

## 基于 2-苯基-1*H*-1,3,7,8-四-氮杂环戊二烯并[*l*]菲的 Pb(II)、Co(II)配合物的晶体结构与发光

李秀颖<sup>1,3</sup> 胡 波<sup>3</sup> 车广波<sup>\*3</sup> 闫永胜<sup>\*2</sup> 关庆丰<sup>1</sup> 李春香<sup>2</sup>

(<sup>1</sup> 江苏大学材料科学与工程学院, 镇江 212013)

(<sup>2</sup> 江苏大学化学化工学院, 镇江 212013)

(<sup>3</sup> 吉林师范大学环境友好材料制备与应用教育部重点实验室, 四平 136000)

**摘要:** 采用水热法合成 2 种配合物 [Pb<sub>2</sub>(ptcp)<sub>2</sub>(DDA)](NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O (**1**) 和 [Co(ptcp)<sub>2</sub>(DDA)(H<sub>2</sub>O)]·0.5H<sub>2</sub>DDA·H<sub>2</sub>O (**2**) (ptcp=2-苯基-1*H*-1,3,7,8-四-氮杂环戊二烯并[*l*]菲, H<sub>2</sub>DDA=1,12-十二烷二酸), 并采用单晶 X-射线衍射、元素分析、红外光谱、X-射线粉末衍射和理论计算对其进行了结构表征。配合物 **1** 和 **2** 分别呈现双核和单核结构, 通过  $\pi$ - $\pi$  和氢键作用形成二维和三维结构。此外, 配合物 **1** 具有较好的发光性质。利用 Gaussian09W 程序, 采用 B3LYP/LANL2DZ 方法对配合物 **1** 进行自然键轨道(NBO)分析。结果表明配位原子与 Pb(II)离子之间存在明显的共价相互作用。

**关键词:** 铅; 钴; 2-苯基-1*H*-1,3,7,8-四-氮杂环戊二烯并[*l*]菲; 1,12-十二烷二酸; 发光

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## Crystal Structure and Photoluminescent Property of Pb(II) and Co(II) Complex Based on 2-Phenyl-1*H*-1,3,7,8-tetra-azacyclopenta[*l*]phenanthrene

LI Xiu-Ying<sup>1,3</sup> HU Bo<sup>3</sup> CHE Guang-Bo<sup>\*3</sup> YAN Yong-Sheng<sup>\*2</sup> GUAN Qing-Feng<sup>1</sup> LI Chun-Xiang<sup>2</sup>

(<sup>1</sup> School of Material Science and Engineering, Jiangsu University, Zhenjiang, Jiangsu 212013, China)

(<sup>2</sup> School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang, Jiangsu 212013, China)

(<sup>3</sup> Key Laboratory of Preparation and Applications of Environmental Friendly Materials,  
Chinese Ministry of Education, Jilin Normal University, Siping, Jilin 136000, China)

**Abstract:** Two complexes, [Pb<sub>2</sub>(ptcp)<sub>2</sub>(DDA)](NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O (**1**) and [Co(ptcp)<sub>2</sub>(DDA)(H<sub>2</sub>O)]·0.5H<sub>2</sub>DDA·H<sub>2</sub>O (**2**) (ptcp=2-phenyl-1*H*-1,3,7,8-tetra-azacyclopenta[*l*]phenanthrene, H<sub>2</sub>DDA=1,12-dodecanedioic acid), have been hydrothermally synthesized and structurally characterized by single-crystal X-ray diffraction, elemental analyses, IR, powder X-ray diffraction and theoretical calculations. Complexes **1** and **2** exhibit binuclear and mononuclear structure, which are further extended to two-dimensional and three-dimensional structure through  $\pi$ - $\pi$  stacking interactions and hydrogen bonds, respectively. Furthermore, complex **1** exhibits excellent photoluminescence at room temperature in the solid state. Natural bond orbital (NBO) analysis was performed by the B3LYP/LANL2DZ method in Gaussian 09W Program. The calculation results show the obvious covalent interaction between the coordinated atoms and Pb(II) ion. CCDC: 997822, **1**; 997823, **2**.

**Key words:** lead; cobalt; 2-phenyl-1*H*-1,3,7,8-tetra-azacyclopenta[*l*]phenanthrene; 1,12-dodecanedioic acid; photoluminescent

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\*通讯联系人。E-mail: guangbochejl@yahoo.com; yys@ujs.edu.cn

The design and syntheses of zero-, one-, two-, three-dimensional complexes is an attractive area of research due to their potential application as functional materials as well as their diversity structures<sup>[1-7]</sup>. In order to obtain the complexes with desirable frameworks and specific functionality, much effort has been devoted to the rational selection of metal ions and multifunctional organic ligands. In this regard, the typical N-donor chelate ligands 1,10-phenanthroline (phen) or its derivatives have been often chosen to construct complexes owing to their excellent binding ability, unique  $\pi$ -electron conjugated systems as well as good hydrogen bonding donors and acceptors<sup>[8-11]</sup>.

Although a large number of complexes constructed by phen or its derivatives have been synthesized, a few complexes in the presence of an auxiliary flexible fatty acid ligands (such as adipic acid, glutaric acid, succinic acid, etc) with diverse coordination modes have appeared in the literature<sup>[12-17]</sup>. In our experiment, we incorporate 2-phenyl-1*H*-1,3,7,8-tetra-azacyclopenta[*l*]phenanthrene (ptcp) and 1,12-dodecanedioic acid (H<sub>2</sub>DDA) into the hydrothermal system including lead and cobalt ions to produce two new complexes, [Pb<sub>2</sub>(ptcp)<sub>2</sub>(DDA)](NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O (**1**) and [Co(ptcp)<sub>2</sub>(DDA)(H<sub>2</sub>O)]·0.5H<sub>2</sub>DDA·H<sub>2</sub>O (**2**). Furthermore, the photoluminescent property and theoretical calculations of complex **1** have also been studied in detail.

## 1 Experimental

### 1.1 Materials and instruments

The ligand ptcp was synthesized according to the literature method<sup>[18]</sup> and all other chemicals were of analytical grade and were used as received. Elemental analyses were recorded on a Perkin-Elmer 240C element analyzer. A Perkin-Elmer 2400LSII spectrometer was used to obtain the IR spectra over the range from 4 000 to 400 cm<sup>-1</sup>. PXRD were obtained with a D/MAX-3C diffractometer with the Cu  $K\alpha$  radiation ( $\lambda=0.154\ 06\ \text{nm}$ ) at room temperature. The  $2\theta$  scanning angle range was 5°~50° at a scanning rate of 5°·min<sup>-1</sup>. Solid state photoluminescent spectrum of **1** at room temperature were recorded with a Perkin-

Elmer LS55 spectrometer. Photoluminescent spectrum was taken on a QuantaMaster and TimeMaster spectrofluorometer (Photon Technology International, Inc.).

### 1.2 Preparation of complexes **1** and **2**

#### 1.2.1 Synthesis of [Pb<sub>2</sub>(ptcp)<sub>2</sub>(DDA)](NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O (**1**)

Pb(NO<sub>3</sub>)<sub>2</sub> (0.165 g, 0.50 mmol), ptcp (0.148 g, 0.50 mmol), H<sub>2</sub>DDA (0.058 g, 0.25 mmol) and NaOH (0.008 g, 0.20 mmol) were dissolved in distilled water (15 mL), and the resulting solution was stirred for about 30 min at room temperature, sealed in a 25 mL Teflon-lined stainless steel autoclave and heated at 428 K for 3 d under autogenous pressure. Upon cooling and opening the bomb, yellow block crystals of **1** were collected with a yield of 67% (based on Pb) by filtration and washed with water and ethanol several times. Anal. Calcd.(%) for C<sub>50</sub>H<sub>48</sub>N<sub>10</sub>O<sub>12</sub>Pb<sub>2</sub>: C, 43.04; H, 3.47; N, 10.04. Found (%): C, 43.01; H, 3.49; N, 10.03. IR (KBr, cm<sup>-1</sup>): 3 477s, 2 913s, 2 846s, 1 573w, 1 532s, 1 513s, 1 460s, 1 427s, 1 388s, 1 351s, 1 075 m, 1 039w, 811w, 735w, 702w, 673w, 637w.

#### 1.2.2 Synthesis of [Co(ptcp)<sub>2</sub>(DDA)(H<sub>2</sub>O)]·0.5H<sub>2</sub>DDA·H<sub>2</sub>O (**2**)

CoSO<sub>4</sub> (0.039 g, 0.25 mmol), ptcp (0.148 g, 0.50 mmol), H<sub>2</sub>DDA (0.115 g, 0.50 mmol) and NaOH (0.016 g, 0.40 mmol) were dissolved in distilled water (15 mL), and the resulting solution was stirred for about 30 min at room temperature, sealed in a 25 mL Teflon-lined stainless steel autoclave and heated at 428 K for 3 d under autogenous pressure. Upon cooling and opening the bomb, brown block crystals of **2** were collected with a yield of 44% (based on Co) by filtration and washed with water and ethanol several times. Anal. Calcd.(%) for C<sub>56</sub>H<sub>59</sub>CoN<sub>8</sub>O<sub>8</sub>: C, 65.23; H, 5.77; N, 10.88. Found (%): C, 65.20; H, 5.79; N, 10.93. IR (KBr, cm<sup>-1</sup>): 3 440s, 2 922s, 2 850s, 1 605s, 1 554s, 1 455s, 1 402s, 1 385s, 1 360m, 1 113m, 1 174 m, 950w, 807w, 733m, 704m, 640w.

### 1.3 Structure determination

The diffraction data were collected at 292 K on a Bruker-AXS Smart CCD diffractometer equipped with a graphite-monochromatized Mo  $K\alpha$  radiation ( $\lambda = 0.071\ 073\ \text{nm}$ ) by using an  $\omega$  scan mode. For **1**, a total of 13 054 reflections were collected in the range

of  $1.67^\circ \leq \theta \leq 26.03^\circ$ , of which 4 743 ( $R_{\text{int}}=0.032\ 6$ ) were independent and 3 762 with  $I > 2\sigma(I)$  were used in the structure determination and refinement. The final  $R=0.027\ 1$  and  $wR=0.059\ 0$  ( $w=1/[\sigma^2(F_o^2)(0.030\ 2P)^2+0.651\ 1P]$ , where  $P=(F_o^2+2F_c^2)/3$ ).  $S=1.015$ ,  $(\Delta\rho)_{\text{max}}=1\ 069\ \text{e}\cdot\text{nm}^{-3}$  and  $(\Delta\rho)_{\text{min}}=-632\ \text{e}\cdot\text{nm}^{-3}$  and  $(\Delta/\sigma)_{\text{max}}=0.001$ . And for **2**, a total of 53 919 reflections were collected in the range of  $1.71^\circ \leq \theta \leq 26.00^\circ$ , of which 10 084 ( $R_{\text{int}}=0.047\ 8$ ) were independent and 6 937 with  $I > 2\sigma(I)$  were used in the structure determination and refinement. The final  $R=0.088\ 1$  and  $wR=0.209\ 8$  ( $w=1/[\sigma^2(F_o^2)(0.053\ 3P)^2+36.442\ 6P]$ , where  $P=(F_o^2+2F_c^2)/3$ ).  $S=1.152$ ,  $(\Delta\rho)_{\text{max}}=843\ \text{e}\cdot\text{nm}^{-3}$  and  $(\Delta\rho)_{\text{min}}=-689\ \text{e}\cdot\text{nm}^{-3}$  and  $(\Delta/\sigma)_{\text{max}}=0.003$ . Crystal structures were solved by the direct method and refined using SHELX-97<sup>[19]</sup> by full-matrix least-squares techniques on  $F^2$ . All non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically. Except the solvent molecules in complex **1**, hydrogen atoms were localized in their calculated positions and refined using a riding model.

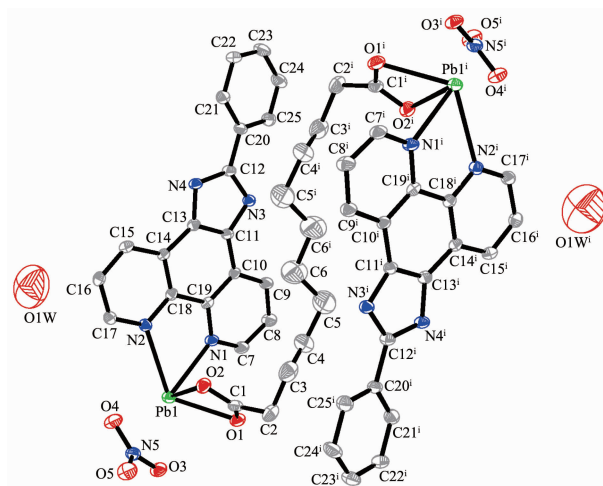
CCDC: 997822, **1**; 997823, **2**.

## 2 Results and discussion

### 2.1 Description of the crystal structure

The X-ray crystallographic study reveals that **1** crystallizes in the monoclinic system,  $P2_1/c$  space group. The molecular structure of **1** contains two Pb(II) cations, two ptcp ligand, one DDA anion fragment, two nitrate and two free water molecules (Fig.1). Each Pb(II) atom adopt distorted tetrahedral coordination geometry coordinated by two N atoms (N(1), N(2)) from one ptcp ligand, two O atoms (O(1), O(2)) from

one DDA ligands. The Pb-O and Pb-N distances are similar to those of reported<sup>[20]</sup>. Selected bond lengths and angles are reported in Table 1. Pb(II) ions are bridged by the carboxylate oxygen atoms to form a novel binuclear Pb(II) cluster with Pb...Pb distance *ca.* 1.443 9 nm. In **1**, there are intramolecular  $\pi$ - $\pi$  interactions between two adjacent ptcp rings with 0.358 6(3) nm between Cg(1) and Cg(2) rings, 0.355 5(3) nm between Cg(3) and Cg(3) rings (defined rings Cg(1): N(3)→C(11)→C(13)→N(4)→C(12), Cg(2): N(2)→C(17)→C(16)→C(15)→C(14)→C(18), Cg(3): C(10)→C(11)→C(13)→C(14)→C(18)→C(19)). Complex **1** is linked by these  $\pi$ - $\pi$  interactions to form a one-dimensional chain, and these chains are further connected to form stabilizing two-dimensional network structure by N-H...O hydrogen bonding involving imidazole rings of ptcp ligands and nitrate anions (Fig.2).



Hydrogen atoms were omitted for clarity, Symmetry code:  $i -x, -y+1, -z+1$

Fig.1 ORTEP view of complex **1** with 30% probability displacement ellipsoids

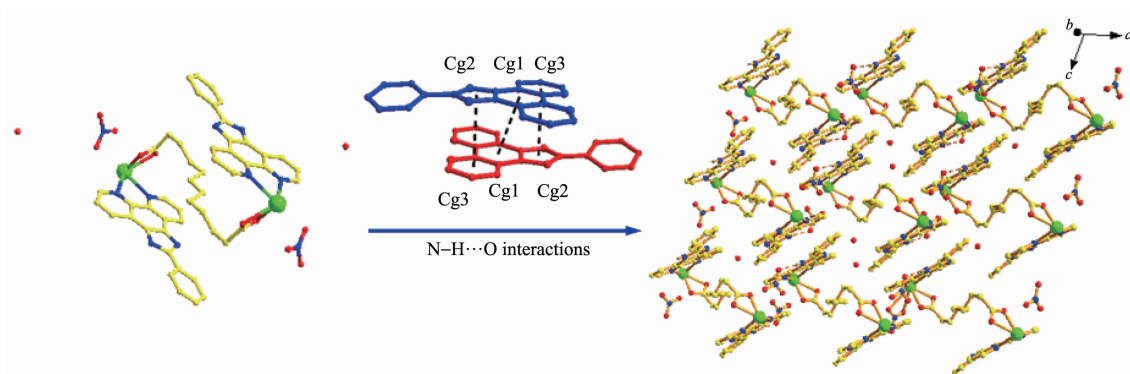


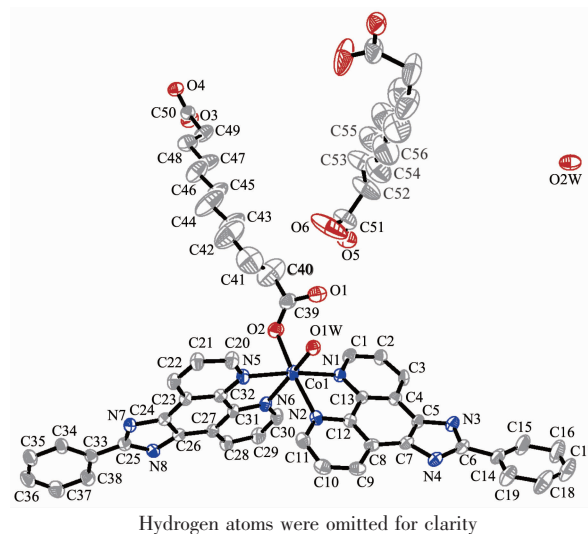
Fig.2 Two-dimensional structure formed through  $\pi$ - $\pi$  stacking and hydrogen-bond interactions

**Table 1** Selected bond lengths (nm) and bond angles (°) of complexes **1** and **2**

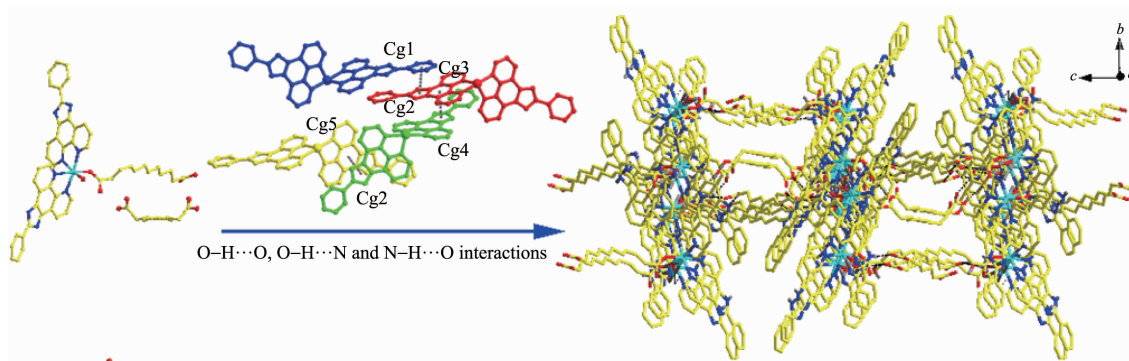
Complex <b>1</b>					
Pb(1)-N(1)	0.249 3(4)	Pb(1)-N(2)	0.263 3(4)	Pb(1)-O(2)	0.237 7(3)
Pb(1)-O(1)	0.246 0(3)				
O(2)-Pb(1)-O(1)	54.07(11)	O(2)-Pb(1)-N(1)	80.79(12)	O(1)-Pb(1)-N(2)	118.34(11)
O(1)-Pb(1)-N(1)	76.31(11)	O(2)-Pb(1)-N(2)	73.86(11)	N(1)-Pb(1)-N(2)	63.93(11)
Complex <b>2</b>					
Co(1)-N(1)	0.213 9(4)	Co(1)-N(2)	0.215 9(4)	Co(1)-N(5)	0.215 6(4)
Co(1)-N(6)	0.213 4(4)	Co(1)-O(2)	0.205 5(4)	Co(1)-O(1W)	0.208 0(4)
O(2)-Co(1)-O(1W)	96.16(19)	O(2)-Co(1)-N(6)	92.25(18)	O(1W)-Co(1)-N(6)	165.30(18)
O(2)-Co(1)-N(1)	96.60(18)	O(1W)-Co(1)-N(1)	94.04(17)	N(6)-Co(1)-N(1)	96.95(16)
O(2)-Co(1)-N(5)	87.68(19)	O(1W)-Co(1)-N(5)	91.53(17)	N(6)-Co(1)-N(5)	76.75(16)
N(1)-Co(1)-N(5)	172.56(17)	O(2)-Co(1)-N(2)	173.21(18)	O(1W)-Co(1)-N(2)	84.60(18)
N(6)-Co(1)-N(2)	88.47(16)	N(1)-Co(1)-N(2)	76.61(16)	N(5)-Co(1)-N(2)	99.05(17)

As shown in Fig.3, the asymmetric unit of complex **2** contains the mononuclear unit [Co(ptcp)<sub>2</sub>(DDA)(H<sub>2</sub>O)], half uncoordinated H<sub>2</sub>DDA ligand and one lattice water molecule. Each Co(II) atom is six-coordinated by four N atoms (N(1), N(2), N(5), N(6)) from two ptcp ligand, one O atoms (O(2)) from one DDA ligands, and one water molecule (O(1W)). The average Co-O and Co-N distances for **2** are near to those of reported (Table 1)<sup>[21]</sup>. As shown in Fig.4, a three-dimensional network are constructed from three different types of hydrogen bonding interactions, described as follows: (i) O(5)–H(5)···O(1) hydrogen bonding involving the carboxylic O atom (O(5)) from uncoordinated H<sub>2</sub>DDA molecule as donors and O atom (O(1)) from the DDA ligands as acceptors. (ii) O–H···O (or O–H···N) hydrogen bonding involving the water molecules (O1W and O2W) as donors and N atom of

ptcp ligand (N7<sup>i</sup>, Symmetry code: <sup>i</sup>  $-x+1/2, y-1/2, z$ ), O atom from water molecule (O2W<sup>ii</sup>, Symmetry code:



**Fig.3** ORTEP view of complex **2** with 30% probability displacement ellipsoids



**Fig.4** Three-dimensional structure of complex **2** formed through hydrogen-bond and  $\pi$ - $\pi$  stacking interactions

**Table 2** Selected natural atomic charges (e) and natural electron configuration for complex **1**

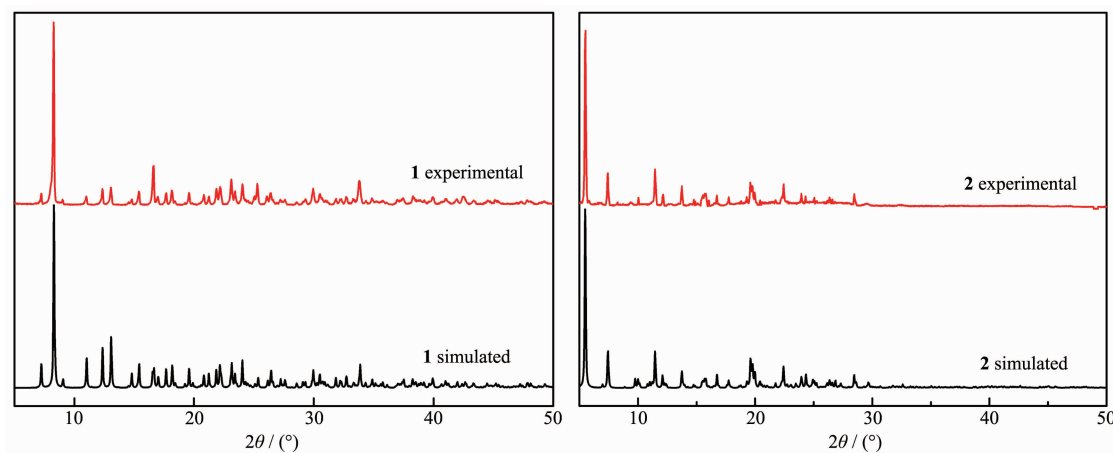
Atom	Net charge	Electron configuration
Pb(1)	1.445	[core]6s(1.92)6p(0.63)7p(0.01)
O(1)	-0.775	[core]2s(1.72)2p(5.04)3p(0.01)
O(2)	-0.804	[core]2s(1.73)2p(5.06)3p(0.01)
N(1)	-0.594	[core]2s(1.37)2p(4.20)3p(0.02)
N(2)	-0.554	[core]2s(1.37)2p(4.16)3p(0.02)

<sup>ii</sup>  $x, y+1, z$ ) or carboxylic O atoms (O4<sup>iii</sup>, O6<sup>iv</sup>, Symmetry code: <sup>iii</sup>  $-x, y-1, -z+1/2$ ; <sup>iv</sup>  $x, y-1, z$ ) as acceptors. (iii) N-H...O hydrogen bonding involving N atoms (N4, N8) from imidazole rings of ptcp ligands as donors and carboxylic O atoms (O3<sup>v</sup>, O4<sup>vi</sup>, Symmetry code: <sup>v</sup>  $x+1, -y+2, z+1/2$ ; <sup>vi</sup>  $-x-1/2, -y+5/2, z+1/2$ ) as acceptors. It is noted that there are apparent  $\pi$ - $\pi$  interactions between the ptcp rings. The face-to-face

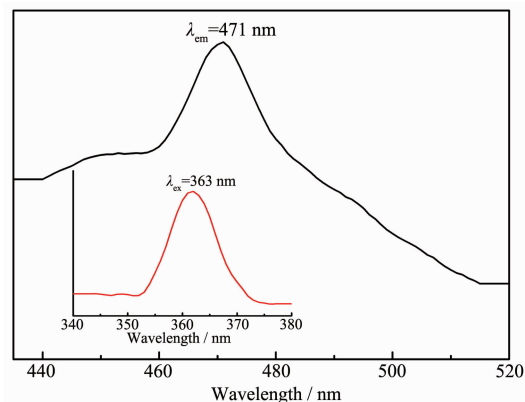
distances are 0.359 8 nm between Cg (1) and Cg(2) rings, 0.358 5 nm between Cg(3) and Cg(4) rings, 0.356 2 nm between Cg(2) and Cg(5) rings (defined rings Cg (1): C(33)→C(34)→C(35)→C(36)→C(37)→C(38), Cg (2): N(7)→C(24)→C(26)→N(8)→C(25), Cg (3): C(23)→C(24)→C(26)→C(27)→C(31)→C(32), Cg(4): N(3)→C(5)→C(7)→N(4)→C(6), Cg(5): C(4)→C(5)→C(7)→C(8)→C(12)→C(13)). Consequently, complex **2** are linked by these  $\pi$ - $\pi$  interactions to form a stabilizing network structure.

## 2.2 Powder X-ray diffraction (PXRD) and photoluminescent properties

The simulated and experimental PXRD pattern of complexes **1** and **2** are showed in Fig.5, the peak positions are in good agreement with each other, indicating the phase purity of products.

Fig.5 Simulated and experimental PXRD patterns of complexes **1** and **2**

As known, Pb(II)-complex has been found to exhibit photoluminescence properties, accordingly, the photoluminescence properties of complex **1** in solid

Fig.6 Emission and excitation spectra (inset) of **1**

state at room temperature were examined. As shown in Fig.6, it can be seen that **1** exhibits photoluminescence in solid state at room temperature with emission maximum at 471 nm upon excitation at 363 nm. According to the literature, the main emission peaks of the free ptcp ligand are at 475 nm ( $\lambda_{ex}$ =393 nm)<sup>[11]</sup>. Relative to the free ptcp ligand the emission spectrum of the **1** is similar to the free ligand, which probably originates from the intraligand transition of the coordinated ligands.

## 2.3 Theoretical calculations

The Gaussian09W program<sup>[22]</sup> was used in the calculation. The parameters of the molecular structure for calculation were all from the experimental data of



the complex **1**. Natural bond orbital (NBO) analysis was performed by density functional theory (DFT)<sup>[23]</sup> with the B3LYP<sup>[24-26]</sup> hybrid functional and the LANL2DZ basis set<sup>[27]</sup>.

The selected natural atomic charges and natural electron configuration for the complex is shown in Table 2. It is indicated that the electronic configurations of Pb(II) ion, O and N atoms are  $6s^{1.92}6p^{0.63}7p^{0.01}$ ,  $2s^{1.72,1.73}2p^{5.04,5.06}3p^{0.01}$  and  $2s^{1.37}2p^{4.16,4.20}3p^{0.02}$ , respectively. Based on the above results, one can conclude that the Pb(II) ion coordination with N and O atoms is mainly on 6s, and 6p orbitals (the electron number of 7p orbit is so small that can be omitted). N atoms and O atoms form coordination bonds with Pb(II) ion using 2s

and 2p orbitals (the electron number of 3p orbit is so small that can be omitted). Therefore, the Pb(II) ion obtained some electrons from two N atoms of ptpc ligand and two O atoms of DDA ligand. Thus, according to valence-bond theory the atomic net charge distribution in the complex shows the obvious covalent interaction between the coordinated atoms and Pb(II) ion.

As can be seen from the Fig.7, the HOMO, HOMO-1 and HOMO-2 are mainly composed of the  $\pi$  orbital of ptpc ligand. The LUMO, LUMO+1 and LUMO+2 are all mainly composed of the  $\pi$  orbital of ptpc ligand. The result further verified our supposition about the type of energy transfer, which is derived from the ligand to ligand charge transition.

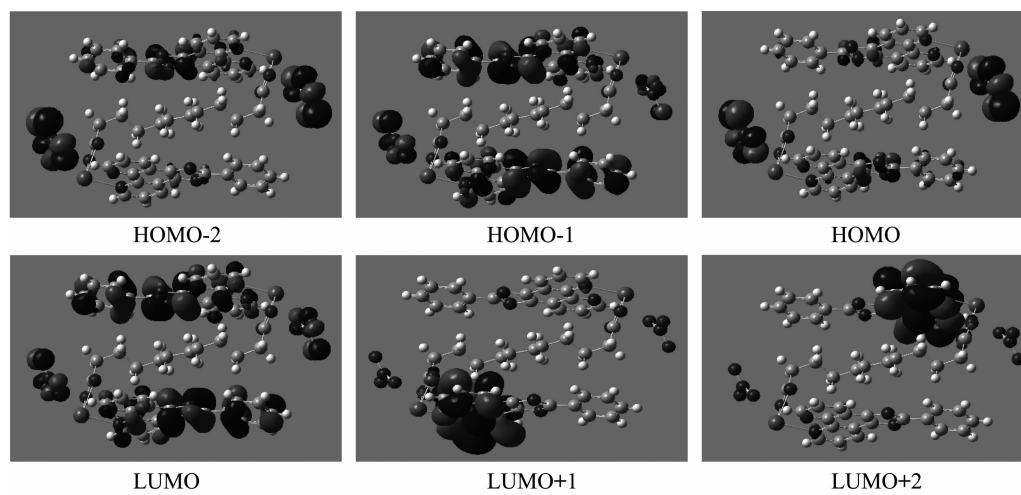


Fig.7 View of frontier orbitals of complex **1**

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