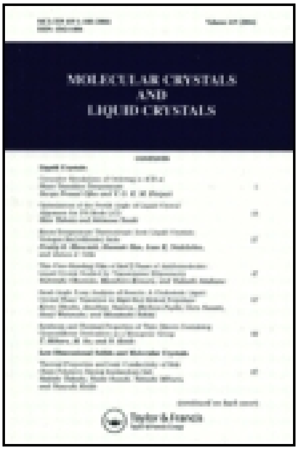

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New Zn Complex Derivatives for Red OLEDs Host Materials

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New two metal complexes, di-(Phenyl dipyrrylmethene)zinc (Zn(PPM)$_2$) and di-(Pentafluorophenyl dipyrrylmethene)zinc (Zn(PFPPM)$_2$) as a host material instead of Alq$_3$ were synthesized. To evaluate electroluminescent properties, multi-layered organic light-emitting devices were fabricated by using 4-(dicyanomethylene)-2-tert-buthyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTB) as a dopant and Alq$_3$ as an electron transporting layer. Alq$_3$ and Zn(PPM)$_2$ host EL devices exhibited DCJTB emission peak at around 617 nm due to energy transfer from Alq$_3$ and Zn(PPM)$_2$ to DCJTB. However Zn(PFPPM)$_2$ host device shows no DCJTB emission peak because Zn(PFPPM)$_2$ device emit EL light of 563 and 700 nm. The Zn(PPM)$_2$ device showed same luminance efficiency as Alq$_3$ device, but showed better power efficiency of 1.2 times than Alq$_3$ device.

Keywords: host material; luminance efficiency; power efficiency; red OLED; zinc complex

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INTRODUCTION

Many research efforts have been focused on the development of full-color displays. To achieve full-color applications, it is required to have red, green and blue materials with good color purity and high efficiency [1]. Organic materials for green and blue organic light emitting diodes (OLEDs) with high luminance, high efficiency, saturated emission color and practical lifetimes have been developed, but there are a few reports on organic materials for red electroluminescence (EL). Presently, development of red OLEDs performance are made by doping a red dye into a suitable host since the first high-performance red OLEDs were obtained by doping a guest red luminescent dye into Alq_3 host matrix in 1989 by Tang *et al.* [2–5].

One of the most commonly used methods to modify the color and luminance efficiency of an emitter is by doping it with a small amount of a highly fluorescent material in a host. Among many known red fluorescent dyes, one prominent example is 4-(dicyanomethylene)-2-tert-buthyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTB). DCJTB is an excellent red dopant with a quantum efficiency $\eta > 90\%$. In our previous paper, we mentioned the synthesis of new Zn metal complexes [6].

In here, we report the synthesis of new two metal complexes, di-(phenyl dipyrrylmethene)zinc ($Zn(PPM)_2$) and di-(pentafluorophenyl dipyrrylmethene)zinc ($Zn(PFPPM)_2$) as host materials.

EXPERIMENTAL

Instrumentation

^{1}H-NMR spectra were recorded on a Brucker DMX300MHz spectrometer at room temperature. The optical absorption spectra were measured by a Shimadzu UV-3100 UV-VIS-NIR Spectrometer. Perkin Elmer luminescence spectrometer LS50 (Xenon flash tube) was used for photo- and electroluminescence (EL) spectroscopy. For EL devices, organic materials were vacuum deposited on top of ITO (1200 Å/30 ohm) under 10^{-6} torr with the deposition rate of 1 Å/sec. Aluminum cathode was continuously deposited under the same vacuum condition to give an emitting area of 9 mm^2. Current-Voltage (I-V) characteristics of the device were measured using Keithley 2400 electrometer. Light intensity was obtained by Minolta CS-1000.

Synthesis of $Zn(PPM)_2$ (I)

Phenyl Dipyrryl Methane

TFA (trifluoroacetic acid) 5 ml was added a solution of benzaldehyde (9.57 ml, 94.2 mmol) and pyrrole (300 ml) under nitrogen with stirring for 20 minutes. After diluted by addition of methylene chloride, the solution was extracted with NaOH aqueous solution. The product was purified by silica gel column chromatography and reprecipitated from methylene chloride/hexane (11.9 g, 57% yield).

^{1}H-NMR(300 MHz, $CDCl_3$): δ (ppm) 7.92(s, 2H), 7.34(t, 2H), 7.26(t, 1H), 7.20(d, 2H), 6.70(d, 2H), 6.17(t, 2H), 5.93(d, 2H), 5.47(s, 1H).

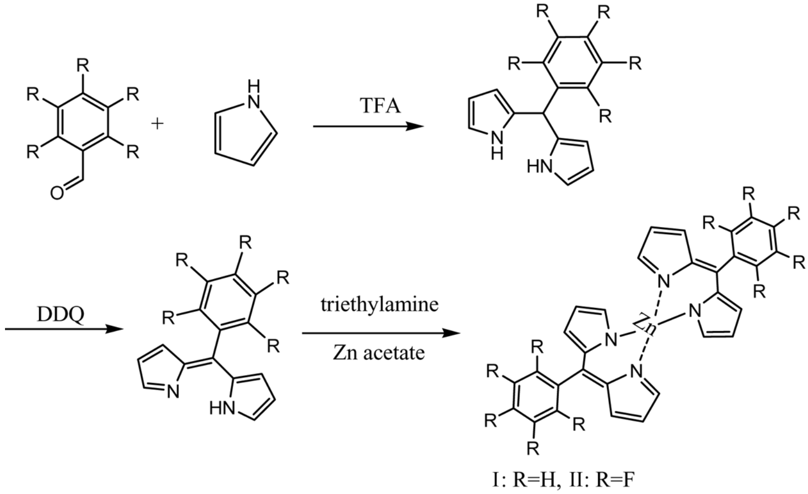
Di-(Phenyl Dipyrrylmethene)Zinc (Zn(PPM)$_2$)

100 ml acetonitrile solution of phenyl dipyrryl methane(4 g, 18.0 mmol) was oxidized for 3 hrs by addition of DDQ(2,3-dichloro-5,6-dicyano-1,4-bezoquinone) 4.9 g and then quenched with 6.3 ml of triethylamine. Saturated of MeOH solution of zinc acetate was added into the solution. The product was purified by silica gel column chromatography and reprecipitated from methylene chloride/MeOH (1.24 g, 27% yield). ^{1}H-NMR(300 MHz, $CDCl_3$): δ (ppm) 7.57(m, 7H), 6.66(d, 2H), 6.45(m, 2H). MS(positive ion FAB) 502(M^+).

Synthesis of Zn(PFPPM)$_2$ (II)

Pentafluorophenyl dipyrryl methene and di-(pentafluorophenyl dipyrrylmethene)zinc (Zn(PFPPM)$_2$) were synthesized through similar procedures of Zn(PPM)$_2$ (Scheme 1).

^{1}H-NMR(300 MHz, $CDCl_3$): δ (ppm) 7.58(s, 2H), 6.67(d, 2H), 6.47(d, 2H) MS(positive ion FAB) 682(M^+).



SCHEME 1 Synthetic route of di-(Phenyl dipyrrylmethene)zinc (Zn(PPM)$_2$) (I) and di-(Pentafluorophenyl dipyrrylmethene)zinc (Zn(PFPPM)$_2$) (II).

RESULTS AND DISCUSSION

New Zn complexes based on phenyl and pyrrole moieties were synthesized according to Scheme 1. These compounds were finally purified with reprecipitation and column methods to have highly pure solid and were identified by ^{1}H-NMR, IR, Fab-Mass analysis.

As the last reaction of making metal complex proceeded, amine proton peak was completely disappeared in ^{1}H-NMR. Phenyl protons of Zn(PPM)$_2$ were overlapped with pyrrole proton peaks at 7.57 ppm. In order to characterize optical property, we analyzed UV-Vis and PL specta of synthetic compounds in a film state.

Figure 1 shows UV-visible absorption of DCJTB and PL emission of Zn complexes films. The absorption peak of DCJTB as a dopant was found to be 517 nm, and PL emission maximum peak of Zn(PPM)$_2$ and Zn(PFPPM)$_2$ as a host was also found to be 540 and 564 nm under the excitation of its own UV-vis maximum value. PL maximum value of Zn(PFPPM)$_2$ was red shifted about 24 nm compared to Zn(PPM)$_2$ because of different metal-ligand interaction. Zn(PFPPM)$_2$ complex shows very weak excimer emission peak at around 700 nm. UV-Vis and PL results offer that the generated excitons of Zn(PPM)$_2$ can transfer to DCJTB molecules better than Zn(PFPPM)$_2$'s when DCJTB is used as a dopant, because the absorption of DCJTB is large overlapped with PL spectra of Zn(PPM)$_2$.

Electrochemical characteristics of new Zn complexes were investigated by cyclovoltammertic method. On set point of the first oxidation

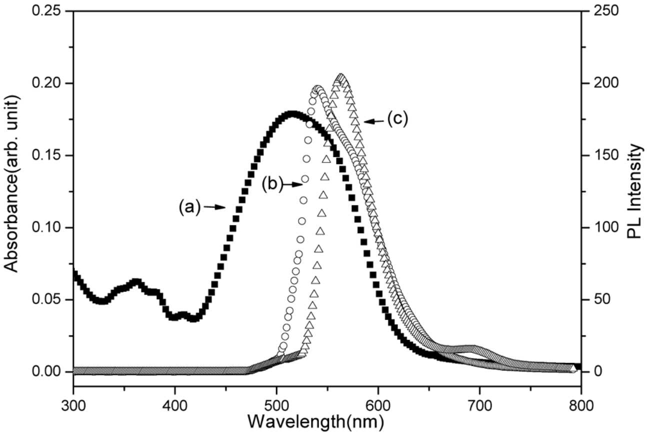


FIGURE 1 UV-visible absorption of (a) DCJTB(■) and PL emission of (b) Zn(PPM)$_2$(○) and (c) Zn(PFPPM)$_2$(△) thin films.

TABLE 1 Optical and Electrochemical Properties of Zn Complex Compounds and DCJTB

Compounds	λ_{max} (nm)	λ_{em} (nm)	HOMO (eV)	LUMO (eV)	Band gap
$Zn(PPM)_2$	514	540	5.27	2.95	2.32
$Zn(PFPPM)_2$	532	564	5.28	3.05	2.23
DCJTB	517	620	5.30	3.10	2.20

potentials accounts that we could get HOMO energy level of Zn complexes. Based on UV-Vis and CV data, we calculated all electronic levels of DCJTB and Zn complexes as shown in Table 1. Band gap of $Zn(PFPPM)_2$ is more squeezed compared to F-free Zn complex(I) and LUMO level of $Zn(PFPPM)_2$ is lower than $Zn(PPM)_2$'s about 0.1 eV. HOMO and LUMO levels of two compounds are matched with DCJTB's.

EL devices were fabricated by using 2-TNATA as a hole injection layer, NPB as a hole transporting layer, $Zn(PPM)_2$, $Zn(PFPPM)_2$ or Alq_3 as a host, DCJTB as a dopant, Alq_3 as an electron transporting layer; ITO/2-TNATA (60 nm)/NPB (15 nm)/Zn complex compounds or Alq_3 + DCJTB 5%(30 nm)/Alq_3(30 nm)/LiF (1 nm)/Al (200 nm).

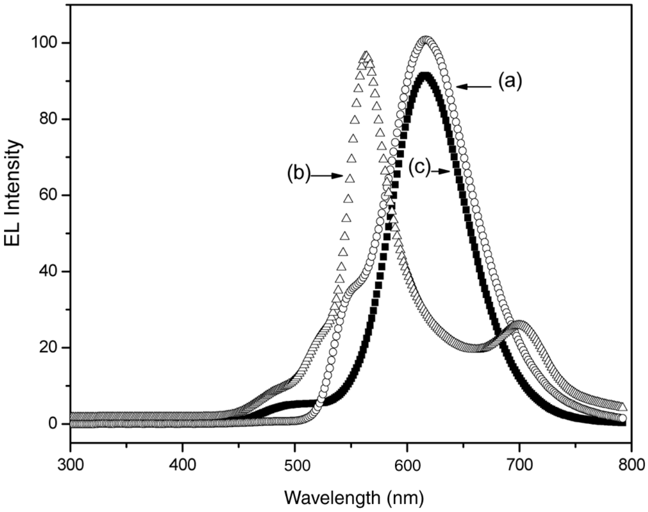
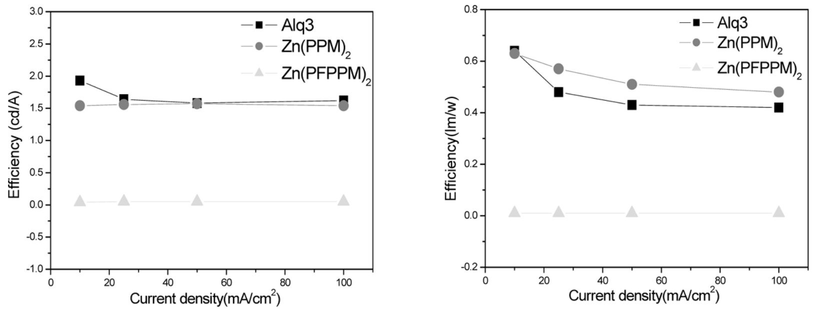


FIGURE 2 EL spectra of ITO/2-TNATA (60 nm)/NPB (15 nm)/ (a) $Zn(PPM)_2$(○), (b) $Zn(PFPPM)_2$(△) or (c) Alq_3(■) + DCJTB 5% (30 nm)/ Alq_3(30 nm)/LiF (1 nm)/Al (200 nm) at current density of 100 mA/cm^2.

Figure 2 shows the EL spectra of the devices with $Zn(PPM)_2$, $Zn(PFPPM)_2$ and Alq_3 host doped with 5% DCJTB. Alq_3 and $Zn(PPM)_2$ host EL devices exhibited DCJTB emission peak at around 617 nm due to energy transfer from Alq_3 and $Zn(PPM)_2$ to DCJTB. However the $Zn(PFPPM)_2$ host device showed no DCJTB emission peak and exhibited EL maximum values of 563 and 700 nm although $Zn(PFPPM)_2$ host material is doped with DCJTB. As shown in Figure 1 (c), this EL maximum value is consistent with PL maximum value of $Zn(PFPPM)_2$. As a result, we believe that there was no energy transfer from $Zn(PFPPM)_2$ to DCJTB. It is not easy to explain it clearly, but we also think of two kinds of reason. One thing could be that the overlapped spectrum area of $Zn(PFPPM)_2$ PL and DCJTB UV-visible spectrum was relatively smaller than $Zn(PFPPM)_2$'s. The other thing might be that the heterogeneous morphology between fluorinated compound host and DCJTB dopant was occurred. Further studies on this are underway.

Figure 3 showed luminance efficiency and power efficiency of ITO/2-TNATA (60 nm)/NPB (15 nm)/Zn complex compounds or Alq_3 + DCJTB 5%(30 nm)/Alq_3(30 nm)/LiF (1 nm)/Al (200 nm) devices. The $Zn(PPM)_2$ device showed same luminance efficiency as Alq_3 device, but showed better power efficiency of 1.2 times than Alq_3 device. One more thing is that efficiency stability of $Zn(PPM)_2$ device at high current density is observed. We believe that the reason why two Zn complexes show quite different efficiency data is no energy transfer from $Zn(PFPPM)_2$ to DCJTB. Further studies of Zn derivatives and devices are underway.



(a) (b)

FIGURE 3 Luminance efficiency (a) and power efficiency (b) of ITO/2-TNATA (60 nm)/NPB (15 nm)/$Zn(PPM)_2$, $Zn(PFPPM)_2$ or Alq_3 + DCJTB 5% (30 nm)/Alq_3(30 nm)/LiF (1 nm)/Al (200 nm) devices.

CONCLUSION

New Zn complexes based on phenyl and pyrrole moieties were synthesized. The absorption peak of DCJTB as a dopant was found to be 517 nm, and PL emission maximum peak of $Zn(PPM)_2$ and $Zn(PFPPM)_2$ as a host was also found to be 540 and 564 nm under the excitation of its own UV-vis maximum value. PL maximum value of $Zn(PFPPM)_2$ was red shifted about 24 nm compared to $Zn(PPM)_2$ because of different metal-ligand interaction.

EL devices were fabricated ITO/2-TNATA (60 nm)/NPB (15 nm)/Zn complex compounds or Alq_3 +DCJTB 5%(30 nm)/Alq_3(30 nm)/LiF (1 nm)/Al (200 nm). Alq_3 and $Zn(PPM)_2$ host EL devices exhibited DCJTB emission peak at around 617 nm due to energy transfer from Alq_3 and $Zn(PPM)_2$ to DCJTB. The $Zn(PPM)_2$ device showed same luminance efficiency as Alq_3 device, but showed better power efficiency of 1.2 times than Alq_3 device. One more thing is that efficiency stability of $Zn(PPM)_2$ device at high current density is observed.

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