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基于三联苯-2,2′,4,4′-四羧酸的二维双层锌(Ⅱ)配位聚合物的水热合成、晶体结构及荧光性质

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摘要:采用水热法合成了一个配合物$[Zn_2(tpta)_{0.5}(H_2tpta)(dpe)(H_2O)_2]_n$ (**1**)(H_4tpta=三联苯-2,2′,4,4′-四羧酸,dpe=1,2-二(4-吡啶基)乙烯),并用元素分析、红外光谱、X-射线单晶衍射、热重分析和荧光分析对其进行了表征。晶体结构分析表明:该配合物属于三斜晶系,空间群为 $P\bar{1}$,a=1.017 4(2) nm,b=1.034 1(2) nm,c=1.883 1(4) nm,α=96.147(4)°,β=96.866(4)°,γ=98.023(4)°,V=1.932 2(7) nm^3,Z=2,D_c=1.640 $g\cdot cm^{-3}$,μ=1.320 mm^{-1},F(000)=974,R_1=0.066 9,wR_2=0.133 2($I>2\sigma(I)$);具有环状双核锌(Ⅱ)连接的二维双层结构,双层之间又进一步通过 O–H···O 氢键组装成三维超分子结构。此外,该配合物具有较好的热稳定性和发光性能。

关键词:配位聚合物;晶体结构;三联苯-2,2′,4,4′-四羧酸;Zn(Ⅱ)
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Hydrothermal Synthesis, Crystal Structure and Luminescence of a 2D Bilayer Zn(Ⅱ) Coordination Polymer Based on Terphenyl-2,2′,4,4′-tetracarboxylic Acid

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Abstract: A complex based on Zn (Ⅱ) and terphenyl-2,2′,4,4′-tetracarboxylic acid, namely, $[Zn_2(tpta)_{0.5}(H_2tpta)(dpe)(H_2O)_2]_n$ (H_4tpta=terphenyl-2,2′,4,4′-tetracarboxylic acid, dpe=1,2-di(4-pyridyl)ethylene) has been hydrothermally synthesized and characterized by elemental analysis, IR spectroscopy, single-crystal X-ray diffraction analysis, thermal stability analysis and fluorescent analysis. The complex crystallizes in triclinic system, space group $P\bar{1}$ with a=1.017 4(2) nm, b=1.034 1(2) nm, c=1.883 1(4) nm, α=96.147(4)°, β=96.866(4)°, γ=98.023(4)°, V=1.932 2(7) nm^3, Z=2, D_c=1.640 $g\cdot cm^{-3}$, μ=1.320 mm^{-1}, F(000)=974, and the final R_1=0.066 9, wR_2=0.133 2 for $I>2\sigma(I)$. Complex **1** features an unusual 2D bilayer motif with ring dinuclear Zn_2 units, which is further linked to each other by O–H···O hydrogen bonds to complete the final 3D supramolecular architecture. In additional, complex **1** shows good thermal stability and luminescent property. CCDC: 913522.

Key words: coordination polymer; crystal structure; terphenyl-2,2′,4,4′-tetracarboxylic acid; Zn(Ⅱ)

The rational design and construction of new coordination polymers have provoked the interest of chemists in recent years due to their potential applications in the fields of magnetism, luminescence, gas adsorption, and catalysis, as well as their fascinating architectures and topologies[1-5]. It is well-

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known that the rational design and reasonable use of the organic multicarboxylate ligands is very important in the construction of the desired coordination polymers. Although, so many studies have recently focused on the use of biphenyl-3,3′,5,5′-tetracarboxylate, biphenyl-2,2′,4,4′-tetracarboxylate, biphenyl-2,2′,3,3′-tetracarboxylate, and terphenyl-2,5,2′,5′-tetracarboxylate[6-10], the use of terphenyl-2,2′,4,4′-tetracarboxylate organic linkers remains largely unexplored.

As an extension of our previous work[11], we report the synthesis and structures of a new complex based on H_4tpta and auxiliary dpe ligands: $[Zn_2(tpta)_{0.5}(H_2tpta)(dpe)(H_2O)_2]_n$ (**1**), and its thermal stability and luminescent property are also reported below in detail.

1 Experimental

1.1 Materials and methods

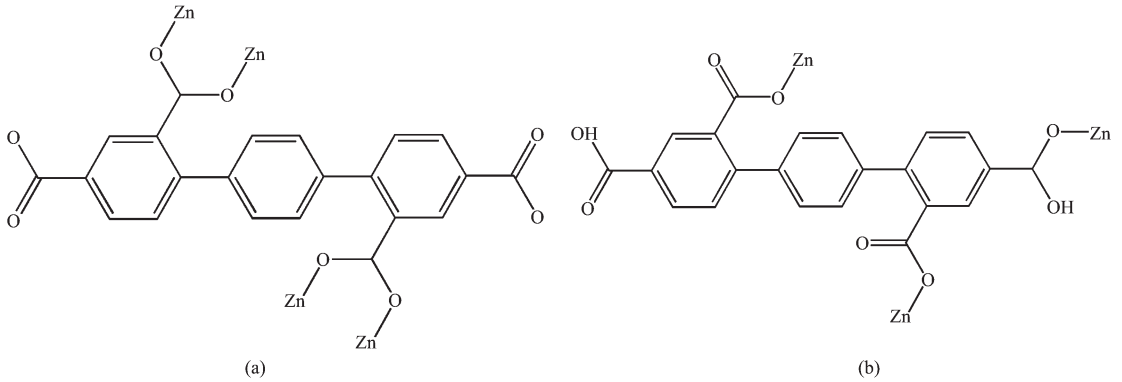
All reagents and solvents employed were commercially available and used without further purification. The C, H and N microanalyses were carried out with a Vario EL Ⅲ elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range of 4 000~400 cm^{-1} on a Shimadzu Prestige-21 spectrometer. Thermogravimetric analyses (TGA) were performed under nitrogen with a heating rate of 10 ℃·min^{-1} using a NETZSCH STA 449F3 thermogravimetric analyzer. Fluorescence spectra were performed on a Hitachi F-4500 fluorescence spectrophotometer at room temperature.

1.2 Syntheses of complex 1

A mixture of $Zn(NO_3)_2·6H_2O$ (0.20 mmol), H_4tpta (0.15 mmol), dpe (0.10 mmol) and 10 mL H_2O was stirred for 30 min. The mixture was then placed in a 25 mL Teflon-lined stainless steel vessel and heated for 160 ℃ for 4 d. Colorless block crystals were obtained when the mixture was cooled to room temperature. Yield: *ca.* 56% based on Zn. Calcd. for $C_{45}H_{31}N_2O_{14}Zn_2$ (%): C, 56.62; H, 3.27; N, 2.93. Found (%): C, 56.59; H, 3.28; N, 2.95. IR (KBr pellet, cm^{-1}): 3 444w, 3 057w, 1 691w, 1 612s, 1 541w, 1 431m, 1 369s, 1 249w, 1 101w, 1 064w, 1 028w, 999w, 918m, 833s, 746w, 775s, 551s, 451w.

1.3 Crystal structure determination

Diffraction intensities for the complex **1** was collected at 293(2) K on a Bruker Smart APEX Ⅱ CCD diffractometer equipped with a graphite-monochromated Mo $K\alpha$ radiation (λ=0.071 073 nm) using an ω-φ scan mode. A semiempirical absorption correction was applied using the SADABS program[12]. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXS 97 and SHELXL 97 programs, respectively[13-14]. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in geometrically calculated positions. The O3 and H3 of the $(H_2tpta)^{2-}$ anion in **1** was found to be disordered over two orientations. The occupancies of the disordered positions O3/O3A, H3A/H3B were refined to 0.38/0.62. The $(H_2tpta)^{2-}$ anion in **1** is disordered into two positions and some soft constraints were also applied. A total of 10148 reflections of complex **1** were collected in the range of $1.10°<\theta<25.50°$ ($-12 \leqslant h \leqslant 12$, $-6 \leqslant k \leqslant 12$, $-22 \leqslant l \leqslant 22$) and 7 127 were independent with R_{int}=0.051 2, of which 4 095



Scheme 1 Coordination modes of L^{4-} and $(H_2L)^{2-}$ in complex **1**

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

Zn(1)-O(2)	0.198 2(4)	Zn(1)-N(1)	0.202 2(6)	Zn(2)-O(13)	0.206 9(5)
Zn(1)-O(9)	0.194 3(4)	Zn(2)-O(4B)	0.203 3(4)	Zn(2)-O(14)	0.209 4(5)
Zn(1)-O(10A)	0.197 8(4)	Zn(2)-O(5)	0.200 9(4)	Zn(2)-N(2C)	0.209 3(5)
O(9)-Zn(1)-O(10A)	115.50(18)	O(2)-Zn(1)-N(1)	120.7(2)	O(4B)-Zn(2)-O(14)	87.7(2)
O(9)-Zn(1)-O(2)	114.61(19)	O(5)-Zn(2)-O(4B)	90.74(19)	O(13)-Zn(2)-O(14)	125.1(2)
O(10A)-Zn(1)-O(2)	102.62(18)	O(5)-Zn(2)-O(13)	121.56(19)	O(5)-Zn(2)-N(2C)	94.3(2)
O(9)-Zn(1)-N(1)	105.6(2)	O(4B)-Zn(2)-O(13)	88.11(18)	O(4B)-Zn(2)-N(2C)	172.6(2)
O(10A)-Zn(1)-N(1)	96.8(2)	O(5)-Zn(2)-O(14)	113.4(2)	O(13)-Zn(2)-N(2C)	94.0(2)

Symmetry operations: A: $-x+1, -y, -z+2$; B: $x+1, y+1, z$; C: $x, y-1, z$.

with $I>2\sigma(I)$ (refinement on F^2) were observed and used in the succeeding structure calculation. The final R_1=0.066 9, wR_2=0.133 2 (w=1/[$\sigma^2(F_o^2)$+(0.061 3P)^2], where P=(F_o^2+2F_c^2)/3), $(\Delta\rho)_{max}$=957 e·nm^{-3} and $(\Delta\rho)_{min}$ =−998 e·nm^{-3}. Selected bond lengths and bond angles are listed in Table 1.

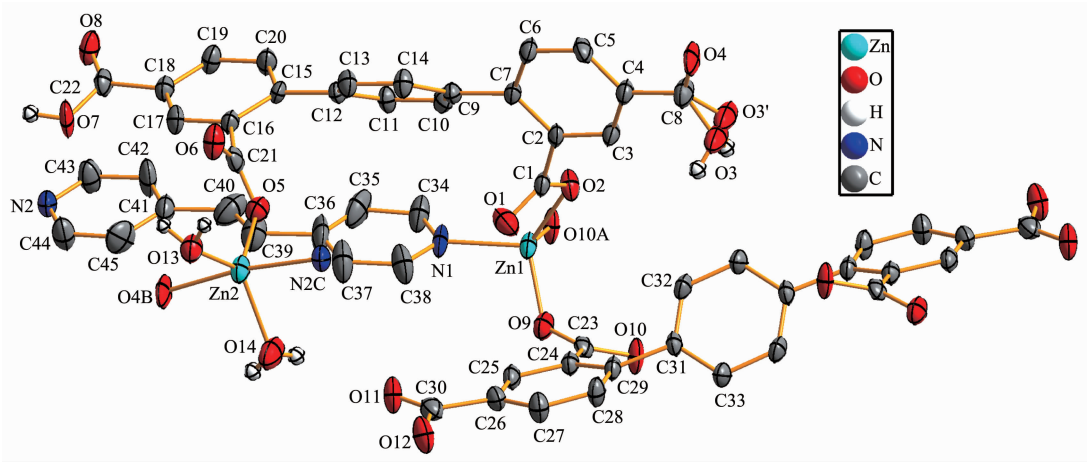
CCDC: 913522.

2　Results and discussion

2.1　Description of crystal structure

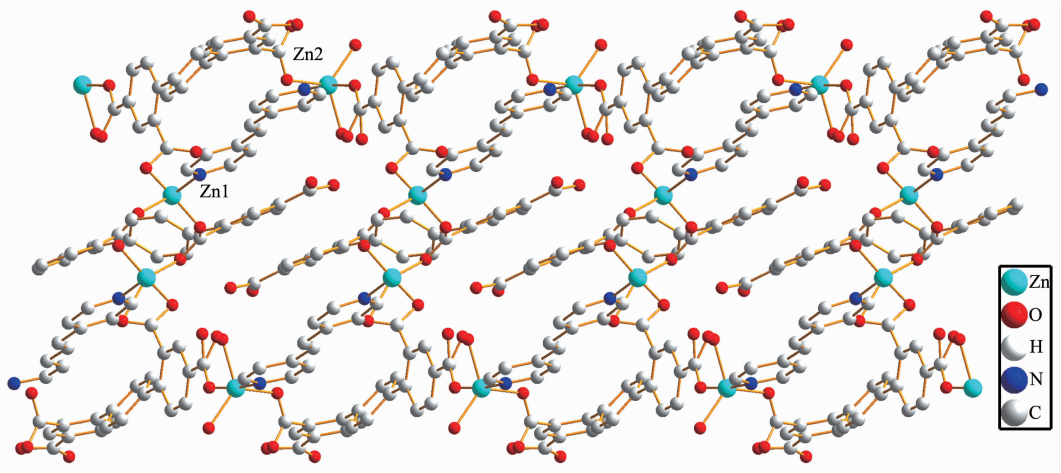
Complex **1** features an unusual 2D bilayer motif with ring dinuclear Zn_2 units acting as the junctures between the two layers. The asymmetric unit of **1** contains two crystallographically independent Zn(Ⅱ) ions, a half of tpta^{4-} anion, one $(H_2tpta)^{2-}$ anion, one dpe ligand, and two coordinated water molecules. As depicted in Fig.1, Zn(1) is located in a distorted tetrahedral environment formed by two oxygen atoms from two different tpta^{4-} anions, one oxygen atom from one $(H_2tpta)^{2-}$ anion, and one nitrogen atom from one dpe ligand. Different from those of Zn(1), Zn(2) adopts a distorted trigonal bipyramidal coordination geometry and is five-coordinated by two oxygen atoms from two different $(H_2tpta)^{2-}$ anions, one nitrogen atom from one dpe ligand, and two coordinated water molecules. All the Zn-O (0.194 3(4)~0.209 4(5) nm) and Zn-N (0.202 2(6) and 0.209 3(5) nm) bond lengths and bond angles around Zn(Ⅱ) (87.7(2)°~172.6(2)°) fall into the normal ranges (Table 1).

In complex **1**, two crystallographically independent tpta^{4-}/$(H_2tpta)^{2-}$ anions display two different coordination modes: μ_2-η^1:η^1-bidentate bridging mode (Scheme 2a) and μ_1-η^1:η^0-monodentate bridging mode (Scheme 2b), respectively. On the basis of the connection mode, the Zn(1) ions are bridged by the 2(2′)-carboxyl groups of tpta^{4-} anions to give a dimeric Zn_2 units (Zn⋯Zn, 0.374 83(13) nm), which is linked by tpta^{4-} anions to form a 1D $[Zn(tpta)_{0.5}]_n$ ring-like chain;



Symmetry code: A: $-x+1, -y, -z+2$; B: $x+1, y+1, z$; C: $x, y-1, z$; F: $-x+1, -y-1, -z+2$; 50% thermal ellipsoids

Fig.1 Coordination environments of Zn(Ⅱ) in complex **1**



All hydrogen atoms are omitted for clarity

Fig.2 2D bilayer network constructed by 1D $[Zn(1)(tpta)_{0.5}]_n$ and $[Zn(2)(H_2tpta)]_n$ chains in complex **1**

while the Zn(2) ions are connected by the 2(2′),4(4′)-carboxyl groups of $(H_2tpta)^{2-}$ anions to lead to a 1D $[Zn(H_2tpta)]_n$ zigzag chain. Interestingly, two such adjacent 1D chain are further associated together by ring dinuclear Zn_2 units of 1D $[Zn(tpta)_{0.5}]_n$ chain, and a 2D bilayer structure of **1** is thus formed. Furthermore, each 2D bilayer is further strengthened by dpe ligands with Zn-N distances of 0.202 1(6) and 0.209 3(5) nm, respectively (Fig.2). Although several types of double-layered architectures have been fabricated by the assembly of T-shaped[15] or rectangular building blocks[16], this type of molecular double-layered motif is, to the best of our knowledge, unprecedented. It is noteworthy that the adjacent 2D bilayer are further linked to each other by O–H⋯O hydrogen bonds (O(7)⋯O(6G) 0.266 5(7) nm, O(13)⋯O(8G) 0.290 3(7) nm, O(14)⋯O(11) 0.292 0(7) nm (symmetry code: G $-x+2$, $-y+1$, $-z+1$)) to complete the final 3D supramolecular architecture.

2.2 IR analysis

The IR spectrum of **1** exhibits a band at 1 691 cm^{-1}, assignable to the protonated carboxylate group of $(H_2L)^{2-}$ anion. The broad bands centered at ca. 3 444 cm^{-1} indicate the O-H stretching of water molecule. The absorption band at 1 612 cm^{-1} may be assigned to the asymmetric stretching vibrations of the carboxylate group, and the bands at 1 431 and 1 369 cm^{-1} are attributed to the symmetric stretching vibrations. These data are consistent with the crystal structure.

2.3 Thermal analysis

The thermal behaviors of **1** were studied on the crystal samples under N_2 atmosphere with a heating rate of 10 ℃·min^{-1}, shown in Fig.3. The first weight loss of 3.82% for **1** is in the range from 209 to 236 ℃ corresponding to the removal of two coordinated H_2O (calcd. 3.77%). Upon further heating, the 3D supramolecular framework is stable up to 287 ℃, followed by another weight loss at high temperature.

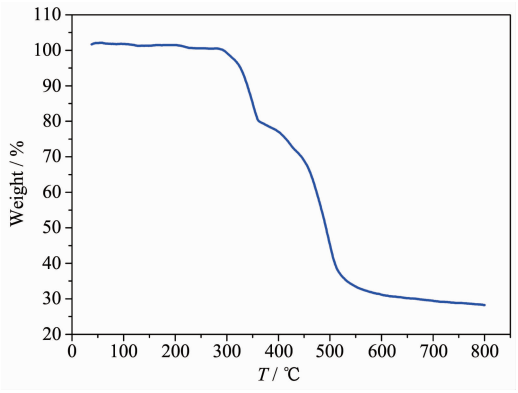


Fig.3 TG of the complex **1**

2.4 Photoluminescent property

Concerning the photoluminescent spectra, as shown in Fig.4, free H_4tpta has excitation peak at 327 for 410 nm emission. Complex **1** shows an intense emission peak at 420 nm (λ_{ex}=327 nm), which means a red shift of ca. 10 nm relative to that of the free H_4tpta. As complex **1** exhibits the similar emission peak to the free H_4tpta, we tentatively assign it to the intraligand photoluminescence[17-18]. In complex **1**, the

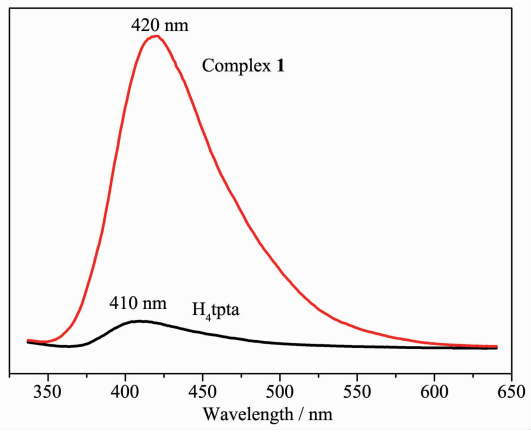


Fig.4 Emission spectra of H_4tpta and complex **1** in the solid state at room temperature

enhancement of photoluminescence may be attributed to ligand chelation to the metal center which effectively increases the rigidity of the ligand and reduces the loss of energy by radiationless decay[19-20]. The observation indicates that complex **1** may be excellent candidates for potential photoluminescent materials.

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