

Enforced Effects of Side Group Substitution Position on Luminescence Properties; Synthesis of Bis(dipyrrinato)zinc Complex Derivatives

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New yellow-green emitting materials using bis(dipyrrinato)zinc complex moiety were synthesized by substituting phenyl group and 1- or 2-positioned naphthalene group. Bis[5-(1-naphthalenyl)-dipyrrinato]zinc complex ($\text{Zn}(1\text{-NaPN})_2$) substituted at position 1 of naphthalene group showed about 10 times stronger photoluminescence (PL) property and sharper PL spectrum compared to bis[5-(phenyl)-dipyrrinato]zinc complex ($\text{Zn}(\text{PPN})_2$) and bis[5-(2-naphthalenyl)-dipyrrinato]zinc complex ($\text{Zn}(2\text{-NaPN})_2$). Optical properties in film state were almost identical to the result of non-doped organic light emitting diodes (OLEDs) device.

Luminance efficiency (cd/A) of $\text{Zn}(1\text{-NaPN})_2$ was $0.33 \text{ cd}/\text{A}$, which was about 4~8 times higher than $\text{Zn}(\text{PPN})_2$, $0.04 \text{ cd}/\text{A}$ and $\text{Zn}(2\text{-NaPN})_2$, $0.08 \text{ cd}/\text{A}$. Quantum efficiency was also about 2~3 times higher.

Keywords Bis(dipyrrinato)zinc complex; OLED; π - π^* stacking; yellow-green emitting material

Introduction

OLED based on organic π -conjugation molecules is receiving the spotlight as next generation flat panel display and many researchers are actively conducting studies on OLED [1–5]. For full color achievement in OLED, a highly efficient and pure emitting material in the red, blue and green regions is necessary. In order to control emission wavelength of π -conjugation molecules, π -conjugation length of molecules can be adjusted [6]. Also to make pure emission and highly efficient emission property, a bulky side group must be introduced to prevent interaction between molecules by π - π^* stacking and remove undesirable red shift or luminescence reduction [7]. However, it is difficult to control molecular interaction in solid or film state

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because of difficulty in estimating molecular stacking. Therefore, studies on molecular interaction in emitting materials are deemed important.

Bis(dipyrrinato)metal complex was first reported by Fischer in 1924 [8] and several research groups synthesized derivatives of bis(dipyrrinato)metal complex. However, there is still lack of studies on molecular packing and optical and electrical properties of bis(dipyrrinato)metal complex derivatives.

Accordingly, positions 1 and 2 of naphthalene group were used as links at 5,5'-position of bis(dipyrrinato)zinc complex for substitution, and the changes in optical properties according to naphthalene substitution position were observed. Phenyl group was substituted for use as comparison material. Large difference in luminance efficiency was verified according to molecular interaction in solution and film states of these materials. Based on such changes in optical properties, newly synthesized materials were used as emitting layers of a non-doped OLED device for observation.

Experimental

Synthesis

Bis[5-(phenyl)-dipyrrinato]zinc Complex ($Zn(PPN)_2$). The following compounds have been synthesized following literature procedures [9–12].

1H -NMR (300 MHz, $CDCl_3$) δ (ppm): 7.54–7.45 (m, 7H), 6.71–6.69 (m, 2H), 6.41–6.40 (m, 2H). Fab^+ -MS 502 m/z.

Bis[5-(1-naphthalenyl)-dipyrrinato]zinc Complex ($Zn(1-NaPN)_2$). 5-(1-naphthalenyl)-dipyrromethane (1 g, 4.5 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (1.124 g, 4.95 mmol) stirred in acetonitrile (AN) (20 ml) at room temperature for 3 h. And then quenched with triethylamine (TEA) (0.05 ml, 0.45 mmol). Saturated methanol solution of zinc acetate (0.413 g, 2.25 mmol) was added to the reaction mixture and stirred for 5 h. After completion of the reaction, the solvent was evaporated under vacuum and the product was extracted with dichloromethane (CH_2Cl_2). The CH_2Cl_2 solution was washed with water and dried with magnesium sulfate anhydrous ($MgSO_4$). The solvent was evaporated to give $Zn(1-NaPN)_2$ as orange solid, which was recrystallized from tetrahydrofuran (THF) and methanol. (yield 56%) 1H -NMR(500 MHz, $DMSO-d_6$) δ (ppm): 8.11–8.10 (t, 1H), 8.05–8.03 (d, 1H), 7.80–7.78 (d, 1H), 7.72 (s, 1H), 7.67–7.66 (t, 3H), 7.56–7.53 (t, 1H), 7.50–7.47 (t, 1H), 6.39 (s, 2H), 6.33–6.32 (d, 2H). Fab^+ -MS 603 m/z.

Bis[5-(2-naphthalenyl)-dipyrrinato]zinc Complex ($Zn(2-NaPN)_2$). The synthetic procedure is similar to that of $Zn(1-NaPN)_2$. After completion of the reaction, product was purified by column chromatography on silica gel and recrystallized from dichloromethane and Methanol (yield 35%).

1H NMR(500 MHz, $DMSO-d_6$) δ (ppm): 8.16 (s, 1H), 8.08–8.05 (t, 3H), 7.73–7.71 (m, 1H), 7.65–7.62 (m, 4H), 6.62–6.61 (d, 2H), 6.48–6.47 (m, 2H). Fab^+ -MS 602 m/z.

Fabrication of Non Doped OLED

OELD devices were fabricated as the following structure: ITO/2-TNATA (60 nm)/NPB (15 nm)/ $Zn(PPN)_2$ or $Zn(1-NaPN)_2$ or $Zn(2-NaPN)_2$ (30 nm)/Bphen

(30 nm)/LiF (1 nm)/Al (200 nm). All organic layers were deposited on indium-tin-oxide (ITO) coated glass where 4,4',4''-tris(*N*-(2-naphthyl)-*N*-phenyl-amino)-triphenylamine (2-TNATA) as hole injection layer, *N,N'*-bis(naphthalen-1-yl)-*N,N'*-bis(phenyl)benzidine (NPB) as hole transporting layer, 4,7-diphenyl-1,10-phenanthroline (Bphen) as electron transporting layer, the synthesized materials as emitting layers, lithium fluoride (LiF) as electron injection layer, ITO as anode and Al as cathode. The organic layer was vacuum-deposited using thermal evaporation at a vacuum base pressure of 10^{-6} torr and the rate of deposition being 1.0 \AA/s to give an emitting area of 4 mm^2 , and the Al layer was continuously deposited under the same vacuum condition.

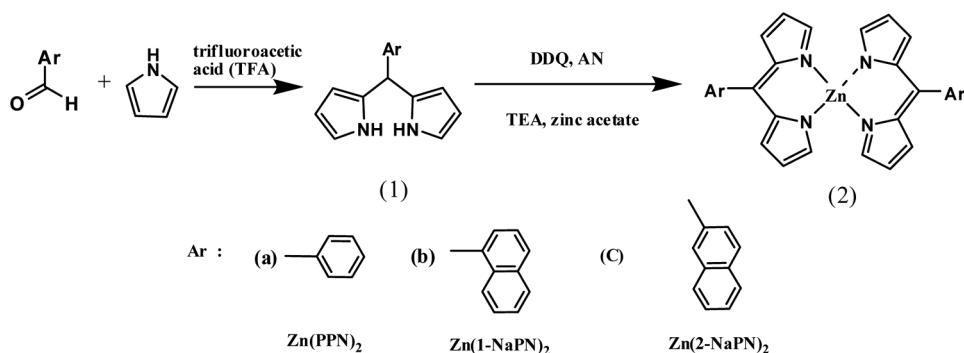
Measurements

$^1\text{H-NMR}$ spectra were recorded on Bruker Avance 300 and Avance 500 spectrometers. The UV-visible absorption spectra were obtained by HP 8453 UV-VIS-NIR spectrometer. Photoluminescence (PL) was obtained by Perkin Elmer luminescence spectrometer LS50 (Xenon flash tube). The current-voltage (I-V) characteristics of the fabricated EL devices were obtained by Keithley 2400 electrometer. Electroluminescence (EL) spectroscopy was obtained by Minolta CS-1000.

Results and Discussion

As shown in Scheme 1, bis(dipyrinato)zinc complex derivatives substituted at 5,5'-position with positions 1 and 2 of naphthalene and phenyl comparison materials were firstly synthesized. As the method of synthesis, pyrrole and aromatic aldehyde substituted with phenyl or naphthalene are reacted together at room temperature with a Lewis acid called trifluoroacetic acid (TFA). Once it is purified, aromatic substituted dipyrromethane (1) can be obtained. Oxidant DDQ is used to oxidize dipyrromethane and then Zn complex is synthesized by reacting oxidized dipyrromethane with zinc acetate.

Optical properties of synthesized materials were measured through ultraviolet-visible (UV) and photoluminescence (PL) spectra and they are summarized in Figure 1 and Table 1. In solution state, UV maximum value of $\text{Zn}(\text{PPN})_2$, $\text{Zn}(1\text{-NaPN})_2$ and $\text{Zn}(2\text{-NaPN})_2$ was respectively 482, 485 and 486 nm. PL maximum



Scheme 1. Synthetic route of $\text{Zn}(\text{PPN})_2$, $\text{Zn}(1\text{-NaPN})_2$, and $\text{Zn}(2\text{-NaPN})_2$.

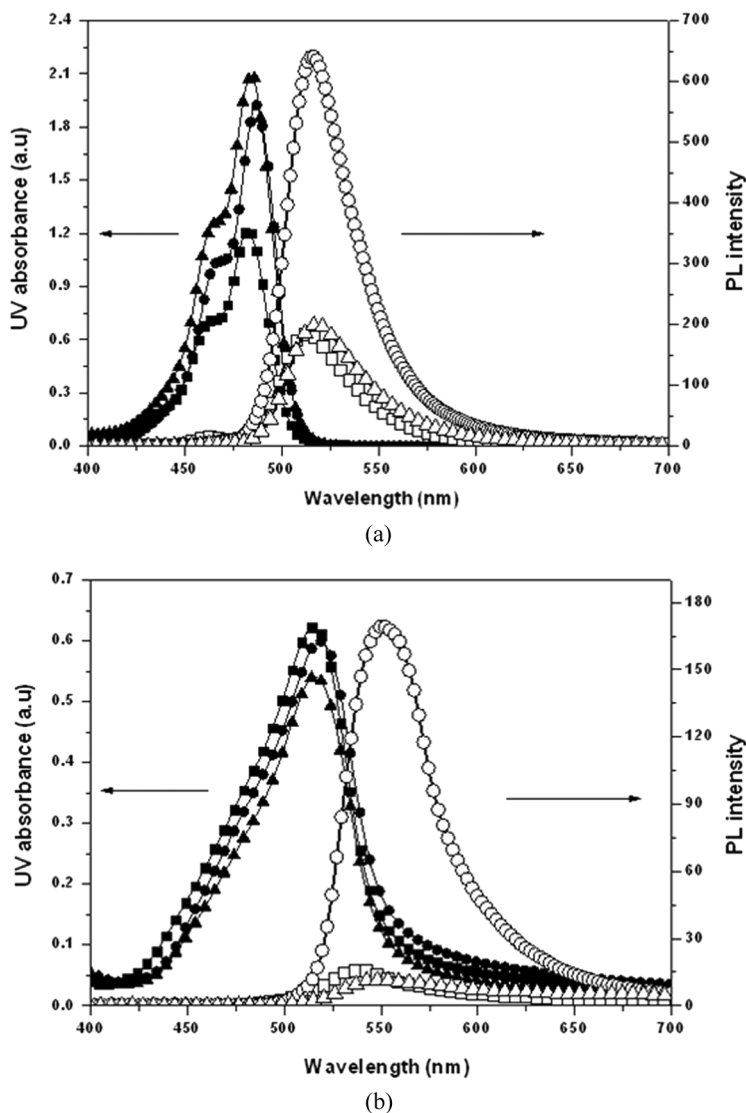


Figure 1. UV-visible and PL spectra of Zn(PPN)₂ (■, □), Zn(1-NaPN)₂(●, ○), and Zn(2-NaPN)₂ (▲, Δ) at (a) Solution 1×10^{-5} M concentration in THF solution (b) Film on glass (thickness: 30 nm).

value was also in the green region at 513, 516, and 518 nm. Although synthesized materials were all measured under THF solvent condition with same concentration of 1×10^{-5} M, but as shown in Figure 1(a), PL spectrum intensity is about three times higher in Zn(1-NaPN)₂ than Zn(PPN)₂ and Zn(2-NaPN)₂ despite the fact that UV spectrum intensities are similar. This probably resulted from increased luminescence and quantum efficiencies in Zn(1-NaPN)₂ compared to Zn(PPN)₂ and Zn(2-NaPN)₂ by steric constraints of dipyrinato and naphthalene [13–16]. Also in film state as summarized in Table 1 and Figure 1(b), UV and PL spectra maximum values were respectively about 516 nm and 546 nm region. They had similar PL

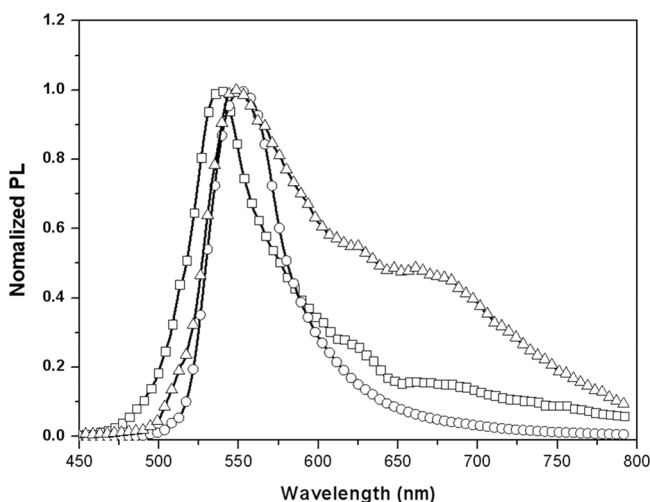
Table 1. Optical and Electronic properties of Zn complexes

| Compound | Solution ^a | | Film ^b | | HOMO (eV) | LUMO (eV) | Band gap (eV) |
|-------------------------|---------------------------|---------------------------|---------------------------|---------------------------|--------------|--------------|------------------|
| | UV _{max} (nm) | PL _{max} (nm) | UV _{max} (nm) | PL _{max} (nm) | | | |
| Zn(PPN) ₂ | 482 | 513 | 515 | 539 | 5.27 | 2.95 | 2.32 |
| Zn(1-NaPN) ₂ | 485 | 516 | 518 | 550 | 5.27 | 2.99 | 2.28 |
| Zn(2-NaPN) ₂ | 486 | 518 | 516 | 549 | 5.27 | 2.98 | 2.29 |

^aSolution 1×10^{-5} M in THF.^bOn glass (thickness: 30 nm).

values each other in the yellow-green region. Film state was verified to show about 30 nm further red shift compared to the solution state in both UV and PL spectra. Most importantly, PL intensity in film state with same thickness was over 10 times higher in Zn(1-NaPN)₂ than Zn(PPN)₂ and Zn(2-NaPN)₂ (See Fig. 1(b)). Such tendency of luminance efficiency had similar trend as in solution state, and film state showed larger difference in luminescence than solution state. In addition, as shown by Figure 2, Zn(PPN)₂ and Zn(2-NaPN)₂ are broadened at 600~800 nm region in comparison to Zn(1-NaPN)₂. Such phenomenon can be interpreted as more efficient blocking of molecular π - π^* stacking interaction in Zn(1-NaPN)₂ than Zn(PPN)₂ and Zn(2-NaPN)₂. More excellent luminescence property and sharper PL spectrum are shown in Zn(1-NaPN)₂ film state.

Accordingly, the authors performed a series of calculations to interpret optical properties of synthesized molecules, and the results are summarized in Figure 3 Bis(dipyrrinato)zinc complexes were optimized using the DMol [3] program of Materials Studio 4.3[®] based on quantum mechanical code using density functional theory (DFT). The Perdew, Burke and Ernzerhof (PBE) functional and double

**Figure 2.** Normalized PL spectra of Zn(PPN)₂ (□), Zn(1-NaPN)₂ (○), and Zn(2NaPN)₂ (Δ). (film on glass).

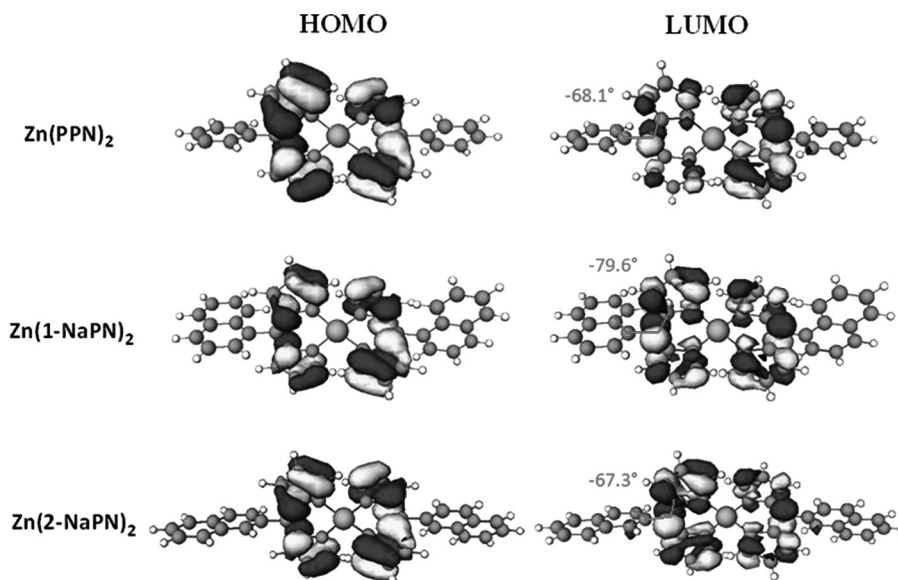


Figure 3. HOMO and LUMO levels diagrams of Zn(PPN)_2 , Zn(1-NaPN)_2 , and Zn(2-NaPN)_2 .

numeric polarization basis set were used in calculations [17–19]. As a result, as illustrated in Figure 3, electron distribution in highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of Zn(PPN)_2 , Zn(1-NaPN)_2 , and Zn(2-NaPN)_2 was verified to be clustered around the location of dipyrrinato center group regardless of phenyl or naphthalene. This result can explain similar UV and PL spectra values in solution state as well as similar HOMO and LUMO levels of the synthesized compounds. Table 1 shows HOMO and LUMO level results at 5.27 and 2.9 eV, which were obtained by cyclic voltammetry, absorption edge analysis using a plot of $(h\nu)$ vs. $(h\nu)^2$ where h and ν are

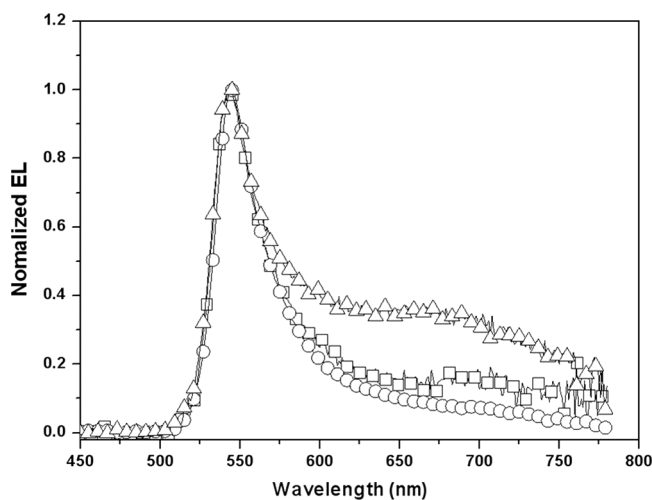


Figure 4. Normalized EL spectra of Zn(PPN)_2 (\square), Zn(1-NaPN)_2 (\circ), and Zn(2NaPN)_2 (Δ).

Table 2. Electroluminescent properties of multi-layered devices at current density 10 mA/cm² (Device configuration: ITO/2-TNATA(60 nm)/NPB(15 nm)/Zn(PPN)₂ or Zn(1-NaPN)₂ or Zn(2-NaPN)₂(30 nm)/Bphen(30 nm)/LiF(1 nm)/Al(200 nm))

| Compound | EL _{max} (nm) | Luminance efficiency (cd/A) | Power efficiency (lm/W) | Quantum efficiency (%) | CIE* (x, y) |
|-------------------------|---------------------------|-----------------------------------|-------------------------------|------------------------------|----------------|
| Zn(PPN) ₂ | 543 | 0.04 | 0.02 | 0.035 | (0.370, 0.470) |
| Zn(1-NaPN) ₂ | 544 | 0.33 | 0.15 | 0.12 | (0.400, 0.569) |
| Zn(2-NaPN) ₂ | 545 | 0.08 | 0.04 | 0.05 | (0.439, 0.480) |

CIE*: Commission Internationale de l'Eclairage.

the absorbance, Plank's constant, and the frequency of light. Also as shown in Figure 3, comparing the optimized calculation structures, dihedral angle between dipyrinato and substituting unit was larger in Zn(1-NaPN)₂ at 79.6° than 68.1 and 67.3° shown by Zn(PPN)₂ and Zn(2-NaPN)₂. Dipyrinato and naphthalene at position 1 are more twisted by steric hindrance. Therefore, such twisted naphthalene blocks π - π^* stacking of dipyrinato, thereby it provides increasing luminance efficiency and showing sharper PL spectrum of Zn(1-NaPN)₂ in film state, in comparison to Zn(PPN)₂ and Zn(2-NaPN)₂ for which phenyl or 2-positioned naphthalene was substituted.

Lastly, synthesized materials were used as emitting layer of a non-doped OLED device to examine whether the difference in optical properties is also shown in actual OLED devices. The properties are summarized in Figure 4 and Table 2. As a result, EL spectrum maximum was about 544 nm for Zn(PPN)₂, Zn(1-NaPN)₂, and Zn(2-NaPN)₂, and broader EL spectrum was only shown by Zn(PPN)₂ and Zn(2-NaPN)₂ compared to Zn(1-NaPN)₂ at 600~800 nm. Such phenomena correspond well to PL spectrum result in film state. For EL device efficiency shown in Table 2, luminance efficiency (cd/A) of Zn(1-NaPN)₂ was about 4~8 times higher at 0.33 cd/A than Zn(PPN)₂ and Zn(2-NaPN)₂ at 0.04 and 0.08 cd/A, respectively. Also, quantum efficiency of Zn(1-NaPN)₂ was about 2~3 times higher compared to other compounds. Zn(1-NaPN)₂ was verified through actual OLED device to show increased luminance efficiency and sharper EL spectrum by efficient blocking of molecular stacking.

Conclusions

Bis(dipyrinato)zinc complex derivatives substituted at 5,5'-position with 1- or 2-positioned naphthalene or phenyl group were firstly synthesized for new yellow-green emission. Optical properties of synthesized materials in solution and film states were compared through UV and PL spectra. As a result, Zn(1-NaPN)₂ substituted with dipyrinato at position 1 of naphthalene group showed about 10 times stronger luminescence property and sharper PL spectrum than Zn(PPN)₂ and Zn(2-NaPN)₂. Molecular calculation verified that position 1 naphthalene blocks π - π^* stacking of dipyrinato.

Optical properties in film state were almost identical to the results of application in OLED device. Therefore, luminance efficiency (cd/A) of Zn(1-NaPN)₂ was 4~8

times higher than luminance efficiency of Zn(PPN)_2 and Zn(2-NaPN)_2 and quantum efficiency was 2~3 times higher. In addition, EL spectrum was also verified to show sharper results in Zn(1-NaPN)_2 .

As a result, it was found that optical- and electrical properties could be controlled by side group connection position as well as kind of side group.

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