研究简报

4,4′-喹啉酸锌(Ⅱ)配位聚合物

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Zinc(Ⅱ) Coordination Polymer with 4,4′-quinoline Ligand

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Abstract: Hydrothermal treatment of racemic atropisomeric ligand diethyl (*R*,*S*)-7,7′-dimethyl-4,4′-biquinoline-3,3′-dicarboxylate (DDBD) in the presence of pyridine over 4 days at 140 ℃ with $Zn(OAc)_2$ offers zinc coordination polymer $[\{Zn(DBD)(pyridine)_2(H_2O)\}_n\{Zn(DBD)(H_2O)_{1/2}\}]_n$ (**1**), which shows weak fluorescence at about 490 nm at solid state at room temperature. CCDC: 631007.

Key words: zinc coordination polymer; 4,4′-quinoline acid; crystal structure; fluorescence

Recently, many attentions have been paid to the design, synthesis and characterization of organic-inorganic coordination compounds. These compounds bear the potential application such as reversible guest-exchange, shape selectivity, catalysis, gas storage, molecular recognition, photoluminescence, unusual magnetic, nonlinear, semiconducting properties, chirality and clathration ect[1~3]. However, such self-assembly processes involving metal ions and well-designed organic ligands haven′t been controlled by people, the crystal engineering of coordination frameworks with desired topologies and specific properties still remains a large challenge since it depends on a variety of factors that can influence the self-assembly process. Herein, we would like to report the synthesis of a novel zinc coordination compound with 4,4′-quinoline acid ligand displaying fluorescence and interesting frameworks.

1 Experimental

1.1 Preparation and analysis of polymer 1

Hydrothermal treatment of Zn $(OAc)_2$ (1 mmol), diethyl (*R*,*S*)-4,4′-biquinoline-7,7′-dimethyl-3,3′-dicarboxylate (1 mmol), H_2O (1 mL), pyridine (1 mL) and C_2H_5OH (2 mL) over 4 days at 140 ℃ yielded colorless block crystal $[\{Zn(DBD)(pyridine)_2(H_2O)\}_n\{Zn(DBD)(H_2O)_{1/2}\}]_n$ (**1**). IR (KBr, cm^{-1}): 3 424(m), 3 035(s), 1 618(s), 1 580(s), 1 569(s) 1 540(s), 1 510(m) 1 487(m), 1 460(m), 1 440(s), 1 380(s), 1 336(s), 1 267(s), 1 220(m), 1 130(m), 1 060(m), 1 010(m), 807(s), 769(s), 702(s), 611(m), 425(m).

Crystal date for **1**: $C_{54}H_{38}Zn_3N_6O_{10}$, Monoclinic, space group $P2_1/c$, M_r=1 127.01, a=1.419 4(8) nm, b=0.917 9(5) nm, c=1.825 9(11) nm, β=106.06(1)°, V=2.334 7(2) nm^3, Z=2, D_c=1.603 $Mg\cdot m^{-3}$, μ=1.599 mm, S=0.828, R_1=0.060 3, wR_2=0.134 7, T=296(2) K.

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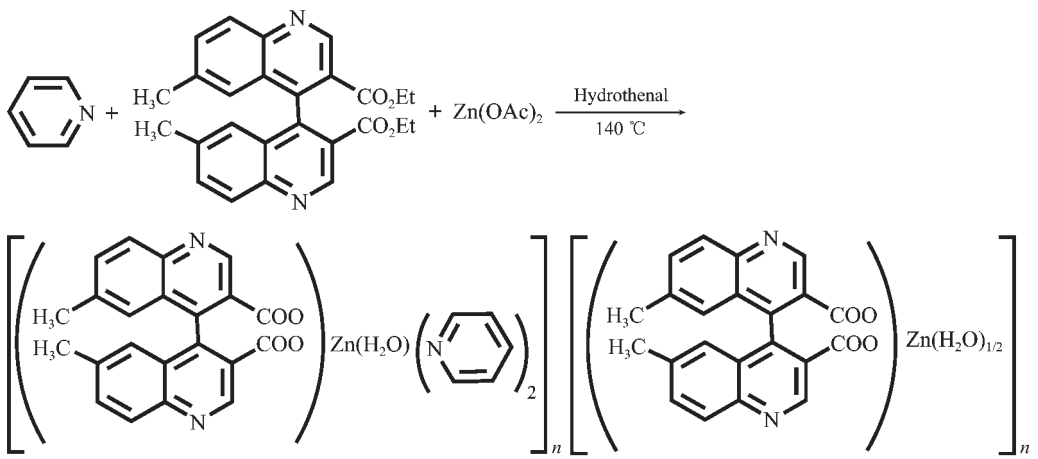


Scheme 1

CCDC: 631007.

2 Results and discussion

Treat with diethyl (*R*,*S*)-6,6′-dimethyl-4,4′-biquinoline-3,3′ -dicarboxylate (DDBD) and Zn $(OAc)_2$ presenting pyridine as the catalyst of hydrolyzing reaction under hydrothermal condition, afford two dimensional plane zinc coordination polymer. The analogy IR spectrum certify the successful synthesis of complex $[\{Zn(DBD)(pyridine)_2(H_2O)\}_n\{Zn(DBD)(H_2O)_{1/2}\}]_n$ (**1**).

In the crystal structure of coordination polymer **1**, there are two crystallographically independent zinc centers (Zn1 and Zn2) (Fig.1). The coordination environment of Zn1 can be best described as slightly distorted tetrahedron with one nitrogen atom from ligand DBD, one bridging oxygen atom from water and two oxygen atoms from ligand DBD. At the same time, one nitrogen atom and two oxygen atoms come independently from three different ligands DBD. While another zinc center (Zn2) was surrounded by two N atoms from pyridine in the axial positions and four oxygen atoms in the plane, two of the oxygen atoms are from two bridging water and the remained are from two different ligands. At the meantime, two Zn1 are connect together trough one Zn2, two bridging water and two bridging ligand DBD to form a node. Additionally, every ligand as a quadridentate compound coordinates to three Zn1 and a Zn2 through a nitrogen atom of quinoline ring and three oxygen atoms from carboxylate group. It needs to note that the three oxygen atoms connect to three zinc centers and one of carboxylate group of ligand connect to two zinc centers (Zn1 and Zn2) through its two O atoms. That is, only one nitrogen atom of quinoline ring and one oxygen atom of carboxylate group haven′t taken part in the coordination. Then, the ability of the DBD to act as a bridging ligand result in the formation of 2D layered coordination network. Simplify the nodes and the ligands as balls (as shown in Fig.2), we can find that in the zinc polymer′s 2D frameworks, every node connect to its surrounding six same nodes through six ligands which act as a tridentate bridging compound this time. Seen from the packing structure of **1**, 2D layered structure stack together with AA sequence to extend in three-dimension direction (Fig.3).

The bond length of Zn1-N (0.204 9 nm) (Table 1) is shorter than those of $[Zn\{(E)\text{-}3\text{-}C_5H_4N\text{-}C(NH_2)=CH\text{-}$

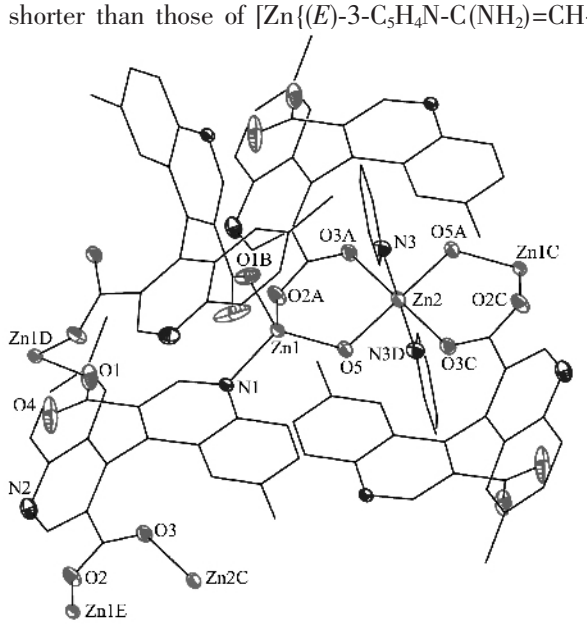
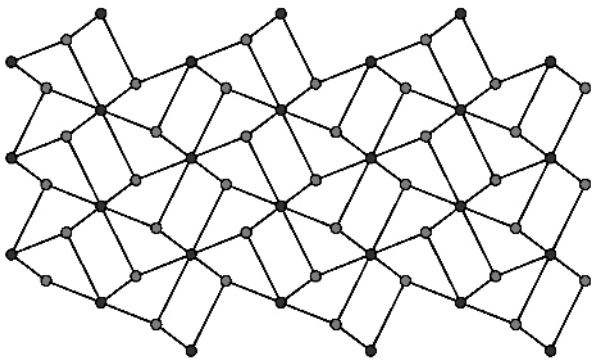


Fig.1 Crystal structure of **1**



Balls represent  and  alternately

Fig.2 2D plane framework of $[\{Zn(DBD)(pyridine)_2(H_2O)\}_n\{Zn(DBD)(H_2O)_{1/2}\}]_n$ (**1**)

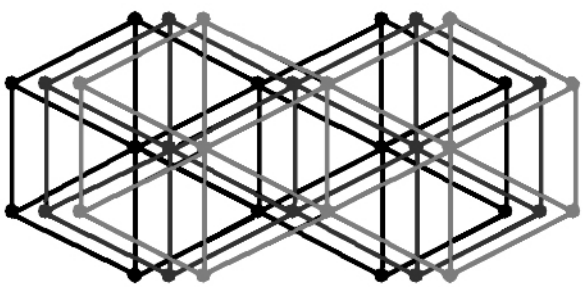


Fig.3 Packing view of $[\{Zn(DBD)(pyridine)_2(H_2O)\}_n\{Zn(DBD)(H_2O)_{1/2}\}]_n$ (**1**)

COO}]ClO_4 (**1**) (0.202 4(7)~0.202 9(8) nm), [Zn{(*E*)-3-C_5H_4N-CH=CH-COO}(OH)] (0.205 5(2) nm) and [Zn(3-(3-pyridyl)-3-aminopropionic acid)(NO_3)] (0.205 4(5)~0.208 6(4) nm)[4]. while the bond distance of Zn2-N (0.221 3) is longer than those of above-mention coordination polymer. In addition, the Zn-O distances (0.188 8~0.220 7 nm) is comparable to those found in above coordination compounds (0.196 7(7)~0.200 5(7) nm, 0.194 4(2)~0.195 1(2) nm and 0.204 6(4)~0.205 4(4) nm). Finally, the environment of Zn2 is near to ideal octahedron seen from the bond angles of compound **1**. All of the angles of two quinoline rings plane of the ligand in this polymer are about 85.9° which is close to rectangle since DBD is retricted rotation due to the bulky substituents in 3,3′, 4,4′and 6,6′ exsition.

From the Fig.4, it is easy to find that **1** displays blue luminescent spectrum at about 490 nm[5,6].

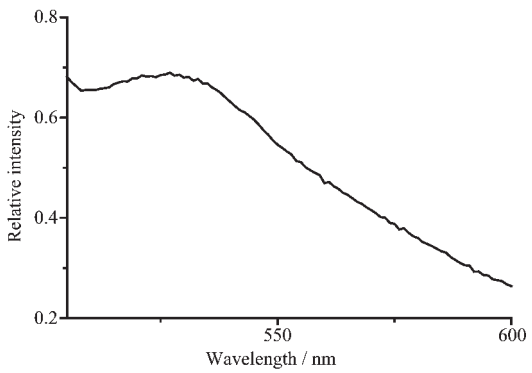


Fig.4 Solid-state emission spectrum of **1** at room temperature

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

Zn1-O5	0.188 8(2)	Zn1-O1B	0.191 0(2)	Zn1-O2A	0.198 9(2)
Zn1-N1	0.204 9(2)	Zn2-O5	0.202 0(2)	Zn2-O5A	0.202 0(2)
Zn2-O3C	0.220 7(2)	Zn2-O3D	0.220 7(2)	Zn2-N3	0.221 3(3)
Zn2-N3D	0.221 3(3)				
O5-Zn1-O1B	120.34(12)	O5-Zn1-O2A	105.62(10)	O1B-Zn1-O2A	97.67(11)
O5-Zn1-N1	119.81(9)	O1B-Zn1-N1	112.46(11)	O2A-Zn1-N1	93.38(10)
O5-Zn(2)-O5A	180.00(16)	O5-Zn2-O3A	96.46(8)	O5A-Zn2-O3A	83.54(8)
O5-Zn2-O3C	83.54(8)	O5A-Zn2-O3C	96.46(8)	O3A-Zn2-O3C	180.00(14)
O5-Zn2-N3	90.39(10)	O5A-Zn2-N3	89.61(10)	O3A-Zn2-N3	89.98(9)
O3C-Zn2-N3	90.02(9)	O5-Zn2-N3D	89.61(10)	O5A-Zn2-N3D	90.39(10)
O3A-Zn2-N3D	90.02(9)	O3-Zn2-N3D	89.98(9)	N3-Zn2-N3D	180.00(19)

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