and angles are listed in Table 2.

Table 2. Selected bond distances (Å) and angles (deg) for the complexes **I** and **II***

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
			I		
Ca(1)–O(6)$^{\#1}$	2.2845(17)	Ca(1)–O(2)	2.332(2)	Ca(1)–O(7)	2.3647(16)
Ca(1)–O(1)	2.4237(16)	Ca(1)–O(12)$^{\#2}$	2.4802(18)	Ca(1)–O(7)$^{\#3}$	2.5173(17)
Ca(1)–N(1)	2.546(2)				
			II		
Cd(1)–O(8)	2.275(3)	Cd(1)–O(5)$^{\#1}$	2.275(3)	Cd(1)–N(2)	2.289(4)
Cd(1)–O(9)	2.334(3)	Cd(1)–O(7)	2.339(5)	Cd(1)–O(1)	2.422(3)
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
			I		
O(6)$^{\#1}$Ca(1)O(2)	88.41(7)	O(6)$^{\#1}$Ca(1)O(7)	93.09(6)	O(2)Ca(1)O(7)	167.06(6)
O(6)$^{\#1}$Ca(1)O(1)	87.41(6)	O(2)Ca(1)O(1)	84.04(7)	O(7)Ca(1)O(1)	83.18(6)
O(6)$^{\#1}$Ca(1)O(12)$^{\#2}$	82.02(7)	O(2)Ca(1)O(12)$^{\#2}$	81.93(7)	O(7)Ca(1)O(12)$^{\#2}$	111.00(6)
O(1)Ca(1)O(12)$^{\#2}$	162.64(5)	O(6)$^{\#1}$Ca(1)O(7)$^{\#3}$	121.65(6)	O(2)Ca(1)O(7)$^{\#3}$	114.49(8)
O(7)Ca(1)O(7)$^{\#3}$	75.49(7)	O(1)Ca(1)O(7)$^{\#3}$	144.24(5)	O(12)$^{\#2}$Ca(1)O(7)$^{\#3}$	52.43(5)
O(6)$^{\#1}$Ca(1)N(1)	153.97(6)	O(2)Ca(1)N(1)	82.59(6)	O(7)Ca(1)N(1)	90.58(5)
O(1)Ca(1)N(1)	67.45(6)	O(12)$^{\#2}$Ca(1)N(1)	120.44(6)	O(7)$^{\#3}$Ca(1)N(1)	84.20(5)
			II		
O(8)Cd(1)O(5)$^{\#1}$	93.99(10)	O(8)Cd(1)N(2)	111.96(10)	O(5)$^{\#1}$Cd(1)N(2)	93.05(19)
O(8)Cd(1)O(9)	84.41(10)	O(5)$^{\#1}$Cd(1)O(9)	177.79(8)	N(2)Cd(1)O(9)	88.97(19)
O(9)Cd(1)O(7)	87.9(2)	O(8)Cd(1)O(1)	174.58(7)	O(5)$^{\#1}$Cd(1)O(1)	89.42(9)
N(2)Cd(1)O(1)	71.99(9)	O(9)Cd(1)O(1)	92.06(10)	O(7)Cd(1)O(1)	84.03(11)

* Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $x + 1, y, z$; $^{\#2}$ $-x + 2, -y + 2, -z + 1$; $^{\#3}$ $-x + 2, -y + 2, -z$ (**I**). $^{\#1}$ $-x + 1/2, -y + 1/2, -z + 1$ (**II**).

Supplementary material for structures **I** and **II** has been deposited with the Cambridge Crystallographic Data Centre (nos. 929826 (**I**), 959841 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

X-ray single crystal diffraction analyses reveal that compound **I** is a 2D network. The asymmetrical unit of **I** consists of a crystallographic independent Ca^{2+} cation which surrounded by four *p*-$CPhH_2IDC^{2-}$ ligands and one coordinated H_2O molecules. As shown in Fig. 2a, the central Ca^{2+} ion has a seven-coordinate environment occupied by five O atoms and one N atom of carboxy groups from four individual *p*-$CPhH_2IDC^{2-}$ ligands and the remaining one site occupied by one O atoms from one coordinated water molecule. The Ca–O bond lengths are in the range of 2.2845(17)–2.5173(17) Å, while the Ca–N bond lengths are 2.546(2) Å are in good with the bond lengths observed in other Ca(II) compounds [11–14].

The ligand *p*-$CPhH_2IDC^{2-}$ in **I** adopts the coordination mode linking four Ca atoms by μ_4-kN, O : kO' : kO', O'' : kO''' mode (Fig. 1a). The distance between the two dinuclear Ca^{2+} ions is 3.862(2) Å. Two crystallographically equal Ca(II) centers are bridged by two O atoms of carboxylate groups from two distinct *p*-$CPhH_2IDC^{2-}$ ligands in bidentate into a binuclear unit which is further jointed by *p*-$CPhH_2IDC^{2-}$ ligands to form a 1D infinite chain (Fig. 2b). These 1D chains are further bridged by the *p*-$CPhH_2IDC^{2-}$ form a extended 2D layer (Fig. 2c). In a word, polymer **I** is a useful example of the complex which is composed of Ca(II) and *p*-$CPhH_4IDC$.

Compound **II** is a binuclear coordination compound (Fig. 3a). The unit of **II** consists of two Cd^{2+} cations, two discrete *o*-$CPhH_2IDC^{2-}$ ligands, as well as six coordinated water molecules. What's more, two Cd atoms in the center position here are associated with a center inversion operation and they are in the same coordinate environment (Fig. 3a). Each of them is in a slightly distorted octahedral geometry [$CdNO_5$]: one imidazole nitrogen N(2) and two carboxylate O(1) and O(5*A*) atoms from two individual *o*-$CPhH_2IDC^{2-}$ anions, and three O(7), O(8) and O(9) atoms from the coordinated water molecule (Fig. 3a). The Cd–O bond lengths are in the range of 2.275(3)–2.422(3) Å

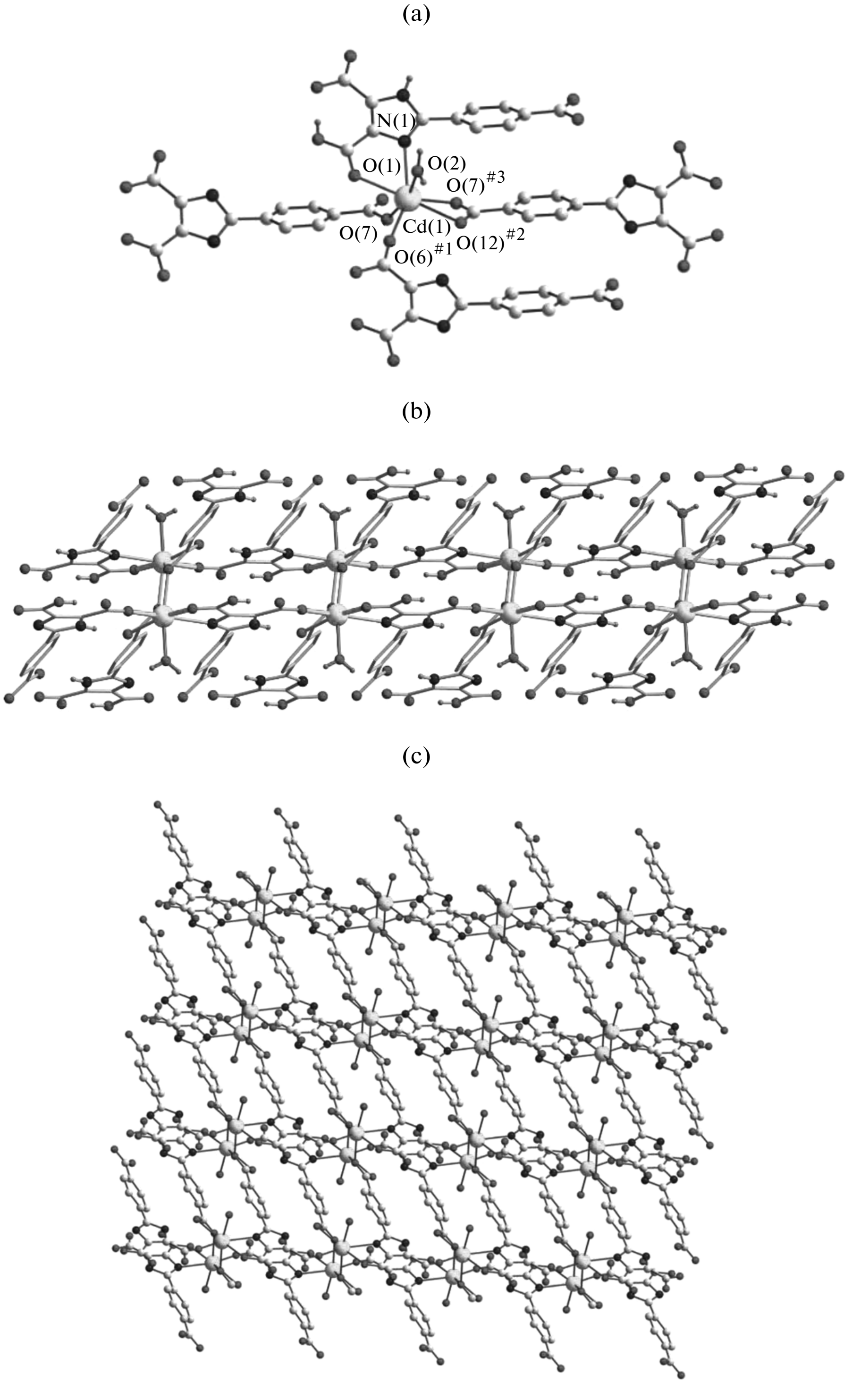


Fig. 2. Coordination environment of the Ca(II) atom in **I** (a); view of the infinite chain structure of **I** (b); view of the 2D framework of **I** with 1D channels in **I** (c).

and the Cd–N bond lengths are 2.289(4) Å are consistent with those of previous reported compounds [15].

Each *o*-$CPhH_2IDC^{2-}$ ligand provides both chelating ligand and bridging ligand, which adopts the same coordination mode μ_2-kN, O : kO' (Fig. 1b). There are both intramolecular hydrogen bonds (O(2)–H(3)···O(3), and intermolecular hydrogen bonds (O(7)–H(7*A*)···O(5*A*), O(7)–H(7*B*)···O(11),

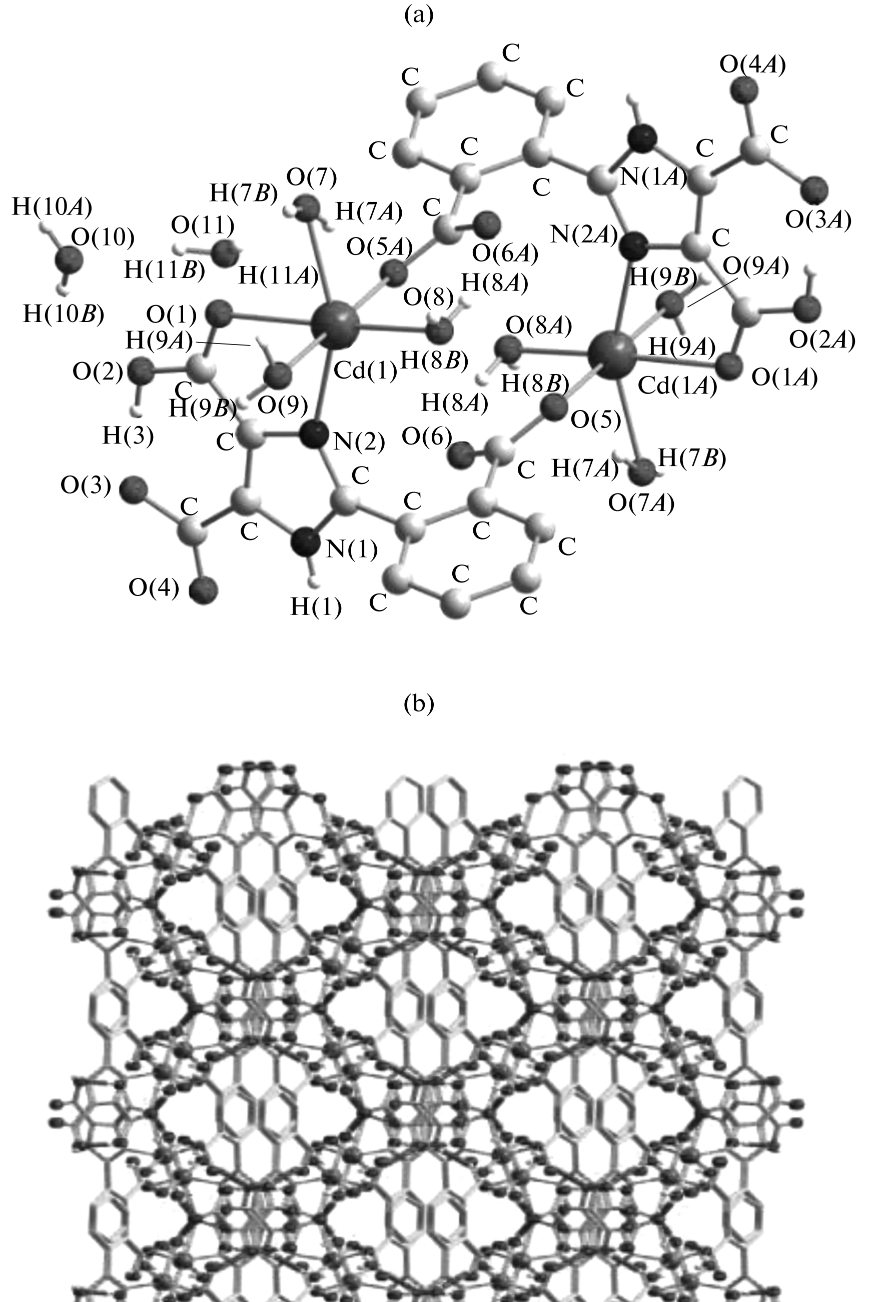


Fig. 3. Coordination environment of the Cd(II) atom in **II** (a); the crystal packing diagram of compound **II** which contains intra- and inter-molecular hydrogen bonds (b).

O(8)–H(8A)···O(6A), O(8)–H(8B)···O(1A), O(9)–H(9A)···O(11), O(9)–H(9B)···O(3A), N(1)–H(1)···O(6A), O(10)–H(10A)···O(5A), O(10)–H(10B)···O(4A), O(11)–H(11A)···O(10A) and O(11)–H(11B)···O(10)) in complex **II**. The O(2), H(3) and O(3) built up a intramolecular hydrogen bond. A H_2O in one $[Cd_2(o\text{-}CPhH_2IDC)_2(H_2O)_6]$ unit and the oxygen atom of carboxylate group in another

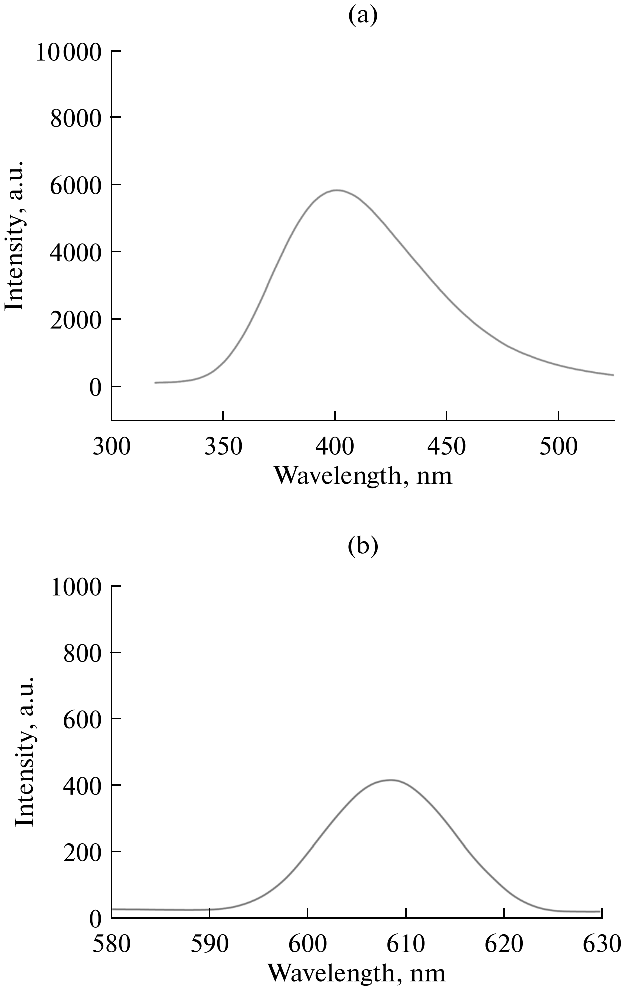


Fig. 4. The fluorescent spectra of complexes **I** (a) and **II** (b).

$[Cd_2(o\text{-}CPhH_2IDC)_2(H_2O)_6]$ unit formed a intermolecular hydrogen bond. A free of water molecule and a H_2O in one $[Cd_2(o\text{-}CPhH_2IDC)_2(H_2O)_6]$ unit also composed a intermolecular hydrogen bond. A free of water molecule and the oxygen atom of carboxylate group in another $[Cd_2(o\text{-}CPhH_2IDC)_2(H_2O)_6]$ unit made up a intermolecular hydrogen bond. Thus, a solid-state supramolecular structure (Fig. 3b) was constructed by intramolecular hydrogen bond, intermolecular hydrogen bonds and the van der waals interactions.

As far as we know, only four kinds of complexes with the ligand p-$CPhH_4IDC$ and three types of complexes with the ligand o-$CPhH_4IDC$ have been prepared [7, 8]. The successful preparation of polymers in our experiments and their various architectures demonstrate the versatile coordination abilities of the two imidazole-based multi-carboxylate ligands give us more confidence to study its affluent properties.

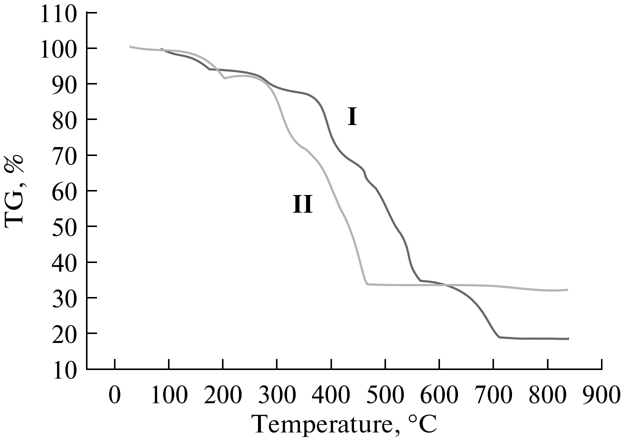


Fig. 5. TG analysis profiles of **I** and **II**.

Photoluminescent properties of complexes have attracted much attention due to their potential optical applications [16, 17]. It has been reported that the emission wavelength and intensity of the organic material can be affected through the coordination with metal. The solid-state photoluminescent spectra of polymers **I**, **II** are investigated at room temperature under the same experimental condition (Fig. 4).

The free ligands show luminescence with emission maximum at 498 nm (λ_{ex} = 445 nm) for o-$CPhH_4IDC$, 492 nm (λ_{ex} = 412 nm) for p-$CPhH_4IDC$, which may be attributed to ligand-centered $\pi^* \rightarrow n$ or $\pi \rightarrow \pi^*$ electronic transitions [7]. Emission bands are observed at 608 nm (λ_{ex} = 580 nm) for **I** and present red shifts 110 nm. Compared with the free ligand, the emissions of **II** (λ_{em} = 405 nm, λ_{ex} = 320 nm) undergo a blue-shift from 492 to 405 nm. Owning to that metal Cd(II) is difficult to oxidize or reduce, then the emissions of the olymers are neither metal-to-ligand charge transfer nor ligand-to-metal charge transfer in nature. This may be assigned to the mixture characteristics of intraligand and ligand-to-ligand charge transfer [18–20]. It is possible that various factors devote to this phenomenon, for instance, a charge-transfer transition between ligands and metal centers, and a joint contribution of the intraligand transitions or charge-transfer transitions between the coordinated ligands and the metal centers. The different emission bands of **I** and **II** may be attributed to the coordination diversities of the metal centers and the rigid differences of coordination modes.

In order to estimate the thermal stabilities of the polymers, TG analyses of **I** and **II** were carried out in the air (Fig. 5).

The TG curve of polymer **I** suggests that it has good thermal stability before 90.8°C. When the temperature is higher than 90.8°C, the 2D framework starts decomposing. The first weight loss from 90.8 to 226.1°C corresponds to the removal of the coordination water molecules (obsed. 6.28%, calced. 5.42%). It keeps losing weight from 226.1 to706.8°C, which may be ascribed to the decomposition of the organic p-CPhH_2IDC^{2-} ligand (obsed. 75.09%, calced. 76.02%). Finally, a plateau region is observed from 706.8 to 830.0°C. The remaining weight residue is CaO (obsed. 18.63%, calced. 17.70%).

The TG curve of dimer **II** reveals that the first weight loss from 91.0 to 281.8°C corresponds to the removal of the four free water molecules (obsed. 8.06%, calced. 7.55%). It keeps losing weight from 281.8 to 458.3°C, which may be ascribed to the decomposition of the two organic o-CPhH_2IDC^{2-} ligand (obsed. 58.52%, calced. 57.90%). Subsequently, the weight loss from 718.3 to 829.6°C corresponds to the removal of the coordination water molecules (obsed. 1.30%, calced. 1.88%). Finally, a plateau region is observed from 458.3 to 718.3°C and the remaining weight residue is CdO (obsed. 32.12%, calced. 32.67%).

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