

## Electron Transport Properties of Zn(phen)q Compared with Alq<sub>3</sub> in OLED

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**Abstract** – We synthesized new electroluminescence materials [(1,10-phenanthroline)(8-hydroxyquinoline)] Zn(phen)q and investigated their electron transport properties. We used Zn(phen)q and Alq<sub>3</sub> for the conductive materials and measured their electron transport properties as a function of the organic layer thickness. The difference between Zn(phen)q and Alq<sub>3</sub> as electron transporting materials suggests that the electrical properties depends on the carrier injection.

**Keywords:** OLED, Zn Complex, Electron Transport Properties, Cyclic Voltammetry

### 1. Introduction

Organic light-emitting diodes (OLED) based on compounds with a low molecular weight are attractive for the next generation of flat panel displays due to their low power consumption, high contrast, ease of fabrication, and low production costs [1]. Since the first report on an LED based on Tris-(8-hydroxyquinoline) aluminum (Alq<sub>3</sub>), a number of organic materials have been synthesized and many researchers have attempted to build high-performance OLED. Recently, high luminance and efficiency were realized in OLED with a multi-layer structure and light-emitting materials such as the metal-chelate complex [2-4].

The OLED can produce light of any color, depending on the type of organic emitting material is selected. The best-known metal chelate compound is Alq<sub>3</sub> where q is the 8-hydroxyquinolinato ligand [5]. This material has both good emission properties and efficient electron transportation. Modifying the ligand of the metal chelate compound changes the emission color and other properties, such as thermal stability and carrier mobility may also improve [6,7].

For synthesis, we used 1,10-phenanthroline (phen) and 8-hydroxyquinoline (q) for this study. Phen is a good ligand for metal ions, and it can be used to construct supramolecular structures via hydrogen bonds and  $\pi$ - $\pi$  aromatic interactions [8]. Thus, its metal complexes show increased thermal stability. In addition, phen enhances the luminescent properties of metal complexes due to the antenna effect, and its hole blocking ability enhances the recombination probability for carriers in the emitting layer [9-10].

We synthesized and characterized the electrical properties of Zn(phen)q, which was used as an electron transport layer in our previous report [11]. In this study, we investigated the difference between Zn(phen)q and Alq<sub>3</sub> as electron transporting materials; the results suggest that the electrical properties depend on the carrier injection.

### 2. Experiment

We synthesized Zn(phen)q for use as a light-emitting materials. In a round-bottomed flask, 1, 10-phenanthroline (0.18 g) was dissolved in 20 ml of absolute ethanol at room temperature under a nitrogen atmosphere. The solution was stirred for 1 h, after which a zinc acetate dihydrate (0.219 g) in water (3 ml) was added dropwise under stirring. Then, the reaction solution was stirred for 3 h, and an ethanol solution of 8-hydroxyquinoline (0.145 g) was added dropwise under stirring. The yellow precipitate was collected by filtration, purified by re-crystallization in acetone and ethanol and dried under overnight. The calculated atomic percentages were (%): C: 67.28, O: 4.52, N: 11.07, and Zn: 17.12; the measured atomic percentages were (%): C: 68.11, O: 4.32, N: 11.35, and Zn: 17.57.

The FT-IR spectra of Zn(phen)q, phen, and q are shown in Figure 1. The high-wavenumber region (3600-1700cm<sup>-1</sup>) has absorption bands due to localized hydrogen stretching vibrations. The mid-wavenumber region (1700-1000cm<sup>-1</sup>) corresponds to heavy atom in-plane stretching and bending vibrations. In the low-wavenumber region (below 1000cm<sup>-1</sup>), out-of-plane modes are observed. The bands centered at 1604 and 1577cm<sup>-1</sup> are assigned to a C=C stretching vibration involving the quinoline ligand. The bands observed 1500 and 1469cm<sup>-1</sup> correspond to a C=C/C=N stretching associated with both the pyridyl and phenyl groups in Zn(phen)q. The vibrations at 1391 and 1329cm<sup>-1</sup> are due to C=C/C=N stretching in the quinoline fragments of Zn(phen)q. Charles et al. have suggested that the absorption band close to about 1100cm<sup>-1</sup> is due to a C-O stretching vibration wavenumber at the C-O-M site; The spectrum

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they measured showed a sharp absorption band near  $1110\text{cm}^{-1}$ [12]. In the region below  $1000\text{cm}^{-1}$ , out-of-plane vibrations are usually observed. The most intense out-of-plane absorption in this region was found at  $743\text{cm}^{-1}$  [13-14].

Fig. 2 gives the UV-Vis spectra of the Zn(phen)q in a THF solution. The spectra of Zn(phen)q show four major bands. The first two bands group located at 260 and 289nm can be assigned to the moderate energy ( $\pi$ - $\pi^*$ ) transitions of the aromatic rings[15], while the second two bands group at 342 and 390nm are due to the coordination of zinc and organic ligands (phen and q). The XPS spectra reveal the elements present and their relative concentrations, which provided a confirmation of the Zn(phen)q structure. The observed elemental composition, was in good agreement with the calculated values. From the binding energies of Zn, N and O that were found from the XPS spectra, we also confirm that there is a coordination bond between these atoms.

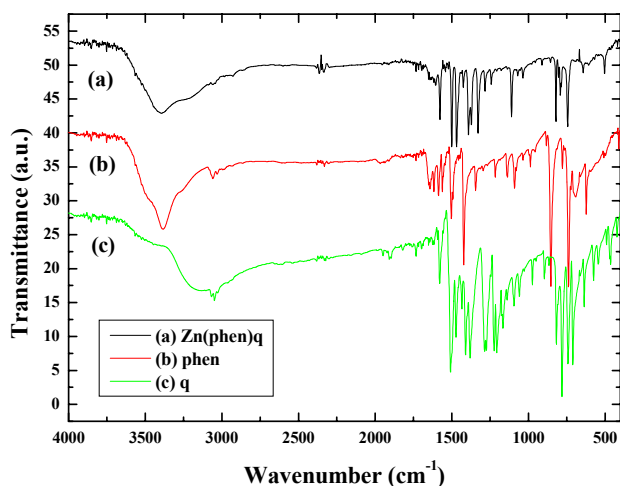


Fig. 1. The FT-IR spectra of (a) Zn(phen)q, (b) phen and (c) q.

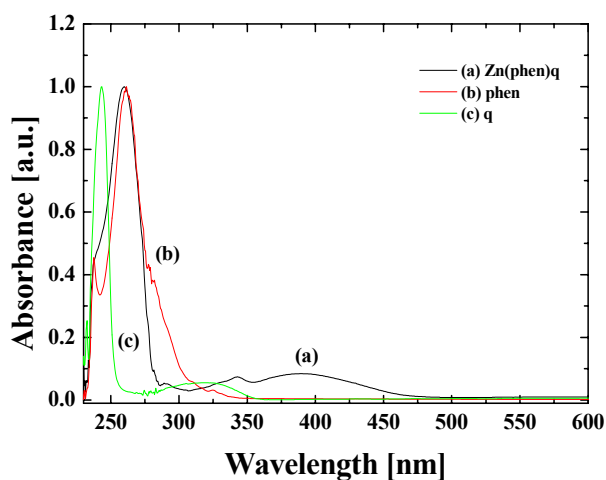


Fig. 2. The UV-vis absorption spectra of (a) Zn(phen)q, (b) phen and (c) q.

In this experiment, the glass substrates coated with indium tin oxide (ITO) had a thickness and a sheet resistance

of 100 nm and  $10\ \Omega/\square$ , respectively. Prior to film deposition, the ITO substrate surface was treated with UV/ozone for 1 minute. In an organic layer evaporation chamber, organic thin films were deposited with an evaporation source equipped with automated temperature controllers. The organic materials were successively evaporated on top of the ITO substrate under  $5 \times 10^{-6}$  Torr at a deposition rate of about 0.1 nm/s. After the organic layer was deposited, the substrates were moved into a metallization chamber for electrode evaporation. The cathodes were constructed from evaporated Al under  $5 \times 10^{-6}$  Torr; the deposition rates was about 1 nm/s (Al). We fabricated the following devices and found the electrical transporting properties of Zn(phen)q: ITO / NPB(40nm) / LiBq<sub>4</sub>(60nm) / LiF(0.05nm) / Al(100nm) [Device 1], ITO / NPB(40nm) / LiBq<sub>4</sub>(60nm) / Alq<sub>3</sub>(10nm) / LiF(0.05nm) / Al(100nm) [Device 2] and ITO / NPB(40nm) / LiBq<sub>4</sub>(60nm) / Zn(phen)q(10nm) / LiF(0.05nm) / Al(100nm) [Device 3].

The NPB(Sigma-Aldrich) and LiBq<sub>4</sub>(Sigma-Aldrich) were used as a hole transporting and emitting materials, respectively. The emission areas for all devices were  $3 \times 3\text{mm}^2$ . The current density versus voltage and luminance versus voltage characteristics were measured with a flat panel display analysis system IVL 300 series (JBS Inc.). The redox potential of Zn(phen)q was determined by cyclic voltammetry using a Potentiostat 263A. Electrochemical measurement was performed with three electrodes: (Ag / Ag<sup>+</sup> (0.1M AgNO<sub>3</sub>) as a reference electrode, Pt wire as a counter electrode and an ITO or Al electrode. The constant scan rate was 400 mV/sec in 0.1M tetrabutylammonium-perchlorate (Bu<sub>4</sub>ClO<sub>4</sub>) with acetonitrile.

We fabricated an electron only device in order to investigate the difference between Zn(phen)q and Alq<sub>3</sub> as electron transporting materials. The devices had a single-layer structure composed of Al/Zn(phen)q or Alq<sub>3</sub>/Al. The thicknesses of the organic layers varied from 140nm to 200nm

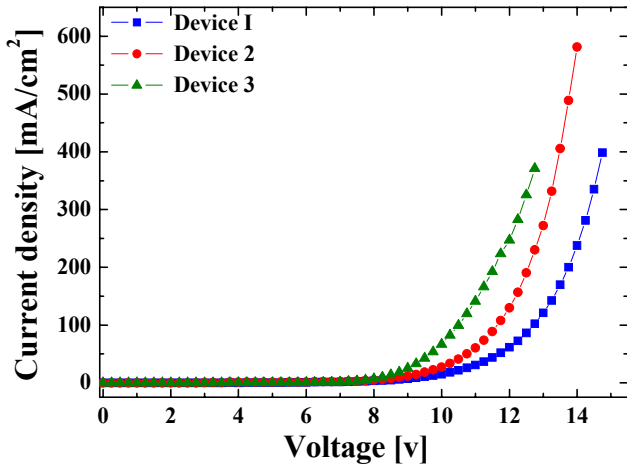
### 3. Results and discussion

We used cyclic voltammetry to measure the energy gap of Zn(phen)q. The oxidation and reduction onset potentials of Zn(phen)q were measured to be +2.5 and -1.6V, respectively. The EA of Zn(phen)q was determined to be 3.2 eV and the IP of Zn(phen)q was determined to be 7.3 eV. The EA and IP of Alq<sub>3</sub> were 3.1 and 5.7eV, respectively. We expect that the injection of carriers into the organic layer will be similar for the devices because Alq<sub>3</sub> and Zn(phen)q have the same EA same.

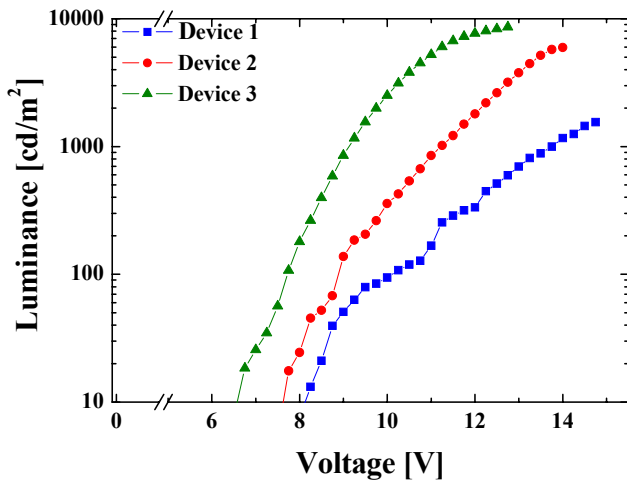
Fig. 3 (a), (b) and (c) show the I-V-L-E characteristics for the fabricated devices. We found that using Zn(phen)q as the electron transport material decreased the driving voltage of the OLED. This result indicates that our experiment data is higher than other experiment data using Zn complexes[16].

The differences in the current densities suggest that the electron injection in Zn(phen)q is higher than that in Alq<sub>3</sub>. Also, the maximum luminance of the devices based on

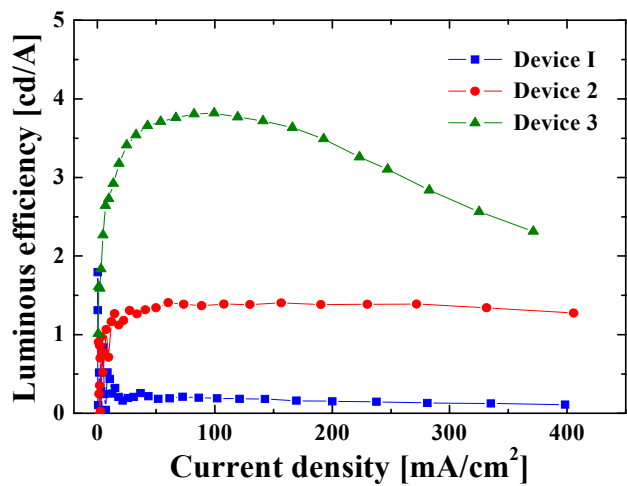
Zn(phen)q is 8900 cd/m<sup>2</sup> higher than the device containing Alq<sub>3</sub>.



(a) Current density - voltage characteristics of devices



(b) Luminance - voltage characteristics of devices



(c) Current density - Efficiency characteristics of devices

Fig. 3. The I-V-L-E characteristics of devices

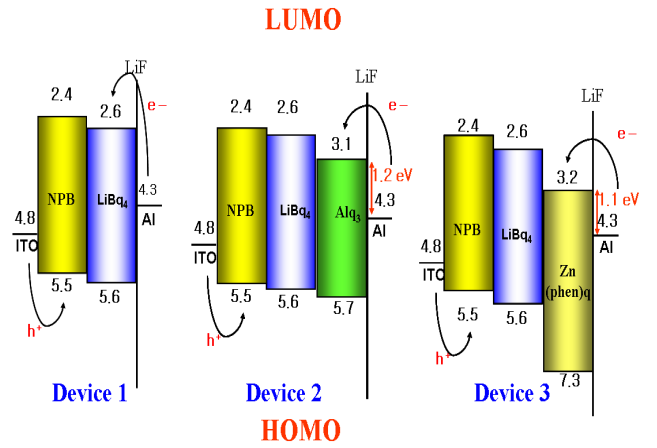
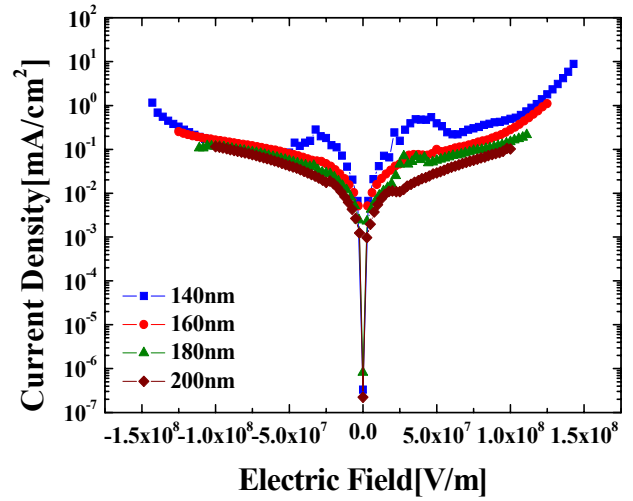
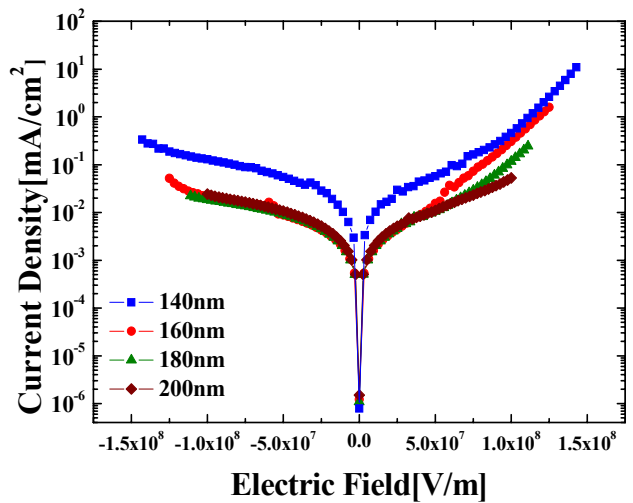


Fig. 4. Schematic energy level diagrams using Zn(phen)q and Alq<sub>3</sub> as an electron transport material



(a) Alq<sub>3</sub>



(b) Zn(phen)q

Fig. 5. Current density-electric field characteristics of the electron only device

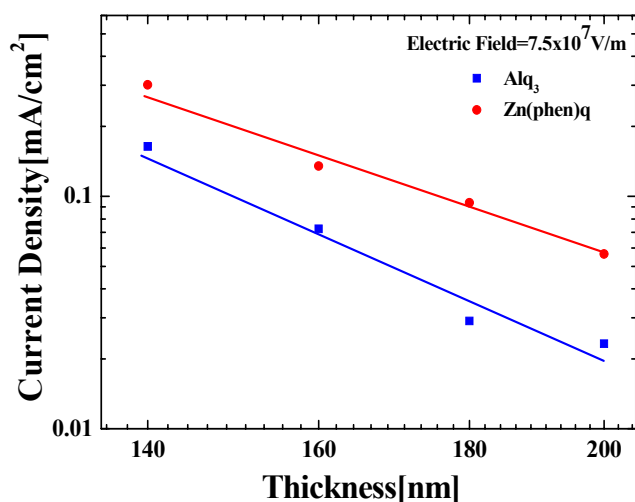


Fig. 6. Current density-thickness characteristics of the electron only device using Alq<sub>3</sub> and Zn(phen)q at constant electric field ( $7.5 \times 10^7$  V/m).

This result is attributed to the LUMO level, which leads Zn(phen)q 3.2 eV and the Zn(phen)q will enhance the electron injection from the cathode.

Fig. 4 is a schematic energy-level diagram for the various devices and is useful for understanding the mechanisms responsible for the operation of OLED. The differences between the devices are attributed to the role of the Zn(phen)q layer. As Fig. 4 shows the LUMO level of Zn(phen)q is 3.2 eV lower than the LUMO level of Alq<sub>3</sub>, 3.1 eV; thus, the electron injection barrier is reduced for the latter. At the same time, the HOMO level of Zn(phen)q is 7.3 eV, which is far greater than the HOMO level of Alq<sub>3</sub> 5.7 eV; hence, the Zn(phen)q layer will block hole transport from the ITO substrate. These characteristics indicate a decrease in the leakage of carriers and thus improved device performance.

We fabricated an electron only device in order to investigate the difference between Zn(phen)q and Alq<sub>3</sub> as electron transporting materials. The device had a single-layer structure of Al/Zn(phen)q or Alq<sub>3</sub>/Al. The thicknesses of organic layers varied from 140 nm to 200 nm, while the thickness of Al electrode was fixed at 120 nm.

Fig. 5 shows the comparison between the current density versus the electric field of the electron only device using Alq<sub>3</sub> and Zn(phen)q, and Fig. 6 gives the current density versus thickness characteristics at constant electric field ( $7.5 \times 10^7$  V/m). According to Fig. 6, the carrier concentration of the device containing Zn(phen)q is higher than devices containing Alq<sub>3</sub>. This result indicates a higher trap density for the Alq<sub>3</sub>, causing more injection carriers to be captured. The higher concentration of captured carriers increases the amount of radiative centers.

#### 4. Conclusion

We investigated the electrical properties of Alq<sub>3</sub> and Zn(phen)q for use as electron transporting materials. We

found that the carrier concentration of the device containing Zn(phen)q was higher than devices containing Alq<sub>3</sub>. We found an increase in the carrier concentration for the Zn(phen)q devices, giving rise to an electric field that increases carrier injection. In order to improve the electron injection behavior, Alq<sub>3</sub> was inserted between the cathode and the emitting layer. Using this material is an effective method of improving the electron injection. We expect that the increased trap density causes more injection carriers, giving rise to carrier balance and recombination between the hole and electron in the emitting layer.

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