

两个 7-氧杂-二苯苈-3,11-二磺酸镉化合物的 合成、结构与荧光性质研究

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摘要: 通过使用浓硫酸对 2,2'-二羟基-1,1'-二萘的磺化与成环反应得到一种新配体, 7-氧杂-二苯苈-3,11-二磺酸。通过水热方法得到了它的两个化合物, $[\text{CdL}(\text{bipy})_2(\text{H}_2\text{O})][\text{Cd}(\text{bipy})_2(\text{H}_2\text{O})_2] \cdot \text{L} \cdot \text{H}_2\text{O}$ (**1**) 和 $[\text{CdL}(\text{phen})_2(\text{H}_2\text{O})] \cdot 5\text{H}_2\text{O}$ (**2**), 并通过 X-射线单晶衍射分析进行结构表征。化合物 **1** 以 $P\bar{1}$ 空间群结晶, 晶胞参数为 $a=1.205\ 5(6)$, $b=1.576\ 4(8)$, $c=1.954\ 5(10)$ nm, $\alpha=75.755(9)^\circ$, $\beta=88.093(10)^\circ$, $\gamma=89.035(10)^\circ$ 。化合物 **2** 以 $P2_1/c$ 空间群结晶, 晶胞参数为 $a=2.104\ 0(7)$, $b=1.358\ 0(4)$, $c=1.428\ 9(5)$ nm, $\beta=94.543(6)^\circ$ 。在化合物 **1** 中, 有两个独立的镉(II)离子不对称单元, 在其中镉(1)离子和两个联吡啶上的四个氮原子, 磺酸配体上的一个氧原子及一个水分子配位; 镉(2)离子和两个联吡啶上的四个氮原子和两个水分子配位。两种固体化合物在室温下均显示强的蓝色荧光。

关键词: 7-氧杂-二苯苈-3,11-二磺酸; 镉化合物; 结构; 荧光

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Synthesis, Structures, and Photoluminescence Studies of Two Cadmium(II) Complexes of 7-Oxa-dibenzofluorene-3,11-disulfonate

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Abstract: A new ligand, 7-oxa-dibenzofluorene-3,11-disulfonic acid (H_2L), was synthesized by sulfonation and ring closure of 2,2'-dihydroxyl-1,1'-binaphthalene with concentrated sulfuric acid. Its two complexes, $[\text{CdL}(\text{bipy})_2(\text{H}_2\text{O})][\text{Cd}(\text{bipy})_2(\text{H}_2\text{O})_2] \cdot \text{L} \cdot \text{H}_2\text{O}$ (**1**) (bipy=2,2'-(bipyridyl) and $[\text{CdL}(\text{phen})_2(\text{H}_2\text{O})] \cdot 5\text{H}_2\text{O}$ (**2**) (phen=1,10-phenanthroline), were obtained by a hydrothermal route, and structurally characterized by X-ray single-crystal diffraction. Compound **1** crystallized in space group $P\bar{1}$ with cell parameters $a=1.205\ 5(6)$, $b=1.576\ 4(8)$, $c=1.954\ 5(10)$ nm, $\alpha=75.755(9)^\circ$, $\beta=88.093(10)^\circ$, and $\gamma=89.035(10)^\circ$. In **1**, there are two independent Cd(II) ions in the asymmetric unit, in which one Cd(1) ion is coordinated with four nitrogen atoms from two bipy molecules, one oxygen atom of L^{2-} anion, and one water molecule; the Cd(2) ion is coordinated with four bipyridyl nitrogen atoms and two water molecule. Compound **2** crystallized in space group $P2_1/c$ with cell parameters $a=2.104\ 0(7)$, $b=1.358\ 0(4)$, $c=1.428\ 9(5)$ nm, and $\beta=94.543(6)^\circ$. In **2**, the coordination environment of Cd(II) ion is similar to that of Cd(1) ion in **1**, producing a mononuclear unit. Both compounds exhibit strong blue photoluminescence in the solid state at room temperature. CCDC: **1**, 258028; **2**, 258029.

Key words: 7-oxa-dibenzofluorene-3,11-disulfonic acid; cadmium complex; structures; photoluminescence

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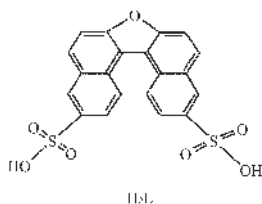
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0 Introduction

Interest in coordination polymers built from aromatic multi-acid has mushroomed recently^[1-3], not only for the interesting molecular topologies and crystal packing motifs that they exhibit, but also for the fact that they may possess potential exploitable properties. More recently, Wen et al^[1,2] reported a series of coordination polymers of 2,2'-dihydroxy-[1,1']-binaphthalene-6,6'-dicarboxylate and its derivative with different size of cavities and channels, and some of them show interesting and useful chiral catalytic properties with high e.e.%^[2]. Complexes of d10 metal with an analogical ligand (2,2'-dihydroxy-[1,1']-binaphthalene-3,3'-dicarboxylate) display photoluminescent properties in the blue/green range^[4].

In comparison with the arene multicarboxylate ligands, the arene multisulfonates have better solubility and higher acidity in aqueous solution, and their metal complexes show higher thermal stability^[5,6]. So we use sulfonate instead of dicarboxylate to synthesize a new ligand (7-oxa-dibenzofluorene-3,11-disulfonic acid, H_2L) and its Cd(II) complexes, and try to know what properties they will show. In this paper, we report on the synthesis and photoluminescent properties of the free ligand and its two cadmium(II) complexes, $[CdL(bipy)_2(H_2O)][Cd(bipy)_2(H_2O)_2] \cdot L \cdot H_2O$ (**1**) and $[CdL(phen)_2(H_2O)] \cdot 5H_2O$ (**2**).



1 Experimental

1.1 Materials and physical measurements

2,2'-dihydroxyl-1,1'-binaphthalene was prepared according to a literature method^[7]. All reagents and solvents were commercially available and were used as received.

Elemental analyses were carried out with an elemental Vario EL elemental analyzer. FTIR spectra were recorded in the 4000~400 cm^{-1} region using KBr pellets and a Bruker EQUINOX 55 FTIR spectrometer. The emission/excitation spectra were recorded on a

HITACHI F-4500 fluorescence spectrophotometer.

1.2 Synthesis

1.2.1 Preparation of H_2L

2,2'-Dihydroxyl-1,1'-binaphthalene (DBN) (5.0 g, 17.5 mmol) was added slowly to an ice-water cooled solution of concentrated sulfuric acid (5.3 mL) under stirring. The reaction temperature was rose to 100 °C and kept at this temperature for 20 h. After cooling to room temperature, 40 mL of water was added; the resulting mixture was filtered to separate the unreacted DBN, the filtrate was extracted with ethyl acetate (3 × 15 mL) to remove trace amount of byproduct. To the water extracts, $NaHCO_3$ (2.9 g, 34.5 mmol) was added carefully to neutralize the solution, and then NaCl (8.0 g, 0.137 mol) and activated carbon were added. The resulting mixture was boiled for about 10 minutes and filtered while still hot. Cooling of the filtrate to room temperature leaded to Na_2L , which was collected by suction filtration. Acidification the saturated solution of Na_2L with concentrated hydrochloric acid gave the product of H_2L . Yield: 43 %. ESI-MS: $m/z=427.1$.

1.2.2 Preparation of $[CdL(bipy)_2(H_2O)][Cd(bipy)_2(H_2O)_2] \cdot L \cdot H_2O$ (**1**)

A mixture of H_2L (0.100 g, 0.233 mmol), bipy (0.054 g, 0.346 mmol), $Cd(CH_3COO)_2 \cdot 2H_2O$ (0.046 g, 0.173 mmol), and H_2O (10 mL) were sealed in a Parr Teflon-lined stainless steel vessel (23 mL) after brief stirring, heated to 160 °C and held at that temperature for 80 h, then cooled to 100 °C at a rate of 10 °C·h⁻¹, followed by further cooling to room temperature. Pale-red crystals of **1** were collected, washed with small amount of water and ethanol, and dried in air (39% yield based on Cd). Elemental analysis (%) Calcd. for $C_{80}H_{67}N_8O_{21.5}S_4Cd_2$ (**1**·3.5 H_2O): C, 52.29; H, 3.68; N, 6.10. Found: C, 52.22; H, 3.43; N, 6.10. IR spectra (KBr, cm^{-1}): 3 418m, 3 111w, 3 073w, 1 596m, 1 574w, 1 517w, 1 475w, 1 438s, 1 396w, 1 372w, 1 320w, 1 235vs, 1 178vs, 1 159s, 1 120m, 1 097m, 1 063w, 1 034vs, 1 016s, 988w, 941w, 904w, 813w, 766s, 736w, 704w, 681s, 652m, 626m, 608w, 561w, 534w, 484w.

1.2.3 Preparation of $[CdL(1,10-phen)_2(H_2O)] \cdot 5H_2O$ (**2**)

A mixture of H_2L (0.100 g, 0.233 mmol), phen (0.068 g, 0.346 mmol), $Cd(CH_3COO)_2 \cdot 2H_2O$ (0.046 g, 0.173 mmol), and H_2O (10 mL) were sealed in a Parr Teflon-lined stainless steel vessel (23 mL) after brief

stirring, heated to 160 °C and held at that temperature for 80 h, then cooled to 100 °C at a rate of 5 °C·h⁻¹, followed by further cooling to room temperature. Pale-yellow crystals of **2** were collected, washed with water and ethanol, and dried in air (74% yield based on Cd). Elemental analysis (%) Calcd. for C₄₄H₄₀N₄O₁₄S₂Cd (**2**·H₂O): C, 51.54; H, 3.93; N, 5.46. Found: C, 51.81; H, 3.97; N, 5.54. IR spectra (KBr, cm⁻¹): 3 424m, 3 059m, 1 621m, 1 582w, 1 515m, 1 451w, 1 426s, 1 372w, 1 341w, 1 228vs, 1 167vs, 1 121s, 1 098s, 1 032vs, 986w, 941w, 900w, 848s, 809m, 726s, 704w, 680s, 651m, 627s, 607m, 560w, 535w, 426w.

1.3 Determination of the crystal structure

Single-crystal data for **1** and **2** were collected on a Bruker Smart 1000 CCD diffractometer with Mo K α

radiation ($\lambda=0.071\ 073\ \text{nm}$) at 288(2) K and 296(2) K, respectively. The structures were solved using direct methods, which yielded the positions of all non-hydrogen atoms. These atoms were refined first with isotropic and then with anisotropic thermal parameters to convergence. All of the hydrogen atoms bound to carbon were placed in calculated positions with fixed isotropic thermal parameters and included in structure factor calculations in the final stage of full-matrix least-squares refinement. All calculations were performed using the SHELXTL system of computer programs^[8]. The crystal data are listed in Table 1, and selected bond distances and angles are present in Table 2.

CCDC: **1**, 258028; **2**, 258029.

Table 1 Crystal data and structure refinement for compounds **1** and **2**

Compound	1	2
Chemical formula	C ₈₉ H ₆₀ N ₈ O ₁₈ S ₄ Cd ₂	C ₄₄ H ₃₈ N ₄ O ₁₃ S ₂ Cd
Molecular weight	1774.46	1007.33
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a / nm	1.205 5(6)	2.104 0(7)
b / nm	1.576 4(8)	1.358 0(4)
c / nm	1.954 5(10)	1.428 9(5)
$\alpha / (^\circ)$	75.755(9)	90
$\beta / (^\circ)$	88.093(10)	94.543(6)
$\gamma / (^\circ)$	89.035(10)	90
V / nm^3	3.598(3)	4.070(2)
Z	2	4
$D(\text{calc.}) / (\text{g}\cdot\text{cm}^{-3})$	1.639	1.644
Absorption coefficient / mm ⁻¹	0.789	0.715
$F(000)$	1802	2056
θ range for data collection / (°)	1.33 to 25.00	0.97 to 27.14
Reflections collected / unique	25 681 / 12 488	26 737 / 8 903
Transmission factors	0.890 9~0.693 8	0.900 3~0.777 8
Data / restraints / parameters	12 488 / 0 / 1 009	8 903 / 0 / 577
Goodness of fit	1.050	1.030
$R(F)$; $R_w(F)$ ($I > 2\sigma(I)$)	0.062 5, 0.177 3	0.041 6, 0.108 0

Table 2 Selected bond distances (nm) and angles (°) for **1** and **2**

[CdL(bipy) ₂ (H ₂ O)] [Cd(bipy) ₂ (H ₂ O) ₂]·L·H ₂ O (1)					
Cd(1)-O(W1)	0.226 9(6)	Cd(1)-N(2)	0.230 3(7)	Cd(1)-N(4)	0.230 5(6)
Cd(1)-N(1)	0.231 2(7)	Cd(1)-O(12)	0.231 9(6)	Cd(1)-N(3)	0.234 0(7)
Cd(2)-N(8)	0.229 2(7)	Cd(2)-N(6)	0.230 4(7)	Cd(2)-N(5)	0.230 8(7)
Cd(2)-O(W2)	0.230 6(6)	Cd(2)-N(7)	0.236 4(7)	Cd(2)-O(W3)	0.237 8(6)
O(W4)···O(2)	0.276 1(7)	O(W1)···O(W4)	0.266 4(10)	O(W4)···O(2)	0.276 1(7)

O(W1)-Cd(1)-N(2)	91.6(3)	O(W1)-Cd(1)-N(4)	99.9(2)	N(2)-Cd(1)-N(4)	166.2(2)
O(W1)-Cd(1)-N(1)	160.5(3)	N(2)-Cd(1)-N(1)	71.6(3)	N(4)-Cd(1)-N(1)	98.3(2)
O(W1)-Cd(1)-O(12)	85.4(3)	N(2)-Cd(1)-O(12)	89.0(3)	N(4)-Cd(1)-O(12)	99.5(3)
N(1)-Cd(1)-O(12)	84.6(3)	O(W1)-Cd(1)-N(3)	83.5(2)	N(2)-Cd(1)-N(3)	102.6(2)
N(4)-Cd(1)-N(3)	71.4(2)	N(1)-Cd(1)-N(3)	109.2(3)	O(12)-Cd(1)-N(3)	164.1(2)
N(8)-Cd(2)-N(6)	156.1(3)	N(8)-Cd(2)-N(5)	125.3(3)	N(6)-Cd(2)-N(5)	71.3(3)
N(8)-Cd(2)-O(W2)	88.6(2)	N(6)-Cd(2)-O(W2)	85.6(2)	N(5)-Cd(2)-O(W2)	139.1(2)
N(8)-Cd(2)-N(7)	70.5(3)	N(6)-Cd(2)-N(7)	88.3(3)	N(5)-Cd(2)-N(7)	109.0(2)
O(W2)-Cd(2)-N(7)	103.4(2)	N(8)-Cd(2)-O(W3)	93.7(3)	N(6)-Cd(2)-O(W3)	107.3(2)
N(5)-Cd(2)-O(W3)	79.1(2)	O(W2)-Cd(2)-O(W3)	76.1(2)	N(7)-Cd(2)-O(W3)	164.2(2)
[CdL(1,10-phen) ₂ (H ₂ O)]·5H ₂ O (2)					
Cd(1)-N(2)	0.231 2(3)	Cd(1)-N(1)	0.232 0(3)	Cd(1)-O(W1)	0.232 2(3)
Cd(1)-N(4)	0.233 3(3)	Cd(1)-N(3)	0.233 6(3)	Cd(1)-O(4)	0.233 6(3)
O(2)···O(W2)	0.277 6(6)	O(W1)···O(6)	0.272 4(3)	O(5)···O(W5)	0.282 2(4)
N(2)-Cd(1)-N(1)	71.85(11)	N(2)-Cd(1)-O(W1)	106.30(11)	N(1)-Cd(1)-O(W1)	89.11(11)
N(2)-Cd(1)-N(4)	94.84(11)	N(1)-Cd(1)-N(4)	112.43(10)	O(W1)-Cd(1)-N(4)	153.85(10)
N(2)-Cd(1)-N(3)	162.63(11)	N(1)-Cd(1)-N(3)	102.37(11)	O(W1)-Cd(1)-N(3)	89.71(10)
N(4)-Cd(1)-N(3)	71.85(10)	N(2)-Cd(1)-O(4)	81.90(11)	N(1)-Cd(1)-O(4)	147.17(10)
O(W1)-Cd(1)-O(4)	79.51(11)	N(4)-Cd(1)-O(4)	88.65(10)	N(3)-Cd(1)-O(4)	108.20(10)

2 Results and discussion

2.1 Crystal structures

As illustrated in Fig.1, the asymmetric unit of **1** contains two six coordinated Cd(II) ions, two L²⁻ anions, four bipy and four water molecules. The Cd(1) atom is coordinated with four nitrogen atoms from two bipy molecules, one oxygen atom of L²⁻ anion, and one water molecule. The Cd(1)-N(3) and Cd(1)-O(12) axial distances (0.234 0(7) and 0.231 9(6) nm) are slightly longer than the Cd(1)-N equatorial distances (0.230 3(6)~0.231 2(7) nm). The Cd(2) atom has a similar coordination environment as that in Cd(1) atom instead of one coordinated oxygen atom of L²⁻ is replaced by a water molecules. The Cd(2)-N(7) and Cd(2)-Ow(3) axial distances (0.236 4(7) and 0.237 8(6) nm) are also longer than the Cd(2)-N and Cd(2)-O equatorial distances (0.229 2(7)~0.230 8(6) nm). In compound **1**, one of the L²⁻ ligands exhibits the monodentate coordination mode with the dihedral angle of 18.8° between two naphthyl rings; the other one simply serves as a free linking group (dihedral angle=20.5°), which connects the [Cd(bipy)₂(H₂O)₂]²⁺ unit via hydrogen bond between sulfonic O(4) atom and Ow(2) atom (O(4)···Ow(2)=0.262 1 nm), and the other [CdL(bipy)₂(H₂O)] unit through the uncoordinated Ow(4) atom (Ow(4)···O(2)=

0.276 1, Ow(4)···Ow(1)=0.266 4 nm). There are intermolecular $\pi \cdots \pi$ interactions between the uncoordinated L²⁻ plane and one of bipy plane (0.340 nm), and between the two adjacent bipy plane (0.349 nm).

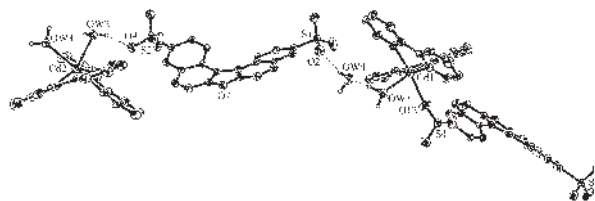


Fig.1 ORTEP drawing of **1** with atomic numbering scheme

Thermal ellipsoids are drawn at the 30% level.

The structure of complex **2** (see Fig.2a) is different from that of **1**, in which there is only one Cd(II) atom in the asymmetric unit. The coordination geometry of Cd(II) atom in **2** is similar to that of Cd(1) in **1**, which is six-coordinated with four nitrogen atoms of two phen, one oxygen atom of L²⁻, and one water molecule. The Cd(1)-N distances (0.231 2(3)~0.233 6(3) nm) are closed to the Cd(1)-N distances in **1** (0.230 3(7)~0.234 0(7) nm), while the Cd(1)-Ow(1) and Cd(1)-O(4) distances (0.232 2(3) and 0.233 6(3) nm) are longer than the Cd(1)-Ow(1) and Cd(1)-O(12) distances (0.227 8(6) and 0.231 9(6) nm) in **1**. There is intramolecular π - π stacking interaction between one phen molecule and L²⁻ anion in **2** with the face-to-face

distance of 0.343 nm and dihedral angle of 2.1° , while the intramolecular π - π interaction is not formed in **1** due to the smaller bipy plane. The above phen also forms intermolecular π - π interaction with adjacent L^{2-} with the face to face distance of 0.332 nm, resulting in 1D polymer along c axis (see Fig.2b). The 1D polymers are held together via π - π interactions between the two adjacent phen molecules to form 2D polymer.

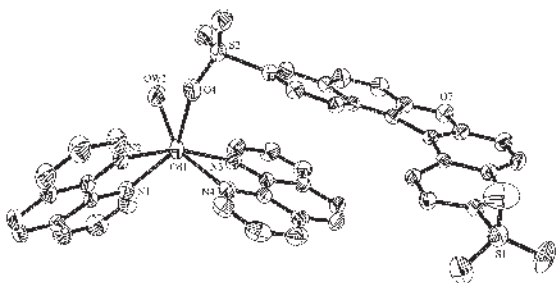


Fig.2a ORTEP drawing of **2** with atomic numbering scheme
Thermal ellipsoids are drawn at the 30% level.

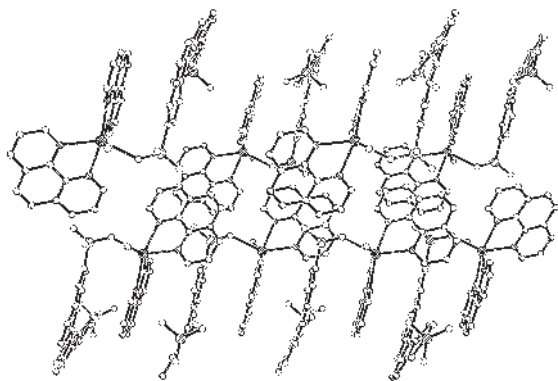


Fig.2b 2D polymer constructed by intermolecular π - π interactions

2.2 Photoluminescent properties

The free ligand H_2L , and its sodium salt Na_2L , complex **1** and **2** display intense blue luminescence with emission maximum at 441, 447, 456 and 460 nm, respectively, upon excitation at 383 nm in the solid state at ambient temperature (Fig.3), which can be attributed to the $\pi \rightarrow \pi^*$ transitions of the ligand^[9,10]. Among the all four compounds, Na_2L shows the highest photoluminescent intensity due to its rich electro-density^[10]. In **1**, the coordination interactions as well as intermolecular hydrogen bond and π - π interactions lead to the electroreduction of L^{2-} anions, and this causes the decreasing of the photoluminescent intensity. In **2**, the strong intra- and intermolecular π - π interactions make the electro-density of L^{2-} anion even more decreasing, and this further weakens the photo-

luminescent intensity of **2**.

In summary, the weaker coordination ability of sulfonate groups leads to mono- and di-nuclear compounds instead of coordination polymers, and the strong intra- and intermolecular π - π interactions decrease the photoluminescent intensity of the ligand (L^{2-} anions).

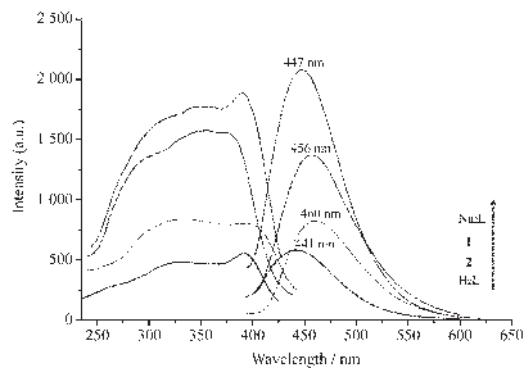


Fig.3 Photoluminescent spectra of H_2L , Na_2L , **1** and **2** in the solid state at room temperature

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