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Synthesis and Electron Transport Layer Properties of Zinc Metallic Complexes Containing Quinoline Moieties in OLED

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Metal chelate complexes are often studied as a carrier transport material in OLEDs, because they have a good electron transport property. We have synthesized metal chelate complexes, Bis(8-hydroxyquinolinato)zinc (Znq_2) and Bis(10-hydroxybenzo[h]quinolinato)zinc ($Zn(bq)_2$) as well as Bis(10-hydroxybenzo[h]quinolinato)beryllium $Be(bq)_2$ and compared EL performance with commercialized Alq_3.

We will report the basic EL performance of synthesized complex materials such as EL spectrum, current efficiency and CIE value. When we applied Znq_2 and $Zn(bq)_2$ to conventional blue OLED device, the device exhibited better power efficiency of 0.4 lm/w and 0.28 lm/w compared to 0.2 lm/w of Alq_3 device. We also introduce overall EL performance of metal chelate device including $Be(bq)_2$.

Keywords: electron transport layer; metal chelate; OLED; quinoline; zinc complex

INTRODUCTION

Since Tang and Vanslyke developed multi-layer organic light-emitting devices (OLEDs) [1], OLEDs are of considerable importance for their potential as a generation of flat panel displays because of their high brightness, high luminance efficiency, wide color range, easy fabrication process, low operation voltage and possibility for flexible displays [2]. Therefore, tremendous efforts have been made toward improving the device performance. It was known that the performance

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of OLEDs depends heavily on the efficiency of carrier injection and their recombination, which generate molecular excitons, as well as the balance of the holes and electrons [3,4]. In order to achieve maximum efficiency, more carrier injection into the emission layer is needed in the device. The injected hole is easily movable in OLED compared to the injected electron, because of its relatively fast mobility.

In order to balance hole and electron carrier, there are two ways to slow hole carrier or to make electron movement fast. Many attempts of new electron transporting materials for fast electron transport have been focused on metal complexes for fluent recombination center. As we already understood, Alq_3 is a representative ETL material but it can not still satisfied with perfect charge balance [5,6]. Although several papers also mentioned $Be(bq)_2$ issues for new electron transporting material, to our knowledge there was no obvious EL data with $Be(bq)_2$ as an ETL in OLED [7,8].

In this study, we proposed new Zn complex materials and report its EL properties including $Be(bq)_2$ compound.

EXPERIMENTAL

Material and Characterization

8-Hydroxyquinoline (99.0%), 10-Hydroxybenzo[h]quinoline (98%), Diethyl zinc (1.0M in hexanes), Zinc acetate (98%), Beryllium sulfate tetrahydrate (99.99%) were purchased from Aldrich and Lancaster used without further purification unless otherwise noted. Solvents were purified by normal procedures and handled under moisture free atmosphere.

^{1}H-NMR spectra were recorded with Bruker, Avance DPX-300 NMR spectrometer in $CDCl_3$ and chemical shift were recorded in ppm units with the residual proton solvent resonance. FAB-Mass spectra were measured with JEOL, JMS-AX505WA.

The optical absorption spectra were measured by a HP 8453 UV-VIS-NIR Spectrometer. Perkin Elmer luminescence spectrometer LS55 was used for photoluminescence spectroscopy.

Synthesis

Synthesis of Bis(8-hydroxyquinolinato)zinc[Znq_2]

8-Hydroxyquinoline (30 mmol) was dissolved in 50 ml ethanol in a flask. Zinc acetate (15 mmol) was dissolved in 200 ml pure water in another flask. 8-hydroxyquinoline solution was slowly poured into the Zinc acetate solution while the solution was stirred. Znq_2

precipitation was deposited after the mixed solution was adjusted to pH 6 using NaOH. Znq_2 was filtered and solidified (2.15 g, 83%).

^{1}H NMR(DMSO)δ: 8.71(d,2H), 8.40(d,2H), 7.58(q,2H), 7.40(t,2H), 6.91(d,2H), 6.79(d,2H); Fab^+-Mass: 353.69.

Synthesis of Bis(10-hydroxybenzo[h]quinolinato)zinc[$Zn(bq)_2$]

A solution of diethyl zinc (2.42 ml, 2.43 mmol) was stirred under N_2 and cooled to -78°C in a dry ice/acetone bath during 1 hr. 10-hydroxybenzo[h]quinoline (4.86 mmol) was dissolved in 40 ml anhydrous THF under N_2 and slowly dropped to the diethyl zinc solution. $Zn(bq)_2$ precipitation was deposited after the mixed solution was adjusted to pH6 using NaOH. $Zn(bq)_2$ was filtered and solidified (0.89 g, 80.9%).

^{1}H NMR(DMSO)δ: 8.99(d,2H), 8.59(d,2H), 7.95(d,2H), 7.88(d,2H), 7.79(q,2H), 7.66(t,2H), 7.53(d,2H), 7.15(d,2H); Fab^+-Mass: 453.81.

Synthesis of Bis(10-hydroxybenzo[h]quinolinato)-beryllium[$Be(bq)_2$]

10-Hydroxybenzo[h]quinoline (80 mmol) was dissolved in 50 ml ethanol in a flask. $BeSO_4 \cdot 4H_2O$ (40 mmol) was dissolved in 200 ml pure water in another flask. 10-Hydroxybenzo[h]quinoline solution was slowly poured into the $BeSO_4 \cdot 4H_2O$ solution while the solution was stirred. $Be(bq)_2$ precipitation was deposited after the mixed solution was adjusted to pH10 using NaOH. $Be(bq)_2$ was filtered and solidified (1.47 g, 93.6%).

^{1}H NMR(DMSO)δ: 8.30(d,4H), 7.91(d,2H), 7.71(t,2H), 7.62(d,2H), 7.36–7.26(m,6H); Fab^+-Mass: 694.74.

Fabrication of OLEDs

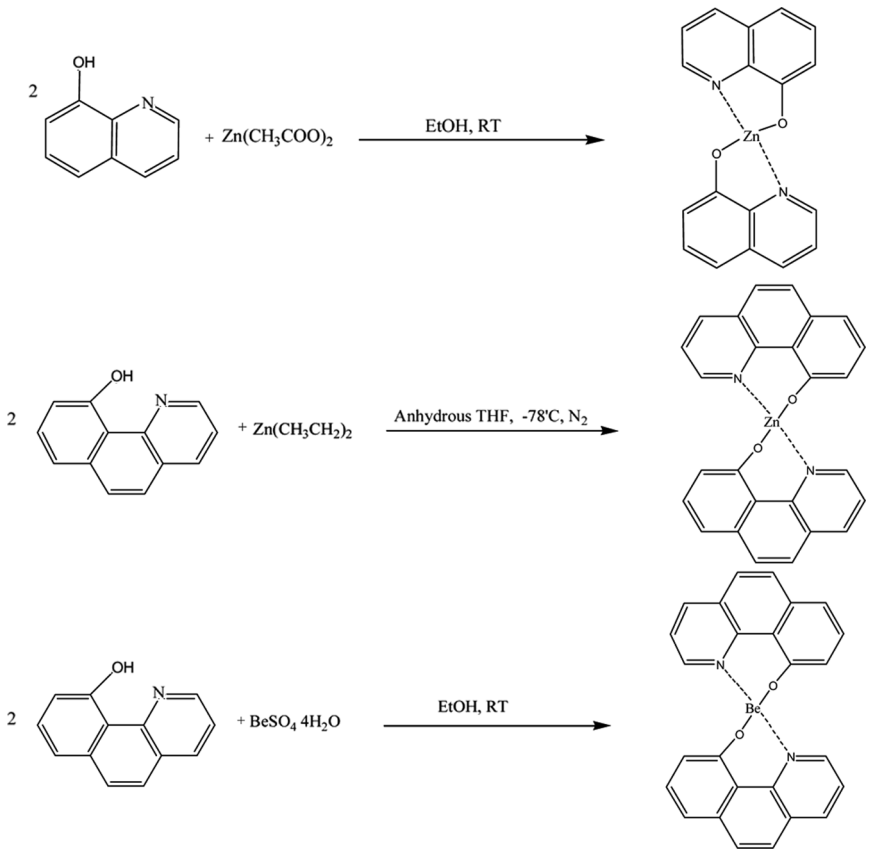
For EL device, Znq_2, $Zn(bq)_2$ and $Be(bq)_2$ were vacuum-deposited on top of ITO(1200 Å/30 ohm) under 10^{-6} torr, rate of deposition being 1 Å/sec to give an emitting area of 4 mm^2 and other organic layer and aluminum layer were continuously deposited with same vacuum condition. Redox potential of the compounds were determined by cyclic voltammetry (CV) using an EG&G 362 electrochemical workstation with a scanning rate of $30 \sim 200$ mV/s. The compound of interest was dissolved in N,N-Dimethylformamide (DMF) with 0.1 M tetrabutylammonium tetrafluoroborate as the electrolyte. We used a platinum working electrode and saturated $Ag/AgNO_3$ referenced electrode. Ferrocene was used for potential calibration (all reported potentials are referenced against ferrocene/ferrocenium, FOC) and reversibility criteria. Light intensity was obtained by Minolta CS-1000.

RESULTS AND DISCUSSION

We synthesized metal chelate complexes, Znq_2, $Zn(bq)_2$ and $Be(bq)_2$ by the reaction of metals and ligands. The structure was identified by NMR, UV-visible spectroscopy and FAB-Mass analysis.

As shown in Scheme 1, Znq_2, $Zn(bq)_2$ and $Be(bq)_2$ were synthesized by facile one step reaction which provides high yield of 80 ~ 90%.

Figure 1 shows UV-visible and photoluminescence (PL) spectra of Znq_2, $Zn(bq)_2$ and $Be(bq)_2$ films on glass. The maximum absorbance of metal chelate complexes appeared at 384 nm, 382 nm and 424 nm. The PL peaks of these complexes were located between 527 nm and 594 nm. Znq_2 showed 543 nm maximum PL value and $Zn(bq)_2$ shifted



SCHEME 1 Synthesis Bis(8-hydroxyquinolinato)zinc(Znq_2), Bis(10-hydroxybenzo[h]quinolinato)zinc($Zn(bq)_2$), Bis(10-hydroxybenzo[h]quinolinato)beryllium($Be(bq)_2$).

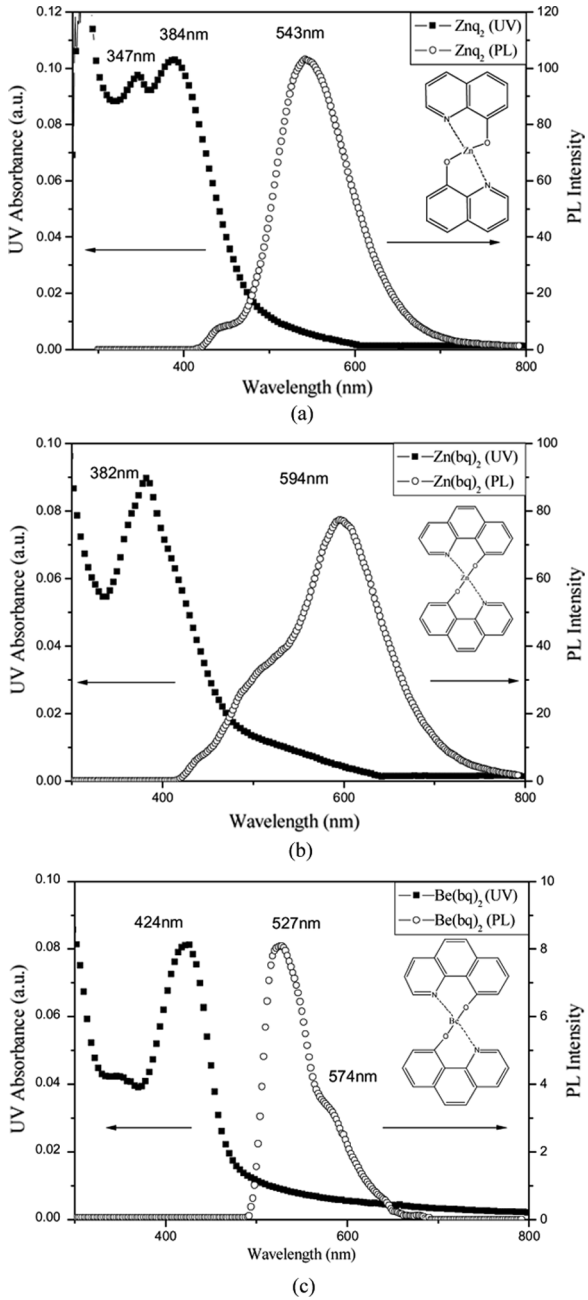


FIGURE 1 UV-visible (-■-) and PL spectra (-○-) of (a) Znq_2, (b) $Zn(bq)_2$ and (c) $Be(bq)_2$ films.

TABLE 1 HOMOs, LUMOs and Optical Band Gaps Values of Metal Chelate Complexes

	HOMO (eV)	LUMO (eV)	Eg (eV)
Znq_2	–	–	2.72
$Zn(bq)_2$	5.87	2.74	3.13
$Be(bq)_2$[7]	5.5	2.7	2.8
Alq_3[7]	5.6	2.8	2.8

red PL maximum value to 594 nm. It could be explained by the longer conjugation lengths of benzoquinoline. In case of $Be(bq)_2$, it showed PL maximum and shoulder values of 527 nm and 574 nm due to different core metal.

The electronic energy level for these metal chelate complexes is listed in Table 1. Each value was measured by calculation of cyclic-voltammetry (CV) data and on set point of UV-visible spectroscopy. Znq_2 showed relatively unstable electrochemical property especially on oxidation process in CV result. It means that Znq_2 can not be applied to use it as a hole transport layer (HTL), because the reversible process of oxidation and neutral state is always happened at HTL. $Zn(bq)_2$ and $Be(bq)_2$ exhibited 5.87 and 5.5 eV of HOMO levels and 2.74 and 2.7 eV of LUMO levels. The electronic energy level of $Zn(bq)_2$ and $Be(bq)_2$ is almost similar value with Alq_3, which is commercialized as an ETL, as shown in Table 1.

TABLE 2 Performance of ETL in Multi-Layered Blue Devices at 10 mA/cm^2: i) ITO/2-TNATA(60 nm)/NPB(15 nm)/DPVBi(30 nm)/ETL(30 nm)/Al device. ii) ITO/2-TNATA(60 nm)/NPB(15 nm)/DPVBi(30 nm)/ETL(30 nm)/LiF(1 nm)/Al device

ETL	EL λ_{max} (nm)	C.I.E. (x, y)	Brightness (cd/m^2)	Luminescence efficiency (cd/A)	Power efficiency (lm/W)
Znq_2[i]	463	(0.149, 0.151)	139	1.39	0.42
$Zn(bq)_2$[i]	467	(0.154, 0.191)	91.3	0.91	0.28
$Be(bq)_2$[i]	469	(0.151, 0.169)	276	2.76	1.02
Alq_3[i]	464	(0.154, 0.167)	57.8	0.58	0.19
Znq_2[ii]	465	(0.149, 0.158)	423	4.23	1.94
$Zn(bq)_2$[ii]	462.5	(0.149, 0.155)	309	3.09	1.18
$Be(bq)_2$[ii]	466.5	(0.151, 0.174)	358	3.58	1.99
Alq_3[ii]	465	(0.150, 0.155)	417	4.17	1.71

TABLE 3 Performance of ETL or Host in Multi-Layered Blue, Green and Red Devices at 10 mA/cm^2: ITO/ 2-TNATA(60 nm)/NPB(15 nm)/EML(30 nm)/ETL(30 nm)/LiF(1 nm)/Al Device

Device	EML	ETL	Voltage (V)	EL λ max (nm)	C.I.E. (x, y)	Brightness (cd/m^2)	Luminescence efficiency (cd/A)	Power efficiency (lm/W)
Blue	DPVBi	Alq_3	9.6	465	(0.150, 0.155)	417	4.17	1.71
		$Be(bq)_2$	5.7	466.5	(0.151, 0.174)	358	3.58	1.99
Green	Alq_3	Alq_3	4.8	516	(0.316, 0.512)	365	3.65	2.4
		$Be(bq)_2$	5.6	510	(0.308, 0.510)	228	2.23	1.25
Red	Alq_3:DCM2 (7.5%)	Alq_3	4.9	622	(0.643, 0.353)	72	0.72	0.46
		$Be(bq)_2$	4.7	621.5	(0.640, 0.357)	94	0.94	0.63
	$Be(bq)_2$:DCM2 (7.5%)	Alq_3	4.8	619	(0.637, 0.360)	85	0.85	0.56
		$Be(bq)_2$	4.6	622	(0.639, 0.357)	91	0.91	0.63

We fabricated blue EL devices with ITO/2-TNATA(60 nm)/NPB(15 nm)/DPVBi(30 nm)/ETL(30 nm)/LiF(1 nm or not)/Al device configuration. Blue EL performance of these devices were summarized in Table 2. OLED blue devices of synthesized compounds without LiF layer showed better overall power efficiency. We observed that Znq_2, $Zn(bq)_2$ and $Be(bq)_2$ have 2.2, 1.4 and 5 times compared to Alq_3's in power efficiency, and Znq_2 also showed slightly better C.I.E. value of (0.149, 0.151) than others. We suppose that Alq_3 device without LiF layer decreased EL efficiency because of poor interface between Alq_3 and cathode metal. When LiF layer is used in devices, Znq_2 and $Be(bq)_2$ only exhibited better power efficiency as 1.94 and 1.99 lm/W compared to Alq_3 device. Kido *et al*. also reported that Alq_3 and LiF are very good combination pair compared to other metal complexes [9].

At present, Alq_3 has been widely used as green and red host as well as an ETL material. In our blue device data, $Be(bq)_2$ showed overall better EL performance than Alq_3. Therefore we also applied $Be(bq)_2$ as a red emitting host material and ETL of green and red device (Table 3). Although green device using $Be(bq)_2$ as an ETL showed half power efficiency of Alq_3 device, red device including $Be(bq)_2$ ETL material exhibited better power efficiency of 0.63 lm/W compared to 0.46 lm/W of Alq_3 device. The reason why Alq_3 green device gave better efficiency is that there is no divided interface between emitting layer and ETL by using Alq_3 layer as a whole. We suppose that there is no electron barrier to move from ETL to emitting layer in Alq_3 system as a whole. In contrast, when we use ETL of $Be(bq)_2$ in green device, we believe that there is different interface effect between Alq_3 and $Be(bq)_2$ layers unlike whole Alq_3 layer.

Regarding on using $Be(bq)_2$ as a red host in EL device, we prepared not only red host EL device with only $Be(bq)_2$ emitting layer, but also red EL device including $Be(bq)_2$ compound as an emitting and electron transporting layer. Red device using $Be(bq)_2$ material as shown in Table 3 shows overall better EL performance with 0.56 and 0.63 lm/W W value compared to 0.46 lm/W of Alq_3 device.

CONCLUSION

We synthesized metal chelate complexes, Znq_2, $Zn(bq)_2$ and $Be(bq)_2$ by the reaction of metals and ligands. They were synthesized by facile one step reaction which provides high yield of $80 \sim 90\%$. In OLED blue devices of synthesized compounds without LiF layer showed that Znq_2, $Zn(bq)_2$ and $Be(bq)_2$ have 2.2, 1.4 and 5 times compared to Alq_3's in power efficiency, and Znq_2 also showed slightly better C.I.E. value of (0.149, 0.151) than others. And when LiF layer is used in devices,

Znq_2 and $Be(bq)_2$ only exhibited better power efficiency as 1.94 and 1.99 lm/W. They could be replaced as an ETL material in OLED device, because of good electron transport property.

Although green device using $Be(bq)_2$ as an ETL showed half power efficiency of Alq_3 device, red device using $Be(bq)_2$ material shows overall better EL performance with 0.56 and 0.63 lm/W value compared to 0.46 lm/W of Alq_3 device.

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