

## 二维配合物 $\{[\text{Cd}(\text{bpds})(\text{bpp})_2] \cdot 2\text{H}_2\text{O}\}_n$ 的水热合成、 晶体结构和荧光性质研究

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### Hydrothermal Synthesis, Crystal Structure and Photoluminescence of a Novel Two-Dimensional Cadmium(II) Complex: $\{[\text{Cd}(\text{bpds})(\text{bpp})_2] \cdot 2\text{H}_2\text{O}\}_n$

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**Abstract:** A novel two-dimensional cadmium(II) complex  $\{[\text{Cd}(\text{bpds})(\text{bpp})_2] \cdot 2\text{H}_2\text{O}\}_n$  (**1**) with 4,4'-biphenyldisulfonic acid ( $\text{H}_2\text{bpds}$ ) and 1,3-bis(4-pyridyl)propane ( $\text{bpp}$ ) has been synthesized by means of hydrothermal method and characterized by elemental analysis, IR spectrum, thermal analysis and single-crystal X-ray diffraction. The crystal is of triclinic, space group  $P\bar{1}$  with  $a=0.900\ 96(12)$  nm,  $b=1.098\ 84(14)$  nm,  $c=1.125\ 71(15)$  nm,  $\alpha=115.907(2)^\circ$ ,  $\beta=92.307(2)^\circ$ ,  $\gamma=105.383(2)^\circ$ ,  $V=0.950\ 8(2)$  nm<sup>3</sup>,  $D_c=1.497$  g·cm<sup>-3</sup>,  $Z=1$ ,  $F(000)=440$ ,  $\text{Goof}=1.046$ ,  $R_1=0.028\ 2$ ,  $wR_2=0.074\ 9$ . Complex **1** shows a novel two-dimensional (2D) lamellar structure and further extended into a 3D supramolecular structure through O—H···O and C—H···O hydrogen bonding interactions. Luminescent studies show that complex **1** exhibits intense blue fluorescent emission. CCDC: 769593.

**Key words:** Cadmium(II) complex; crystal structure; 4,4'-biphenyldisulfonic acid; luminescence

## 0 Introduction

There has been significant interest in the design and synthesis of mixed inorganic-organic hybrid materials owing to their potential application in catalysis, gas storage and separation, ion exchange and magnetism<sup>[1-5]</sup>. Metal phosphonates have been extensively

studied due to their inorganic-organic lamellar structures which possess potential functionality of host-guest interactions<sup>[6-9]</sup>. The sulfonate group,  $\text{R-SO}_3$ , bearing a structural analogue of phosphonate  $\text{R-PO}_3$ , could be utilized as a synthon to build inorganic-organic lamellar structure similar to that of its phosphonate analog. On the other hand, the coordination chemistry of sulfonates

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is a less-well explored territory, as is also indicated by the limited number of references on structures of metal sulfonates, and sulfonate anions show weak coordination strength with transition metals<sup>[10-15]</sup>. Most of the transition metal sulfonates obtained from aqueous solution are aqua-metal sulfonate salts<sup>[16-17]</sup>. However, after introducing other organic ligands as auxiliaries to the metal centers, sulfonate anions can compete with water molecules and coordinate with transition metals<sup>[18-19]</sup>. This observation indicates that the coordination strength of sulfonate anions is tunable. With the infinite number of organic auxiliary ligands available, it opens up a novel research area that could produce numerous materials with interesting coordination and structural features. 4,4'-Biphenyldisulfonate anions are rigid spacers with potential multiple binding sites which can be used to construct coordination polymers with multiple dimensions and variant topologies, as demonstrated previously<sup>[14-15,18-19]</sup>. Herein, we report its synthesis, crystal structure and luminescent properties of a new coordination polymer  $[\text{Cd}(\text{bpds})(\text{bpp})_2] \cdot 2\text{H}_2\text{O}$  (**1**) based on 4,4'-biphenyldisulfonic acid ( $\text{H}_2\text{bpds}$ ) and 1,3-bis(4-pyridyl)propane ( $\text{bpp}$ ).

## 1 Experimental

### 1.1 Materials and general methods

All the reagents and solvents for syntheses and analyses were commercially available and employed as received without further purification. Elemental analyses (C, H and N) were performed on a Vario EL III elemental analyzer. Infrared spectra were performed on a Nicolet AVATAR-360 spectrophotometer with KBr pellets in the  $400\sim 4\,000\text{ cm}^{-1}$  region. The luminescent spectra for the powdered solid samples were measured at room temperature on a Hitachi F-4500 fluorescence spectrophotometer with a xenon arc lamp as the light source. In the measurements of emission and excitation spectra the pass width is 5 nm. All the measurements were carried out under the same experimental conditions. Thermal gravimetric analyses (TGA) were performed on a Netzsch STA-409PC instrument in flowing  $\text{N}_2$  with a heating rate of  $20\text{ }^\circ\text{C} \cdot \text{min}^{-1}$ .

### 1.2 Synthesis of $[\text{Cd}(\text{bpds})(\text{bpp})_2] \cdot 2\text{H}_2\text{O}$ (**1**)

The single crystals of **1** were prepared by hydrothermal reaction. A mixture of  $\text{bpp}$  (0.20 g, 1.00 mmol),  $\text{H}_2\text{bpds}$  (0.31 g, 1.0 mmol),  $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (0.27 g, 1.00 mmol),  $\text{NaOH}$  (0.08 g, 2.00 mmol), and  $\text{H}_2\text{O}$  (10 mL) was stirred for 1 h and then sealed in a 25 mL Teflon-lined stainless steel container. The container was heated to  $150\text{ }^\circ\text{C}$  and held at that temperature for 96 h, then cooled to room temperature at a rate of  $5\text{ }^\circ\text{C} \cdot \text{h}^{-1}$ . Colorless block crystals of **1** were collected in 43% yield based on  $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ . Anal. Calcd. for  $\text{C}_{38}\text{H}_{40}\text{N}_4\text{O}_8\text{S}_2\text{Cd}$ (%): C 53.24, H 4.70, N 6.54; found(%): C 53.20, H 4.75, N 6.51. IR spectrum:  $3\,427, 3\,109, 3\,085, 2\,031, 1\,923, 1\,634, 1\,595, 1\,485, 1\,319, 1\,243, 1\,157, 1\,185, 1\,062, 1\,035, 1\,005, 912, 873, 838, 815, 773, 734, 712, 676$  and  $631\text{ cm}^{-1}$ .

### 1.3 X-ray crystallography

A colorless block single crystal of **1** with  $0.24\text{ mm} \times 0.22\text{ mm} \times 0.18\text{ mm}$  was carefully selected under a polarizing microscope and glued at the tip of a thin glass fiber with cyanoacrylate (super glue) adhesive. Single crystal structure determination by X-ray diffraction was performed on a Bruker Smart Apex II CCD diffractometer equipped with a normal focus, 3 kW sealed tube X-ray source ( $\text{Mo K}\alpha$  radiation,  $\lambda = 0.071\,073\text{ nm}$ ) operating at 50 kV and 30 mA. A total of 4,906 reflections were collected in the range ( $2.04 \leq \theta \leq 25.50, -10 \leq h \leq 9, -13 \leq k \leq 12, -13 \leq l \leq 11$ ), of which 3 468 are unique ( $R_{\text{int}}=0.019\,5$ ) and 3 384 with  $I > 2\sigma(I)$  were used in the refinement of the structure of **1**. Absorption corrections were applied using multiscan technique<sup>[20]</sup>. The structure was solved by the direct method and refined by full-matrix least squares on  $F^2$  using the SHELX 97 software<sup>[21-22]</sup>. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the ligands were placed in the geometrically calculated positions. The hydrogen atoms of the water molecule were located in a difference Fourier map. The detailed crystallographic data and structure refinement parameters for **1** are summarized in Table 1. Selected bond lengths and bond angles for **1** are listed in Table 2.

CCDC: 769593.

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

Formula	C <sub>38</sub> H <sub>40</sub> N <sub>4</sub> O <sub>8</sub> S <sub>2</sub> Cd	<i>D</i> <sub>c</sub> / (g·cm <sup>-3</sup> )	1.497
Formula weight	857.26	Absorption coefficient / mm	0.741
Temperature / K	293(2)	<i>F</i> (000)	440
Crystal system	Triclinic	$\theta$ range / (°)	2.04~25.50
Space group	<i>P</i> $\bar{1}$	Limiting indices	-10 ≤ <i>h</i> ≤ 9, -13 ≤ <i>k</i> ≤ 12, -13 ≤ <i>l</i> ≤ 11
<i>a</i> / nm	0.900 96(12)	Reflections collected	4 906
<i>b</i> / nm	1.098 84(14)	Independent reflections ( <i>R</i> <sub>int</sub> )	3 468 (0.019 5)
<i>c</i> / nm	1.125 71(15)	Reflections observed [ <i>I</i> > 2σ( <i>I</i> )]	3 384
α / (°)	115.907(2)	Data / restraints / parameters	3 468 / 2 / 245
β / (°)	92.307(2)	Goodness-of-fit on <i>F</i> <sup>2</sup>	1.046
γ / (°)	105.383(2)	<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.028 2, 0.074 9
<i>V</i> / nm <sup>3</sup>	0.950 8(2)	Largest difference peak and hole / (e·nm <sup>-3</sup> )	390, -538
<i>Z</i>	1		

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

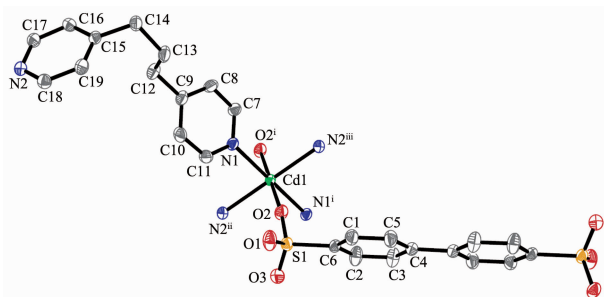
Cd(1)-N(1) <sup>i</sup>	0.231 04(18)	Cd(1)-N(2) <sup>ii</sup>	0.233 60(18)	Cd(1)-O(2) <sup>i</sup>	0.234 09(16)
Cd(1)-N(1)	0.231 04(18)	Cd(1)-N(2) <sup>iii</sup>	0.233 60(18)	Cd(1)-O(2)	0.234 09(16)
N(1)-Cd(1)-N(2) <sup>ii</sup>	93.34(6)	N(1)-Cd(1)-N(2) <sup>iii</sup>	86.66(6)	N(1) <sup>i</sup> -Cd(1)-O(2)	90.46(6)
N(1)-Cd(1)-O(2)	89.54(7)	N(2) <sup>iii</sup> -Cd(1)-O(2)	91.54(6)	N(2) <sup>ii</sup> -Cd(1)-O(2)	88.46(6)

Symmetry code: <sup>i</sup> -*x*+1, -*y*+1, -*z*+2; <sup>ii</sup> *x*, *y*+1, *z*+1; <sup>iii</sup> -*x*+1, -*y*, -*z*+1.

## 2 Results and discussion

### 2.1 Structure description of {[Cd(bpds)(bpp)]<sub>2</sub>·2H<sub>2</sub>O}<sub>n</sub>

Complex **1** crystallizes in the triclinic with space group *P* $\bar{1}$ . The asymmetric unit contains one unique Cd(II) atom, one unique bpp ligand, a half of bpds dianion and one solvated water molecule. As shown in Fig.1, Cd(II) lies on an inversion center and shows a slightly distorted octahedral geometry with four nitrogen atoms from four different bpp ligands in the equatorial



Symmetry code: <sup>i</sup> 1-*x*, 1-*y*, 2-*z*; <sup>ii</sup> *x*, 1+*y*, 1+*z*; <sup>iii</sup> 1-*x*, -*y*, 1-*z*; <sup>iv</sup> *x*, 1-*y*, 3-*z*. Hydrogen atoms and water molecule are omitted for clarity

Fig.1 ORTEP drawing of **1** showing the labeling of atoms with thermal ellipsoids at 30% probability

basal plane and two oxygen atoms from different bpds at the axial positions. The Cd-N distances are in the range of 0.231 04 (18)~0.233 60 (18) nm and the Cd-O distance is 0.234 09 (16) nm, which are similar to the reported Cd-O and Cd-N distances in other Cd(II) coordination polymers<sup>[14]</sup>. The angles of cis O(N)-Cd-O(N) are in the range of 86.66(6)°~93.34(6)°.

Bpds in a bis-monodentate fashion bridges two Cd(II) atoms forming a one-dimensional zigzag chain. The shortest Cd···Cd distance within a chain is 1.308 2 nm, which is similar to those in other bpds complexes<sup>[14,19]</sup>. The zigzag chains are further linked by bpp into a two-dimensional lamellar structure (Fig.2), the

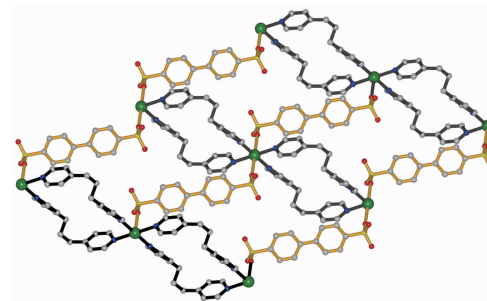


Fig.2 View toward the *bc* plane of the two-dimensional lamellar structure in **1**

$\text{Cd} \cdots \text{Cd}$  distances separated by bpp is 1.180 6 nm. The pyridyl rings of bpp are twisted with dihedral angle of  $61.87^\circ$ . Crystalline water molecules reside in adjacent

layers and extend the 2D layer into a 3D architecture through extensive hydrogen-bonding interactions. Hydrogen-bonding details for **1** are given in Table 3.

Table 3 Distance and angles of hydrogen-bonding for **1**

D-H $\cdots$ A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle(\text{DHA}) / (^\circ)$
O1W-H1WA $\cdots$ O3 <sup>i</sup>	0.082	0.242	0.294 6(5)	123
O1W-H1WB $\cdots$ O1 <sup>ii</sup>	0.085(4)	0.236(7)	0.305 3(5)	140(9)
C11-H11 $\cdots$ O1W <sup>ii</sup>	0.093	0.256	0.325 5(5)	132
C17-H17 $\cdots$ O3 <sup>ii</sup>	0.093	0.243	0.336 2(3)	175
C18-H18 $\cdots$ O2 <sup>iii</sup>	0.093	0.257	0.322 7(3)	128

Symmetry code: <sup>i</sup>  $x, y, -1+z$ ; <sup>ii</sup>  $1-x, -y, 1-z$ ; <sup>iii</sup>  $x, -1+y, -1+z$ .

## 2.2 IR spectra

The IR spectral data show features attributable to the sulfonate stretching vibrations of the complex. The broad bands centered at *ca.*  $3\,427\text{ cm}^{-1}$  indicate the O-H stretching of water. The well-resolved frequencies of aromatic rings span over the regions of  $1\,250\sim 1\,750$  and  $600\sim 900\text{ cm}^{-1}$ . Bands characteristic of the fundamental and split  $\nu_3$  S-O stretching modes are observed in the range of  $1\,000\sim 1\,240\text{ cm}^{-1}$  [23].

## 2.3 Thermogravimetric analyses

Thermal gravimetric analyses (TGA) were carried out to examine the thermal stability of **1**. The samples were heated up in flowing  $\text{N}_2$  with a heating rate of  $20\text{ }^\circ\text{C} \cdot \text{min}^{-1}$ , as shown in Fig.3. The weight loss of 4.15% (calcd. 4.20%) below  $100\text{ }^\circ\text{C}$  is attributed to the release of two solvated water molecules per formula. Then a sharp weight-loss step was observed between  $280$  and  $550\text{ }^\circ\text{C}$ , which can be attributed to the decomposition of organic ligands.

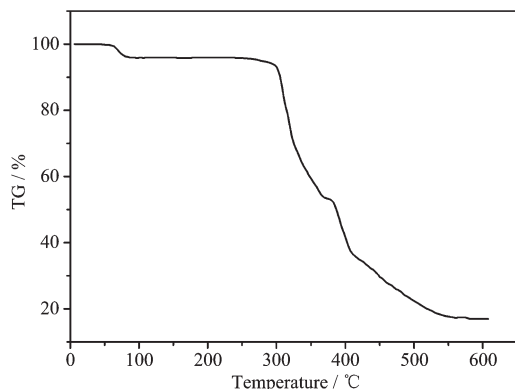


Fig.3 TG curve of complex **1**

## 2.4 Luminescent properties

Luminescent compounds are of great current

interest because of their various applications in chemical sensors, photochemistry, and electroluminescent (EL) displays [24-27]. The luminescent properties of cadmium carboxylate complexes have been investigated extensively [28-30], however, studies concerning cadmium sulfonates are limited [14,19]. As shown in Fig.4, complex **1** exhibits both blue photoluminescence with an emission maximum at 476 nm upon excitation at 338 nm and the strongest excitation peak at 342 nm upon emission at 472 nm. The main emission peaks of  $\text{H}_2\text{bpds}$  and bpp are at 312 and 369 nm, respectively. The removal of a proton from  $\text{H}_2\text{bpds}$  and the coordination of the  $\text{bpds}^{2-}$  anion and bpp to the cadmium(II) centers play important roles in the red shift of the emission. The luminescence of complex **1** should originate from the transitions between the energy levels of sulfonate anion, neutral ligand, or both. The shifts of the emission bands are attributed to both the deprotonation of the sulfonic acid and the coordination action of the sulfonate anion and neutral ligand to cadmium(II) ions [31]. These observations indicate that **1** may be excellent candidates for potential photoactive materials.

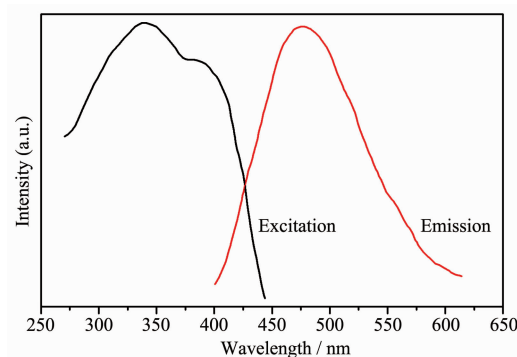


Fig.4 Solid-state excitation and emission spectra of **1** at room temperature

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