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A Zinc Complex Based on 4-Bromoisophthalic Acid and 1,2-Bi(4-pyridyl)ethane: Hydrothermal Synthesis, Crystal Structure, and Fluorescent Properties

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A novel zinc complex formulated as [Zn(Bript)(bpa)(H_2O)]$_n$ (1) (H_2Bript = 4-bromoisophthalic acid, bpa = 1,2-bi(4-pyridyl)ethane) has been synthesized through hydrothermal reaction. It was structurally characterized by elemental analysis and x-ray single-crystal diffraction. The x-ray crystal structure shows that the complex belongs to monoclinic systems, $P2_1/n$ space group, and $a = 10.997(6)$ Å, $b = 14.578(8)$ Å, $c = 12.963(7)$ Å, $\beta = 105.993(6)°$. The adjacent Zn atoms are bridged by Bript to form a one-dimensional (1D) chain. Such 1D chains are further connected by hydrogen bonding to generate a three-dimensional (3D) supramolecular network. Fluorescence measurements show that 1 has medium fluorescent emissions at 404 nm and 468 nm upon excitation at 288 nm.

Keywords 1, 2-bi(4-pyridyl)ethane, 4-bromoisophthalic acid, crystal structure, fluorescent properties

INTRODUCTION

During the past two decades, design and synthesis of metal–organic hybrid materials have been of great interest because of their intriguing topologies and potential applications as functional materials, such as in gas adsorption,[1] luminescence, [2] catalysis,[3] ion exchange,[4] nonlinear optics,[5] and magnets.[6] One of the current interesting topics is to rationally design and synthesize coordination polymers and supramolecular assemblies by coordination bonds or noncovalent contacts such as hydrogen bonding. The key step in building these complexes is to use suitable organic ligands, metal cations, and auxiliary ligands. For instance, 1,*n*-benzenedicarboxylate ($n = 2, 3, 4$), 1,3,5-benzenetricarboxylate, 1,2,4-benzenetricarboxylate, 1,2,3-benzenetricarboxylate, 1,2,4,5-benzenetetracarboxylate, and their derivatives are often selected as versatile coordinating ligands to coordinate with metal ions in a variety of modes.[7–15] 4-Bromoisophthalic acid is a versatile ligand that can coordinate to transition metals in a variety of modes with donor atoms.[16–20]

Among the N-donor ligands, *exo*-bidentate rodlike N,N′-donor ligands, such as 4,4′-bipyridine, can have significant influence on the assembly systems of multicarboxylate ligands and metal centers. Its derivatives bpe (1,2-bi(4-pyridyl)ethene), bpp (1,3-bi(4-pyridyl)propane), and bpa (1,2-bi(4-pyridyl)ethane) with certain spacers between the two 4-pyridyl rings may also lead to fascinating architectures with interesting properties. So they are always employed to construct one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) coordination polymers. In addition, they could act as both hydrogen-bond acceptors and donors.[21,22]

In this study, we reacted 4-bromoisophthalic acid (H_2Bript) bpa with Zn(II) ion, yielding a new polymer, [Zn(Bript)(bpa)(H_2O)]$_n$ (**1**). Herein, we report its hydrothermal synthesis, structural characterization, thermal stabilities, and luminescent properties.

EXPERIMENTAL

Materials and Physical Measurements

All chemicals were commercially purchased and used without further purification. Elemental analyses (C, H, and N) were performed on a Thermo Science Flash 2000 element analyzer. Thermogravimetric analysis (TGA) was performed on a SII EXStar6000 TG/DTA6300 analyzer heated from 15 to 895°C under nitrogen. The photoluminescent properties were measured on an F-4500 FL spectrophotometer.

Synthesis of Complex 1

A mixture of 4-bromoisophthalic acid (24.5 mg, 0.1 mmol), bpa (18.5 mg, 0.1 mmol), $Zn(Ac)_2{\bullet}4H_2O$ (24 mg, 0.1 mmol), and KOH (5.6 mg, 0.1 mmol) was added into water (12 mL) in a Teflon-lined stainless-steel vessel. The mixture was heated at 433 K for 3 days, and then slowly cooled down to room temperature. Colorless block crystals of **1** were obtained. Anal. (%): Calc. for $C_{20}H_{17}BrN_2O_5Zn$: C, 47.04; H, 3.33; N, 5.48. Found: C, 47.00; H, 3.28; N, 5.40.

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TABLE 1
Crystal data and structure refinement details for compound **1**

Empirical formula	$C_{20}H_{17}BrN_2O_5Zn$
fw	510.64
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	10.997(6)
b (Å)	14.578(8)
c (Å)	12.963(7)
β (°)	105.993(6)
V (Å^3)	1997.7(19)
Z	4
T (K)	296(2)
D_{calc} (g•cm^{-3})	1.698
μ(mm^{-1})	3.264
F(000)	1024
Max./min. transmission	0.7666/0.5804
θ range (°)	2.38 to 25.50
Reflections collected	11051
Independent reflections (R_{int})	3691
Restraint/parameters	0/262
Goodness-of-fit (GOF) on F^2	1.045
R_1,[a] wR_2 [$I > 2\sigma(I)$]	0.0309, 0.0698
R_1,wR_2 (all data)	0.0458, 0.0749
Largest diff. peak and hole (e •Å^{-3})	0.778/–0.381

[a] $R = [\sum ||F_0| - |F_c|| / \sum |F_0|]$, $R_W = \sum w\,[|F_0^2 - Fc^2|^2 / \sum w\,(|F_w|^2)^2]^{1/2}$.

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

Zn(1)–O(5)#1[a]	1.933(2)	Zn(1)–O(2)	1.969(2)
Zn(1)–O(1)	2.001(2)	Zn(1)–N(1)	2.016(2)
O(5)#1–Zn(1)–O(2)	109.97(9)	O(5)#1–Zn(1)–O(1)	102.78(9)
O(2)–Zn(1)–O(1)	100.36(9)	O(5)#1–Zn(1)–N(1)	130.55(10)
O(2)–Zn(1)–N(1)	106.96(10)	O(1)–Zn(1)–N(1)	101.66(10)

[a] Symmetry transformations used to generate equivalent atoms: #1: x – 1/2, –y + 1/2, z + 1/2.

Crystallographic Data Collection and Structure Determination

Single-crystal diffraction data for **1** were collected on a Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) at room temperature. The structures were solved using direct methods and successive Fourier difference synthesis (SHELXS-97)[23] and refined using the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all nonhydrogen atoms (SHELXL-97).[24] An empirical absorption correction was applied using the SADABS program. The hydrogen atoms were placed in calculated positions and refined using a riding on attached atoms with isotropic thermal parameters 1.2 times those of their carrier atoms. Corrections for L_p factors were applied and all non-hydrogen atoms were refined with anisotropic thermal parameters. Crystallographic and experimental details and the selected bond lengths and bond angles are are summarized in Table 1, Table 2, and Table 3, respectively.

RESULTS AND DISCUSSION

Crystal Structure Description

The asymmetric unit of 1 contains one Zn^{II} center, one Bript dianion, and one bpa ligand, as well as one coordinated water molecule. Both of the carboxylate groups of the H_2Bript are deprotonated. Each Bript acts as a bis-monodentate bridge linking two zinc atoms. The Zn ion is four-coordinated with a distorted tetrahedral geometry, as shown in Figure 1. The four coordinated atoms come from one nitrogen atoms of bpa ligand, two carboxylate oxygen atoms of two Bript ligands, and one water

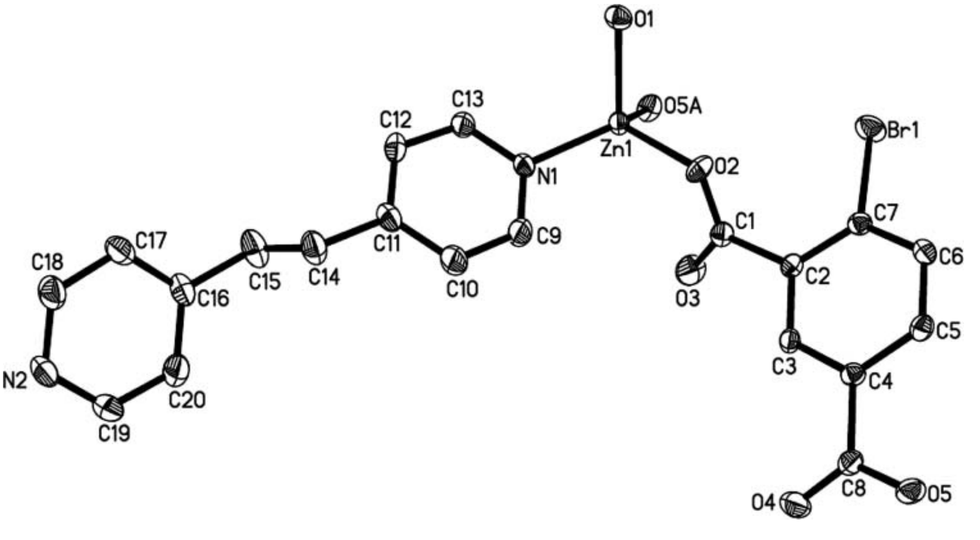

FIG. 1. Coordination environment of Zn(II) ion in **1.** Hydrogen atoms are omitted for clarity. Symmetry codes: A, x – 1/2, –y + 1/2, z + 1/2.

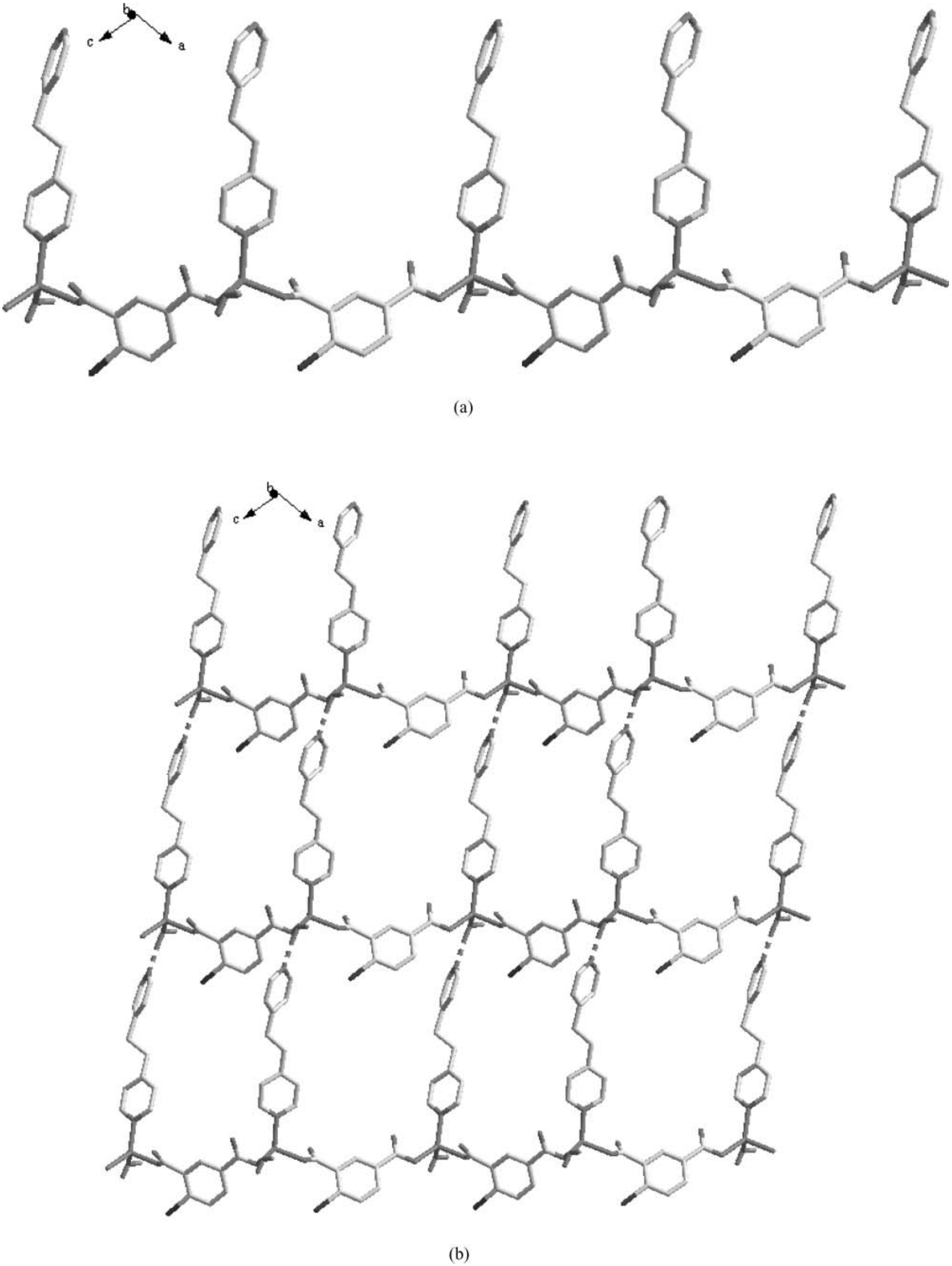

FIG. 2. (a) Perspective view of the 1D chain in **1**. (b) 2D view in **1** linked by hydrogen bonding O-H. . .N. Hydrogen bonds are represented as dashed lines.

TABLE 3
Distance (Å) and angles (°) of hydrogen bonding for complex **1**

D–H. . .A[a]	d(D–H)	d(H. . .A)	d(D. . .A)	∠(DHA)
O(1)–H(2W). . .O(2)#3	0.83	1.94	2.750(3)	165.2
O(1)–H(1W). . .N(2)#4	0.83	1.87	2.699(3)	174.3

[a] Symmetry transformations used to generate equivalent atoms: #3: –x + 2, –y, –z + 1; #4: x + 1, y, z + 1.

molecule. The Zn–N bond length is 2.013(10) Å and the Zn–O ones are in the range of 1.929(8)–2.019(11) Å, respectively.

The adjacent Zn atoms are bridged by Bript to form a 1D chain, as shown in Figure 2a. Such 1D chains are further connected by hydrogen bonding, between the coordinated-water molecules and the nitrogen of bpa (d(O. . .N) = 2.699(3) Å, EMBED Equation.3 (OHN) = 174.3°) to generate a 2D network (Figure 2b). The 2D networks are further linked by hydrogen bonding, between the coordinated water molecules and the carboxylate oxygen groups of the Bript ligands (d(O. . .O) = 2.750(3) Å, ∠ (OHO) = 165.2°), to form a 3D supramolecular architecture (Figure 3).

Thermal Analysis

To investigate its thermal stabilities, the TGA of **1** was studied in our laboratory. The experiment was performed on samples consisting of numerous single crystal of **1** under N_2 atmosphere with a heating rate of 10°C min^{-1}. The framework of **1** can be stable up to 340°C, which make it a potential candidate for practical applications. Compound **1** lost its coordinated water molecules and bpa molecules from 340 to 507°C (obsd. 39.4%, calcd. 39.6%). Then the compound begins to slowly decompose at 507°C, as shown in Figure 4.

Fluorescence Spectrum

Coordination polymers with d^{10} metal centers and organic ligands are promising candidates for photoactive materials with potential applications such as chemical sensors and photochemistry.[25] The solid-state photoluminescent property of compound **1** has been investigated at room temperature. The fluorescence and emission peaks are shown in Figure 5. The

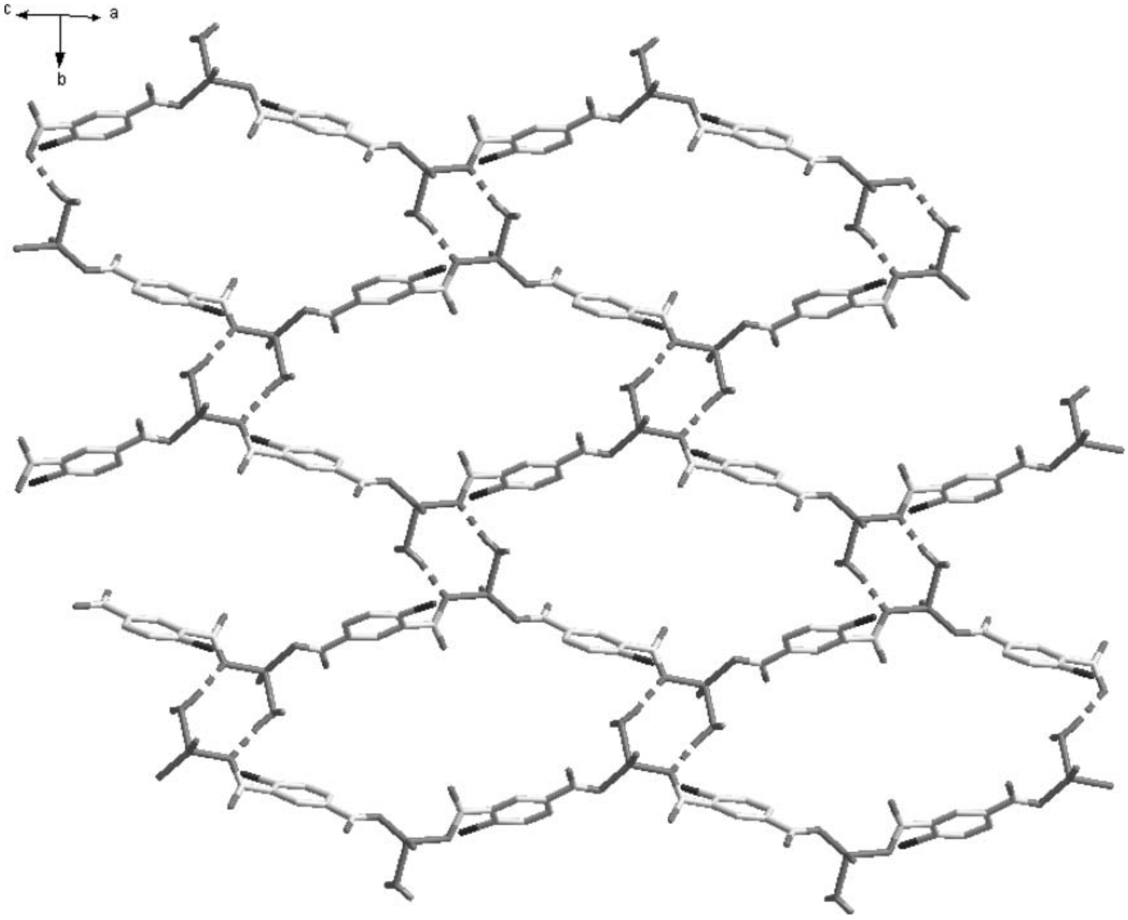

FIG. 3. 2D view in **1** linked by hydrogen bonding O-H. . .O. Hydrogen bonds are represented as dashed lines.

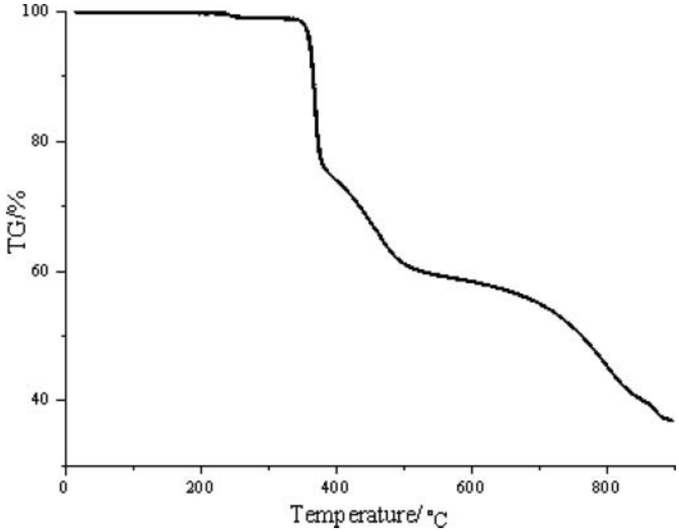

FIG. 4. TGA plot of complex **1**.

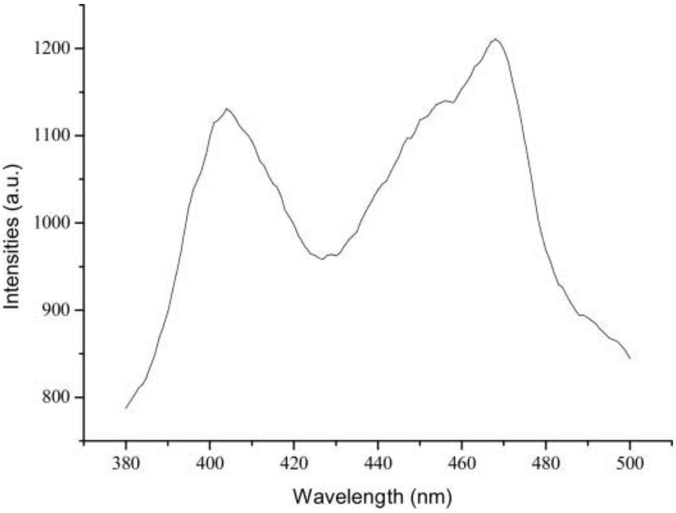

FIG. 5. Fluorescence and emission spectra of **1** in the solid state at room temperature.

measurement of photoluminescence spectra of **1** shows a fluorescence emission at 404 nm and 468 nm upon excitation at 288 nm.

CONCLUSIONS

In summary, a new zinc complex has been synthesized and characterized. Complex **1** contains 1D infinite chains, and these 1D chains are further linked by hydrogen bonding to form a 3D supramolecular network. Fluorescence measurement show that **1** has medium fluorescent emission. Further syntheses and studies of structures and properties of coordination frameworks with the H_2Bript ligand and other metal ions are under way in our laboratory.

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