

两个含三唑环有机配体的 Hg(II)配聚物的合成、晶体结构及其荧光性质

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摘要: 以碘化汞为原料, 分别与 3,5-二(4-吡啶基)-1,2,4-三唑(L1), 4-氨基-3,5-二(4-吡啶基)-1,2,4-三唑(L2)在 *N,N*-二甲基甲酰胺(DMF)溶液中反应, 合成了 2 个一维链状 Hg(II)配聚物 $[\text{Hg}_2\text{I}_4(\text{L1})_2] \cdot 3\text{DMF}_n$ (**1**), $[\text{Hg}_2\text{I}_4(\text{L2})] \cdot \text{DMF}_n$ (**2**)。用红外光谱、元素分析、X-射线单晶衍射对配合物进行了表征。X-射线单晶衍射表明, 配聚物 **1** 中汞离子位于扭曲的配位四面体中心, 相邻汞离子通过分别与 L1 的 2 个端基 N 原子配位, 桥连形成了一维 zig-zag 链结构, 碘离子占据配位四面体的剩余两配位点, 配聚物 **1** 的一维链平行于 *bc* 平面。配合物 **2** 中汞离子位于扭曲的配位四面体中心, 分别与 L2 的一个吡啶 N 原子和 3 个碘离子配位, 其中 2 个碘离子充当桥联配体将相邻汞离子连接, 形成了一维-Hg-I-Hg-I-的 zig-zag 链, 相邻的-Hg-I-Hg-I-链进一步通过作为双齿配体的 L2 连接, 形成一独特的一维双链梯状聚合物, 配聚物 **2** 一维链平行于 *a* 方向。室温固态荧光测试显示, 配聚物 **1** 在 383.7nm 处具有强的荧光发射, 而配聚物 **2** 在 299.7 nm 和 376.5 nm 处具有强的荧光发射。

关键词: 三唑; 配位聚合物; 晶体结构; 荧光性质

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Synthesis, Crystal Structures and Luminescent Properties of Two Coordination Polymers Generated from Triazole-Containing Organic Ligands and Inorganic Hg(II) Salts

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Abstract: Two 1D chain Hg(II) coordination polymers $[\text{Hg}_2\text{I}_4(\text{L1})_2] \cdot 3\text{DMF}_n$ (**1**) and $[\text{Hg}_2\text{I}_4(\text{L2})] \cdot \text{DMF}_n$ (**2**) (where L1=3,5-bis(4-pyridyl)-1,2,4-triazole, L2=4-amino-3,5-bis(4-pyridyl)-1,2,4-triazole) have been synthesized in DMF solution with HgI_2 and L1, L2, respectively. The polymers were characterized by elemental analysis, IR and X-ray single crystal diffraction analysis. Complex **1** crystallizes in the triclinic system, space group $P\bar{1}$ with cell parameters $a=0.820\ 3(2)$ nm, $b=1.631\ 0(5)$ nm, $c=1.845\ 8(5)$ nm, $\alpha=69.026(3)^\circ$, $\beta=88.521(4)^\circ$, $\gamma=83.355(4)^\circ$, $V=2.290\ 1(11)$ nm³, $Z=2$, $\mu(\text{Mo } K\alpha)=9.439$ mm⁻¹, $F(000)=1\ 448$, $R_1=0.046\ 1$, $wR_2=0.133\ 1$ [$I>2\sigma(I)$]. In the complex **1**, each Hg(II) ion atom locates in a distorted coordination tetrahedron and coordinates with two pyridine N atoms from two L1 ligands. The remaining two coordination sites of Hg(II) ion are occupied by two I ions. Each L1 acts as a bridge to bond neighboring two Hg(II) ions to form an infinite 1D chain. The 1D chain is parallel to the *bc* plane. Complex **2** crystallizes in the monoclinic system, space group $P2_1/c$ with cell parameters $a=0.433\ 0(3)$ nm, $b=2.465\ 7(15)$ nm, $c=2.459\ 2(16)$ nm, $\beta=91.267(14)^\circ$, $V=2.625(3)$ nm³, $Z=4$, $\mu(\text{Mo } K\alpha)=16.407$ mm⁻¹, $F(000)=$

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2 144, $R_1=0.0515$, $wR_2=0.1140$ [$I>2\sigma(I)$]. In the complex **2**, each Hg(II) ion atom locates in a distorted coordination tetrahedron and coordinates with one pyridine N atom from L2 ligand and the remaining three coordination sites of Hg(II) ion are occupied by three crystallographically distinct Ions. Two Ions act as bridging ligands, which link the Hg(II) centers forming a 1D zig-zag -Hg-I-Hg-I- chain. The adjacent-Hg-I-Hg-I- chains are further connected by bidentate L2 ligand, resulting in a unique 1D double chain. The double chain structure of **2** can be regarded as a ladder-like chain containing two chains -Hg-I-Hg-I- and L2 spacers. The ladder-like chain extends in the *a* direction. The experimental results show that the title complexes have good luminescent properties and could be used as potential optical materials. CCDC: 751327, **1**; 991983, **2**

Key words: triazole; coordination polymer; crystal structure; luminescent property

During the past decades, tremendous effort has been devoted to the study of coordination complexes, including discrete coordination complexes and coordination polymers, for their utilitarian properties and versatile structural motifs and intriguing topological structures. The rapid development of materials science and crystal engineering has considerably promoted the uses of coordination complexes as functional materials with potential applications in the fields of catalysis, gas absorption, nonlinear optics, ion-exchange, luminescence, magnetism and many other fields^[1-13].

In principle, the diversity in the polymeric structures of such materials is highly influenced by the choice of the metal centers (nodes), organic ligands (spacers), as well as on the reaction pathways^[14-15]. Among these factors, the choice of the organic spacers is the greatest influence in determining the type and topology of the product. Properties of organic spacers, such as solubility, coordination activity, length, geometry, and relative orientation of the donor groups, play a very important role in dictating polymer framework topology. As we know, the rigid linear ligands, such as 4,4'-bipyridine (4,4'-bpy) and 4,4'-bipyridine-like N,N'-donor ligands are often used as spacers to form open metal-organic frameworks^[10-13]. 3,5-bis(4-pyridyl)-1,2,4-triazole (Hbpt), which is introduced the 1,2,4-triazole moiety between the two 4-pyridyl groups, has attracted considerable interest due to its excellent behaviors^[5]. First, it can act as an excellent organic spacer, which can exhibit diverse coordination fashions and bridge metal centers to assemble one, two or multidimensional architectures.

Second, the prototropy and conjugation between the 1,2,4-triazole and 4-pyridyl groups not only alter the electron density in different parts of the molecule, but also make the ligand more flexible, in addition, the wide application in spin-crossover materials and pharmacologically active compounds also makes this moiety more attractive^[5,16-18].

On the other hand, one special class of such compounds is the coordination polymers based on Hg(II) halides and aromatic N-donor ligands which show a great structural diversity, which in part arises from the adjustable coordination numbers and geometries of d¹⁰ Hg(II) center particularly suited for the construction of coordination polymers and networks^[19-23]. Owing to the ability of organic materials to affect wavelength emissions, syntheses of inorganic-organic coordination polymers by the judicious choice of organic spacers and metal centers (such as Zn, Cd, Hg, Ag, Cu, etc.) can be an efficient method to obtain types of luminescent materials^[24-27].

With this understanding, in this paper we describe the synthesis and crystal structures of two 1D Hg(II) coordination polymers $\{[\text{Hg}_2\text{I}_4(\text{L1})_2] \cdot 3\text{DMF}\}_n$ (**1**) and $\{[\text{Hg}_2\text{I}_4(\text{L2})] \cdot \text{DMF}\}_n$ (**2**). Their luminescent properties are also presented.

1 Experimental

1.1 Materials and instruments

With the exception of the ligands L1 and L2, which were prepared according to the literature procedure^[28], all reagents and solvents for the synthesis and analysis were commercially available and used as

received (without further purification). Elemental analyses for carbon, hydrogen and nitrogen were performed by a PerkinElmer 240C elemental instrument. IR spectra were measured with KBr pellets on a Nicolet AVATAR360 FT-IR spectrometer in the range of 4 000~400 cm^{-1} .

1.2 Synthesis of $\{[\text{Hg}_2\text{I}_4(\text{L1})_2] \cdot 3\text{DMF}\}_n$ (**1**)

HgI_2 (0.454 g, 1 mmol) was added to DMF (6 mL), and the resulting mixture was stirred at room temperature for 5 min. L1 (0.444 g, 2 mmol) was then added to the solution with stirring, during which time a colorless solution was formed. The resulting solution was further stirred for about 20 min. The reaction mixture was filtered and the filtrate was then transferred to a test tube and carefully layered by *i*-PrOH (10 mL). Colorless block crystals were obtained after 15 days. The colorless products were collected and single crystals of the title complex suitable for X-ray measurements were obtained. Anal. Calcd.(%) for $\text{C}_{33}\text{H}_{39}\text{Hg}_2\text{I}_4\text{N}_3\text{O}_3$: C 25.17, H 2.50, N 11.56. Found (%): C 25.03, H 2.82, N 11.71. IR (KBr disc, cm^{-1}): 3 107m, 3 083m, 3 034m, 2 239m, 1 602s, 1 547m, 1 413s, 1 220s, 1 089m, 1 066s, 1 008s, 827vs, 783m, 558s, 472m.

1.3 Synthesis of $\{[\text{Hg}_2\text{I}_4(\text{L2})_2] \cdot \text{DMF}\}_n$ (**2**)

Compound **2** was synthesized by the same

procedure as described for **1** except the addition of L2 (0.476 g, 2 mmol) instead of L1 (0.444 g, 2 mmol). Light-yellow block-like crystals were obtained and collected in the same way as for compound **1**. Anal. Calcd. (%) for $\text{C}_{15}\text{H}_{17}\text{Hg}_2\text{I}_4\text{N}_7\text{O}$: C 14.76, H 1.40, N 8.04. Found (%): C 14.63, H 1.48, N 8.11. IR (KBr disc, cm^{-1}): 3 332s, 1 654m, 1 608vs, 1 560m, 1 466 m, 1 410m, 1 217s, 1 066m, 1 010s, 950m, 831m, 738 m, 702m, 611m, 508m.

1.4 Crystal structure determination

Single crystal data were collected at room temperature using a Bruker Smart Aepex II CCD diffractometer equipped with a graphite-monochromatic Mo $K\alpha$ radiation ($\lambda=0.071\ 073$ nm) at 296 K using a φ - ω scan mode. Data reductions and cell refinement were performed with the SAINT program, and the absorption correction program SADABS was employed to correct the data for absorption effects^[29-30]. The structures were solved by direct methods using SHELXS program and refined with SHELXL program^[31]. Final refinements were performed by full matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms on F^2 . Hydrogen atoms were theoretically added. The crystal data and structure refinement results are summarized in Table 1.

CCDC: 751327, **1**; 991983, **2**.

Table 1 Crystallographic data of the complexes

Compound	1	2
Empiric formula	$\text{C}_{33}\text{H}_{39}\text{Hg}_2\text{I}_4\text{N}_3\text{O}_3$	$\text{C}_{15}\text{H}_{17}\text{Hg}_2\text{I}_4\text{N}_7\text{O}$
Formula weight	1 574.55	1 220.14
Color	Colorless	Yellow
Size / mm	0.22×0.24×0.28	0.06×0.07×0.07
θ range for data collection / (°)	1.2~25.0	1.9~26.0
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
<i>a</i> / nm	0.820 3(2)	0.433 0(3)
<i>b</i> / nm	1.631 0(5)	2.465 7(15)
<i>c</i> / nm	1.845 8(5)	2.459 2(16)
α / (°)	69.026(3)	90
β / (°)	88.521(4)	91.267(14)
γ / (°)	83.355(4)	90
<i>V</i> / nm ³	2.290 1(11)	2.625(3)
<i>Z</i>	2	4
<i>D_c</i> / (g·cm ⁻³)	2.283	3.087

Continued Table 1

$F(000)$	1 448	2 144
μ (Mo $K\alpha$) / mm^{-1}	9.439	16.407
Reflections collected	16 238	14 824
Reflections unique (R_{int})	7 975 (0.041)	5 162 (0.061)
GOF on F^2	0.972	0.988
R_1, wR_2 [$I > 2\sigma(I)$]	0.046 1 ^a , 0.133 1 ^a	0.051 5 ^b , 0.114 0 ^b
R_1, wR_2 (all data)	0.082 2 ^a , 0.111 4 ^a	0.097 1 ^b , 0.101 7 ^b
Limiting indices	$-9 \leq h \leq 9, -19 \leq k \leq 19, -21 \leq l \leq 21$	$-5 \leq h \leq 5, -30 \leq k \leq 25, -27 \leq l \leq 30$
Largest diff. peak and hole / ($\text{e} \cdot \text{nm}^{-3}$)	1 940 and -1 190	1 040 and -1 210

^a $w=1/[\sigma^2(F_o^2)+(0.0668P)^2]$, where $P=(F_o^2+2F_c^2)/3$; ^b $w=1/[\sigma^2(F_o^2)+(0.0467P)^2]$, where $P=(F_o^2+2F_c^2)/3$.

2 Results and discussion

2.1 Crystal structures of the complex 1 and the complex 2

The molecules and polymers structures of the title complexes are depicted in Fig.1 and Fig.2, with crystal data being given in Table 1. Selected bond lengths and angles are listed in Table 2. The complex **1** crystallizes in the triclinic, $P\bar{1}$ space group with two asymmetric units in one unit cell. The asymmetric unit of the title complex **1** consists of two Hg(II) atoms, four iodine atoms, two L1 ligands and three solvent DMF molecules (Fig.1). As shown in Fig.1 and Fig.2, each Hg atom has a distorted tetrahedral geometry and is coordinated by two pyridine N atoms of bridging L1 ligands and two iodine ions. Two

adjacent Hg atoms are asymmetrically bridged by two pyridine N atoms of bridging L1 ligands with bond lengths range: 0.242 4(10) (Hg(2)-N(5)) to 0.249 7(9) nm (Hg (2)-N (10)ⁱ), which are comparable to the values in related Hg(II) complexes^[21]. Hg atoms linked by L1 ligands and form a 1D zig-zag chain polymer (Fig.2). The 1D chain is parallel to bc plane. In the 1D polymer chain, the remaining coordination sites of the approximate octahedron of each mercury atom are occupied by two iodine ions. For the complex **1**, the bond angles of N-Hg-N are within 91.2(3) $^\circ$ (N(5)-Hg(2)-N(10)ⁱ) ~ 93.3(3) $^\circ$ (N(4)-Hg(1)-N(9)), which are close to 90 $^\circ$ and different from the bond angle of 109 $^\circ$ 28' for an ideal tetrahedron. Additionally, the N-Hg-I bond angles ranged from 98.7(2) $^\circ$ to 108.3(2) $^\circ$, the I-Hg-I bond angles ranged from 145.35(4) $^\circ$ to

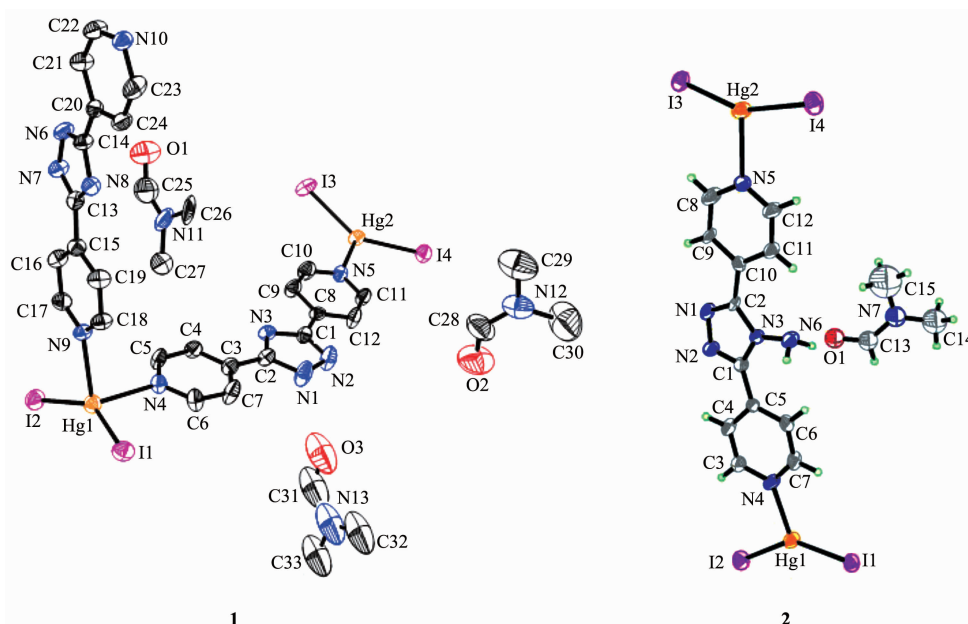


Fig.1 Asymmetric units of the title complexes and the labeling scheme used with 30% ellipsoidal probability

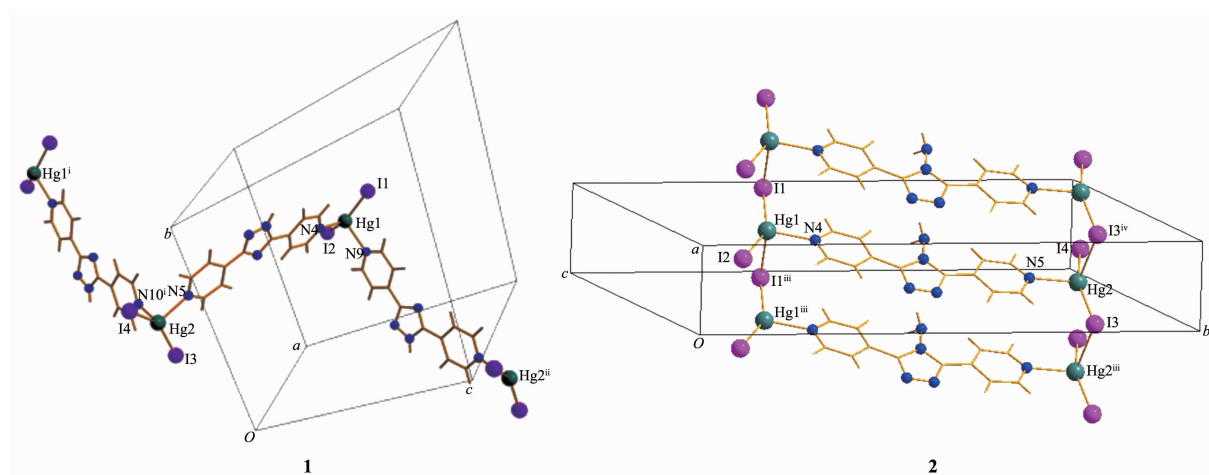
Free DMF are omitted for clarity; Symmetry code: ⁱ $-1+x, 1+y, -1+z$; ⁱⁱ $1+x, -1+y, 1+z$; ⁱⁱⁱ $-1+x, y, z$; ^{iv} $1+x, y, z$

Fig.2 Part of the title 1D chain polymers

Table 2 Selected bond lengths (nm) and bond angles ($^{\circ}$) for the title complex

Compound 1					
Hg(1)-I(1)	0.265 61(13)	Hg(1)-I(4)	0.263 20(14)	Hg(1)-I(2)	0.264 32(13)
Hg(2)-I(3)	0.264 00(13)	Hg(1)-N(4)	0.243 6(9)	Hg(2)-I(4)	0.263 20(14)
Hg(1)-N(9)	0.248 0(10)	Hg(2)-N(5)	0.242 4(10)	Hg(1)-I(3)	0.264 00(13)
Hg(2)-N(10) ⁱ	0.249 7(9)				
I(1)-Hg(1)-I(2)	145.35(4)	N(5)-Hg(2)-N(10) ⁱ	91.2(3)	I(1)-Hg(1)-N(4)	100.1(2)
Hg(1)-N(4)-C(5)	122.0(8)	I(1)-Hg(1)-N(9)	101.4(2)	Hg(1)-N(4)-C(6)	121.3(8)
I(2)-Hg(1)-N(4)	105.7(2)	Hg(2)-N(5)-C(10)	120.6(9)	I(2)-Hg(1)-N(9)	100.0(2)
Hg(2)-N(5)-C(11)	124.5(8)	N(4)-Hg(1)-N(9)	93.3(3)	Hg(1)-N(9)-C(17)	122.5(8)
I(3)-Hg(2)-I(4)	145.97(4)	Hg(1)-N(9)-C(18)	120.9(7)	I(3)-Hg(2)-N(5)	100.3(2)
Hg(1)-N(4)-C(5)	122.0(8)	I(3)-Hg(2)-N(10) ⁱ	98.7(2)	Hg(2) ⁱⁱ -N(10)-C(22)	121.5(8)
I(4)-Hg(2)-N(5)	108.3(2)	Hg(2) ⁱⁱ -N(10)-C(23)	121.7(8)	I(4)-Hg(2)-N(10) ⁱ	98.8(2)
Compound 2					
Hg(1)-I(1)	0.265 5(2)	Hg(2)-I(3)	0.264 4(2)	Hg(1)-I(2)	0.262 1(2)
Hg(2)-I(4)	0.262 5(2)	Hg(1)-N(4)	0.234 6(10)	Hg(2)-N(5)	0.240 9(10)
Hg(1)-I(1) ⁱⁱⁱ	0.321 1(2)	Hg(2)-I(3) ^{iv}	0.323 3(2)		
I(1)-Hg(1)-I(2)	146.28(4)	I(4)-Hg(2)-N(5)	101.6(2)	I(1)-Hg(1)-N(4)	103.2(3)
I(3) ^{iv} -Hg(2)-I(4)	95.11(3)	I(1)-Hg(1)-I(1) ⁱⁱⁱ	94.67(3)	I(3) ^{iv} -Hg(2)-N(5)	92.8(2)
I(2)-Hg(1)-N(4)	108.4(3)	Hg(1)-I(1)-Hg(1) ^{iv}	94.67(4)	I(1) ⁱⁱⁱ -Hg(1)-I(2)	97.46(3)
Hg(2)-I(3)-Hg(2) ⁱⁱⁱ	94.39(3)	I(1) ⁱⁱⁱ -Hg(1)-N(4)	88.6(3)	Hg(1)-N(4)-C(3)	123.4(9)
I(3)-Hg(2)-I(4)	154.08(4)	Hg(1)-N(4)-C(7)	122.6(9)	I(3)-Hg(2)-N(5)	102.0(2)
Hg(2)-N(5)-C(8)	117.6(9)	I(3)-Hg(2)-I(3) ^{iv}	94.39(3)	Hg(2)-N(5)-C(12)	125.8(8)

Symmetry code: ⁱ $-1+x, 1+y, -1+z$; ⁱⁱ $1+x, -1+y, 1+z$; ⁱⁱⁱ $-1+x, y, z$; ^{iv} $1+x, y, z$.

145.97(4) $^{\circ}$. These are in accordance with the distorted tetrahedron configuration.

The complex **2** crystallizes in the monoclinic, $P2_1/c$ space group with four asymmetric units in one unit cell. The asymmetric unit of the complex **2**

consists of two Hg(II) atoms, four iodine ions, one L2 ligand and one solvent DMF molecular (Fig.1). In the complex **2**, each Hg(II) ion atom locates in a distorted coordination tetrahedron and coordinates with one pyridine N atom from L2 ligand and the remaining

three coordination sites of Hg(II) ion are occupied by crystallographically distinct iodine ions. One is terminal iodine ion and two iodine ions act as bridging ligands, which link the Hg(II) centers forming a 1D zig-zag -Hg-I-Hg-I-chain along *a*-axis with bond lengths range: 0.262 1(2) (Hg(1)-I(2)) to 0.323 3(2) nm (Hg(2)-I(3)^{iv}). The adjacent -Hg-I-Hg-I- chains are further connected by bidentate L2 ligand, resulting in a unique 1D double chain with Hg⋯Hg separation of 1.526 6(9) nm (Fig.2). The double chain structure of **2** can be regarded as a ladder-like chain containing two chains -Hg-I-Hg-I- and L2 spacers. The ladder-like chain extends in the *a* direction. To the best of our knowledge, 1D double chain as complex **2** constructed from two -Hg-I-Hg-I- repeating units is not found in literature. Obviously, the structural features of the complex **2** consisting of infinite chain vary significantly with that of the complex **1**. For the complex **2**, the bond lengths of Hg-N are in the range of 0.234 6(10)~0.240 9(10) nm, with the average bond length of 0.237 8 nm. The bond angles of I-Hg-N are within 88.6(3)° (I(1)ⁱⁱⁱ-Hg(1)-N(4)) ~108.4(3)° (I(2)-Hg(1)-N(4)), which

are close to 90° and different from the bond angle of 109°28' for an ideal tetrahedron. These are in accordance with the distorted tetrahedron configuration.

As shown in Fig.3(a), in the crystal lattice of complex **1**, there exist some H-bonding interactions (Table 3) between the lattice DMF molecules and the ligand, including intra-molecular H-bonding interactions (N(2)-H(2)⋯O(3), C(26)-H(26C)⋯O(1)) and intermolecular interactions (N(6)-H(6A)⋯O(1)^v, C(26)-H(26C)⋯O(3)^{vi}) between 1D zig-zag chains. The polymeric chains are held together by these weak interactions, which help to stabilize the molecular and crystal structure. The nitrogen and carbon atoms of the ligand act as hydrogen bond donors, while the DMF molecules serve as acceptors. Also, there are some H-bonding interactions between the lattice DMF molecules and the ligands (L2) in the crystal lattice of complex **2** (Fig.3 (b)), including intramolecular H-bonding interactions (N(6)-H(6B)⋯O(1)) and intermolecular interactions (N(6)-H(6A)⋯O(1)^{iv}). These interactions exist in the ladder-like chain. The parameters of the H-bonds are listed in Table 3.

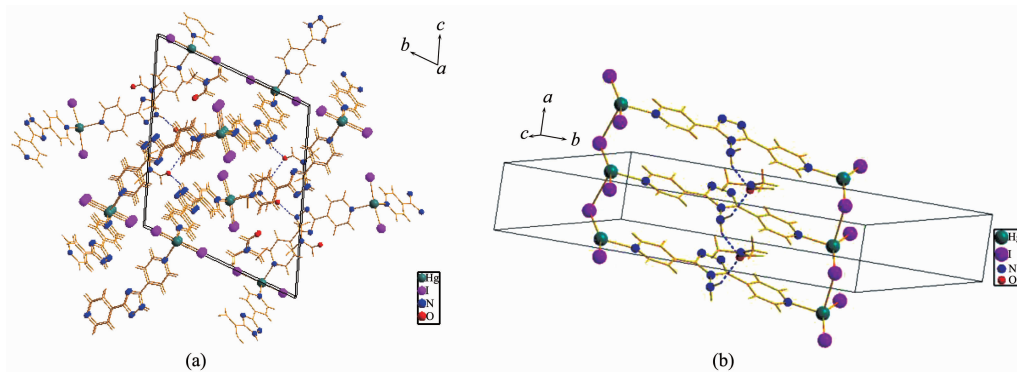


Fig.3 H-bonding interactions for the complexes **1** (a) and **2** (b)

Table 3 Hydrogen bonds and angles for the title complexes

D-H⋯A	<i>d</i> (D-H) / nm	<i>d</i> (H⋯A) / nm	<i>d</i> (D⋯A) / nm	∠DHA / (°)
Compound 1				
N(2)-H(2)⋯O(3)	0.086 00	0.218 00	0.301(2)	160.00
N(6)-H(6A)⋯O(1) ^v	0.086 00	0.199 00	0.283 1(18)	165.00
C(26)-H(26C)⋯O(1)	0.096 00	0.259 00	0.293(2)	101.00
C(26)-H(26C)⋯O(3) ^{vi}	0.096 00	0.224 00	0.301(2)	136.00
Compound 2				
N(6)-H(6B)⋯O(1)	0.090 00	0.213 00	0.289 9(13)	142.00
N(6)-H(6A)⋯O(1) ^{iv}	0.090 00	0.246 00	0.301 0(13)	120.00

Symmetry code: ^{iv} 1+x, y, z; ^v 1-x, -y, 1-z; ^{vi} 1-x, 1-y, 1-z.

2.2 Fluorescence spectra

It is well known that polymeric coordination complexes with d^{10} metal ions and conjugated ligands may be regarded as promising candidates for potential fluorescent materials^[5,32-35]. As shown in Fig.4, the title complexes showed strong luminescent properties in the solid state at ambient temperature. When excited at $\lambda=236$ nm, the luminescent spectrum of the complex **1** exhibited emission peaks at 383.7 nm. Slightly different emission maxima ($\lambda=376.5$ nm) was observed

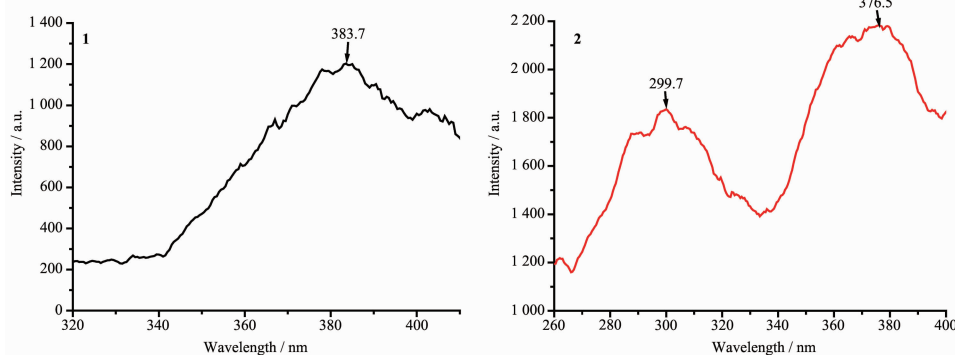


Fig.4 Solid-state fluorescence spectra for the complexes

in complex **2**. These emissions likely originate from ligand-centered $\pi-\pi^*$ or $\pi-n$ electronic transitions^[36] within either the aromatic ring systems of the L1 or L2 ligands, which is a commonly encountered feature within d^{10} -metal coordination polymers^[37-39]. Additionally, the luminescent spectrum of the complex **2** exhibited the second emission peaks at 299.7 nm. The experimental results show that this class of materials may provide potential functional luminescent solids for light-emitting diode applications.

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