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# Single-crystal Structure and Luminescent Property of Bi-nuclear Bis[ 2-(5-methyl-2-hydroxyphenyl) benzothiazolate ] Zinc

XU Hui-xia<sup>1,2</sup>, CHEN Liu-qing<sup>1,2</sup>, MENG Wei-xin<sup>3</sup>,  
WANG Hua<sup>1,2</sup>, HAO Yu-ying<sup>1,3</sup>, XU Bing-she<sup>1,2\*</sup>

(1. Key Laboratory of Interface Science and Engineering in Advanced Materials, Ministry of Education, Taiyuan University of Taiyuan, Taiyuan 030024, China;

2. College of Materials Science and Engineering, Taiyuan University of Technology, Taiyuan 030024, China;

3. College of Science, Taiyuan University of Technology, Taiyuan 030024, China)

**Abstract:** Bi-molecular bis[ 2-(5-methyl-2-hydroxyphenyl) benzothiazolate ] zinc [ Zn(5-MeBTZ)<sub>2</sub> ] was synthesized. Its molecular structure was confirmed by single-crystal X-ray diffraction. Single-crystal data are as follow: space group triclinic,  $P-1$ ;  $a = 0.9719(2)$  nm,  $b = 1.1248(2)$  nm,  $c = 1.1902(2)$  nm;  $\alpha = 73.099(3)^\circ$ ,  $\beta = 81.498(3)^\circ$ ,  $\gamma = 76.476(3)^\circ$ . Zn(5-MeBTZ)<sub>2</sub> has a good thermal stability. The double-layer devices was employed using Zn(5-MeBTZ)<sub>2</sub> as emitter and NPB as hole-transport material, in which Zn(5-MeBTZ)<sub>2</sub> gave rise to unusually large width in electroluminescence (EL) spectrum, covering almost the range of visible light. The broadened EL spectra were demonstrated to be originated from the exciplexes formed at the interface between NPB and Zn(5-MeBTZ)<sub>2</sub>. White OLEDs could be expected to be realized by designing of reasonable device structure.

**Key words:** bi-molecular structure; thermal stability; exciplex

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## 1 Introduction

Recently, white organic light-emitting diodes (WOLED) have gained importance<sup>[1]</sup> because of their potential application in full color displays with the help of color filter. A number of strategies have been reported to fabricate WOLED, including multi-layer OLED structures, doping host<sup>[2]</sup> and use of exciplex formation<sup>[3]</sup>. Multilayer OLED structure results in a high cost and complicated structure. For the way of doping, it is very difficult to emit white light because of intermolecular Förster energy transfers. However, those problems become solvable if a single emitting material in a single emitting structure

can give rise to broad emission with desirable color coordinates. Luckily, metal complexes are good candidates for such application and have been reported to yield broad emission or formation of exciplexes<sup>[4,5]</sup>.

Exciplex is a two site excitation formed from two distinct chromophors, a donor D and an acceptor A, with the one in the excited state and the other in the ground state. It is metastable as a result of resonant contribution from exciton and charge transfer configuration. Exciplex has been exploited to develop bi-functional devices with photovoltaic and EL performances to tune emission color<sup>[6]</sup> and to design white OLEDs<sup>[7]</sup>.

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**Biography:** XU Hui-xia, female, was born in 1981, Henan Province. Ph. D. Her work focuses on synthesising and properties of emitting materials.

E-mail: xuhuixia08242@163.com

\* : Corresponding Author; E-mail: xubs@tyut.edu.cn, Tel/Fax: (0351)6010311

## 2 Experiments

### 2.1 Materials and Instruments

All materials were purified by high vacuum gradient-temperature sublimation before analysis. C, H and N microanalysis was carried out with an Elemental Vario EL Elemental analyzer.  $^1\text{H}$  NMR data were recorded with Switzerland Bruker DR  $\times$  300 NMR spectrometers. FT-IR spectra were determined with a Nicolet 7199B spectrometer in KBr pellets in the range of  $4\ 000 \sim 400\ \text{cm}^{-1}$ . UV-vis absorption spectra were recorded by Lambda Bio 40, American PE Co. The PL (photoluminescent) and EL (electroluminescent) spectra were measured by SPR-920D spectrofluorometer. The fluorescence spectra were examined by Cary Eclipse fluorescence spectrophotometer.

Thermal analysis was conducted using STA 409PC thermogravimeter. Pure polycrystalline samples were placed in aluminum pans and heated at a heating rate of  $10\ \text{°C}/\text{min}$  under a dry argon gas at a flow rate of  $30\ \text{mL}/\text{min}$ . Melting point (Mp) of the complexes were determined by thermal gravimetric (TG) and differential scanning calorimetry (DSC) analysis.

### 2.2 Device Fabrication

The OLED structure employed in this study was double layered. Emitting layer was fabricated by high-vacuum ( $1.33 \times 10^{-4}\ \text{Pa}$ ) thermal evaporation onto a glass substrate precoated with an indium-tin-oxide (ITO) layer. Prior to use, the ITO surface was ultrasonicated in a detergent solution followed by deionized water rinse and dip into acetone. N,N'-diphenyl-N,N'-bis(1-naphenyl)-1,1'-biphenyl-4,4'-diamine (NPB) was used as hole-transporting material. Aluminum (Al) was evaporated as cathode. All testing was carried out in air at room temperature. Luminance-current-voltage characteristics of OLED were recorded on Keithley 2400 Source Meter and L-2188 spot Brightness Meter.

### 2.3 Single-crystal XRD

The single crystals of  $\text{Zn}(5\text{-MeBTZ})_2$  were grown by vacuum sublimation in a tube furnace under a base pressure at  $395\ \text{°C}$  and collected at room

temperature. They were measured on SMART APEX CCD diffractometer, Mo  $\text{K}\alpha$  ( $\lambda = 0.071\ 073\ \text{nm}$ ). Cell constants and an orientation matrix for data collections were obtained by Full-matrix least-squares on  $F^2$ . The structures were solved by direct methods with SHELXL-97. The powder X-ray diffraction (XRD) spectra were measured by Rigaku D/max 2500.

### 2.4 Materials Characterization

Preparation of 2-(5-methyl-2-hydroxyphenyl) benzothiazolate (5-MeBTZ):

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.359 (3H, s), 6.996-7.024 (2H, d), 7.182-7.212 (2H, d), 7.405-7.431 (2H, m), 7.479-7.505 (1H, d), 7.891-7.919 (1H, d), 7.971-7.994 (1H, d), 12.331 (1H, s).

Anal. calcd for  $\text{C}_{14}\text{H}_{11}\text{NOS}$ : C, 69.68; H, 4.59; N, 5.80; found: C, 70.56; H, 4.49; N, 5.276;

FT-IR (KBr)  $\text{cm}^{-1}$ : 3 442, 2 921, 2 360, 1 624, 1 594, 1 497, 1 438, 1 274, 1 222, 984, 828, 724.

Preparation of Bis[2-(5-methyl-2-hydroxyphenyl)benzothiazolate]zinc [ $\text{Zn}(5\text{-MeBTZ})_2$ ]:

$\text{Zn}(5\text{-MeBTZ})_2$  was synthesized from the reaction between 5-MeBTZ and  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  in ethanol solution. The mixed solution is stirred for 2 h at room temperature. The precipitation of  $\text{Zn}(5\text{-MeBTZ})_2$  was obtained, and it was then purified by vacuum sublimation.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.325 (6H, s), 6.899-6.927 (2H, d), 7.172-7.198 (8H, m), 7.404-7.430 (2H, d), 7.767-7.790 (2H, d);

Anal. calcd for  $\text{C}_{28}\text{H}_{20}\text{N}_2\text{O}_2\text{S}_2\text{Zn}$ : C, 61.59; H, 3.69; N, 5.13; found: C, 61.40; H, 3.602; N, 4.562;

FT-IR (KBr)  $\text{cm}^{-1}$ : 3 431, 2 857, 1 620, 1 535, 1 495, 1 444, 1 393, 1 246, 1 187, 982, 823, 724, 707, 591.

## 3 Results and Discussion

### 3.1 The Molecular Structure and Crystal Packing

The molecular structure of  $\text{Zn}(5\text{-MeBTZ})_2$  was elucidated by X-ray crystallography, as shown in

Fig. 1. The crystal data and selected bond lengths and angles are listed in Table 1 and Table 2. The crystal data for Zn(5-MeBTZ)<sub>2</sub> are triclinic, space group  $P-1$ ,  $a = 0.971\ 9(2)$  nm,  $b = 1.124\ 8(2)$  nm,  $c = 1.190\ 2(2)$  nm,  $\alpha = 73.099(3)^\circ$ ,  $\gamma = 76.476(3)^\circ$ ,  $\beta = 81.498(3)^\circ$ . Anhydrous Zn(5-MeBTZ)<sub>2</sub> has two crystallographically independent Zn<sup>2+</sup> ions, each in distorted four-coordinate geometry. This crystal was of bi-molecular structure. There is distinct intermolecular  $\pi$ - $\pi$  interaction between monomers. The bond length of Zn(1)-O(2) is 0.201 5(2) nm, while the bond length of Zn(2)-O(4) is 0.195 7(2) nm. The bond angle of O(1)-Zn(1)-N(2) is 132.1(9)°, while the bond angle of O(3)-Zn(2)-N(4) is 122.6(8)°. Other bond lengths and angles have similar phenomena, as can be seen in Table 2, suggesting that the coordinate ability of the center Zn<sup>2+</sup> ions is different in bi-molecular structure. The  $\pi$ - $\pi$  stacking occurs in the phenoxide and benzothiazolyl moieties of adjacent 2-(2-hydroxyphenyl) benzothiazole ligands, as shown in Fig. 2. There is also weak H···O hydrogen bond

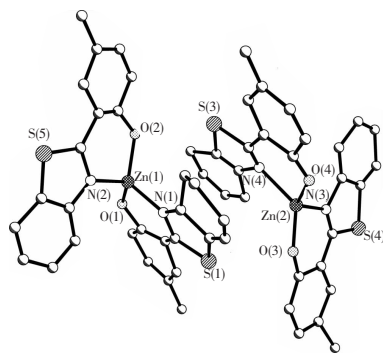


Fig. 1 The crystal structure of Zn(5-MeBTZ)<sub>2</sub>

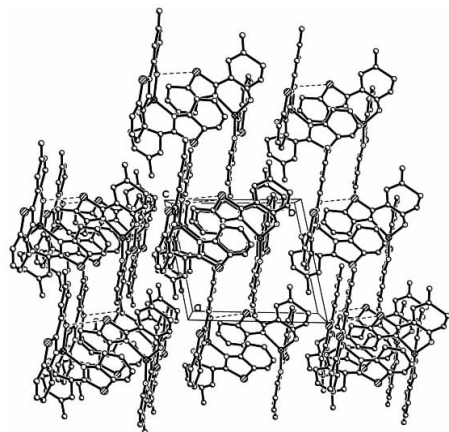


Fig. 2 The solid-state  $\pi$ - $\pi$  stacking of Zn(5-MeBTZ)<sub>2</sub>

**Table 1** Summary of crystal data including data collection and refinement for Zn(5-MeBTZ)<sub>2</sub>

Identical code	Zn(5-MeBTZ) <sub>2</sub>
empirical formula	C <sub>56</sub> H <sub>40</sub> N <sub>4</sub> O <sub>4</sub> S <sub>4</sub> Zn <sub>2</sub>
temperature, K	293(2)
wavelength, nm	0.071 073
crystal system	Triclinic
space group	$P-1$
$a$ , nm	0.971 9(2)
$b$ , nm	1.124 8(2)
$c$ , nm	1.190 2(2)
$\alpha$ , (°)	73.099(3)
$\beta$ , (°)	81.498(3)
$\gamma$ , (°)	76.476(3)
volume, nm <sup>3</sup>	1.205 8(4)
$Z$	11
density, calcd mg/cm <sup>3</sup>	2.112
absorption, coefficient, mm <sup>-1</sup>	5.889
$F(000)$	737
reflections collected / unique	4 385 / 3 838 [ $R(\text{int}) = 0.031\ 4$ ]
Refinement method	Full-matrix least-squares on $F^2$
data / restraints / parameters	3 838/0/631
goodness-of-fit on $F^2$	1.014
final $R$ indices [ $I > 2\sigma(I)$ ]	$R1 = 0.067\ 0$ , $wR2 = 0.163\ 4$
$R$ indices (all data)	$R1 = 0.097\ 0$ , $wR2 = 0.212\ 7$

**Table 2** The selected bond and bond angles for Zn(5-MeBTZ)<sub>2</sub>

Selected bond (nm)	Bond angles (°)
Zn(1)-O(2) 0.201 5(2)	O(2)-Zn(1)-O(1) 117.5(7)
Zn(1)-N(1) 0.200(2)	O(2)-Zn(1)-N(2) 89.7(8)
Zn(1)-O(1) 0.179 2(2)	O(1)-Zn(1)-N(2) 132.1(9)
Zn(1)-N(2) 0.215(3)	O(2)-Zn(1)-N(1) 123.8(8)
Zn(2)-O(4) 0.195 7(2)	O(1)-Zn(1)-N(1) 92.1(7)
Zn(2)-O(3) 0.186 3(1)	N(2)-Zn(1)-N(1) 104.7(8)
Zn(2)-N(3) 0.197 5(1)	O(4)-Zn(2)-O(3) 116.5(8)
Zn(2)-N(4) 0.198 5(2)	O(4)-Zn(2)-N(4) 95.2(7)
	O(3)-Zn(2)-N(4) 122.6(8)
	O(4)-Zn(2)-N(3) 120.5(7)
	O(3)-Zn(2)-N(3) 97.1(6)
	N(4)-Zn(2)-N(3) 106.5(6)

interaction between adjacent molecules. This intermolecular interaction is expected to lead to good carrier transport properties.

### 3.2 Thermal Stability

Thermal stability is an important factor which dramatically influence on the physical performance of OLEDs. The TG and DSC curves for bi-molecular  $\text{Zn}(5\text{-MeBTZ})_2$  are shown in Fig. 3. A single endothermic transition was accompanied by no weight loss measured following Mp at 319 °C. The TG curve reveals a high decomposition temperature ( $T_d$ ) at 490 °C. The reported Mp and  $T_d$  for Bis[2-(2-hydroxyphenyl) benzothiazolate] zinc [ $\text{Zn}(\text{BTZ})_2$ ] are 287 and 453 °C<sup>[8]</sup>, respectively. The higher Mp and  $T_d$  of  $\text{Zn}(5\text{-MeBTZ})_2$  can be ascribed to its stronger intermolecular interaction.

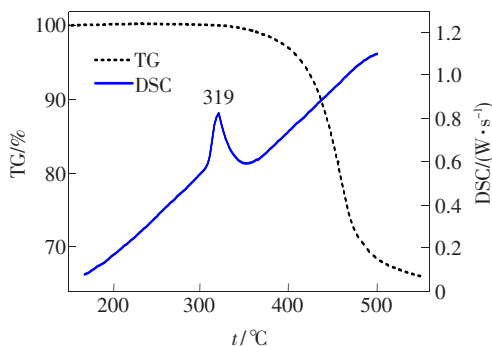


Fig. 3 TG and DSC curves of the  $\text{Zn}(5\text{-MeBTZ})_2$

### 3.3 Photoluminescent Property

The photoluminescent (PL) and electroluminescent (EL) properties of  $\text{Zn}(5\text{-MeBTZ})_2$  were investigated. The devices was fabricated using  $\text{Zn}(5\text{-MeBTZ})_2$  as emitting-layer materials and NPB as hole-transport material. The structures of OLEDs used in this work are typical bilayer device, employing ITO as anode and Al as cathode.

The peaks on PL spectra of solid state are 446 nm for NPB and 490 nm for  $\text{Zn}(5\text{-MeBTZ})_2$ . The EL spectra of the device show a broad emission band in 447 ~ 650 nm region with the peak at 524 nm and a weak shoulder at 638 nm with the full width at half maximum (FWHM) of 100 nm, can be seen in Fig. 4. A broaden EL spectra is attributed to the formation of exciplex at the interface between emitting [ $\text{Zn}(5\text{-MeBTZ})_2$ ] and hole-transport (NPB) layers. The formation of exciplex

requires an electron donor with low ionization potential ( $I_p$ ) so that it can donate an electron to the second molecule, which has high electron affinity ( $E_A$ ). In this paper, NPB is used as donor with  $I_p$  value of 5.5 eV and  $\text{Zn}(5\text{-MeBTZ})_2$  is used as acceptor with  $E_A$  of 3.76 eV<sup>[8]</sup>. High barrier for hole injection would make the hole locate in the donor layer. Donor molecule would react with hole to form  $D^+$  and donates an electron. Consequently, the adjacent acceptor molecule accepts the electron to form  $A^-$ , which is resonant with  $D^+$ , forming metastable exciplex exciton ( $D^+ - A^-$ )\*.

The current-voltage and luminance-voltage curves of the EL device are shown in Fig. 5. Luminance starts at lower voltage of 6 V (turn-on voltage) and maximum luminance of 681  $\text{cd}/\text{cm}^2$  is achieved at 22 V.

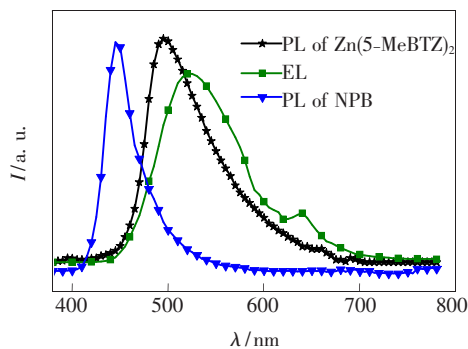


Fig. 4 The PL spectra of NPB and  $\text{Zn}(5\text{-MeBTZ})_2$  and EL spectra of ITO/NPB/ $\text{Zn}(5\text{-MeBTZ})_2$ /Al

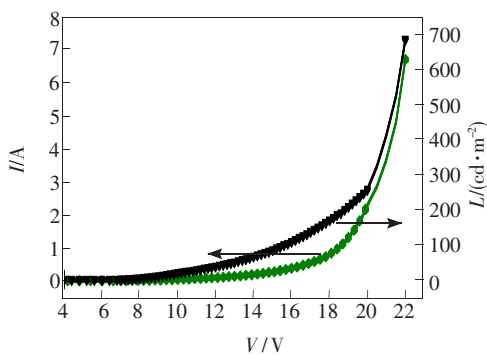


Fig. 5 The  $I$ - $V$ - $L$  characteristics of EL for the bilayer device

## 4 Conclusion

The molecular structure, thermal stability, PL and EL properties of bi-molecular  $\text{Zn}(5\text{-MeBTZ})_2$  were reported in this paper. There is weak  $S \cdots O$  hydrogen bond interaction between adjacent ligands

besides the  $\pi$ - $\pi$  intermolecular interaction. Zn(5-MeBTZ)<sub>2</sub> has a better thermal stability with Mp of 319 °C. The EL spectra of the bi-layer device showed a

peak at 524 nm and a weak shoulder at 638 nm with FWHM of 100 nm. The turn-on voltage is 6 V and the maximum luminance of 681 cd/cm<sup>2</sup> at 22 V.

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# 具有双分子结构的[2-(5-甲基-2-羟基苯基)苯并噻唑]锌的单晶结构和光学性能

许慧侠<sup>1,2</sup>, 陈柳青<sup>1,2</sup>, 孟维新<sup>3</sup>, 王 华<sup>1,2</sup>, 郝玉英<sup>1,3</sup>, 许并社<sup>1,2\*</sup>

(1. 新材料界面科学与工程省部共建教育部重点实验室, 山西 太原 030024;

2. 太原理工大学 材料科学与工程学院, 山西 太原 030024; 3. 太原理工大学 理学院, 山西 太原 030024)

**摘要:** 合成了一种具有双分子结构的[2-(5-甲基-2-羟基苯基)苯并噻唑]锌[Zn(5-MeBTZ)<sub>2</sub>]。通过 X 射线单晶衍射的方法确定了它的分子结构。单晶数据如下:空间群为三斜,*P*-1 晶系,*a*=0.971 9(2) nm,*b*=1.124 8(2) nm,*c*=1.190 2(2) nm; $\alpha$ =73.099(3)°, $\beta$ =81.498(3)°, $\gamma$ =76.476(3)°。两个分子间存在有  $\pi$ - $\pi$  相互作用。Zn(5-MeBTZ)<sub>2</sub>具有良好的热稳定性,熔点为 319 °C。以 Zn(5-MeBTZ)<sub>2</sub> 为发光层,NPB 为空穴传输层材料的双层结构器件的电致发光光谱有较大的半峰全宽,几乎覆盖整个可见光区域。这种宽的 EL 谱是由于在 NPB 和 Zn(5-MeBTZ)<sub>2</sub>界面的激基复合物产生的。优化的 OLED 器件结构和性能将在以后的论文中介绍。

**关键词:** 双分子结构;热稳定性;激基复合物

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作者简介: 许慧侠(1981-),女,河南长垣人,博士研究生,主要从事有机电致发光材料的制备与性能的研究。

E-mail: xuhuixia0824@163.com

\*: 通讯联系人; E-mail: xubs@tyut.edu.cn, Tel/Fax: (0351)6010311