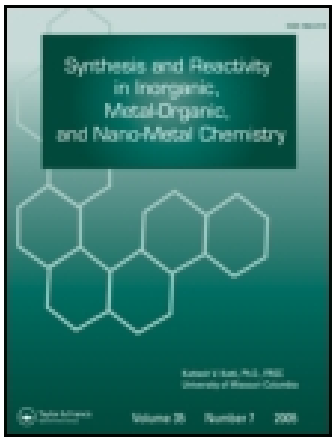

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

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A Novel 4-Connected Zn(II) Compound With 4,4′-Oxydiphthalic Acid: Synthesis, Structure and Luminescence

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A Novel 4-Connected Zn(II) Compound With 4,4′–Oxydiphthalic Acid: Synthesis, Structure and Luminescence

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A novel Zn(II) coordination polymer, $[Zn(H_2ODPT)(bpp)]_n$ (1) (H_4ODPT = 4,4′–oxydiphthalic acid, bpp = 1,3–bis(4–pyridyl)–propane), was hydrothermally synthesized by the reactions of Zn(II) nitrate, H_4ODPT, and bpp. Single crystal X-ray analysis reveals that 1 is a two-dimensional (2D) layer structure. In this 2D layer structure, H_4ODPT is half deprotoned into H_2ODPT^{2-}. Moreover, the luminescent property of this compound was also investigated in the solid state at room temperature.

Keywords coordination polymer, 4, 4′–oxydiphthalic acid, luminescence

INTRODUCTION

Design and synthesis of coordination polymers have experienced explosive development in the past few decades not only because of their intriguing topological frameworks but also because of their potential applications in the areas of luminescence, magnetism, nonlinear optics, gas storage, and so on.[1–4] Generally speaking, the basic strategy for fabricating novel metal-organic frameworks is to combine the transition metal ions and organic bridging ligands under appropriate conditions.[2] As a matter of fact, crystal engineering of desired coordination polymers is still a challenge to chemists. Thus, the key factor for constructing of coordination polymers with desired structure and properties is the judicious selection of metal centres and organic ligands with suitable shape, functionality, flexibility, and symmetry. Among various organic ligands, polycarboxylate ligands, such as isophthalic acid, terephthalic acid, benzenetricarboxylic acid, and so on, have been widely used by researchers to construct coordination polymers owing to their variety of coordination modes and sensitivity to pH values of the carboxylate groups.[5,6] Recently, 4, 4′–oxydiphthalic acid because of its flexibility to construct various interesting interpenetrating or self-penetrating networks have attracted our attention.[7] Therefore, in this work, we used 4, 4′–oxydiphthalic acid and bpp as the organic bridging ligands to assemble with Zn(II) ions under hydrothermal conditions, and successfully isolated a new luminescent coordination polymer, namely $[Zn(H_2ODPT)(bpp)]_n$ (**1**). In this article, we report the synthesis, structure, and luminescence of this compound.

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EXPERIMENTAL

Materials and Pyhsical Measurements

All reagents and solvents employed were commercially available and used without further purification. The synthesis was carried out in 23-mL polytetrafluoroethylene lined stainless steel containers under autogenous pressure. Elemental analyses (C, H, and N) were determined with an elemental Vairo EL III analyzer. The fluorescence spectra were measured on polycrystalline samples at room temperature using an Edinburgh FLS920 TCSPC fluorescence spectrophotometer. Single-crystal X-ray diffraction data for compound 1 were recorded on Oxford Xcalibur E diffractometer (Mo$K\alpha$ radiation, $\lambda = 0.71073$, graphite monochromator) at 293(2) K.

*Synthesis of $[Zn(H_2ODPT)(bpp)]_n$ (**1**)*

A mixture of $Zn(NO_3)_3{\cdot}6H_2O$ (0.20 mmol, 0.060 g), H_4ODPTA (0.20 mmol, 0.062 g), and bpp (0.2 mmol, 0.0396 g) in distilled water (12 mL) was placed in a Teflon-lined stainless steel vessel, heated to 160°C and held at that temperature for 3 days, then cooled to room temperature. Colorless block crystals were obtained. Yield: 43%. Elemental analysis: Anal. Calcd. for $C_{29}H_{22}N_2O_9Zn$ (%): C, 46.27; H, 1.23; N, 3.22. Found (%):C, 46.27; H, 1.23; N, 3.22.

Crystallographic Data Collection and Structures Determination

Suitable single crystal of **1** was carefully selected under an optical microscope and glued to thin glass fibers. Structural measurements were performed on a computer-controlled Oxford Xcalibur E diffractometer with graphite-monochromated

TABLE 1
Crystal data and structure refinements for compound **1**

Empirical formula	$C_{29}H_{22}N_2O_9Zn$
Temperature (K)	293(2)
Crystal color	colorless
Crystal size	0.20 × 0.20 × 0.20 mm^3
Formula weight	605.86
Crystal system	Monoclinic
Space group	*P21/n*
a (Å)	11.637(6)
b (Å)	10.905(6)
c (Å)	21.023(12)
α (°)	90.00
β (°)	97.947(11)
γ (°)	90.00
Volume (Å^3)	2642(3)
Z	4
Density (calculated)	1.523 g/cm^3
Abs. coeff. (mm^{-1})	0.990
F(000)	1240
Refinement method	Full-matrix least-squares on F^2
Reflections collections	18062
Independent reflections	4631 (R_{int} = 0.1082)
θ range for data collection	2.57–25.00
h,k,l range	$-13 \le h \le 13$, $-11 \le k \le 12$, $-25 \le l \le 24$
Goodness-of-fit on F^2	1.033
Final *R* indices [*I*>2sigma(*I*2)]	$R = 0.0696$, $wR_2 = 0.2124$
R (all data)	$R = 0.0957$, $wR_2 = 0.2395$
Largest difference peak and hole	0.626 and −0.738 Å^3

Mo-*Kα* radiation (λ=0.71073 Å) at T = 293(2) K. Absorption correction was made using the SADABS program.[8] The structure was solved using the direct method and refined by full-matrix least-squares methods on F^2 by using the SHELXL-97 program package.[9]

TABLE 2
Selected bond lengths (Å) and angles (°) for compound **1**

Zn(1)-O(1)	1.961(4)	Zn(1)-N(2)^a	2.035(5)
Zn(1)-N(1)	2.039(5)	Zn(1)-O(8)^b	2.098(5)
O(1)-Zn(1)-N(2)^a	101.94(18)	O(1)-Zn(1)-N(1)	118.87(19)
N(2)^a-Zn(1)-N(1)	109.08(18)	O(1)-Zn(1)-O(8)^b	97.56(18)
N(2)^a-Zn(1)-O(8)^b	133.32(18)	N(1)-Zn(1)-O(8)^b	97.38(17)

Symmetry codes: (a): x − 1/2, −y + 1/2, z - 1/2; (b): x − 1, y, z.

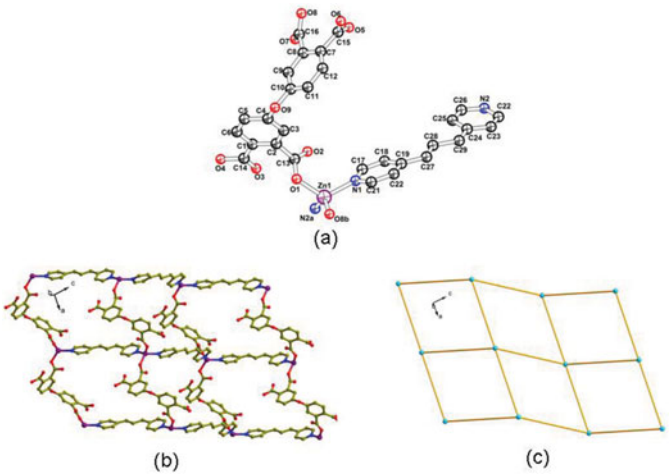

FIG. 1. (a) Coordination environment of compoud **1**, all hydrogen atoms were omitted for clarity (symmetry code: (a) –0.5 + *x*, 0.5 – *y*, –0.5 + *z*; (b) –1 + *x*, *y*, *z*. (b) 2D layer structure of **1**. (c) Schematic representation of 4-connected **sql** topological net.

RESULT AND DISCUSSION

Crystal Structure Description

Single-crystal X-ray diffraction analysis reveals that **1** crystallizes in $P2_1/n$ space group with an asymmetric unit containing one crystallographic independent Zn(II) ion, one H_2ODPTA^{2-} anion and one bpp ligand. The partial structure of **1** is shown in Figure 1a. It can be clearly seen that each Zn(II) ion is four-coordinated by two nitrogen atoms from two different bpp ligands and three carboxylate oxygen atoms from two different H_2ODPTA^{2-} anions. The average of Zn-O/N distance is 2.031(4) Å, 2.037(5) Å, respectively, which are comparable to those reported Zn(II) coordination polymers.[10] In 1, H_4ODPTA is half deprotoned into H_2ODPTA^{2-}, which acts as a bidentate ligand with its two carboxylate groups in uniform monodentate mode. The dihedral angle between the two phenyl rings of

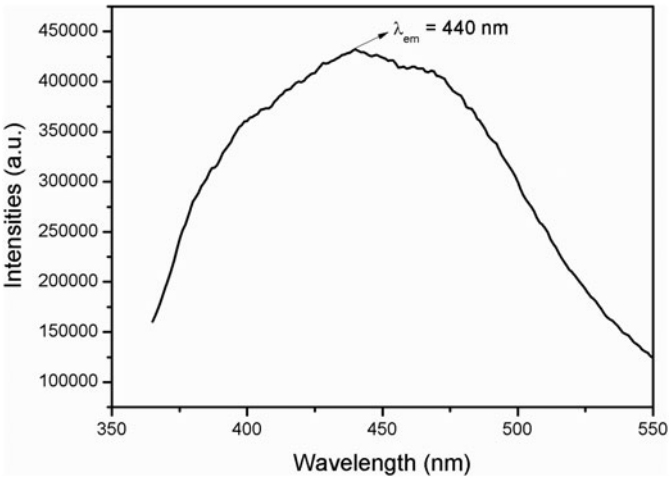

FIG. 2. Emission spectrum of **1** in the solid state at room temperature.

H_2ODPTA^{2-} is 89.197°. Therefore, Zn(II) ions are bridged by H_2ODPTA^{2-} and bpp into a 2D wave-like layer (Figure 1b). If each Zn(II) is simplified into a 4-connected nodes, and each bridged ligand (H_2ODPTA^{2-} and bpp) can be looked as linkers, this 2D layer can be simplified into a 4-connected **sql** net with the short schläfli symbol of $\{4^4.6^2\}$ (Figure 1c).

Photoluminescent Property

Considering the excellent photoluminescent properties of d^{10} metal-organic frameworks, the luminescence of **1** was investigated at room temperature. As shown in Figure 2, intense emission maximum at 440 nm can be observed upon excitation of 330 nm. According to previously reported document, H_4ODPTA showed the emission maximum at 371 nm upon excitation of 339 nm.[7] Therefore, the luminescent emission of **1** may be tentatively attributed to the ligand-to-metal-charge-transfer (LMCT).

CONCLUSIONS

In summary, a new luminescent compound has been successfully synthesized and characterized. The compound is a 2D wave-like layered structure and can be simplified into a 4-connected **sql** net with the short schläfli symbol of $\{4^4.6^2\}$.

SUPPLEMENTAL MATERIAL

CCDC No. 926460 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via htt://www.ccdc.cam.ac.uk/data_request/cif.

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