

4'-羟基联苯-4-甲酸、1,3-二吡啶基丙烷构筑的一维 镉配位聚合物的晶体结构和荧光性质

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摘要: 水热条件下采用 $\text{Cd}(\text{NO}_3)_2 \cdot 4(\text{H}_2\text{O})$, 4'-羟基联苯-4-甲酸和 1,3-二吡啶基丙烷作为反应物合成出一个新的一维镉配位聚合物 $[\text{Cd}(4',4\text{-Hhbc})_2(\text{bpp})_2]_n$ (**1**) (4',4-H₂hbc=4'-羟基联苯-4-甲酸, bpp=1,3-二吡啶基丙烷), 并分别用元素分析、红外光谱、差热分析、X-射线粉末衍射、紫外吸收光谱和 X-射线单晶衍射等表征了该结构。晶体结构分析结果表明: μ_2 桥联的 1,3-二吡啶基丙烷将镉金属离子连接成一维链结构。荧光分析表明常温固态下配合物 **1** 发射蓝色荧光, 且在 440 nm 处的荧光寿命为 3.2 ns。

关键词: 镉配位聚合物; 水热合成; 晶体结构; 荧光性质

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One-Dimensional Cadmium Coordination Polymer Involving 4'-Hydroxybiphenyl-4-carboxylate and 1,3-Bis(4-pyridyl)propane Ligands: Structure and Luminescence

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Abstract: A new 1D cadmium(II) coordination polymer, $[\text{Cd}(4',4\text{-Hhbc})_2(\text{bpp})_2]_n$ (**1**, 4',4-Hhbc=4'-Hydroxylbiphenyl-4-carboxylate, bpp=1,3-bis(4-pyridyl)propane), has been hydrothermally synthesized and structurally characterized by elemental analysis, IR spectroscopy, TGA, powder X-ray diffraction, UV-Vis and single crystal X-ray diffraction. Structural determination reveals that **1** exhibits an interesting 1D chain structure. Solid-state **1** emits the intensely indigotin photoluminescence with fluorescence lifetime of 3.2 ns (440 nm) at room temperature. CCDC: 854723.

Key words: cadmium(II) coordination polymer; hydrothermal synthesis; crystal structure; luminescence

Metal-organic coordination polymers have attracted considerable interests because of their intriguing topological structures^[1-3] and potential applications, such as magnetism, conductivity, photoluminescence, non-linear optics, catalysis, chemical separation, ion-exchange, adsorption, sensor and molecular recognition^[4-10]. Rational selection of organic ligands and metals play an important role in constructing

functional coordination polymers, and the weaker non-covalent interactions, such as hydrogen bonds, π - π stacking interactions also play key roles in the recognition process forming final 3D architectures^[11-13]. In recent decades, a variety of fascinating coordination polymers have been constructed by carboxylate ligands and N-containing ligands as the auxiliary ligands^[14-15]. As a multidentate ligand, the anion of the 4' -

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hydroxyl-biphenyl-4-carboxylate (4',4-hbc) molecule possesses one oxygen of the hydroxyl group and two oxygen atoms of carboxylate group, and might be utilized as a versatile linker for constructing interesting coordination polymers with abundant hydrogen bonds interactions. Moreover, it is widely recognized that the flexible 1,3-bis(4-pyridyl)propane (bbp) ligand is an excellent candidate for constructing novel structures as the auxiliary ligands and may act as a bidentate bridge with different conformations or in a monodentate terminal mode, leading to the formation of a variety of 1D chain, 2D layer and 3D network motifs^[16-17]. However, so far, work on the construction of new transition metals coordination polymers based on 4',4-H₂hbc ligand is still scarce, especially for N-containing auxiliary ligands^[18-20]. On the basis of above considerations, we chose 4'-hydroxyl-biphenyl-4-carboxylic acid (4',4-H₂hbc) and 1,3-bis (4-pyridyl)propane (bbp) as starting materials to construct the title 1D cadmium coordination polymer, $\{[\text{Cd} (4',4\text{-Hhbc})_2 (\text{bbp})_2]\}_n$ (**1**), under hydrothermal conditions. Structural characterization and photoluminescent properties of **1** are reported here.

1 Experimental

1.1 Materials and measurements

All chemicals were commercially available and used as received without further purification. Elemental analyses for C, H, and N were carried out by using a Vario EL III Elemental Analyzer. Infrared spectra were recorded (4 000~400 cm⁻¹) as KBr disks on Shimadzu IR-440 spectrometer. Powder XRD investigations were carried out on a Bruker AXS D8-Advanced diffractometer at 40 kV and 40 mA with Cu K α (λ =0.154 06 nm) radiation. Luminescence spectra for crystal solid samples were recorded at room temperature on an Edinburgh FLS920 phosphorimeter. Thermogravimetry analyses (TGA) were performed on an automatic simultaneous thermal analyzer (DTG-60, Shimadzu) under a flow of N₂ at a heating rate of 10 °C·min⁻¹ between ambient temperature and 800 °C. UV-Vis spectra were recorded at room temperature on a Shimadzu UV-160A spectrophotometer in barium

sulfate based paint.

1.2 Synthesis of complex 1

A mixture of Cd (NO₃)₂·4H₂O (0.15 g, 0.5 mmol), 4',4-H₂hbc (0.107 g, 0.5 mmol), 1,3-bis (4-pyridyl)propane (0.099 g, 0.5 mmol) and H₂O (15 mL) was sealed in a 23 mL Teflon reactor and kept under autogenous pressure at 150 °C for 72 h. The mixture was cooled to room temperature at a rate of 5 °C·h⁻¹ and colorless block crystals were obtained in a yield of 49% based on the Cd. Calcd.(%) for C₅₂H₄₆CdN₄O₆: C, 66.71; H, 4.92; N, 5.99. Found(%): C, 66.78; H, 4.98; N, 5.90. IR bands (KBr pellets, cm⁻¹): 3 250(s), 2 930(m), 1 612(s), 1 524(s), 1 401(s), 1 263(s), 1 221(m), 1 187(s), 1 102(w), 1 071(m), 1 018(s), 964(w), 934(w), 862(m), 838(s), 791(s), 735(s), 862(m), 838(s), 791(s), 735(s), 708(m).

1.3 Crystal structure determination

A colorless crystal with dimensions of 0.30 mm×0.29 mm×0.21 mm was selected for X-ray analyses. All diffraction data were collected on a Bruker Smart Apex II CCD diffractometer operating at 50 kV and 30 mA using a Mo K α radiation (λ =0.071 073 nm) at 296(2) K by using a ω scan mode. In the range 2.15° ≤ θ ≤ 25.19°, a total of 11 776 reflections were collected, of which 3 863 were unique (R_{int} =0.021 2) and 3 362 observed ones ($I > 2\sigma(I)$) were used in the succeeding structure calculations. Data collection and reduction were performed using the APEX II software^[21]. Multi-scan absorption corrections were applied for all the data sets using the SADABS^[21]. The structure was solved by direct methods and refined by full matrix least squares on F^2 using the SHELXTL program package^[22]. All non-hydrogen atoms were treated anisotropically. The hydrogen atoms attached to C were added according to theoretical models. The final $R = 0.026 3$ and $wR = 0.089 4$ ($w = 1/[\sigma^2(F_o^2) + (0.086 5P)^2 + 0.496 1P]$, where $P = (F_o^2 + 2F_c^2)/3$) for 3 362 observed reflections with $I > 2\sigma(I)$. $S = 1.052$, $(\Delta/\sigma)_{\text{max}} = 0.000$, $(\Delta\rho)_{\text{max}} = 374 \text{ e} \cdot \text{nm}^{-3}$ and $(\Delta\rho)_{\text{min}} = -416 \text{ e} \cdot \text{nm}^{-3}$. Crystal parameters and details of the data collection and refinement are given in Table 1. The selected bond lengths and bond angles are shown in Table 2.

CCDC: 854723.

Table 1 Crystal data and structure refinements of complex **1**

Empirical formula	C ₅₂ H ₄₆ CdN ₄ O ₆	<i>V</i> / nm ³	2.160 2(3)
Formula weight	935.33	<i>Z</i>	2
Temperature / K	296(2)	μ / mm ⁻¹	0.563
Size/ mm	0.30×0.29×0.21	<i>D_c</i> / (g·cm ⁻³)	1.438
θ range for data collection / (°)	2.15 to 25.19	<i>F</i> (000)	964
Crystal system	Monoclinic	Reflections collected	11 776
Space group	<i>P</i> 2 ₁ / <i>n</i>	Independent reflections (<i>R</i> _{int})	3 863 (0.021 2)
<i>a</i> / nm	1.075 58(10)	Goodness of fit on <i>F</i> ²	1.052
<i>b</i> / nm	1.810 42(17)	<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>))	0.026 3, 0.089 4
<i>c</i> / nm	1.184 61(11)	<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.033 1, 0.116 6
β / (°)	110.532(2)	($\Delta\rho$) _{max} , ($\Delta\rho$) _{min} / (e·nm ⁻³)	374, -416

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

Cd(1)-O(1)	0.226 7(2)	Cd(1)-N(1)	0.234 1(2)	Cd(1)-N(2) ⁱⁱ	0.241 1(2)
O(1)-Cd(1)-O(1) ⁱ	180.0	O(1)-Cd(1)-N(1)	89.44(8)	O(1)-Cd(1)-N(1) ⁱ	90.56(8)
N(1)-Cd(1)-N(1) ⁱ	180.0	O(1)-Cd(1)-N(2) ⁱⁱ	90.97(8)	O(1) ⁱ -Cd(1)-N(2) ⁱⁱ	89.03(8)
N(1)-Cd(1)-N(2) ⁱⁱ	89.70(8)	N(1)-Cd(1)-N(2) ⁱⁱⁱ	90.30(8)	N(2) ⁱⁱ -Cd(1)-N(2) ⁱⁱⁱ	180.0

Symmetry codes: ⁱ 1-*x*, -*y*, 2-*z*; ⁱⁱ 1-*x*, -*y*, 1-*z*; ⁱⁱⁱ *x*, *y*, 1+*z*.

2 Results and discussion

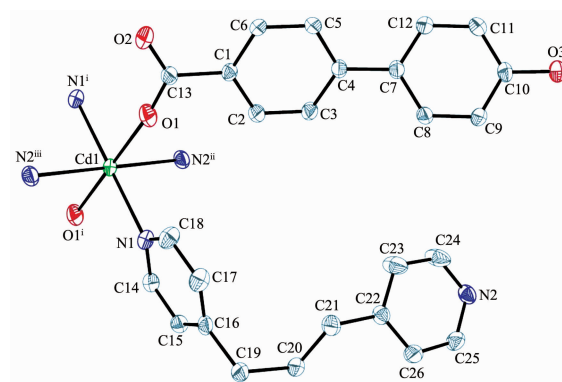
2.1 IR spectra

The IR spectra of complex **1** shows broad bands in the 3 250 cm⁻¹, which may be assigned to the ν (O-H) stretching vibrations of the hydroxyl of 4',4-Hhbc ligands. The moderate absorption band observed at 2 930 cm⁻¹ is attributed to the ν (C_{methylene}-H) vibration of bbp ligand. The features at 1 612 and 1 401 cm⁻¹ are associated with the asymmetric (COO) and symmetric (COO) stretching vibrations. The $\Delta\nu$ ($\nu_{as}(\text{COO}^-) - \nu_s(\text{COO}^-)$) value is 211 cm⁻¹ (greater than 200 cm⁻¹), indicating the coordination of carboxylate with Cd(II) in monodentate mode^[25], which is well consistent with X-ray diffraction structural analysis.

2.2 Structure description

Single-crystal X-ray diffraction analysis reveals that compound **1** crystallizes in the *P*2₁/*n* space group and has a 1D infinite chain structure. A thermal ellipsoid plot of the asymmetric unit of **1** is shown in Fig.1. The Cd(II) ion, lying on an inversion centre, is defined by two oxygen atoms from two different 4',4-Hhbc ligands and four nitrogen atoms from four different bbp ligands in an octahedral geometry. The

equatorial plane is defined by N(1), N(1)ⁱ, N(2)ⁱⁱ and N(2)ⁱⁱⁱ atoms, while O(1) and O(1)ⁱ occupy the axial position (symmetry codes: ⁱ 1-*x*, -*y*, 2-*z*; ⁱⁱ 1-*x*, -*y*, 1-*z*; ⁱⁱⁱ *x*, *y*, 1+*z*). The Cd-O, Cd-N bond lengths and O-Cd-O, O-Cd-N angles, all of which are within the range of those observed for other analogical Cd complexes^[23-24], are ranging from 0.267(2) to 0.241 1(2) nm and 89.03(8)° to 180.0°, respectively.

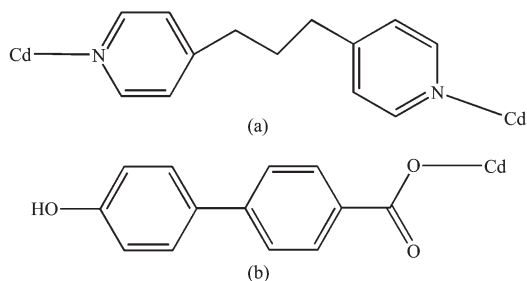


All hydrogen atoms are omitted for clarity; Symmetry codes: ⁱ 1-*x*, -*y*, 2-*z*; ⁱⁱ 1-*x*, -*y*, 1-*z*; ⁱⁱⁱ *x*, *y*, 1+*z*

Fig.1 Thermal ellipsoids plot of the asymmetric unit of **1** with 30% probability ellipsoids

In the intricate polymeric structure of **1**, the 4',4-Hhbc ligand is terminal and adopts monodentate

coordination mode (Scheme 1a), and bbp ligand take a trans coordination motif and bidentate bridging to link two Cd^{II} ions (Scheme 1b). The carboxylate oxygen atoms of two 4',4'-Hhbc ligands connect one Cd atom to construct a monocyclic cadmium building block, which can be regarded as a knot. Every two bbp ligands bridges two neighbouring knots to form a one-dimensional infinite chain along the *b* axis of the unit cell (Fig.2a). The distance between two knots is 1.184 (6) nm, which is equal to the unit length of the *c* axis. The C-H $\cdots\pi$ stacking interactions assemble neighbouring chains into a corrugated layer (Fig.3). The H-to-centroid distances of $\text{H}(11)\cdots\text{Cg}(1)^{\text{iv}}=0.276(2)$ nm ($\text{Cg}(1)$ is the centroid of the C1-C6 ring, symmetry code: $^{\text{iv}} -0.5+x, 0.5-y, -0.5+z$). Moreover, intramolecular O3-H3a \cdots O2 hydrogen bonds are also observed.



Scheme 1 Coordination modes of 4',4'-Hhbc and bbp ligands in the structure of **1**

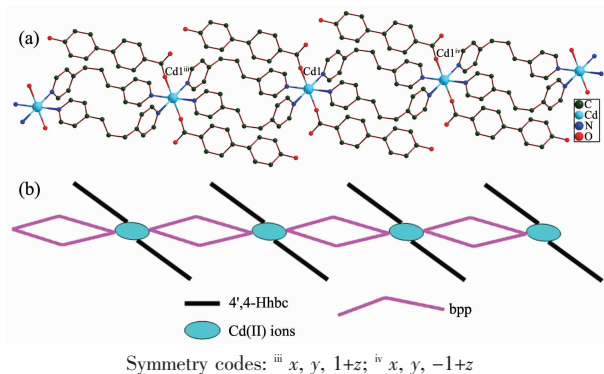


Fig.2 (a) View of the 1D infinite chain of **1** along the *b* axis of the unit cell; (b) and the corresponding schematic mode

2.3 Thermal analysis

The thermogravimetric analyses (TGA) of compound **1** were performed in a N_2 atmosphere when the sample was heated to 800 $^{\circ}\text{C}$ at a constant rate of 10 $^{\circ}\text{C}\cdot\text{min}^{-1}$. The TG and DTA curves are depicted in

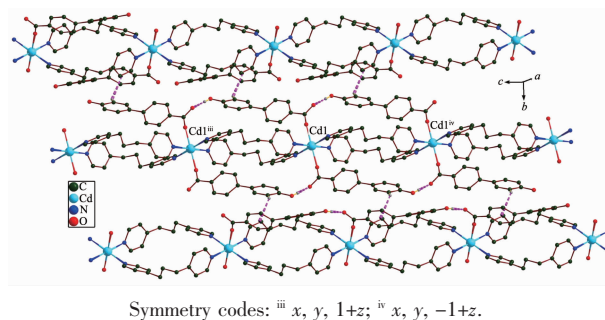


Fig.3 View of the 2D layer structure of **1** formed by C-H $\cdots\pi$ stacking interactions (dash lines)

Fig.4, which shows that compound **1** has good thermal stability as no strictly clean weight loss step occurs below 280 $^{\circ}\text{C}$. The weight-loss step occurred above 280 $^{\circ}\text{C}$ which corresponds to the decomposition of framework structure. Finally, **1** was completely degraded into CdO with total loss of 87.51% (Calcd. 86.23%).

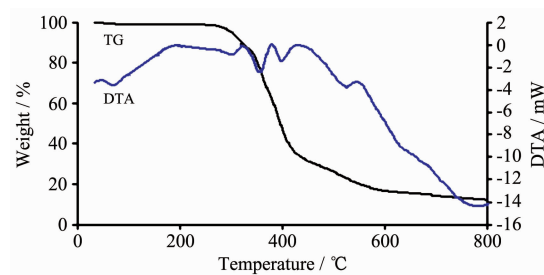


Fig.4 Thermogravimetric curves (DTA and TG) for compound **1**

2.4 Powder X-ray diffraction Analysis

Samples of complex **1** were measured by X-ray powder diffraction at room temperature. As shown in Fig.5, the peak positions of the experimental patterns are in a good agreement with the simulated patterns, which clearly indicates the good purity of the complex.

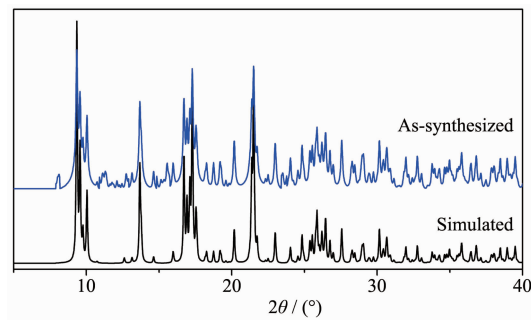


Fig.5 PXRD patterns in complex **1**

2.5 UV-Vis absorption spectra

Fig.6 illustrates the UV-Vis absorption spectra of

1 in solid state. In the exploited wavelength domain from 200~450 nm, the B band of 4',4-Hhbc and bbp ligands which is attributed to the π - π^* transition is observed with the absorptions at 254 and 278 nm. The second-most intense absorption at 355 corresponds to the K band of the L \rightarrow M (charge transfer) transition involving 4',4-Hhbc, bbp ligands and Cd²⁺ ions^[26].

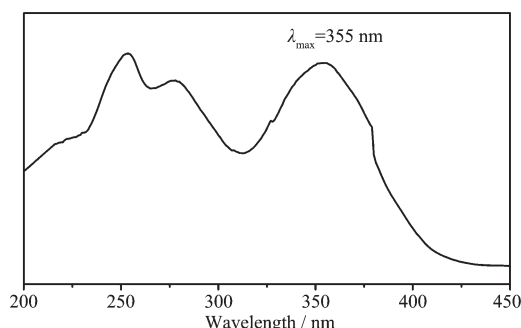


Fig.6 UV-Vis absorption spectroscopy of **1** in solid state

2.6 Luminescent properties

The photoluminescence properties of compound **1**, 4',4-H₂hbc and bbp were studied in the solid state at room temperature. Luminescent emissions for the free ligands of 4',4-H₂hbc (λ_{em} =407 nm, λ_{em} =342 nm)^[18] and bbp (λ_{em} =441 nm, λ_{em} =315 nm)^[27] were detected under experimental conditions. In contrast to the 4',4-H₂hbc and bbp ligands, complex **1** shows a rather intense luminescence with emission maxima at ca. 440 nm upon excitation at 339 nm (Fig.7). Obviously, the emission maximum of compound **1** is almost equal to the bbp ligand, which indicates that the emission of title compound probably origins from the bbp ligand. This phenomenon observed for title compound is in contrast to the observations for other transition metal complexes involving bbp ligand^[28-30], which are unexp-

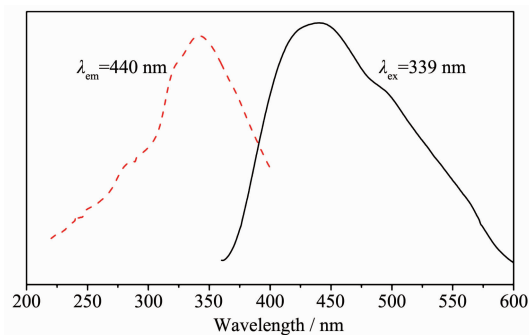


Fig.7 Solid-state excitation and emission spectra of complex **1** at room temperature

ected. The luminescent lifetime of solid complex **1** using an Edinburgh FLS920 phosphorimeter with 450 W xenon lamp as excitation source show lifetime for complex **1** of 3.2 ns at 440 nm (Fig.8).

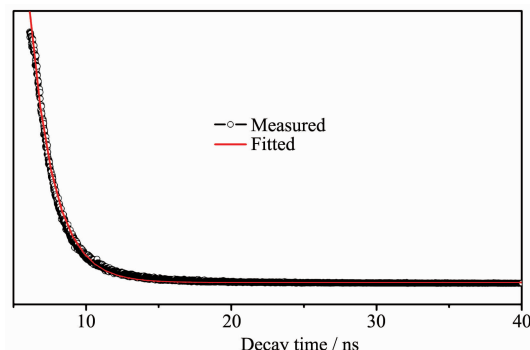


Fig.8 Luminescent lifetime for complex **1** in solid state at room temperature

3 Conclusions

In conclusion, a new 1D cadmium(II) complex based on 4',4-Hhbc and bbp ligands, $[[Cd_2(4',4-Hhbc)_2(bbp)_2]]_n$, has been hydrothermal synthesized and structurally characterized. This successful preparation of the title compound indicates that the bbp can be an excellent candidate for the construction of supramolecular complexes. Complex **1** emits the intensely indigotin luminescence with the fluorescence lifetime of 3.2 ns (440 nm) in the solid state at room temperature.

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