

Organic electroluminescent device using Zn(phen)q as emitting layer

Won Sam Kim, Jung Min You, Burm-Jong Lee*

Dept. of Chemistry and BPRC, Univ. of Inje, Kimhae, Korea

Yoon-Ki Jang, Young-Soo Kwon

Dept. of Electrical Engineering, Univ. of Dong-A, Busan, Korea

Abstract

A novel zinc complex, Zn(phen)q, was synthesized from 1,10-phenanthroline (phen) and 8-hydroxyquinoline (q) as organic ligands and its electroluminescent (EL) properties were characterized. The structure of Zn(phen)q was elucidated by FT-IR, UV-Vis and XPS. The complex Zn(phen)q showed thermal stability up to 300°C under nitrogen flow, which was measured by TGA and DSC. The photoluminescence (PL) of the Zn(phen)q was measured from the THF solution and the solid film on quartz substrate. The PL emission of Zn(phen)q exhibited green light centered at about 505nm. The EL devices were fabricated by the vacuum deposition. The EL devices having the structure of ITO/a-NPD/Zn(phen)q/Li:Al were studied, where 4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl(a-NPD) used as a hole transport layer(HTL). a-NPD has high Tg of 96°C and thus makes the device thermally stable. The EL emission of Zn(phen)q exhibited also green light centered at 532nm.

1. Introduction

Organic light-emitting diodes (OLEDs) based on organic molecules [1] or polymer [2] have been widely studied in science and technology in the past decade due to the potential application in flat panel displays. We called, OLEDs, holes and electrons injected from electrodes recombine and light is emitted from excited molecules in the luminescent layer as a result of excitation decay. Multi-layer device are often employed to balance charge injection and improve efficiency in OLEDs [3]. At the interfaces of these multi-layer devices, important photochemical phenomena such as exciplex and eletroplex formations may occur [4]. The electron transporting emissive materials, the hole transport layer is very important to balance the injection of hole

and electron, to decrease the driving voltage, to increase the luminance brightness, and to increase the efficiency and the device lifetime. Using multilayer structure from an energy ladder is one of the ways to improve the hole injection, because it is easier for carriers to pass through a number of lower energy barriers than to overcome one higher energy barrier.

The devices can produce all emission color depending on what kind of organic emitting materials is selected. The best-known EL metal chelate compound is Alq3 not only a good emitter but also a highly efficient electron-transporting material, where q is the 8-hydroxyquinolinato ligand. Via the modification of the ligand of metal chelate compound, the emission color of a metal chelate compound and be turned and other properties, such as thermal stability and carrier mobility, may also be improved upon.

1,10-phenanthroline (phen) is also good ligand for metal ions and can construct supramolecular structure via C-H-O and C-H-N hydrogen bonds and p-p aromatic interaction [5-6], thus can be increased the thermal stability. In addition, phen can enhance the luminescent properties of metal complexes due to the antenna effect of 1,10-phenanthroline and its hole blocking ability would enhance the recombination probability of carriers in the emitting layer. The phen's derivative is used as useful hole blocking material:2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (bathocuproine, BCP) [7-8].

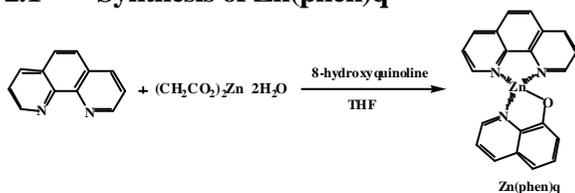
In this paper, we report on a novel green light-emitting organometallic complex. An organozinc complex synthesized from 1,10-phenanthroline (phen) and 8-hydroxyquinoline (q) was found to show PL and EL properties. The PL emission of Zn(phen)q was measured by applying the excitation light with the wavelength of 350nm. The emission peak wavelength was 505nm. EL devices having the structure of ITO/a-NPD/Zn(phen)q/Li:Al were fabricated by

vacuum deposition. An alloy of aluminum and lithium (Al doped Li) was used as a cathode, because the use of Li:Al cathode reduced the driving voltage and increased the quantum EL efficiency. The device showed EL spectrum around $\lambda_{\max}=532\text{nm}$ and 7380cd/m^2 .

2. Experimental

All the chemicals employed in synthesis were purchased from Aldrich Co. Zinc acetate dehydrate, 8-hydroxyquinoline, 1,10-phenanthroline were used without further purification. X-ray photoelectron spectroscopy (XPS) was carried out at Korea Basic Science Institute on Busan branch. UV-Vis absorption spectra were collected on Shimadzu UV-3100S. IR spectra were recorded on a Shimadzu 8201PC and Bruker IFS 66. Thermo gravimetric analyses (TGA) were performed on a Perkin-Elmer thermo gravimeter under a dry nitrogen gas flow at the heating rate of $30^\circ\text{C}/\text{min}$. The melting point (T_m) of materials were determined by differential scanning calorimeter (DSC) of the Perkin-Elmer differential scanning calorimeter. PL spectra were recorded on fluoroluminescence spectrometer (LS45, Perkin Elmer, USA) and fluorophotometer (HITACHI F-4500). Current density-applied voltage and luminance-applied voltage characteristics of the film were measured using IVLT System (JBS, JVLT-1000, Korea).

2.1 Synthesis of Zn(phen)q



Scheme 1. Synthesis of Zn(phen)q

1,10-phenanthroline (1 mmol, 0.18g) was dissolved in 15ml of tetrahydrofuran (THF) at room temperature under a nitrogen atmosphere. The reaction was stirred at 1 h, and then a solution of Zinc acetate dihydrate (1 mmol, 0.22g) in water (3ml) was added dropwise during stirring. After the addition was completed, the reaction solution was further stirred for 3 h, then THF solution of 8-hydroxyquinoline (1 mmol, 0.145g) was slowly added dropwise during stirring. The yellow precipitates was collected by filtration and purified by recrystallization from

acetone. In this way, 0.31g (80% yield) of Zn(phen)q was obtained. m.p: 163°C , Calcd. C: 67.28%, O: 4.52%, N: 11.07%, Zn: 17.12%, Found C: 68.11%, O: 4.32%, N: 11.35%, Zn: 17.57%. IR (KBr, cm^{-1}): 3327, 1604, 1577, 1500, 1469, 1391, 1329, 1110, 743. UV-Vis (nm, in THF): 260, 289, 342, 390. (Reference: 8-hydroxyquinoline: 243, 287, 320. 1,10-phenanthroline: 237, 261, 325.)

3. Results and discussion

The title (Helvetica 14-point bold), authors' names (Helvetica 12-point bold italic) and affiliations (Helvetica 12-point bold) run across the full width of the page – one column wide. We also recommend phone number (Helvetica 10-point) and e-mail address (Helvetica 10-point). Authors with different affiliations would follow on separate lines under the first author's affiliation line.

3.1 The structure characterization of Zn(phen)q

Zn(phen)q was synthesized from 1,10-phenanthroline (phen) and 8-hydroxyquinoline (q) as organic ligands (see Scheme 1). Zinc (II) [(8-hydroxyquinoline)(1,10-phenanthroline)], Zn(phen)q was estimated from FT-IR, UV-Vis and XPS spectra. FT-IR spectra of Zn(phen)q, phen and q itself are shown together in Fig. 1a. The high-frequency region ($3600\text{--}1700\text{ cm}^{-1}$) contains absorption bands mainly originating from localized hydrogen stretching vibrations. The midfrequency region ($1700\text{--}1000\text{ cm}^{-1}$) corresponds to heavy atom in-plane stretching and bending vibrations. In the lowfrequency region (below 1000 cm^{-1}), the out-of-plane are observed. The bands centered at 1604 and 1577 cm^{-1} are assigned to a C=C stretching vibration involving the quinoline group of ligands. The bands observed 1500 and 1469 cm^{-1} should 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 1329 cm^{-1} involve C=C/C=N stretching of the quinoline fragments of Zn(phen)q. Charles et al. have suggested that the absorption band at about 1100 cm^{-1} should be assigned to the C-O stretching vibration frequency at the C-O-M site [9]. The spectrum shows a sharp absorption band at about 1110 cm^{-1} . In the region below 1000 cm^{-1} , the out-of-plane vibrations are usually observed. The most intense absorption in this wavenumber region corresponds to 743 cm^{-1} .

The UV-Vis spectra of Zn(phen)q were measured from THF solution (Fig. 1b). The spectra of

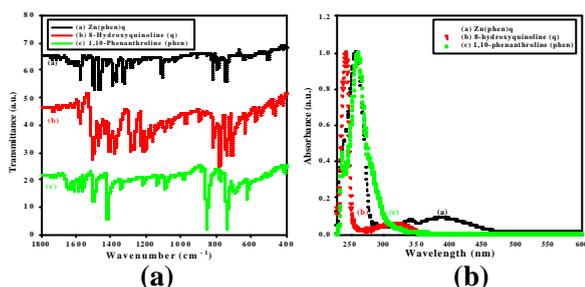


Fig. 1. (a) The FT-IR spectra and (b) absorption spectra of Zn(phen)q, 8-hydroxyquinoline (q) and 1,10-phenanthroline (phen).

Zn(phen)q displayed mainly four bands. The first band located at 260, 289nm can be assigned to the moderate energy (p-p*) transition of the aromatic ring [10] while the second absorption band at 342, 390nm, which led to red-shift from the coordination of zinc and organic ligands (phen and q).

The XPS spectra revealed the kinds of elements and also the confirm Zn(phen)q of the molecular structure, because the measured elemental compositions are in good agreement with the calculated. Fig. 2 shows the XPS spectrum indicating the kinds of elements C, N, O, and Zn composing of Zn(phen)q. From the binding energies of Zn, N, O in each XPS spectrum, we could also confirm that there exists coordination bond between Zn, O, N atoms.

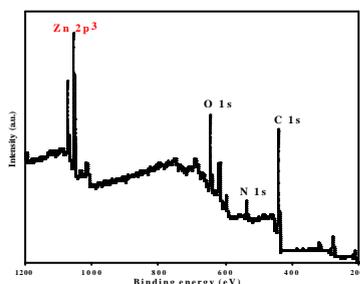


Fig. 2. The XPS spectrum of Zn(phen)q

3.2 Thermal analysis of Zn(phen)q

Fabrication of EL device needs thermal stability of the emitting materials when the vapor deposition is employed. We examined thermal stability of Zn(phen)q from TGA and DSC measurements. The TGA and DSC spectra of Zn(phen)q were measured under nitrogen flow. The TGA spectrum shows the degradation begins around 300 . This degradation was approved by DSC spectrum. By DSC, 163 was found for melting point. From the spectrum, we could confirm that Zn(phen)q complex is stable enough to

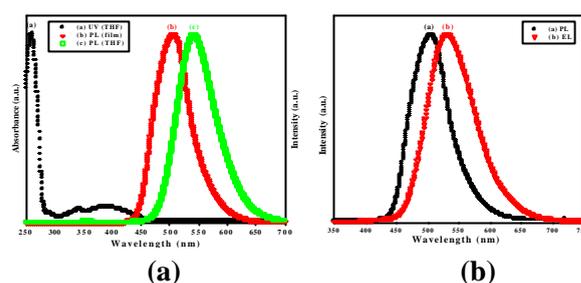


Fig. 3. (a) PL spectra and (b) EL spectra of Zn(phen)q.

EL devices fabrication by vacuum deposition.

3.3 Photoluminescent property

UV-vis and photoluminescence spectra of the complex Zn(phen)q are shown in Fig.3. The spectra are measured from in film states on a quartz glass substrate and in THF solution. Under the excitation of UV-light of wavelength 350nm, in the solid state (quartz), a green emission 505nm in PL spectra. But it was shown a PL peak around 541nm in THF solution which was red-shift of 36nm peak points comparing to film emission (Fig. 3a). The long wavelength of fluorescence emission is undoubtedly due to an intramolecular charge transfer transition and solvents stabilize a twisted intramolecular charge transfer species which has a long wavelength emission [11]. And these difference maybe caused by the different dielectric environments surrounding molecules.

3.5 Electroluminescent property

We are attempted ITO anodes treatments to improve properties of the device. UV-ozone cleaning is a simple method of removing contamination from substrates using exposure to ozone and UV light. The EL property measured from 1min of UV-ozone treatment in ITO anode. Two types of double-layer EL device: ITO(chemical cleaning)/a-NPD(50nm)/Zn(phen)q(50nm)/Li:Al(120nm) (device 1) and ITO(UV-ozone treatments)/a-NPD(50nm)/Zn(phen)q(50nm)/Li:Al(120nm) (device 2). A schematic diagram of device is shown in Fig 4. The maximum EL of Zn(phen)q device was found to be at 532nm (Fig 3b). But it was shown a PL peak around 505nm in thin film which was red-shift of 27nm points. The EL spectra under different forward bias are similar, but their luminescent intensities increase with increasing driven voltage. These results indicate that emission center does not change in

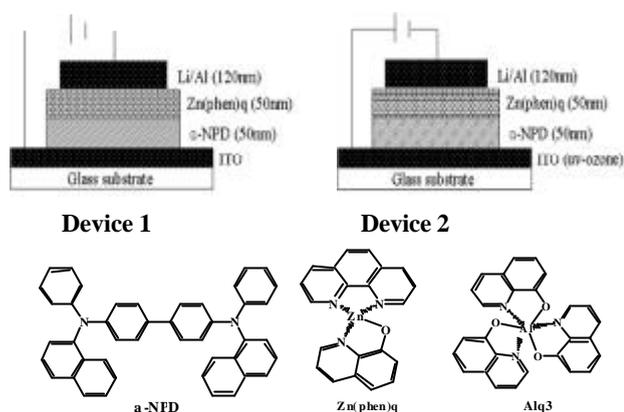


Fig. 4. Schematic diagram of EL device configuration.

depending of different. Fig. 5 show the current density-voltage and luminance-voltage characteristics for the present organic EL device. The turn-on voltage, which is defined as the voltage when the luminance is 1cd/m^2 , were measured and found to be 7V and the maximum luminance of 4750cd/m^2 at 12V in device 1. As to device 2, the turn-on voltage is as low as 4.5 V, and a maximum luminance of 7380cd/m^2 was obtained at 11V. When the bias voltage exceeded the turn-on voltage, EL intensity was proportionally linear to the bias voltage. The maximum current density was found to be each 76.2mA/cm^2 , 105mA/cm^2 at 13V, 11V. And the luminous efficiency was 0.4 lm/W at 10V. In this case, it is expected that adhesion of the organic film to the substrate irradiated by the UV-ozone is stronger than to the substrate without the UV-ozone. Moreover, removal of the organic contaminant on the ITO surface by the UV irradiation has an effect to the hole injection into Zn(phen)q.

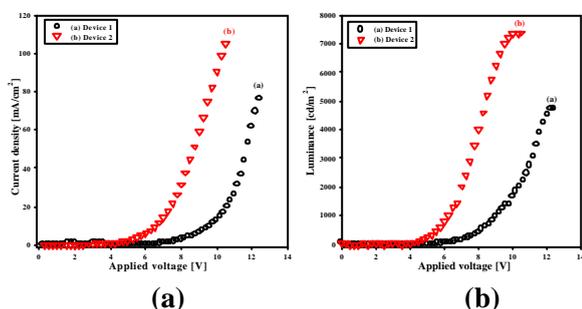


Fig. 5. (a) The current density-applied voltage and (b) luminance-applied voltage characteristic of devices.

4. Conclusion

In this paper, we have synthesized a new green

emitting material for use in OLEDs. Zn(phen)q showed not only high Tg(163 °C), but also good color purity and high efficiency in OLEDs.

The PL emission of Zn(phen)q peak wavelength was 505nm in thin film. EL devices having the structure of ITO/a-NPD/Zn(phen)q/Li:Al were fabricated by vacuum deposition. The device showed EL spectrum around $\lambda_{\text{max}}=532\text{nm}$. The turn-on voltage were measured and found to be 4.5V and maximum luminance of 7380cd/m^2 at 11V. We think that the device structure is important for reducing the turn-on voltage and increasing the brightness. So, we will try to find the best device structure by applying various kinds of hole injection layer, electron transport layer, electrode, and buffer layer.

6. Acknowledgements

This work was supported by Graduate Student Cultivation Program of Korea Industrial Technology Foundation and partly by BPRC of Inje University.

7. References

- [1] C.W. Tang, S.A. VanSlyke, Appl. Phys. Lett. **51** 913 (1987).
- [2] J. H. Burroughes, D.D.C. Bradley, A.R. Brown, B. N. Marks, K. Marckay, R.H. Friend, P.L. Burns, A.B. Holmes, Nature **347** 539 (1990).
- [3] C. Adachi, S. Tokito, T. Tsutsui, S. Saito, Jpn. J. Appl. Phys. **27** 713 (1988).
- [4] C. L. Chao, S. A. Chen, Appl. Phys. Lett. **72** 636 (1998).
- [5] Y. Wan, L. Zhang, L. Jin, S. Gao, S. Lu, Inorg. Chem. **42** 4985 (2003).
- [6] C.-B. Liu, C.-Y. Sun, L.-P. Jin, S.-Z. Lu, New J. Chem. **28** 1019 (2004).
- [7] D.F. O'Brian, M.A. Baldo, M.E. Thompson, S.R. Forrest, Appl. Phys. Lett. **74** 442 (1999).
- [8] N.A.H. Male, O.V. Salata, V. Christou, Synth. Met. **126** 7 (2002).
- [9] J. Yu, Z. Chen, S. Miyata, Synth. Met. **123** 239 (2000).
- [10] A. Jacobson, A. Petric, D. Hogenkamp, A. Sinur, J.R. Barrio, J. Am. Chem. Soc. **118** 5572 (1996).
- [11] W. Chen, D.A. Tomalia, J.L. Thomas, Macromolecules **33** 9169 (2000).