

以 4,4'-二(苯并咪唑-1-甲基)联苯及邻苯二甲酸根构筑的 锌配位聚合物的合成、晶体结构及荧光性质

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摘要: 水热法合成了 1 个新的锌配位聚合物 $[\text{Zn}(\text{bbmb})(\text{Pht})]_n$ (bbmb=4,4'-二(苯并咪唑-1-甲基)联苯; H_2Pht =邻苯二甲酸), 对其进行了红外光谱、元素分析、PXRD 和 TGA 等表征, 并用 X-射线单晶衍射法测定了配合物的单晶结构。该配合物属单斜晶系, $P2_1/c$ 空间群, 为二维层状结构。晶胞参数为 $a=1.085\ 28(10)\ \text{nm}$, $b=2.286\ 7(2)\ \text{nm}$, $c=1.218\ 53(12)\ \text{nm}$, $\beta=102.589(3)^\circ$, $V=2.951\ 3(5)\ \text{nm}^3$, $Z=4$ 。室温固态荧光测试显示, 配合物在 416 nm (λ_{max}) 具有强的荧光吸收。

关键词: 水热合成法; 晶体结构; 锌配合物

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Synthesis, Crystal Structure and Fluorescence Property of Zinc(II) Coordination Polymer with 4,4'-Bis(benzimidazol-1-ylmethyl)biphenyl and Phthalate

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Abstract: A new zinc(II) coordination polymer $[\text{Zn}(\text{bbmb})(\text{Pht})]_n$ (bbmb=4,4'-bis(benzimidazol-1-ylmethyl)biphenyl, H_2Pht =phthalic acid) has been prepared by hydrothermal method and structurally characterized by elemental analysis, IR, PXRD, TGA and single-crystal X-ray diffraction. The title compound crystallizes in monoclinic, space group $P2_1/c$ with $a=1.085\ 28(10)\ \text{nm}$, $b=2.286\ 7(2)\ \text{nm}$, $c=1.218\ 53(12)\ \text{nm}$, $\beta=102.589(3)^\circ$, $V=2.951\ 3(5)\ \text{nm}^3$, $Z=4$, and exhibits a 2D network. Fluorescence spectrum studies reveals that the zinc(II) complex exhibits strong fluorescence absorption at 416 nm (λ_{max}) in the solid state at room temperature. CCDC: 880548.

Key words: hydrothermal synthesis; crystal structure; zinc(II) complex

The designed synthesis and characterization of metal-organic coordination polymers have obtained intense interest in supramolecular chemistry and material science. The intense attention in this field is justified not only for their intriguing aesthetic structures and topological features, but also for their

potential applications such as gas sorption, luminescence, catalysis, molecular magnetism, nonlinear optics, and ion-exchange^[1-6]. To get novel structures, the most common strategies are to modify the building blocks and control the assembled motifs for required products via employing rationally organic ligands and

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suitable metal ions.

The combination of metal ions with neutral and anionic mixed bridging ligands makes the assembly process more controllable than a single ligand. The prospect of introducing the second or more organic ligands into a reaction system provides further urge for researches on metal-organic supramolecular frameworks.

Benzimidazol-1-yl-based ligands are typical examples in coordination and metallosupramolecular chemistry^[7-9]. They have important applications not only in medicinal chemistry owing to the broad spectrum of their pharmaceutical and biological properties, such as antibacterial, antiparasitic, and antitumor activities^[10], but also they can construct different coordination architectures as different spacers, bridges, or terminal auxiliary ligands, which have been discussed in recent years^[11-13]. Besides, as one of the most versatile ligands, carboxyl anion (COO^-) has been utilized widely because it has abundant coordination modes^[14-15]. Up to now, multidentate anionic ligands have been employed in the design and synthesis of numerous novel complexes^[16].

Considering the aforementioned point, we selected a semirigid benzimidazol-1-yl-based ligand, namely 4,4'-bis(benzimidazole-1-ylmethyl)biphenyl (bbmb) together with phthalic acid (H_2Pht) and zinc(II) cation to construct a new functional complex. Herein, we report the synthesis and structure of a Zn (II) complex. The luminescent properties of bbmb, H_2Pht and the complex are also discussed.

1 Experimental

1.1 Reagents and physical measurements

4,4'-bis(benzimidazole-1-ylmethyl)biphenyl (bbmb) was prepared according to the reported method^[17]. All the reagents and solvents were of analytical grade and used without further purification. X-ray crystallographic data were collected on a Bruker Apex Smart CCD diffractometer. Elemental analyses were carried out with Perkin-Elmer 240C element analyses. The infrared spectrum (KBr discs) was recorded in the range of $400\sim 4\,000\text{ cm}^{-1}$ on a FT-IR (VECTOR-22) spectrometer. Powder X-ray diffraction (PXRD)

measurements were performed on a Philips X-pert X-ray diffractometer. The as-synthesized samples were characterized by thermogravimetric analysis (TGA) on a Perkin-Elmer thermogravimetric analyzer Pyris II TGA. Luminescent spectra were recorded with a SHIMAZU VF-320 X-ray fluorescence spectrophotometer at room temperature.

1.2 Synthesis of the title complex

A mixture of bbmb (41.4 mg, 0.1 mmol), H_2Pht (16.6 mg, 0.1 mmol) and $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (29.5 mg, 0.1 mmol), and the solvent of $\text{H}_2\text{O}/\text{DMF}$ (2:2, V/V, 4 mL) was sealed in a 15 mL PTFE-lined stainless-steel vessel under autogenous pressure and heated at $95\text{ }^\circ\text{C}$ for 3 d. Large quantities of colorless leaf-like crystals were obtained, which were filtered off, washed with distilled water, and dried under ambient conditions. The yield of the reaction was ca. 45% based on bbmb ligand. Anal. Calcd. for $\text{C}_{36}\text{H}_{26}\text{O}_4\text{N}_4\text{Zn}$ (%): C, 67.14, H, 4.07, N, 8.70; found (%): C, 66.98, H, 4.16, N, 8.59. IR (KBr, cm^{-1}): 3 104(w), 1 622(s), 1 510 (m), 1 453 (m), 1 372(s), 1 294(w), 1 258(w), 1 188(m), 1 146(w), 918(w), 823(w), 752(m), 710(w), 654(w), 501(w), 423 (w), 463(w).

1.3 Crystal structure determination

A single crystal of dimensions $0.22\text{ mm}\times 0.24\text{ mm}\times 0.28\text{ mm}$ for the complex was selected for single-crystal X-ray diffraction analysis. Crystallographic data were collected at Bruker Apex Smart CCD diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda=0.071\,073\text{ nm}$) with the φ - ω scan mode. The structure was solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using full-matrix least-squares procedures based on F^2 values^[18]. The hydrogen atoms were added according to theoretical models. The pertinent crystallographic data are summarized in Table 1, while the selected bond lengths and angles are listed in Table 2.

CCDC: 880548.

2 Results and discussion

2.1 Crystal structure of the title complex

Single crystal X-ray analysis reveals the

Table 1 Crystal data and structure refinements for the title complex

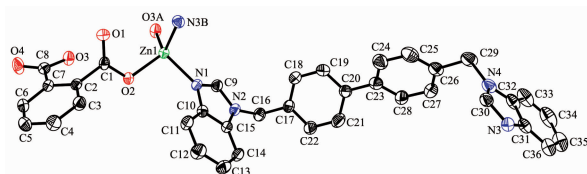
| | | | |
|---|---|---|---|
| Empirical formula | C ₃₆ H ₂₆ ZnN ₄ O ₄ | Index range | -8 ≤ h ≤ 12, -26 ≤ k ≤ 27, -14 ≤ l ≤ 14 |
| Formula Weight | 643.98 | Goodness of fit on F ² | 1.096 |
| Crystal System | Monoclinic | Crystal size / mm | 0.22×0.24×0.28 |
| Space group | P2 ₁ /c | S(all data) | 1.096 |
| a / nm | 1.085 28(10) | Temperature / K | 273(2) |
| b / nm | 2.286 7(2) | Tot., Uniq. Data | 16 351, 5 197 |
| c / nm | 1.218 53(12) | R _{int} | 0.057 6 |
| β / (°) | 102.589(3) | Observed data (I>2σ(I)) | 3 599 |
| V / nm ³ | 2.951 3(5) | Nref, Npar | 5 197, 406 |
| Z | 4 | R ₁ , wR ₂ (I>2σ(I)) | 0.048 8, 0.102 9 |
| D _c / (g·cm ⁻³) | 1.499 | R ₁ , wR ₂ (all data) | 0.081 3, 0.110 4 |
| μ / mm ⁻¹ | 0.881 | Max. and Av. Shift / Error | 0.001, 0.000 |
| F(000) | 1 328 | (Δρ) _{max} , (Δρ) _{min} / (e·nm ⁻³) | 368, -213 |
| θ _{min} , θ _{max} / (°) | 1.78, 25.00 | | |

Table 2 Selected bond lengths (nm) and angles (°) for the title complex

| | | | | | |
|------------|------------|------------|------------|-------------|------------|
| Zn1-O2 | 0.194 5(2) | Zn1-O3A | 0.193 0(2) | Zn1-N1 | 0.201 0(3) |
| Zn1-N3B | 0.203 0(3) | | | | |
| O2-Zn1-N1 | 100.62(10) | O2-Zn1-O3A | 111.22(9) | O2-Zn1-N3B | 114.70(10) |
| N1-Zn1-N3B | 107.27(11) | N1-Zn1-O3A | 115.62(10) | N3B-Zn1-O3A | 107.49(11) |

Symmetry codes: A: 2-x, -y, 1-z; B: 1+x, 0.5-y, -0.5+z.

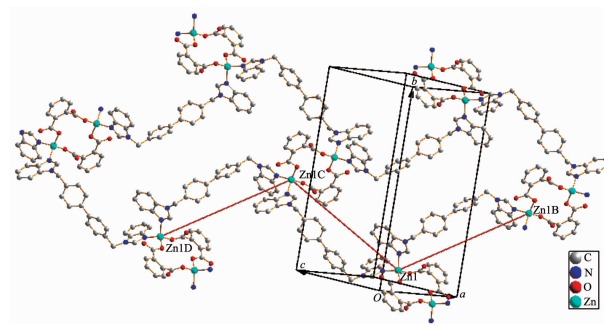
compound crystallized in monoclinic crystal system of *P*2₁/c. As illustrated in Fig.1, the asymmetric unit contains one Zn (II) cation, one bbmb ligand and one Pht²⁻, the Zn center presents a slightly distorted tetrahedron, defined by two oxygen atoms from two carboxylate groups of different Pht²⁻ ligands, and two nitrogen atoms from two different bbmb ligands. The Zn1-O bond lengths are 0.193 0(2) and 0.194 5(2) nm respectively, and the Zn1-N bond lengths are 0.202 0(3) and 0.203 0(3) nm, respectively. They are comparable to those reported in the literature^[13]. The two carboxylate groups of H₂Pht ligand are both deprotonated and adopt the monodentate coordination mode. As shown



Probability of ellipsoid is 30%; Symmetry codes: A: 2-x, -y, 1-z;
B: 1+x, 0.5-y, -0.5+z; Hydrogen atoms are omitted for clarity

Fig.1 Coordination enviroment of Zn(II) in the title complex

in Fig.2, the nitrogen atoms from bbmb ligands link the zinc(II) ions to form a 1D zigzag chain, and the 1D zigzag chain links adjacent 1D zigzag chain via two carboxylate groups of the Pht²⁻ ligand to further generate an infinite 2D network.



Symmetry codes: B: 1+x, 0.5-y, -0.5+z; C: -1+x, 0.5-y, 0.5+z;
D: -2+x, y, 1+z

Fig.2 2D infinite network constructed by bbmb and Pht²⁻ ligands

2.2 IR spectrum

The infrared spectrum of the complex has been recorded and some important assignments are shown in experimental section. The very strong band in the

IR spectrum of the complex at $1\,622\text{ cm}^{-1}$ was assigned to the asymmetrical stretching mode of the COO^- groups, while the shoulder at $1\,372\text{ cm}^{-1}$ corresponds to the symmetrical COO^- stretching modes. As we know, the separation between $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ has often been used to diagnose the coordination modes in the carboxylate ligands. The separation for bidentate carboxylate groups is $<200\text{ cm}^{-1}$, whereas it is $>200\text{ cm}^{-1}$ in monodentate groups^[19]. The separation ($\Delta\nu$) between $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ is 250 cm^{-1} for zinc(II) complex, indicating monodentate coordinating modes for the coordinated carboxylate groups, these IR results are coincident with the crystallographic structural analyses.

2.3 Thermal analysis and XRD result

In flow of N_2 , in the temperature range from 20 to $700\text{ }^\circ\text{C}$, with a heating rate of $20\text{ }^\circ\text{C}\cdot\text{min}^{-1}$, thermal behavior was carried out to estimate the stability of the coordination architecture by TGA. The TGA curve (Fig.3) shows the complex is thermally stable. No weight loss was observed up to $320\text{ }^\circ\text{C}$. An weight loss is observed above $330\text{ }^\circ\text{C}$ because of the decomposition of the ligands. In order to confirm the phase purity of the title complex, PXRD experiment was carried out for the complex. As shown in Fig.4, the experimental PXRD patterns are in agreement with simulated PXRD patterns, demonstrating the single phase purity of the products.

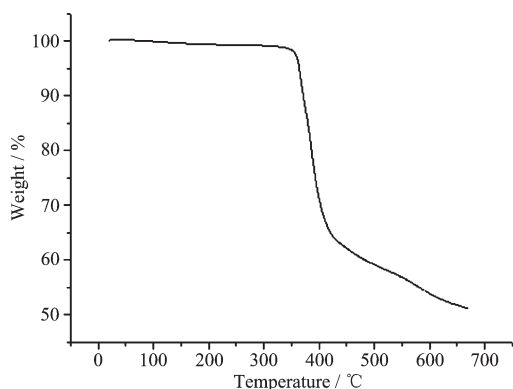


Fig.3 TG curve of the title complex

2.4 Fluorescence spectra

The fluorescence spectra of bbmb, H_2Pht and the zinc(II) complex in the solid state were measured at room temperature. The excitation wavelengths are at

346, 328 and 319 nm , respectively. As shown in Fig. 5, the emission peaks are observed with wavelengths at $370\sim387\text{ nm}$ in bbmb, and $378\sim481\text{ nm}$ in H_2Pht , which may arise from $\pi^*\rightarrow\pi$ transitions of the bbmb and H_2Pht . The emission peak of the zinc(II) complex is at 416 nm (λ_{max}). It is obvious that the emission band of the complex could still be assigned to $\pi^*\rightarrow\pi$ transitions of the ligands.

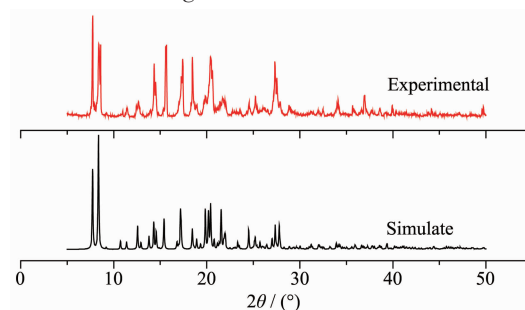


Fig.4 Experimental and simulated PXRD spectra of the title complex

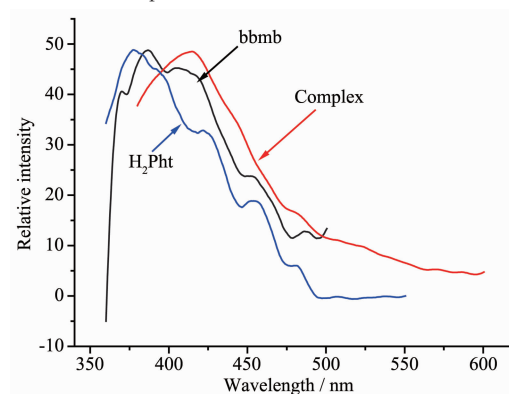


Fig.5 Solid-state fluorescent emission spectra of L (bbmb, H_2Pht) and the title complex at room temperature

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