

两个由两性二酸配体构筑的 Cd(II)低维配合物的合成、 结构及荧光性质

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摘要: 利用合成的两性离子二酸配体 1-(4-carboxylatobenzyl)pyridinium-4-carboxylate(HL), 通过调变合成条件, 制备了 2 个低维的配合物{Cd(L)₂·4H₂O}_n(**1**), 和[[Cd(L)(N₃)]·3H₂O]_n(**2**), 并对其进行了元素分析(EA)、红外光谱(IR)、热重(TG)、荧光光谱及 X-射线单晶衍射测定。分析结果显示化合物 **1** 中八配位的 Cd(II)离子被 4 个 L 配体连接形成一维链状结构。而化合物 **2** 中六配位的 Cd(II)离子被双羧基-叠氮三重桥联形成二维层状结构。固体荧光测试表明配体的配位方式明显影响其荧光发射。

关键词: 两性离子配体; 晶体结构; 配位聚合物; 荧光; Cd(II)配合物

中图分类号: O614.24²

文献标识码: A

文章编号: 1001-4861(2015)10-1929-09

DOI: 10.11862/CJIC.2015.231

Two Low Dimensional Cd(II) Coordination Polymers Constructed from Zwitterionic Dicarboxylate Ligand: Syntheses, Structures, and Fluorescent Properties

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Abstract: By controllable syntheses, two low dimensional Cd(II) complexes with the newly zwitterionic dicarboxylate ligand 1-(4-carboxylatobenzyl)pyridinium-4-carboxylate (HL), {Cd(L)₂·4H₂O}_n(**1**), and [[Cd(L)(N₃)]·3H₂O]_n(**2**) have been synthesized and structurally characterized by IR, elemental analyses, single-crystal X-ray diffraction. In compound **1**, the eight-coordinated Cd(II) ions are chelated by four equivalent L in a bis(chelating) mode, forming a one-dimensional coordination polymer structure. In **2**, six-coordinated Cd(II) ions are triple bridged by two carboxylate groups and an azide ion into 1D uniform [Cd(N₃)(OCO)₂]_n chains, which are further interlinked through the cationic N-benzylpyridinium backbones of the L ligands into 2D sheet. Interestingly, the fluorescence measurements show that all compounds exhibit intense blue emission in the solid state, and the emission bands are correlated to the coordination modes of the L ligand. CCDC:1031439, HL; 1031440, **1**; 1031441, **2**.

Key words: zwitterionic ligand; crystal structure; coordination polymers; fluorescence; cadmium(II) complex

收稿日期: 2015-01-27。收修改稿日期: 2015-06-04。

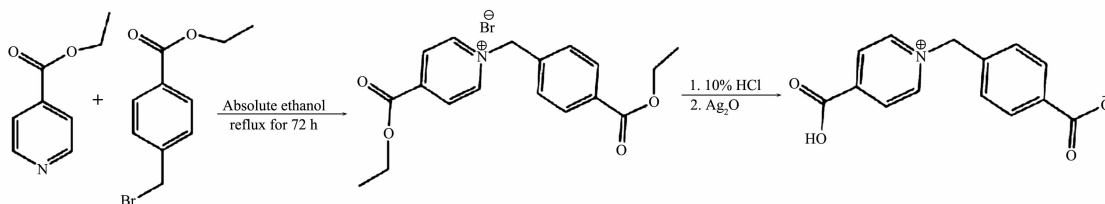
上海市自然科学基金(No.14ZR1447900), 校复合材料学科建设项目(No.10210Q140001)资助。

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0 Introduction

Over the past decade, the construction of coordination polymers (CPs) that are composed of infinite of metal ions connected by functionalized organic linkers, have been carried out by many researchers, because of not only their fascinating structures, but also their potential applications^[1-3], for example in the areas of gas adsorption^[4], catalysis^[5], ion recognition^[6] and luminescent properties^[7]. The multi-dentate ligands with conjugated groups are selected as organic linkers in the design of variable coordination frameworks because the flexibility of organic backbone, conformational preference and symmetry of organic ligands can lead to a remarkable series of materials with various structures and properties. Among them, aromatic multicarboxylate ligands, due to strong and versatile coordination abilities towards metal ions have been widely used for the construction of CPs in recent years. Compared with the usual carboxylate carboxylate ligands, the chemistry of zwitterionic carboxylate ligands have been studied limitedly so far^[8]. As illustrated in Scheme 1, compared with normal

dicarboxylate ligands, such dicarboxylate ligand bearing separated positive (pyridinium) and negative (carboxylate) charges can overcome the unbalanced competition of two anionic bridges in binding metal ions and compensating for metal charge. Our interest lies in the construction of coordination polymers based on various multicarboxylate ligands comprises zwitterionic carboxylate moieties. Recently, we have successfully constructed some newly CPs with dimensionalities from 1D to 3D using a series of zwitterionic carboxylate ligands and systematically studied the influences of metal ions, shape of the different zwitterionic carboxylate ligands on the structures and properties of final compounds formed^[9]. As an extension of this research, we present here two new Cd(II) complex with a flexible zwitterionic dicarboxylate 1-(4-carboxylatobenzyl)pyridinium-4-carboxylate(HL) ligand, $\{Cd(L)_2 \cdot 4H_2O\}_n$ (**1**), and $\{[Cd(L)(N_3)] \cdot 3H_2O\}_n$ (**2**). Their structures have been characterized by X-ray single-crystal diffraction analyses. Interestingly, the fluorescence measurements show that the emission bands can be correlated to the coordination modes of the L ligand.



Scheme 1 Synthetic route to the zwitterionic dicarboxylate ligand 1-(4-carboxylatobenzyl)pyridinium-4-carboxylate ligand (HL)

1 Experimental

1.1 General

All the metal salts and 4-(bromomethyl)benzoic acid ethyl ester, ethyl isonicotinate were purchased and used without further purification.

¹H NMR spectra were recorded on a Bruker AVANCEIII NMR spectrometer at 400 MHz, using DMSO-d₆ as a locking solvent. Elemental analyses (EA) were determined on an Elementar Vario ELIII analyzer. FTIR spectra were recorded in the range of 500 ~4 000 cm⁻¹ using KBr pellets on a Nicolet

NEXUS 670 spectrophotometer. Thermogravimetric analyses (TGA) were carried out on a Mettler Toledo TGA/SDTA851 instrument under flowing air at a heating rate of 10 °C · min⁻¹. Powder X-ray diffraction data were collected on a Bruker D8 ADVANCE diffractometer equipped with Cu K α (λ =0.154 18 nm) at a scan speed of 5° · min⁻¹. Excitation and emission spectra were recorded on an F-4500 luminescence spectrophotometer.

1.2 Synthesis

1.2.1 Synthesis of the ligand HL

The ligand HL was prepared according to the

literature following a method (Scheme 1) as described below^[10]. 4-(bromomethyl)benzoic acid ethyl ester (15.0 mmol, 3.46 g) was dissolved in 20 mL of absolute ethanol followed by the dropwise addition of ethyl isonicotinate (10.0 mmol, 1.52 g) and the reaction mixture was refluxed under vigorously stirred for 72 h. The excess ethanol was then evaporated under reduced pressure, yielding crude products, which was then recrystallized from hot H₂O to give the ester of HL. The resultant was dissolved in 10wt% HCl (100 mL) and was subsequently refluxed for 24h giving colorless powder after removal of the solvent. Removal of bromide and chloride ions with moist silver (I) oxide afforded the colorless HL. Diamond shaped crystals suitable for single-crystal X-ray diffraction analyses were grown by crystallization from H₂O (Yield: 86%). Elemental analysis Calcd. for C₁₄H₁₃NO₅ (*M*=275.26)(%): C, 61.09; H, 4.76; N, 5.09. Found(%): C, 61.16; H, 4.57; N, 5.36. IR (KBr disc, cm⁻¹) 3 448 (s), 3 050 (m), 1 675 (s), 1 634 (s), 1 563 (m), 1 376 (m), 759 (m), 542 (m). ¹H NMR (400 MHz, DMSO-d₆, TMS, 25 °C): δ 12.96(m, 1H, -COOH), 9.22(d, 1H, Py-H), 8.41(d, 1H, Py-H), 7.98(d, 1H, Ph-H), 7.64(d, 1H, Ph-H); 6.05 (m, 1H, -CH₂),

1.2.2 Synthesis of {Cd(L)₂·4H₂O}_n (**1**)

Compound **1** was prepared by the following method. A solution of HL (0.10 mmol, 0.027 g) in DMSO (3 mL) was added dropwise to a stirred aqueous solution (2 mL) of CdCl₂·4H₂O (0.10 mmol, 0.03 g); then NaN₃ (0.2 mmol, 0.013 g) dissolved in H₂O (2 mL) was added slowly. The resulting mixture was stirred for 1 h at room temperature and then filtered to remove any possible precipitate. The clear colorless solution was left to evaporate undisturbed at room temperature. Colorless block crystals of **1** appeared after two days (Yield: 44%). Elemental analysis Calcd. for C₂₈H₂₈N₂O₁₂Cd (*M*=696.92)(%): C, 48.21; H, 4.05; N, 4.02. Found(%): C, 48.07; H, 4.23; N, 3.85. IR (KBr, cm⁻¹): 3 433(br), 3 118(w), 3061(m), 3 020(w), 2 694(m), 2 584(w), 2 551(w), 2 445(w), 2 403(w), 1 795(w), 1 707(vs), 1 641(m), 1 614(m), 1 576(m), 1 510(w), 1 462(m), 1 394(vs), 1 323(w), 1 240(vs), 1 173(s), 1 117(s), 1 045(w), 1 017(w), 928

(m), 906(w), 870(m), 835(m), 746(s), 681(m).

1.2.3 Synthesis of {[Cd(L)(N₃)]·3H₂O}_n (**2**)

Colorless crystals of **2** were obtained by slow diffusion in an H-shaped tube. An aqueous solution (3 mL) containing HL (0.10 mmol, 0.027 g) and NaN₃ (0.50 mmol, 0.033 g) and the solution of CdCl₂·4H₂O (0.10mmol, 0.03 g) in the same solvent (3 mL) were added into, respectively, the two arms of a H-shaped tube, and then about 15 mL of ethanol was carefully added till the bridge of the tube was filled. Slow diffusion between the two solutions afforded rod-shaped crystals of **2** within one week. Yield: 59%. Elemental analysis Calcd. for C₁₄H₁₆N₄O₇Cd (*M* = 464.71)(%): C, 36.18; H, 3.47; N, 12.06. Found (%): C, 40.29; H, 3.56; N, 11.97. IR (KBr, cm⁻¹): 3 444 (br), 3 113(m), 3 049(m), 2 964(w), 2 071(vs), 1 624 (vs), 1 562(vs), 1 456(m), 1 392(vs), 1 192(w), 1 186 (w), 1 134(w), 1 045(w), 864(w), 806(m), 768(s), 690 (m).

1.3 Crystallographic Studies

Single crystal diffraction data of HL, **1** and **2** were respectively collected on a Bruker APEX II diffractometer equipped with a CCD area detector and graphite-monochromated Mo Kα radiation (λ=0.071 073 nm) at room temperature. Empirical absorption corrections were applied using the SADABS program^[11]. The structure was solved by the direct method and refined by the full-matrix least-squares method on *F*², with all non-hydrogen atoms refined with anisotropic thermal parameters^[12]. Hydrogen atoms were placed in calculated positions and refined isotropically using the riding model. For compounds **1** and **2**, the final structures have a large volume fraction of solvent accessible voids (22.5 and 33.7% for **1** and **2**, respectively) containing a number of residual electron density peaks, which may be attributed to solvent H₂O molecules but could not be satisfactorily modeled, perhaps due to the heavy disorder and the limited quality of the dataset. To improve the refinement, the SQUEEZE routine within the PLATON software package^[13] was applied to subtract the scattering contributions of the solvent molecules to the intensity data. In compound **2**, the orthorhombic *Imma* group

imposes C_{2v} point symmetry on the HL ligand, so the pyridyl nitrogen atom (N4) and the benzene carbon atoms (C5) were refined to occupy the same crystallographic position with the same displacement

parameters and bisected occupancy factors. Pertinent crystallographic data and structure refinement parameters are summarized in Table 1.

CCDC: 1031439, HL; 1031440, **1**; 1031441, **2**.

Table 1 Crystallographic data and structure refinements parameters for compounds HL, **1** and **2**

Compound	HL	1	2
Empirical formula	C ₁₄ H ₁₃ NO ₅	C ₂₈ H ₂₈ N ₂ O ₁₂ Cd	C ₁₄ H ₁₆ N ₄ O ₇ Cd
Formula weight	275.25	696.92	464.71
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$C2/c$	$Imma$
a / nm	0.721 05(12)	2.176 50(8)	0.745 94(3)
b / nm	2.684 8(4)	1.063 85(4)	1.419 12(7)
c / nm	0.672 98(11)	1.289 51(5)	1.757 41(7)
β / (°)	104.655(2)	92.607(2)	90
T / K	296	296	293
V / nm ³	1.260 4(4)	2.982 73(19)	1.860 36(14)
Z	4	4	4
D_c / (g·cm ⁻³)	1.451	1.552	1.659
μ / mm ⁻¹	0.111	0.798	1.216
$F(000)$	576	1416	928
θ range for all data collection / (°)	2.92~26.01	1.87~26.00	1.84~26.00
Reflns collected	7 068	17 631	11 497
Unique reflns	2 485	2 933	1 039
R_{int} *	0.030 7	0.033 3	0.016 5
GOF*	1.109	0.937	1.284
R_1, wR_2 [$I > 2\sigma(I)$]*	0.063 9, 0.161 9	0.023 8, 0.069 4	0.025 6, 0.107 4
R_1, wR_2 (all data)*	0.088 7, 0.176 3	0.027 0, 0.071 9	0.026 5, 0.108 7

* Values are for the refinements after the SQUEEZE routine.

2 Results and discussion

Both compounds were prepared by the reaction of cadmium (II) chloride, sodium azide and the HL ligands. However, small changes in the syntheses seem to influence on the final structure. For the synthesis of **1**, although cadmium (II) chloride and sodium azide were first well mixed in water before a DMSO solution of HL ligands was added dropwise, the azide ions did not coordinate to the Cd(II) centers, which may be due to the precipitation of the azide ions by Cd(II) ions. When the cadmium (II) chloride was diffused slowly into the water solution of HL ligands with sodium azide in an H-shaped tube, compound **2** was isolated, in which the azide ion bridged the neighboring Cd(II) centers. It should be noted that in the synthesis of

compound **2**, a large excess of sodium azide was necessary for the crystallization of the compounds. The azide ions not only act as ligands to bind Cd(II) ions, but also could serve to facilitate the deprotonation of HL.

2.1 Thermal analyses and PXRD patterns

Thermogravimetric analysis (Fig.1a) indicates that compound **1** lost its guest water molecules in the range of 25 ~90 °C. The weight loss (10.9%) corresponds to the release of four guest water molecules (Calcd. 10.3%) per formula, and the dehydrated solid shows no weight loss until ca. 280 °C. Compound **2** loses the water molecules (Found 12.3%, Calcd. 11.6%) upon heating from room temperature to 105 °C, and there is no significant weight loss until 270 °C, above which a rapid

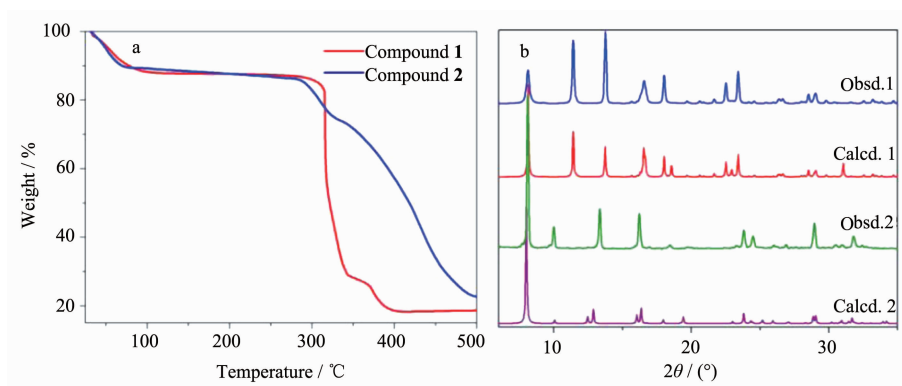


Fig.1 TGA and PXRD patterns for compounds **1** and **2**

decomposition occurs. The phase purity of the two products was also confirmed by comparing the experimental PXRD patterns with those calculated from the single-crystal structural data (Fig.1b).

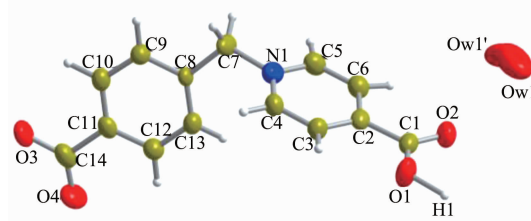
2.2 Description of the structure

As shown in Scheme 1, the zwitterionic dicarboxylate ligand (HL) was synthesized by the reaction of 4-(bromomethyl)benzoic acid ethyl ester with ethyl isonicotinate in absolute ethanol and hydrolysis. Single-crystal X-ray diffraction analyses revealed that HL crystallized in the monoclinic $P2_1/c$ space group. As shown in Fig.2, the HL free ligand adopts a highly twisted conformation, in which the two aromatic rings are perpendicular to each other with a large dihedral angle of $75.97(10)^\circ$, and the $\angle C8-C7-N1$ angle is $114.24(21)^\circ$. Adjacent HL ligands are interlinked into 1D chains through strong hydrogen bonding interactions, which involves the carboxylate oxygen atom (O3) and hydroxyl groups (O1-H) from the other carboxylate groups ($H1 \cdots O3$ $0.127\ 4(51)$ nm, $O1 \cdots O3$ $0.249\ 3(3)$ nm).

X-ray analyses reveal that compound **1** possesses 1D polymeric coordination chain with a space group

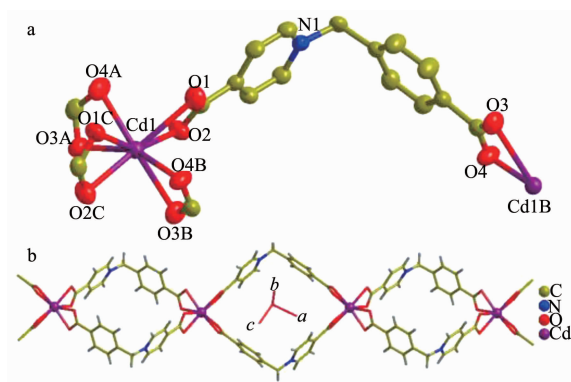
$C2/c$. The molecular structure is shown in Fig.3, and selected bond distances and angles are given in Table 2. The Cd(II) ion is coordinated to four chelating carboxylate groups from four L ligands with the Cd-O bond distances in the range of $0.237\ 6\sim 0.253\ 9$ nm. The L ligand adopts bis (chelate) mode (μ_4, η^2) to bridge neighboring Cd(II) ions forming 1D coordination polymer chains $[Cd(L)_2]_n$, extending along the $(\bar{1}01)$ direction, with a long Cd \cdots Cd distance of 1.293 nm. Due to the V-shaped conformation of the L ligands, the two aromatic rings are tilted to each other giving a dihedral angle of $79.31(07)^\circ$, and the $\angle C8-C7-N1$ angle is $109.54(17)^\circ$. Compared with the free HL ligand, both the angles change larger, maybe due to the coordination to Cd(II), changing the rigidities and conjugation. The L ligands are hump alternately up and down from the chain, resulting in 1D rhombic channel along the b direction, occupied by the guest water molecules. PLATON calculations revealed that the guest-accessible volume is $0.672\ 2\ \text{nm}^3$ per unit cell^[13], comprising 22.5% of the crystal volume.

As shown in Fig.4, the individual ribbon chains are further packed into 3D supramolecular network



Thermal ellipsoids at 30% probability

Fig.2 ORTEP representation of the crystal structure for HL



Thermal ellipsoids at 30% probability; All hydrogen atoms are omitted for clarity; Symmetry codes: A: $-x+0.5, -y+0.5, -z+1$; B: $x-0.5, -y+0.5, z+0.5$; C: $-x, y, -z+1.5$

Fig.3 (a) Coordination environments in **1** (b) View of the 1D ribbon chain of **1** linked by the L ligands

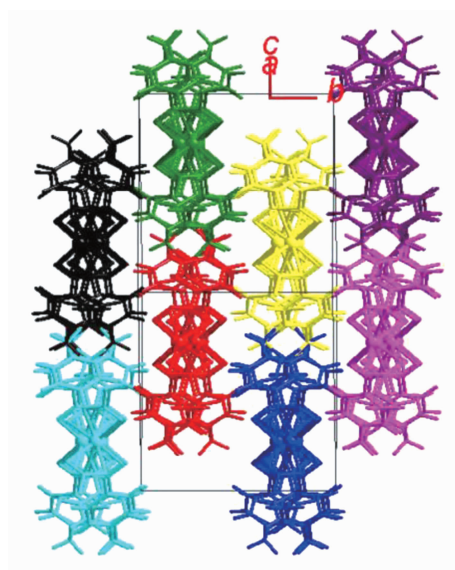


Fig.4 3D supramolecular network constructed via the hydrogen bonds

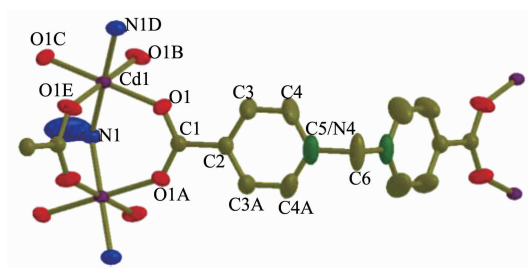
Table 2 Selected bond (nm) and angles ($^{\circ}$) for compound **1**

Cd1-O1	0.254 0(2)	Cd1-O2	0.240 5(2)	Cd1-O3A	0.241 1(2)
Cd1-O4A	0.237 7(2)				
O1-Cd1-O2	52.75(6)	O1-Cd1-O4A	78.15(7)	O1-Cd1-O4B	80.63(7)
O1-Cd1-O2C	151.30(6)	O1-Cd1-O3B	124.07(6)	O1-Cd1-O3A	98.27(6)
O1-Cd1-O1C	103.29(8)	O2-Cd1-O3A	79.27(6)	O2-Cd1-O4A	105.70(7)
O2-Cd1-O4B	81.92(7)	O2-Cd1-O2C	154.69(8)	O2-Cd1-O3B	86.43(6)
O3A-Cd1-O4A	54.33(6)	O3A-Cd1-O4B	156.88(7)	O3B-Cd1-O3A	110.87(8)
O4A-Cd1-O4B	145.49(8)				

Symmetry codes: A: $-x+0.5, -y+0.5, -z+1$; B: $x-0.5, -y+0.5, z+0.5$; C: $-x, y, -z+1.5$

via the hydrogen bonding interactions between the coordinated carboxylate oxygen atoms (O2, O4) and guest water molecules.

Single crystal X-ray analyses revealed that compound **2** crystallized in the orthorhombic space group *Imma* and containing 2D coordination networks.



All hydrogen atoms are omitted for clarity, and the C5 and N4 atoms are disordered; The thermal ellipsoids were drawn at 30%; Symmetry codes: A: $-x, -y+1.5, z$; B: $-x+0.5, -y+1.5, -z+0.5$; C: $-x+0.5, y+0, -z+0.5$; D: $x, -y+1.5, z$; E: $1-x, y, z$

Fig.5 Coordination environments in **2**

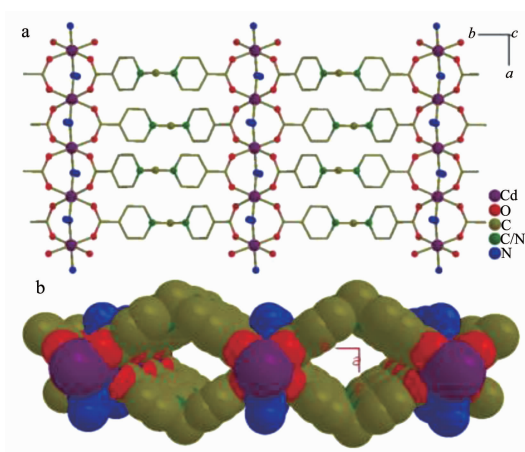


Fig.6 (a) Top view of the 2D network; (b) side view of the space-filling diagram along a direction showing the 1D rhombic channels

The coordination environment of the Cd(II) ion is shown in Fig.5 and the relevant parameters are summarized in Table 3. The unique Cd(II) ion resides at the crystallographic $2/m$ position and adopts *trans*-octahedral $[N_2O_4]$ coordination geometry, completed by four equivalent carboxylate oxygen atoms (O1, O1B, O1C and O1E) and two equivalent nitrogen atoms (N1 and N1D). Different from that in **1**, the L ligand, having the C_{2v} point symmetry, serves as a *syn-syn*- μ_4 bridge using its two carboxylate groups to connect four Cd(II) ions (Cd-O, 0.229 5(2) nm, Table 3), and due to the C_{2v} symmetry, the pyridyl nitrogen atom (N4) and

one (C5) of the benzene carbon atoms are disordered. The azide ion adopts end-on μ -1,1 mode to bridge neighboring Cd(II) ions (Cd-N, 0.215 8(2) nm). Thus the adjacent Cd(II) ions are triply bridged by two carboxylate groups and an azide ion to generate a 1D uniform $[Cd(N_3)(OCO)_2]_n$ chain running along the a direction. The Cd \cdots Cd distance separated by the triple bridges is 0.373(1) nm, and the bridging angle Cd \cdots N \cdots Cd is 109.86(1) $^\circ$.

The compound consists of 2D coordination network parallel to the ab plane, in which identical anionic $[Cd(N_3)(OCO)_2]_n$ chains are further interlinked

Table 3 Selected bond (nm) and angles ($^\circ$) for compound **2**

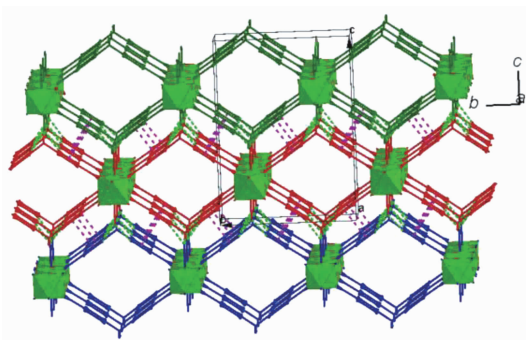
Cd1-O1	0.229 5(2)	Cd1-N1	0.227 8(3)		
O1-Cd1-O1D	94.49(15)	O1-Cd1-O1C	85.51(15)	O1-Cd1-O1B	180.0
O1-Cd1-N1	93.89(9)	Cd1-N1-CdA	109.9(2)	O1-Cd1-N1B	86.11(9)
N1-Cd1-N1B	180.0				

Symmetry codes: A: $-x, -y+1.5, z$; B: $-x+0.5, -y+1.5, -z+0.5$; C: $-x+0.5, y+0, -z+0.5$; D: $x, -y+1.5, z$

through the cationic N-benzylpyridinium backbones of the L ligands, with Cd \cdots Cd distance of 1.419 12(7) nm, which is equal to the *b* dimension of the unit cell (Fig.6a). Due to the V-shaped conformation of the L ligand, the two aromatic rings are tilted to each other with a dihedral angle of 64.01(15) $^\circ$ and the \angle C5-C6-N4 angle is 112.46(23) $^\circ$, and both angles are also smaller than those in the free HL ligand. The layer is tunneled through by 1D rhombic channels along the chain direction (Fig.6b). PLATON calculations revealed that the guest-accessible volume is 0.626 3 nm 3 per unit cell^[13], comprising 33.7% of the crystal volume. The free spaces in the framework are occupied by the structural disordered H $_2$ O guest molecules.

The 2D coordination sheets are stacked in an offset

ABAB fashion (Fig.7), with an interlayer separation of 0.915 4(2) nm. Interlayer interdigitation occurs with the methylene CH groups of a layer protruding towards the mesh centers of the two neighboring layers, and this allows the formation of interlayer C-H \cdots N hydrogen bonds: each N3 atom from one layer interact with six C-H groups from the neighboring layer, including two equivalent methylene C6-H groups and four equivalent aromatic C4-H groups) (H \cdots N 0.274~0.295 nm, C \cdots N 0.362~0.378 nm, \angle C-H \cdots N 144 $^\circ$ ~158 $^\circ$) and the nearest interlayer Cd \cdots Cd distance is 1.129 4(3) nm. Additionally, the 3D supramolecular structure are further sustained by π - π stacking interactions between the parallel aromatic rings (benzene/pyridyl) from different layers, with the center-to-center (0.349 8 (1) nm) and interplanar distances (0.374 79(6) nm).



The hydrogen bonds are highlighted in green colors, and π - π interactions are purple color

Fig.7 3D structure constructed via the hydrogen bonds and π - π interactions between the ABAB stacking sheets

2.3 Luminescent properties

CPs with d^{10} metal centers are desirable candidates for fluorescent materials due to their ability to affect the emission wavelength of the organic materials by metal

coordination^[7a,14]. The luminescent measurements of the HL ligand and corresponding compounds **1** and **2** in the solid state were carried out at room temperature. As can be seen from Fig.8, compounds **1** and **2** exhibit blue

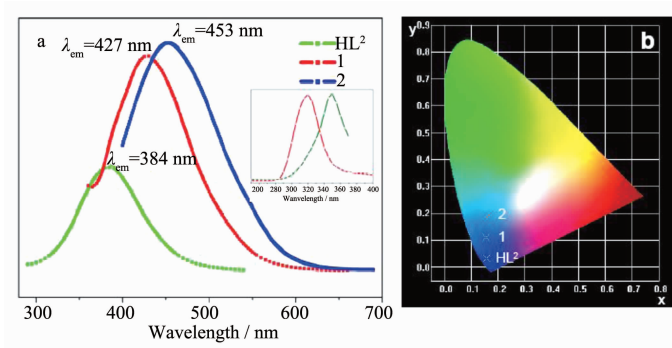


Fig.8 (a) solid-state emission spectra and excitation spectra (inset) of HL ligand and compounds **1**, **2** at room temperature; (b) The CIE chromaticity diagrams

emissions at 427 and 453 nm, respectively, in the similar excitation (about 350 nm). Meanwhile, the maximum emission of the free HL ligand in solid state is observed at 384 nm ($\lambda_{\text{ex}}=319$ nm). In comparison with the emission peak of free HL ligand, the obvious red-shift observed in compounds **1** and **2** can be tentatively assigned to the cooperative effects of intraligand $\pi-\pi^*$ transitions and ligand-to-metal charge transfer (LMCT), which is not rare for the complexes of d^{10} metal like Cd(II)^[7a,14-15]. The bathochromic shifts of emission occurring in **1** and **2** are possibly assigned to different coordination effect between the ligands and metal ions^[16].

Acknowledgements: We are thanking for the financial support of Key Discipline Grant for Composite Materials from Shanghai Institute of Technology (No. 10210Q140001) and the Foundation of Science and Technology Development of Shanghai (No. 14ZR1447900).

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