

# A New 3D Supramolecular Complex (Dimethylammonium 4,4'-([2,2'-Bipyrimidine]-5,5'-diyl)bis(2-hydroxybenzoate) Dihydrate): Synthesis, Structure and Luminescent Property<sup>①</sup>

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**ABSTRACT** A new 3D supramolecular complex, namely dimethylammonium 4,4'-([2,2'-bipyrimidine]-5,5'-diyl)bis(2-hydroxybenzoate) dihydrate, has been synthesized by the reaction of 4,4'-([2,2'-bipyrimidine]-5,5'-diyl)bis(2-hydroxybenzoic acid) with aqueous dimethylamine solution and characterized by single-crystal X-ray diffraction, <sup>1</sup>H NMR spectroscopy and elemental analysis. It belongs to triclinic system, space group  $P\bar{1}$  with  $a = 6.5539(4)$ ,  $b = 9.4977(6)$ ,  $c = 12.1407(8)$  Å,  $\alpha = 72.299(6)$ ,  $\beta = 89.160(5)$ ,  $\gamma = 70.797(8)$ °;  $V = 676.52(8)$  Å<sup>3</sup>,  $Z = 1$ ,  $M_r = 556.57$ ,  $\mu = 0.103$  mm<sup>-1</sup>,  $D_c = 1.366$  g/cm<sup>3</sup>,  $F(000) = 294$ , the final  $R = 0.0828$  and  $wR = 0.2083$  for 1934 observed reflections with  $I > 2\sigma(I)$ . The 4,4'-([2,2'-bipyrimidine]-5,5'-diyl)bis(2-hydroxybenzoic acid) dianion, dimethylammonium cation, and water molecule are interconnected by O–H···O, N–H···N, and N–H···O hydrogen bonds, forming a two-dimensional (2D) layer. Two adjacent 2D layers are further stacked into a three-dimensional supramolecular structure through O–H···O hydrogen bonds. In addition, the luminescent property of this supramolecular complex has also been investigated.

**Keywords:** 4,4'-([2,2'-bipyrimidine]-5,5'-diyl)bis(2-hydroxybenzoic acid), dimethylammonium, crystal structure; DOI: 10.14102/j.cnki.0254-5861.2011-3058

## 1 INTRODUCTION

Aromatic polycarboxylic acids (i.e., terephthalic, isophthalic, trimesic, and pyromellitic acid) have been widely used for constructing metal-organic frameworks (MOFs) and hydrogen-bonded organic frameworks (HOFs)<sup>[1-8]</sup>. A large number of aromatic polycarboxylic acids have been synthesized so far<sup>[9-15]</sup>. Rosseinsky M. J. and co-workers<sup>[16]</sup> used a X-shaped aromatic tetracarboxylic acid 1,3,6,8-tetrakis(*p*-benzoic acid)pyrene for constructing a permanently microporous fluorescent metal-organic framework, [In<sub>2</sub>(OH)<sub>2</sub>(TBAPy)] (guest). Yaghi and co-workers<sup>[17]</sup> utilized an aromatic dicarboxylic acid 2,2'-bipyridine-5,5'-dicarboxylic acid (H<sub>2</sub>bpydc) to react with AlCl<sub>3</sub>·6H<sub>2</sub>O for affording

Al(OH)(bpydc) (MOF-253), which is the first metal-organic framework with open 2,2'-bipyridine (bpy) coordination sites. Lin and co-workers<sup>[18]</sup> synthesized three enantiopure Mn-Salen dicarboxylic acid ligands for constructing chiral MOFs, which were applied in catalyzing enantioselective epoxidation of alkenes. Cao and co-workers<sup>[19]</sup> employed aromatic 1,3,6,8-tetrakis(*p*-benzoic acid)pyrene to get an ultra-robust hydrogen-bonded organic framework. Wu and co-workers<sup>[11]</sup> made use of 3,3',5,5'-tetrakis(4-carboxyphenyl)-1,1'-biphenyl (H<sub>4</sub>TCBP) for constructing an ultrastable and easily regenerated hydrogen-bonded organic framework with permanent porosity. Bian and co-workers<sup>[20]</sup> designed and synthesized a hydrogen-bonded organic framework (MA-IPA) with ultralong organic phosphorescence through self-assembly

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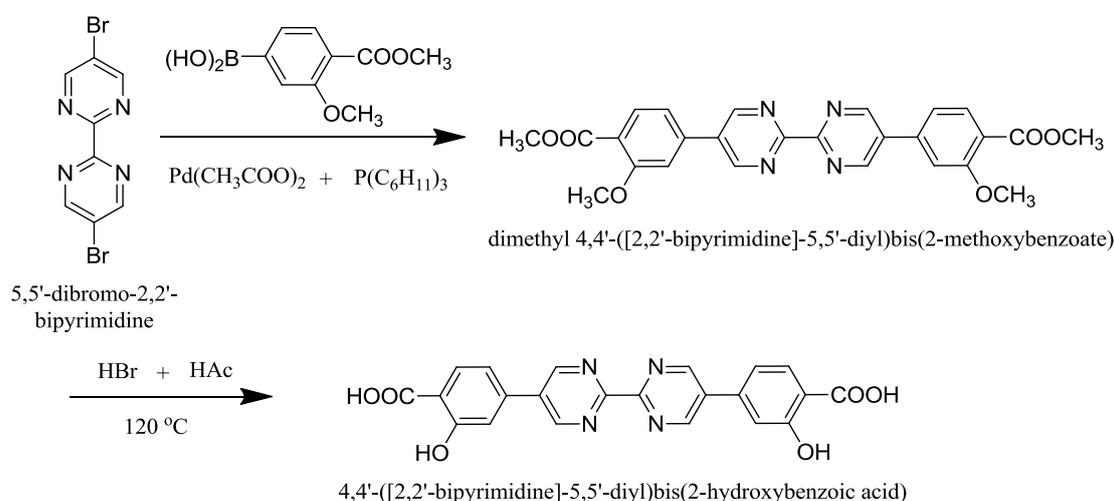
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ly of melamine (MA) and isophthalic acid (IPA) in aqueous media. However, the use of 4,4'-([2,2'-bipyrimidine]-5,5'-diyl)bis(2-hydroxybenzoic acid) with dimethylamine for preparing supramolecular organic frameworks has not been reported to date. In the present paper, we report the synthesis, structure and luminescent property of a new 3D supramolecular complex based on 4,4'-([2,2'-bipyrimidine]-5,5'-diyl)bis(2-hydroxybenzoic acid).

## 2 EXPERIMENTAL

### 2.1 Synthesis of 4,4'-([2,2'-bipyrimidine]-5,5'-diyl)bis(2-hydroxybenzoic acid)



**Scheme 1.** Synthetic pathway for 4,4'-([2,2'-bipyrimidine]-5,5'-diyl)bis(2-hydroxybenzoic acid)

In a 250 mL three-necked round-bottomed flask equipped with a reflux condenser and a magnetic stirring bar were placed 5,5'-dibromo-2,2'-bipyrimidine (3.16 g, 10.00 mmol), 3-methoxy-4-(methoxycarbonyl)phenylboronic acid (6.30 g, 15.00 mmol), potassium carbonate (6.9 g, 50.0 mmol), dioxane (120 mL) and water (24 mL). The mixture was degassed with nitrogen for 30 min, and to the flask were quickly added palladium acetate (0.40 g, 1.78 mmol) and tricyclohexylphosphine (1.00 g, 3.60 mmol) under a N<sub>2</sub> atmosphere. The reaction mixture was heated to reflux for 48 h. After the completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature. The solvents were evaporated with a rotary evaporator. 100 mL of water was added to the residue, then stirred for 30 min. The resulting crude product was filtered at the pump and washed with water. It was recrystallized from DMF, giving 3.43 g (70.0%) of pure dimethyl 4,4'-([2,2'-bipyrimidine]-5,5'-diyl)bis(2-methoxybenzoate). Calcd. for C<sub>26</sub>H<sub>22</sub>N<sub>4</sub>O<sub>6</sub>: C,

All chemicals and solvents were purchased commercially and used without further purification. The 5,5'-dibromo-2,2'-bipyrimidine was prepared according to the literature method<sup>[21]</sup>. <sup>1</sup>H NMR spectrum was taken on a Bruker Avance III 400 MHz spectrometer with TMS as an internal standard. Elemental analyses (C, H, and N) were carried out using an Elemental Vario EL III analyzer. Thermogravimetric analyses were performed under nitrogen with a PerkinElmer TGA-7 TG analyzer. The luminescent properties for the solid samples were measured on a Hitachi F-4500 fluorescent spectrometer at room temperature.

64.19; H, 4.56; N, 11.52%. Found: C, 64.34; H, 4.63; N, 11.39%. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 9.416(s, 4ArH), 7.821 (d, *J* = 8.0 Hz, 2ArH), 7.647 (s, 2ArH), 7.553(d, *J* = 7.6 Hz, 2ArH), 3.994 (s, 2-OCH<sub>3</sub>), 3.848 (s, 2-OCH<sub>3</sub>) ppm.

A 250 mL three-necked flask equipped with a magnetic stirring bar and a reflux condenser was charged with dimethyl 4,4'-([2,2'-bipyrimidine]-5,5'-diyl)bis(2-methoxybenzoate) (486 mg, 1.00 mmol, 1.00 eq.). HBr (50 mL) and AcOH (50 mL) were added, and the non-homogeneous reaction mixture was allowed to stir at reflux for 48 h. The reaction mixture was allowed to cool to room temperature, poured into cold water (100 mL) and filtered. The precipitate was washed with cold water (2 × 50 mL) and then recrystallized from *N,N*-dimethylformamide to yield 4,4'-([2,2'-bipyrimidine]-5,5'-diyl)bis(2-hydroxybenzoic acid) (0.395 g, 91.86%) as a light brown solid. Calcd. for C<sub>22</sub>H<sub>14</sub>N<sub>4</sub>O<sub>6</sub>: C, 61.40; H, 3.28; N, 13.02%. Found: C, 61.53; H, 3.39; N, 12.91%. <sup>1</sup>H

NMR (400MHz, DMSO-*d*<sub>6</sub>):  $\delta$  9.420 (s, 4ArH), 7.949 (s, 2ArH), 7.569 (s, 2ArH), 7.499 (d,  $J = 8.4$  Hz, 2ArH) ppm.

## 2. 2 Synthesis of the dimethylammonium

### 4,4'-([2,2'-bipyrimidine]-5,5'-diyl)bis(2-hydroxybenzoate) dihydrate

0.215 g (0.5 mmol) of 4,4'-([2,2'-bipyrimidine]-5,5'-diyl)bis(2-hydroxybenzoic acid) was dissolved in 40 mL of dimethylamine solution (40%) and then refluxed for about 0.5 h. The resulting clear solution was cooled to room temperature. The undissolved materials were removed by filtration. The filtrate was set aside to crystallize, after one week, giving the title supramolecular complex crystals (0.202 g, 72.6% yield based on 4,4'-([2,2'-bipyrimidine]-5,5'-diyl)bis(2-hydroxybenzoic acid)). Calcd. for C<sub>26</sub>H<sub>32</sub>N<sub>6</sub>O<sub>8</sub>: C, 56.11; H, 5.80; N, 15.10%. Found: C, 56.32; H, 5.98; N, 14.97%. <sup>1</sup>H NMR (400MHz, DMSO-*d*<sub>6</sub>):  $\delta$  9.293 (s, 4ArH), 7.856 (d,  $J = 8.0$  Hz, 2ArH), 7.190 (s, 2ArH), 7.139 (d,  $J = 7.2$  Hz, 2ArH), 2.593 (s, 12H, 4(-CH<sub>3</sub>)) ppm.

## 2. 3 X-ray crystal structure determination of the dimethylammonium 4,4'-([2,2'-bipyrimidine]-5,5'-diyl)bis(2-hydroxybenzoate) dihydrate

Single-crystal X-ray data for the title supramolecular complex were collected on an EosS2 four circle diffractometer equipped with a graphite-monochromatic MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) at room temperature. The crystal structure was solved by direct methods using the SHELXS-97 program<sup>[22]</sup> and refined by full-matrix least-squares methods with the SHELXL-97 program<sup>[23]</sup>. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were added to their calculated positions and refined using a riding model. The final  $R = 0.0828$  and  $wR = 0.2083$  for 1934 observed reflections with  $I > 2\sigma(I)$ .  $(\Delta\rho)_{\max} = 0.55$  and  $(\Delta\rho)_{\min} = -0.23$  e/Å<sup>3</sup>. The goodness-of-fit on  $F^2(S)$  is 1.085. Selected bond lengths and bond angles are listed in Table 1, and the classical hydrogen bonds are shown in Table 2.

Table 1. Selected Bond Lengths (Å) and Bond Angles (°) for the Title Complex

Bond	Dist.	Bond	Dist.
O(1)–C(7)	1.359(3)	N(1)–C(1)	1.328(3)
O(2)–C(11)	1.256(4)	N(1)–C(2)	1.333(3)
O(3)–C(11)	1.245(4)	N(2)–C(1)	1.337(3)
N(2)–C(4)	1.334(3)	C(1)–C(1) <sup>1</sup>	1.500(5)
Angle	(°)	Angle	(°)
C(1)–N(1)–C(2)	116.5(2)	N(1)–C(1)–C(1) <sup>1</sup>	117.2(3)
C(4)–N(2)–C(1)	115.8(2)	N(2)–C(1)–C(1) <sup>1</sup>	116.7(3)
N(1)–C(1)–N(2)	126.1(2)	N(1)–C(2)–C(3)	123.4(2)
N(2)–C(4)–C(3)	123.7(3)	O(1)–C(7)–C(6)	117.0(3)
O(1)–C(7)–C(8)	121.3(3)	O(2)–C(11)–C(8)	117.1(3)
O(3)–C(11)–O(2)	124.8(3)	O(3)–C(11)–C(8)	118.1(3)

Symmetry code: <sup>1</sup> 3–x, –y, 1–z

Table 2. Classical Hydrogen Bonds for the Title Complex

D–H...A	d(D–H)/Å	d(H...A)/Å	d(D...A)/Å	$\angle$ D–H...A <sup>o</sup>
O(1)–H(1)···O(2)	0.82	1.80	2.530(3)	147.3
O(4)–H(4A)···O(2)	0.85	2.02	2.854(3)	166
N(3)–H(3A)···O(3)	0.89	1.80	2.684(3)	174
N(3)–H(3B)···N(2)	0.89	2.19	2.999(3)	152
N(3)–H(3B)···N(1)	0.89	2.33	3.020(3)	134
O(1)–H(1)···O(1) <sup>1</sup>	0.82	2.64	2.774(3)	90
O(4)–H(4B)···O(1)	0.85	2.12	2.954(3)	168

Symmetry code: <sup>1</sup> 3–x, –y, 1–z

## 3 RESULTS AND DISCUSSION

### 3. 1 Synthesis and characterization of the title complex

The 4,4'-([2,2'-bipyrimidine]-5,5'-diyl)bis(2-hydroxybenzoic acid) was synthesized through a Suzuki coupling

reaction, and its purity was determined by <sup>1</sup>H NMR spectroscopy and elemental analysis. The title complex was synthesized from a mixture of 4,4'-([2,2'-bipyrimidine]-5,5'-diyl)bis(2-hydroxybenzoic acid) and aqueous dimethylamine solution at refluxing. During gradient cooling and

evaporating, large amounts of light yellow prismatic crystals were obtained with a high yield of 72.6%. The chemical structure of the title complex was thoroughly characterized

by single-crystal X-ray diffraction,  $^1\text{H}$  NMR spectroscopy and elemental analysis. The phase purity of the crystals was further verified by powder X-ray diffraction shown in Fig. 1.

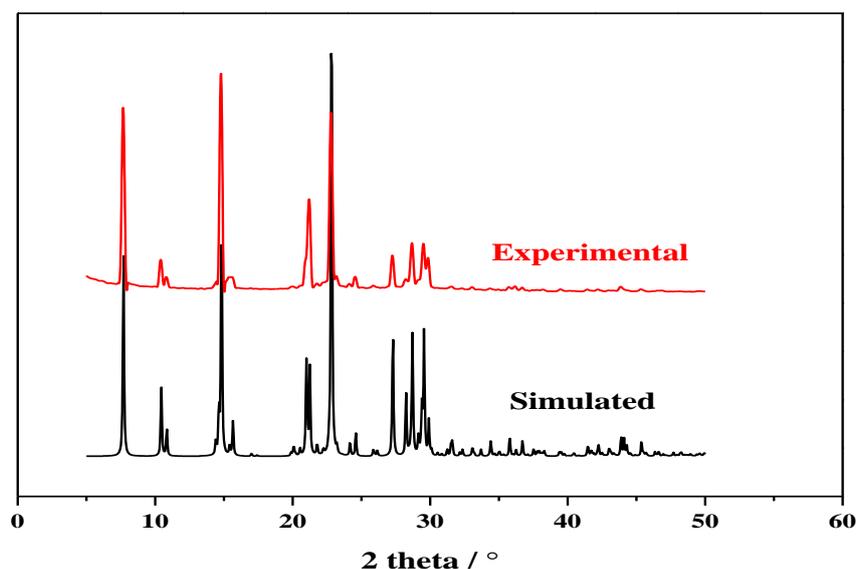


Fig. 1. PXRD patterns for the title complex

X-ray crystallographic analysis reveals that each asymmetric unit of the title complex contains half of a 4,4'-([2,2'-bipyrimidine]-5,5'-diyl)bis(2-hydroxybenzoic acid) anion, one dimethylammonium cation and one water molecule (Fig. 2). Each above anion connects with four dimethylammonium cations, four water molecules and two other such anions through O–H $\cdots$ O, N–H $\cdots$ N, and N–H $\cdots$ O

hydrogen bonds (O(1) $\cdots$ O(1)<sup>1</sup> (2.774(3) Å), O(2) $\cdots$ O(4) (2.854(3) Å), N(3) $\cdots$ N(1) (3.020(3) Å), N(3) $\cdots$ N(2) (2.999(3) Å), N(3) $\cdots$ O(3) (2.684(3) Å)), generating a two-dimensional (2D) supramolecular layer (Fig. 3). Two adjacent 2D layers are further interconnected by O–H $\cdots$ O hydrogen bonds (O(1) $\cdots$ O(4) (2.954(3) Å)), affording a three-dimensional supramolecular structure (Fig. 4).

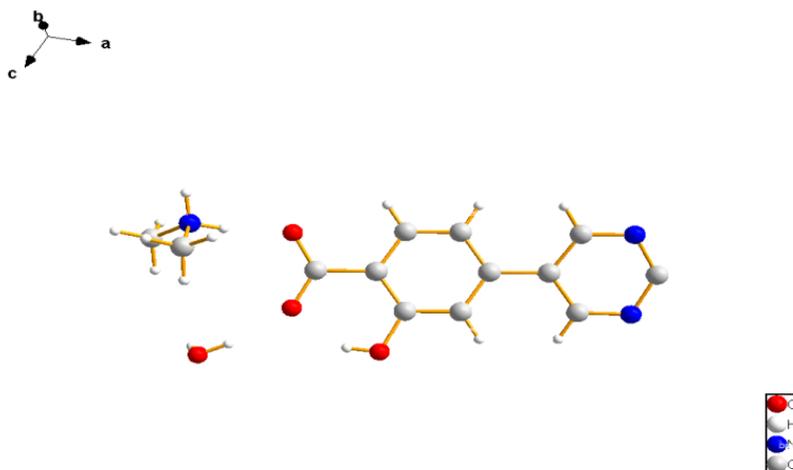


Fig. 2. Asymmetric unit diagram of the title complex

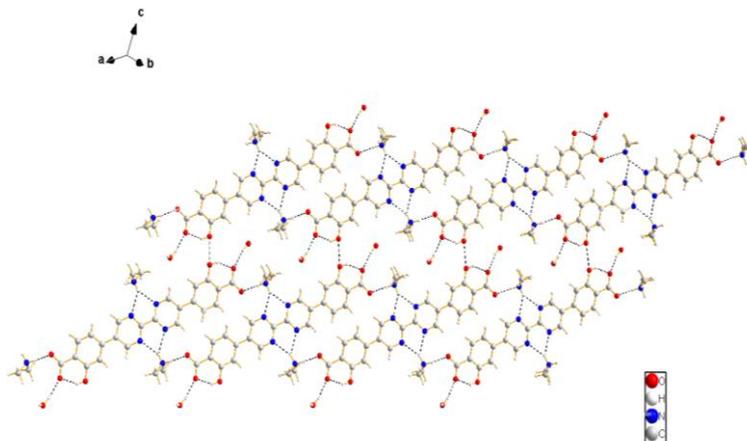


Fig. 3. Two-dimensional (2D) supramolecular layer for the title complex

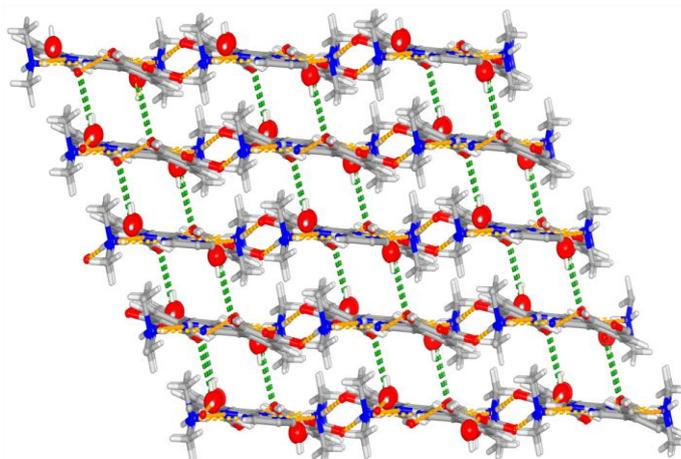


Fig. 4. Three-dimensional (3D) supramolecular structure for the title complex

### 3. 2 Thermogravimetric analysis

To examine the thermal stability of the title complex, TGA experiment was performed. As depicted in Fig. 5, the TGA curve showed weight loss of 6.43% and 16.33% from 68 to

134 °C and from 135 to 280 °C, corresponding to two water molecules (calcd.: 6.46%) and two dimethylamines (calcd.: 16.17%), respectively. Above 285 °C, it starts to decompose.

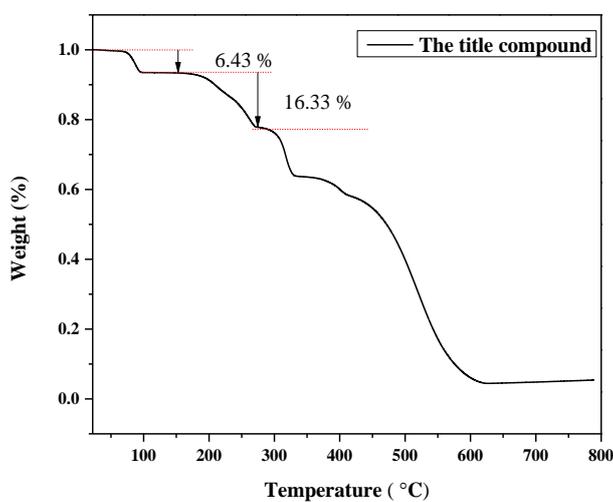


Fig. 5. TGA curve of the title complex

### 3.3 Photoluminescent properties

The photoluminescent properties of the title complex and the free ligand in the solid state at room temperature were studied. The emission peak of the free ligand is observed at about 565 nm upon excitation at 410 nm, which can be attributed to the  $\pi \rightarrow \pi^*$  transition, while that of the title

complex appears at about 564 nm, which increased significantly, compared with the free ligand (Fig. 6) because water molecules in the crystal state make great contributions to hindering the molecular motions for suppressing nonradiative transition of triplet excitation and promoting fluorescence at room temperature<sup>[20]</sup>.

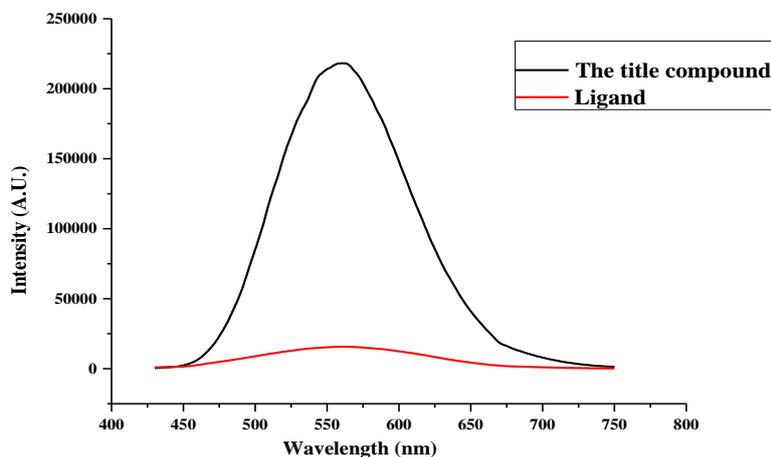


Fig. 6. Fluorescence spectra of the free ligand and the title complex

## 4 CONCLUSION

In summary, we have successfully synthesized and characterized a new 3D complex based on 4,4'-([2,2'-bipyri-

midine]-5,5'-diyl)bis(2-hydroxybenzoic acid) and dimethylamine. This complex has high thermal stability and its luminescent property in solid state was also discussed, indicating it is a potential candidate as luminescent materials.

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