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# High triplet energy Zn complexes as host materials for green and blue phosphorescent organic light-emitting diodes

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ABSTRACT

Two Zn complexes, bis(2-(oxazol-2-yl)phenolate) zinc (ZnOx2) and bis(2-(1-methyl-1H-imidazol-2-yl) phenolate) zinc (ZnIm2), were synthesized as high triplet energy host materials for green and blue phosphorescent organic light-emitting diodes. High triplet energies of 2.71 eV and 2.84 eV were obtained for ZnOx2 and ZnIm2, respectively. Green and blue phosphorescent devices were fabricated using the ZnOx2 and ZnIm2 host materials and high quantum efficiencies of 23.5% and 20.1% were achieved in green and blue devices, respectively.

## 1. Introduction

Organometallic compounds with a metal core and organic ligands have been developed as emitting materials, electron transport materials and host materials for organic light-emitting diodes (OLEDs) [1–10]. Be and Zn have been generally used as the core metal and aromatic ligands with a heteroring unit have been coordinated to the core metal. The coordination of the ligand to the metal core enhanced light-emitting properties of the organometallic complexes.

In general, the organometallic compounds based on Be, Zn and Al were used as the organic materials for fluorescent OLEDs, but they were also effective as the host materials for phosphorescent OLEDs in addition to organic host materials [11–16]. Bis(2-methyl-8-quninolinato)-4-phenylphenolate aluminum (III) was used as the host material and hole blocking layer in red phosphorescent OLEDs and improved lifetime and quantum efficiency [17]. Bis[2-(2-hydroxyphenyl)-pyridinate] beryllium was applied as the host material for green phosphorescent OLEDs and could simplify the device structure without sacrificing the quantum efficiency of green phosphorescent OLEDs [18]. A Zn compound derived from 2-(hydroxyphenyl) benzothiazole was also used as the host material for red phosphorescent OLEDs [19]. However, there has been no work reporting high triplet energy Zn compounds as the host materials for blue phosphorescent OLEDs. Therefore, it is required to develop organometallic compounds with high triplet energy for use in blue phosphorescent OLEDs.

Herein, we describe the synthesis and device application of Zn compounds as the host materials for green and blue phosphorescent OLEDs as an extension of our previous work [20]. Two zinc complexes, bis(2-(oxazol-2-yl)phenolate) zinc (ZnOx2) and bis(2-(1-methyl-1H-imidazol-2-yl)phenolate) zinc (ZnIm2), were synthesized as the host materials and high quantum efficiencies of 23.5% and 20.1% were demonstrated in green and blue phosphorescent OLEDs. This is the first work reporting Zn complexes as the host materials for blue phosphorescent OLEDs.

## 2. Experimental section

### 2.1. General information

Zinc acetate dehydrate and ethanol dihydrate (Aldrich Chem. Co.) were used without further purification. 2-(Oxazol-2-yl)phenol and 2-(1-methyl-1H-imidazol-2-yl)phenol were synthesized according to the method reported in the literature [21]. Detailed chemical analysis of the ZnOx2 and ZnIm2 was performed according to the method reported in our previous work [20].

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### 2.2. Synthesis

#### 2.2.1. Bis(2-(oxazol-2-yl)phenolate) zinc (ZnOx2)

A mixture of 2-(oxazol-2-yl)phenol (1.50 g, 9.31 mmol) and anhydrous ethanol (70 mL) was stirred at 70 °C for 1 h followed by adding zinc acetate dihydrate (1.02 g, 4.65 mmol) dissolved in water (14 mL). The solution was stirred for 48 h under nitrogen and white precipitate was filtered off and washed with ethanol. The product was obtained as a white powder (1.49 g). The product was further purified by vacuum train sublimation. Yield : 83%. $^1$H NMR (500 MHz, DMSO): δ 8.20 (s, 2H), 7.69 (d, $J = 8.00$ Hz, 2H), 7.51 (s, 2H), 7.20 (t, $J = 7.00$ Hz, 2H), 6.76 (d, $J = 8.50$ Hz, 2H), 6.47 (t, $J = 7.00$ Hz, 2H). $^{13}$C NMR (500 MHz, DMSO): δ 167.85, 162.93, 136.79, 132.44, 126.49, 125.17, 122.31, 111.90, 109.34. MS (FAB) *miz* 384 [$(M + H)^+$]. Anal. Calcd for $C_{18}H_{12}N_2O_4Zn$: C, 56.06; H, 3.14; N, 7.26; O, 16.59; Zn, 16.95 Found : C, 56.05; H, 3.01; N, 7.13.

#### 2.2.2. Bis(2-(1-methyl-1H-imidazol-2-yl)phenolate) zinc (ZnIm2)

A mixture of 2-(1-methyl-1H-imidazol-2-yl)phenol (0.50 g, 2.87 mmol) and anhydrous ethanol (23 mL) was stirred at 70 °C for 1 h followed by adding zinc acetate dihydrate (0.31 g, 1.44 mmol) dissolved in water (4 mL). Triethylamine (1.19 mL, 8.61 mmol) was dropwisely added to the solution and the solution was stirred for 48 h under nitrogen. White precipitate was filtered off and washed with ethanol. The product was obtained as a white powder (0.2 g) and was further purified by vacuum train sublimation. Yield: 34%. $^1$H NMR (500 MHz, DMSO): δ 7.19 (s, 4H), 7.05 (t, $J = 7.5$, 2H), 6.91 (s, 4H), 6.43 (s, 2H), 3.70 (s, 6H). MS (FAB) *miz* 411 [$(M + H)^+$]. Anal. Calcd for $C_{20}H_{18}N_4O_2Zn$: C, 58.34; H, 4.41; N, 13.61; O, 7.77; Zn, 15.88 Found C, 58.35; H, 4.40; N, 13.55.

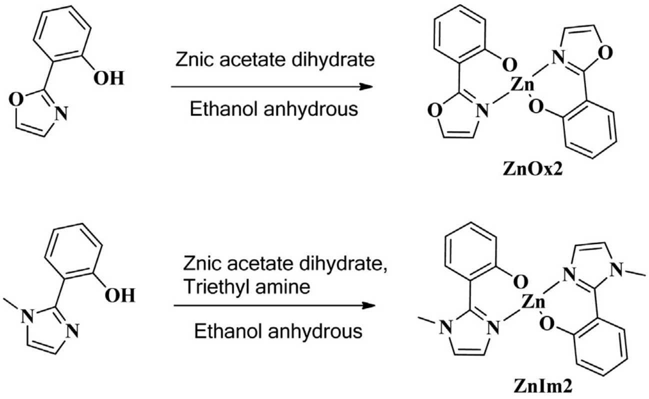
### 2.3. Device fabrication and measurements

A device architecture of indium tin oxide (ITO, 50 nm)/poly(3,4-ethylenedioxythiophene); poly(styrenesulfonate) (60 nm)/4,4′-cyclohexylidenebis[N,N-bis(4-methylphenyl)aniline] (20 nm)/N,N′-dicarbazolyl-3,5-benzene (mCP, 10 nm)/ZnOx2:iridium(III) tris(2-phenylpyridine) ($Ir(ppy)_3$) or ZnIm2:iridium(III) bis((4,6-difluorophenyl)-pyridine) picolinate (FIrpic) (25 nm)/diphenylphosphine oxide-4-(triphenylsilyl)phenyl (30 nm)/LiF (1 nm)/Al (200 nm). Doping concentrations of $Ir(ppy)_3$ and FIrpic were 3%, 5% and 10%. Active area of the device was 4 mm$^2$. All devices were prepared by vaccum thermal evaporation.

Current density–voltage–luminance data and electroluminescence spectra were obtained using Keithley 2400 source measurement unit and Konica-Minolta CS1000 spectroradiometer in ambient condition after encapsulating the fabricated device using a glass lid and CaO getter.

## 3. Results and discussion

ZnOx2 and ZnIm2 were designed to possess high triplet energy by adopting high triplet energy ligands with shortened conjugation length. The 2-(oxazol-2-yl)phenol and 2-(1-methyl-1H-imidazol-2-yl)phenol ligands have an electron donating phenol unit and an electron withdrawing five membered heteroring [10]. Although two aromatic units were directly linked, the less aromatic character of oxazole and imidazole than pyridine reduced the degree of conjugation of the ligands used in this work [20,22,23]. The less conjugation increases the bandgap, singlet energy and triplet energy at the same time, resulting in high triplet energy in the ZnOx2 and ZnIm2. The imidazole unit is better than the pyridine unit to obtain high triplet energy because of electron localization by high dipole moment of the imidazole moiety. Therefore, high triplet energy can be obtained in ZnOx2 and ZnIm2 and those materials can be used as the host materials for green and blue phosphorescent OLEDs.



**Scheme 1.** Synthetic scheme of ZnOx2 and ZnIm2.

ZnOx2 and ZnIm2 were synthesized by modifying the synthetic method described in the literature [20]. Synthetic yields of ZnOx2 and ZnIm2 were 83% and 34%, respectively. The Zn complexes were purified by vacuum train sublimation and high purity over 99% was obtained. Synthetic scheme of ZnOx2 and ZnIm2 is shown in Scheme 1.

Photophysical properties of ZnOx2 and ZnIm2 were analyzed using ultraviolet–visible (UV–Vis) and photoluminescence (PL) spectrometers. UV–Vis and PL data were obtained from a dilute tetrahydrofuran solution of ZnOx2 and ZnIm2. Fig. 1 shows solution UV, solution PL and low temperature PL spectra of ZnOx2 and ZnIm2. The UV–Vis absorption of ZnOx2 was shifted to long wavelength (bathochromic shift) compared to that of ZnIm2 because of large dipole moment of the imidazole moiety. Bandgaps calculated from the UV–Vis absorption edge were 3.18 eV and 3.39 eV, respectively. The bandgap of Zn complexes was smaller than that of Be complexes with the same ligand. Bathochromic shift of the solution PL emission was also observed in ZnOx2 due to the narrow bandgap of ZnOx2. Peak positions of solution PL emission of ZnOx2 and ZnIm2 were 411 nm and 403 nm, respectively. Low temperature PL measurement of ZnOx2 and ZnIm2 was carried out in liquid nitrogen to measure the phosphorescent emission of ZnOx2 and ZnIm2. Delay time for the low temperature PL measurement was 1 ms. Phosphorescent emission was observed at long wavelength, and the first phosphorescent emission peaks of ZnOx2 and ZnIm2 were

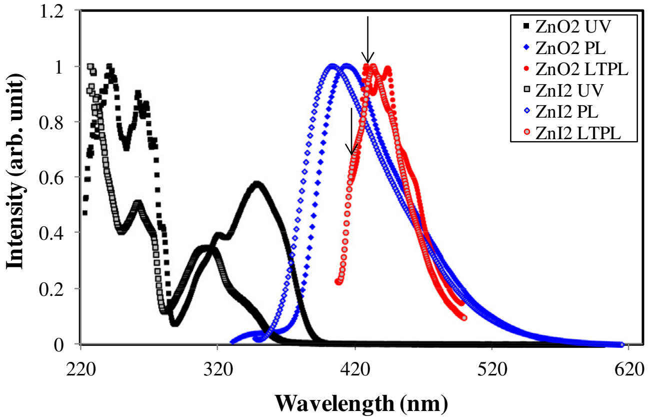


**Fig. 1.** UV–Vis absorption, solution PL and low temperature PL emission spectra of ZnOx2 and ZnIm2.