

Research Article

Synthesis and Electroluminescent Properties of Bis(3H-1,2,3-triazolo-[4,5-b]pyridine-3-ol)zinc $Zn(TAP)_2$

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Received 31 December 2011; Accepted 8 March 2012

Academic Editor: Laécio Santos Cavalcante

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A new light-emissive material, bis(3H-1,2,3-triazolo-[4,5-b]pyridine-3-ol)zinc ($Zn(TAP)_2$), has been synthesized and characterized by FT-NMR, FT-IR, UV-Vis, and elemental analysis. The photoluminescence (PL) of $Zn(TAP)_2$ was measured from the DMF solution at 460 nm. The HOMO (6.5 eV) and LUMO (2.8 eV) energy levels of $Zn(TAP)_2$ were estimated from the measurement of cyclic voltammetry. The devices with structures of ITO/NPB/ $Zn(TAP)_2$ /LiF/Al and ITO/NPB/ $Zn(TAP)_2$ /Alq₃/LiF/Al were constructed to investigate their electroluminescent (EL) performance. $Zn(TAP)_2$ is supposed to be a good emitting material in the EL device.

1. Introduction

Organic light-emitting diodes (OLEDs) are believed to be the next-generation flat panel displays due to low driving voltage, high contrast, ease of fabrication, wide viewing angle, and low cost [1–5]. Even now they have already become cheaper than their inorganic counterparts. In this field, the development of novel luminescent organic/organometallic compounds is a key to enhance the performance of organic and polymeric light-emitting devices. Luminescent chelate complexes have shown to be particularly useful in OLEDs because of their relatively high stability and volatility. Alq₃ is the most well-known example of such chelate compounds, where q is the 8-hydroxyquinolinato ligand, which is both a good emitter and a highly efficient electron-transporting material [6, 7].

Since the first OLEDs with Zn complexes were reported in 1993 [8], synthesis of novel zinc complexes as active materials for OLEDs have focused on improving electron mobility or producing a blue shift emission compared to Znq₂ [9, 10]. The electroluminescent performance of zinc

complexes as the emitter is just comparable with that of Alq₃ [11]. However, in many instances, the electron-transporting mobility of zinc complexes goes beyond that of Alq₃ [12]. So zinc complexes may be potential candidates to enhance the electron-transporting properties for OLEDs.

Zn²⁺ ion is the only oxidation state of zinc atom and has no unoccupied valence electron orbits. Therefore, the oxidation and reduction of zinc complexes are mainly carried out in the ligands, that is, luminescence and charge transporting may be ascribed to intraligand electronic transition. One simple way to adjust the emission wavelength is to manipulate substituents in the 8-hydroxyquinoline rings or to modify the chemical structure. C2 position-substituted bis(2-methyl-8-hydroxyquinoline)zinc ($ZnMq_2$) [13], C5 position-substituted bis(8-hydroxy-5-piperidinylsulfonamidoquinolate)zinc ($Zn(QS)_2$) [14] and ($ZnLn$)₂·2H₂O (Ln = 5-amido-substituted-8-hydroxyquinolate ligand) [11] have been reported one after the other. These complexes showed more or less either blue-shifting or red-shifting with reference to Znq₂. In our previous reports, [2-(2-hydroxyphenyl)benzoxazole]zinc [15] Zn(HPB)₂ and

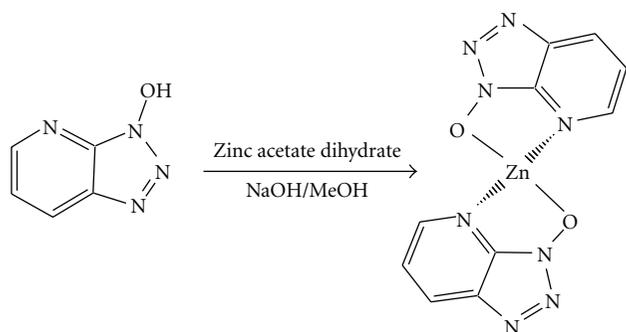


FIGURE 1: Synthetic scheme of $\text{Zn}(\text{TAP})_2$.

zinc [16] $\text{Zn}(\text{MHB})_2$ have shown to be good materials for OLEDs as hole blocking layer and emitting layer.

In this paper, (3H-1,2,3-triazolo-[4,5-b]pyridine-3-ol) zinc $\text{Zn}(\text{TAP})_2$ was synthesized and primarily applied as an emitting layer (EML) based on its energy gap level of 3.7 eV. Two types of OLEDs devices with the structures of ITO/NPB(40 nm)/ $\text{Zn}(\text{TAP})_2$ (60 nm)/ Alq_3 (5 nm)/LiF/A1 and ITO/NPB(40 nm)/ $\text{Zn}(\text{TAP})_2$ (60 nm)/LiF/A1 are fabricated by considering the balance of carriers injection and transportation as well as the matching of the energy level. The photoluminescent (PL) and EL properties of $\text{Zn}(\text{TAP})_2$ were investigated.

2. Experimental Details

2.1. Materials and Characterization Equipments. 3H-1,2,3-triazolo-[4,5-b]pyridine-3-ol (>98%) and sodium hydroxide were purchased from TCI, and Zinc acetate dihydrate (>99%) was purchased from Fluka and used without further purification unless otherwise noted. Solvents were purified by normal procedures and handled under moisture-free atmosphere. The optical absorption spectra were measured by a Shimadzu UV-2501 PC Spectrometer. The PL spectrum was measured using a Perkin-Elmer LS45 luminescence spectrometer. The characteristics of the current density-voltage-luminance (I-V-L) and the efficiency were measured by IVL 300 series (JBS Inc.).

2.2. Synthesis of [3H-1,2,3-triazolo-[4,5-b]pyridine-3-ol]zinc $\text{Zn}(\text{TAP})_2$. The synthetic scheme of $\text{Zn}(\text{TAP})_2$ is shown in Figure 1. The synthesis of $\text{Zn}(\text{TAP})_2$ was followed the closely related literature procedure and our previous works [15–18]. First, a solution of zinc acetate dihydrate (0.211 g, 1 mmol) in methanol (5 mL) was gradually added to a DMF solution of 3H-1,2,3-triazolo-[4,5-b]pyridine-3-ol (TAP) (0.27 g, 2 mmol) and sodium hydroxide (0.08 g, 2 mmol) in 5 mL methanol. After the mixture was stirred for 8 h at room temperature under N_2 , a yellow precipitate was produced. The yellow precipitates were collected by filtration and purified by recrystallization from DMF and water and dried under vacuum. Anal. Calc. for $\text{C}_{10}\text{H}_6\text{N}_8\text{O}_2\text{Zn}$, C: 35.79, H: 1.80, N: 33.39. Found (%) C: 35.02, H: 1.82, N: 33.41. $^1\text{H-NMR}$ (300 MHz, $[\text{D}_6]$ DMSO, ppm) δ 8.25 (2H), 8.20 (2H),

7.22 (2H). $^{13}\text{C-NMR}$ (75 MHz, $[\text{D}_6]$ DMSO, ppm) δ 146.06, 137.85, 134.25, 128.56, 119.90. FT-IR (KBr, cm^{-1}): 3402, 3166, 2305, 1657, 1597, 1394, 1153, 801. UV-Vis (nm, in DMF): 206, 282, 342, 406. (Reference UV-Vis (TAP): 265, 283, 406.).

2.3. Fabrication of EL Devices. The OLEDs containing $\text{Zn}(\text{TAP})_2$ were fabricated by the vacuum deposition. The substrate was ITO-coated glass with a sheet resistance of 10Ω per square. The ITO-coated glass was pretreated according to a regular chemical cleaning procedure using detergent, deionized water and alcohol in sequence, and finished with UV-ozone method. The thermal evaporation of organic materials was carried out at a chamber pressure of 5×10^{-6} torr. The emission area of each device was $3 \times 3 \text{ mm}^2$. All the organics were evaporated with a rate in the range of 0.1–0.3 nm/s. The metallic cathode was evaporated at higher rate (0.8–1 nm/s) with keeping the vacuum level.

3. Results and Discussion

3.1. Structure Characterization and PL Properties of $\text{Zn}(\text{TAP})_2$. The chemical structure of the zinc complex was determined from FT-IR, UV-Vis, and $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$. The FT-IR spectrum of $\text{Zn}(\text{TAP})_2$ is shown in Figure 2(a). The high-frequency region ($3300\text{--}3000 \text{ cm}^{-1}$) contains absorption bands originating mainly from localized C–H stretching vibrations, although the broad band around 3500 cm^{-1} is still shown due to the hydration. The mid-frequency region ($1700\text{--}1000 \text{ cm}^{-1}$) corresponds to in-plane stretching and bending of heavy atom vibrations. In the low-frequency region (below 1000 cm^{-1}), the out-of-plane modes are observed. The bands centered at 1657 and 1597 cm^{-1} are assigned to the C=C stretching vibration involving the TAP ligand. The bands observed at 1496 and 1476 cm^{-1} should correspond to a C=C/C=N stretching associated with the TAP mobility in $\text{Zn}(\text{TAP})_2$. The absorption band at about 1100 cm^{-1} should be assigned to the C–O stretching vibration frequency at the C–O–M site. The spectrum showed a sharp absorption band at about 1153 cm^{-1} . However, the absorption bands by Zn–O or Zn–N were not detected in the lower frequency region. During handling the complex sample, it showed a blue emission in DMF solution under the UV-lamp (exciting wavelength, 365 nm). The UV-vis absorption and photoluminescence (PL) spectra of the $\text{Zn}(\text{TAP})_2$ are, respectively, shown in Figures 2(b) and 3. The UV-vis absorption and PL spectra were measured in the DMF solution. The absorption spectrum of the $\text{Zn}(\text{TAP})_2$ exhibited the peaks at around 265, 282, 342, and 406 nm, which are attributed to $\pi\text{--}\pi^*$ transition of 3H-1,2,3-triazolo-[4,5-b]pyridine-3-ol ligand and the metal complex. The PL spectrum of $\text{Zn}(\text{TAP})_2$ exhibits a maximum at around 460 nm (exciting wavelength, 350 nm). Figure 4(a) shows the $^1\text{H-NMR}$ spectrum of 3H-1,2,3-triazolo-[4,5-b]pyridine-3-ol with chemical shifts (δ) of 7.5 (1H), 8.5 (1H), and 8.7 (1H) ppm, which belong to the aromatic protons, and 13.8 ppm by the OH group. The $^1\text{H-NMR}$ spectrum of the Zn-complex (Figure 4(b)) agrees

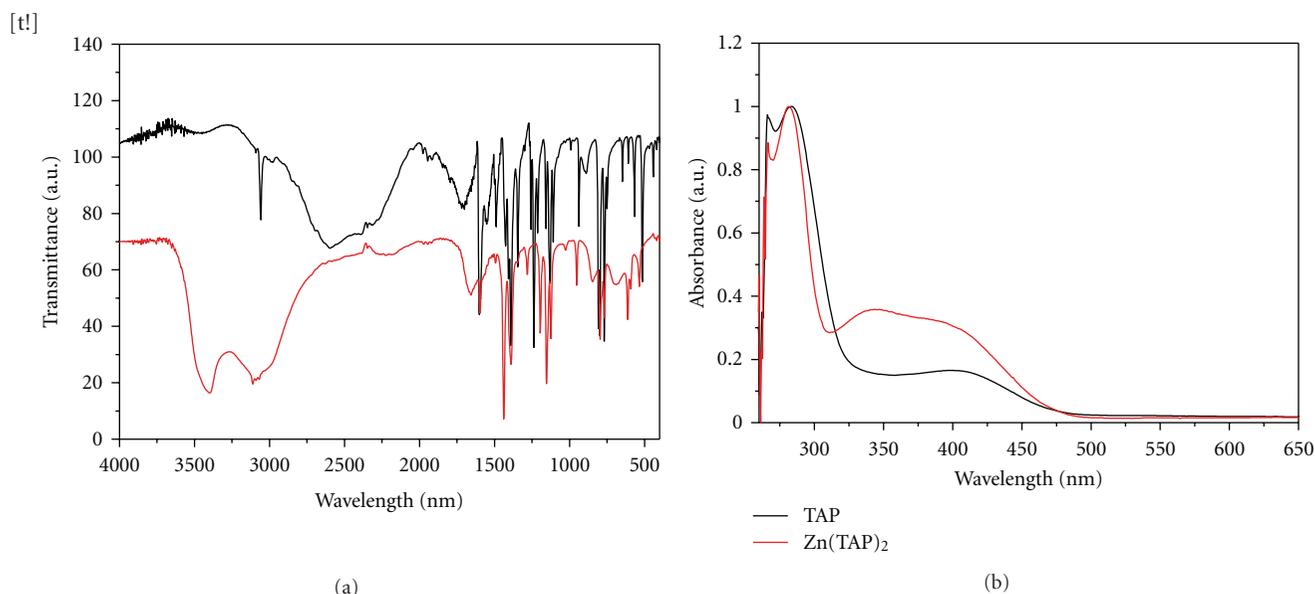


FIGURE 2: (a) FT-IR and (b) UV-vis spectra of Zn(TAP)_2 .

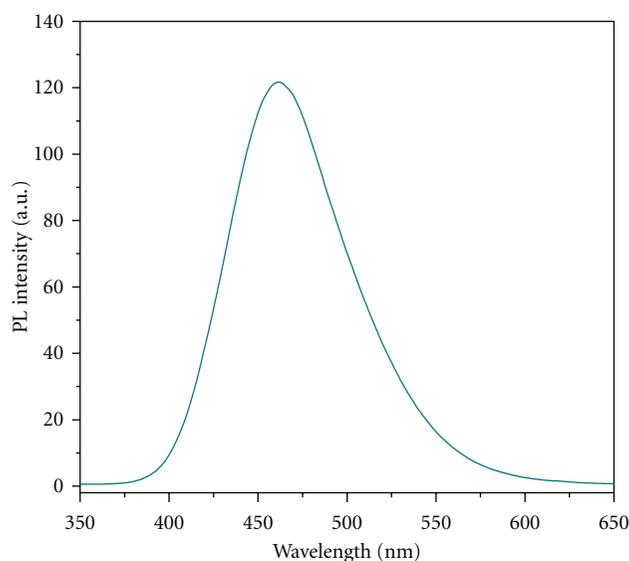


FIGURE 3: Photoluminescence of Zn(TAP)_2 .

with the moiety of 3H-1,2,3-triazolo-[4,5-b]pyridine-3-ol in Figure 4(a) with blue shift. It shows the peaks (δ) of 8.25 (2H), 8.20 (2H), and 7.22 (2H) ppm by the aromatic protons and the peak by the OH group disappears along with the complex formation. The ^{13}C -NMR spectrum (Figure 4(c)) also supports the chemical structure from five ^1H -decoupled ^{13}C -peaks (δ 146.06, 137.85, 134.25, 128.56, and 119.90) due to the aromatic ring.

3.2. Electrochemical Properties of Zn(TAP)_2 . The energy band diagrams of the Zn(TAP)_2 were determined from the HOMO and LUMO energy levels and the band gaps, which were calculated from cyclic voltammetry (C-V) [19].

The C-V measurement was performed with a solution of tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) (0.10 M) in acetonitrile at a scan rate of 400 mV/s at room temperature under the protection of argon. A Pt wire and an Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively. From the onset potential for the oxidation, the HOMO energy level of the Zn(TAP)_2 was estimated by considering the energy level of the reference ferrocene/ferrocenium (Fc/Fc⁺) redox couple [20]. The oxidation onset potential of Zn(TAP)_2 was +1.7 V, and the reduction onset potential was found to be -2.0 V as shown in Figure 5. From these onset potentials of the oxidation and the reduction of cyclic voltammograms, the HOMO and LUMO energy were calculated as 6.5 and 2.8 eV, respectively, with an

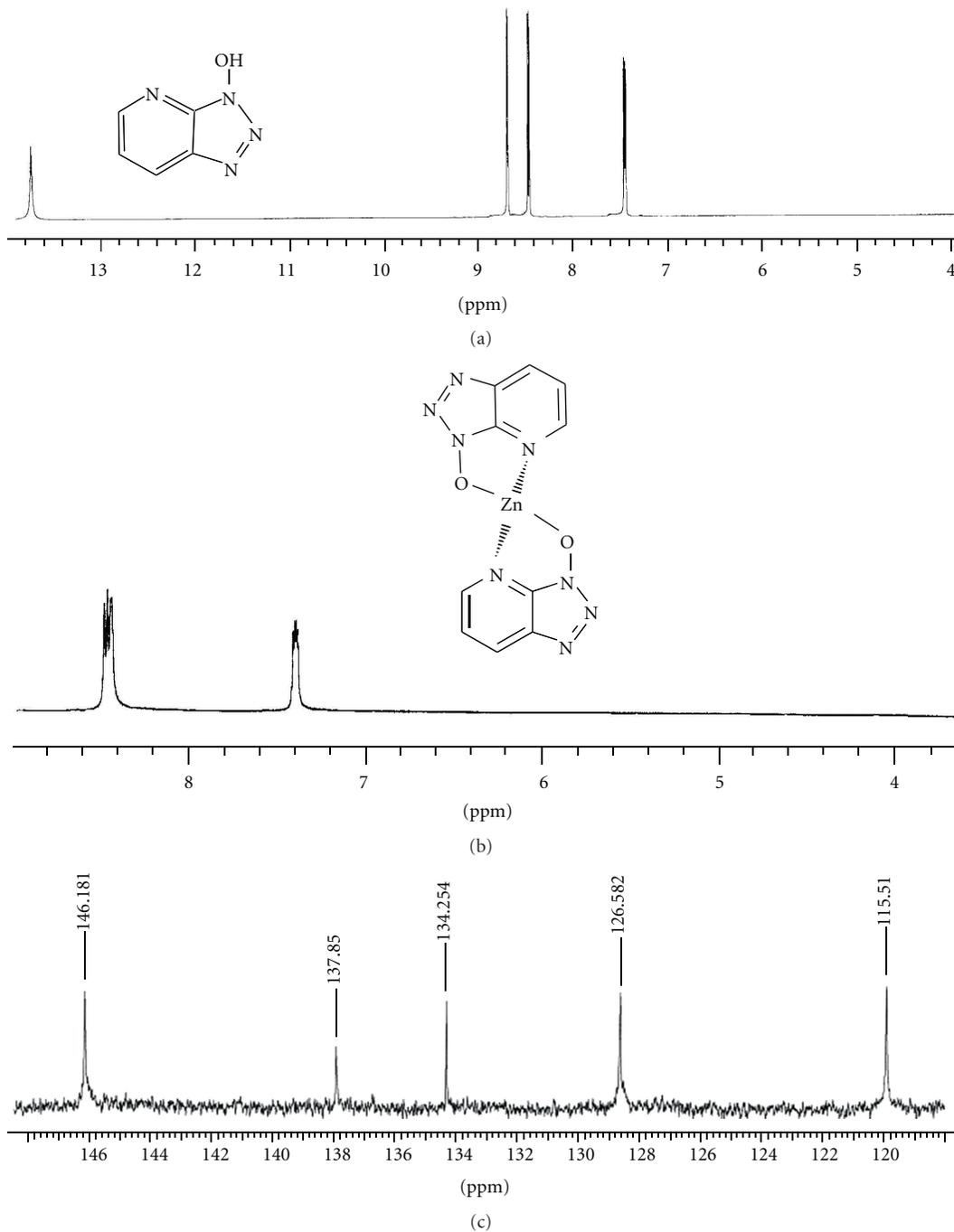
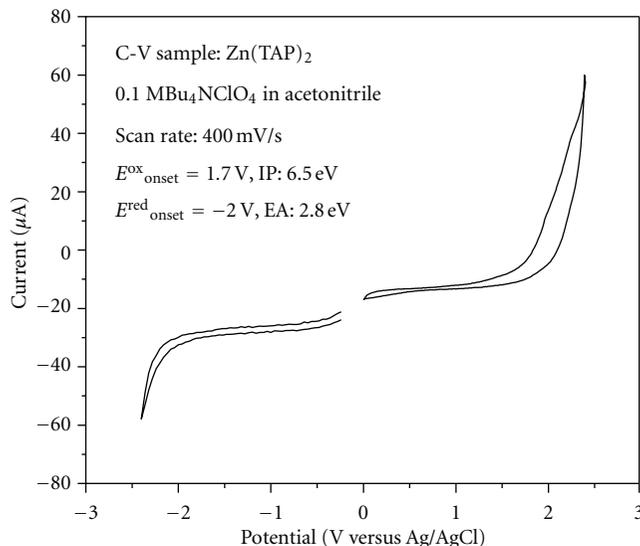
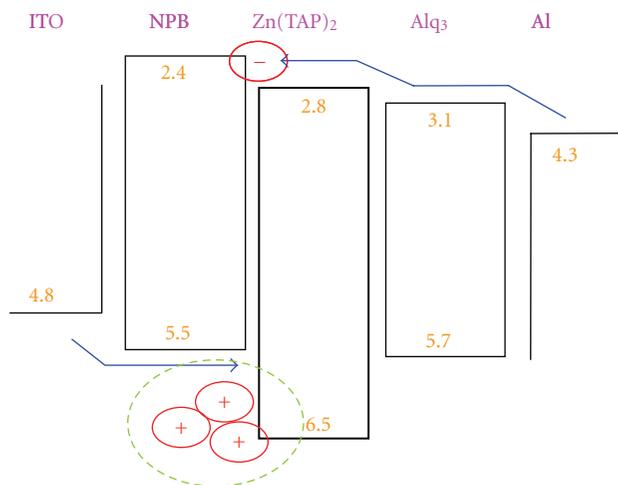


FIGURE 4: ^1H -NMR spectra of (a) TAP and (b) $\text{Zn}(\text{TAP})_2$ and (c) ^{13}C -NMR spectrum of $\text{Zn}(\text{TAP})_2$.

eg of 3.7 eV. Figure 6 shows the work functions of electrodes and HOMO and LUMO energy levels of the materials for ITO/NPB/ $\text{Zn}(\text{TAP})_2/\text{Alq}_3/\text{LiF}/\text{Al}$ device. It illustrates the possible combination of electrons and holes in the $\text{Zn}(\text{TAP})_2$ layer.

3.3. Electroluminescence Properties. The normalized electroluminescence (EL) spectrum is shown in Figure 7(a). To

investigate the EL properties of the $\text{Zn}(\text{TAP})_2$ devices with the configuration of ITO/NPB/ $\text{Zn}(\text{TAP})_2/\text{Alq}_3/\text{LiF}/\text{Al}$ and ITO/NPB/ $\text{Zn}(\text{TAP})_2/\text{LiF}/\text{Al}$ were fabricated. And to decrease the operating voltage and to achieve the best OLEDs performance of the devices, we optimized the thicknesses of emitting layer. The EL spectrum of the device shows maximum emission at the $\lambda_{\text{max}} = 448 \text{ nm}$, considerably blue-shifted compared to the PL spectrum.

FIGURE 5: Cyclic voltammogram of $\text{Zn}(\text{TAP})_2$.FIGURE 6: Work functions of electrodes and HOMO and LUMO energy levels of the materials for ITO/NPB/ $\text{Zn}(\text{TAP})_2$ /Alq₃/LiF/Al device.

The current density-voltage-luminance (I-V-L) and current density-efficiency characteristics of the device are shown in Figures 7(b), 7(c), and 7(d). The device showed a turn-on voltage as low as 5 V. For the ITO/NPB(40 nm)/ $\text{Zn}(\text{TAP})_2$ (60 nm)/Alq₃(5 nm)/LiF/Al device driven at a current density of 2,100 mA/cm², the maximum luminance of 2,800 cd/m² was achieved with an efficiency of 1.85 lm/W. In addition, we constructed another device without Alq₃ as ITO/NPB(40 nm)/ $\text{Zn}(\text{TAP})_2$ (60 nm)/LiF/Al to compare the component performance. In this case, at the current density of 1,500 mA/cm², the maximum luminance of 1,800 cd/m² was achieved with an efficiency of 1.25 lm/V. Therefore, the performance by the first device was better than the later one. It means that the Alq₃ with the thickness of 5 nm played as the electrons transport layer (ETL), which increased the

combination of electrons with the holes in the emitting layer of $\text{Zn}(\text{TAP})_2$. We expect that the EL performance could be further improved by introducing other buffer layers or applying the zinc complex to electron balancing layer.

4. Conclusion

We synthesized a novel blue emitting material, [3H-1,2,3-triazolo-[4,5-b]pyridine-3-ol]zinc $\text{Zn}(\text{TAP})_2$. In DMF solution, $\text{Zn}(\text{TAP})_2$ showed strong blue photoluminescence around 460 nm and the EL device showed blue emission at λ_{max} of 448 nm. The blue emitting device using $\text{Zn}(\text{TAP})_2$ as emitting material showed the luminance of 2,800 cd/m² at 12 V. The preliminary electrical characteristics of $\text{Zn}(\text{TAP})_2$

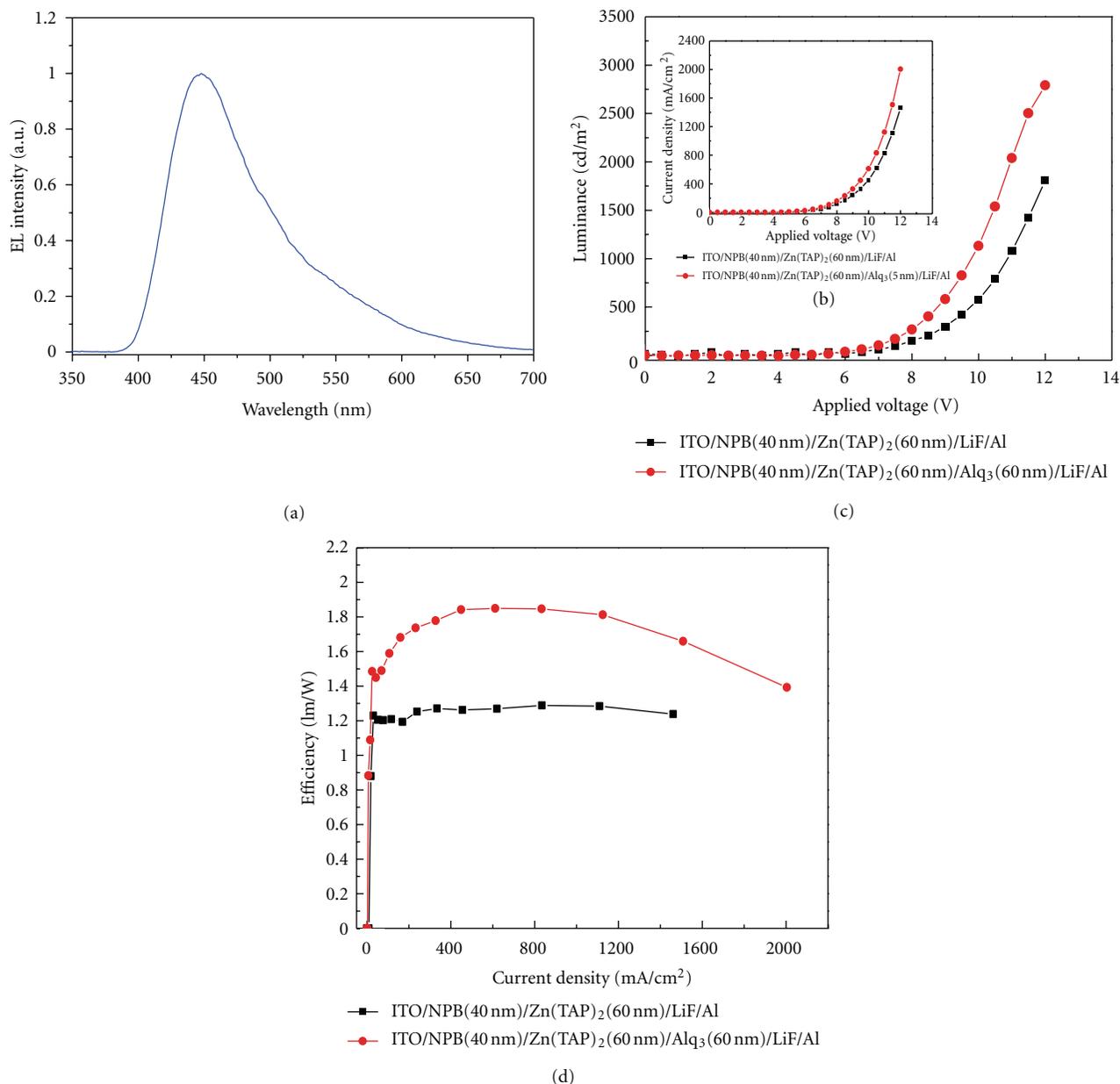


FIGURE 7: (a) EL spectra of OLEDs devices using Zn(TAP)₂ as emitting layer, (b) current density versus applied voltage, (c) luminance versus applied voltage, and (d) efficiency versus applied voltage characteristics of OLEDs devices.

suggest that its related compounds can be possible candidates for the OLEDs materials.

Acknowledgment

This paper was supported by the 2011 Inje University research grant.

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