

Zn(BOX)₂와 Zn(BTZ)₂의 광발광 특성 및 전계발광 특성에 대한 전기 화학적 연구

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(2000년 1월 8일 접수 ; 2000년 3월 30일 채택)

An Electrochemical Study on Photoluminescent and Electroluminescent Characteristics of Zn(BOX)₂ and Zn(BTZ)₂

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(Received January 8, 2000 ; Accepted March 30, 2000)

Abstract : Organic electroluminescent devices(OELD) consisted of multilayer structures have been studied for the application to flat-panel display. Metal-chelate complexes, zinc bis(2-(2-hydroxyphenyl)benzoxazolone) (Zn(BOX)₂) and zinc bis(2-(2-hydroxyphenyl)benzothiazolone) (Zn(BTZ)₂), have been intensively investigated as a white-light emitting layer and recognized to have good electroluminescent(EL) properties. In this study, Zn(BOX)₂ and Zn(BTZ)₂ were synthesized and characterized by FT-IR, ¹H-NMR, UV-VIS and PL. Their EL properties were also studied and their ionization potential(IP) and electron affinity(EA) were also measured by cyclic voltammetry(CV).

INTRODUCTION

Recently electroluminescence(EL) has been studied as a new source of flat-panel display.¹⁻³⁾ Organic electroluminescent devices(OELD) can be applied to full color flat displays and to back-light for liquid crystal displays. These devices have generally multi-layer structures composed of two electrodes, an electron transporting layer, an emitting layer, and/or a hole transporting layer. Accordingly, there has been remarkable development of luminescent materials for application to OELD.

White light emitting materials are necessary to realize full color displays along with a color filter. If red(R), green(G) and blue(B) light emitting materials are employed simultaneously to obtain white emission, the intensities of each RGB peak should be controlled properly, which turns out to

be difficult due to poor reproducibility and complicated multi-layer structures.⁴⁾ Thus, a material which can produce white emission by itself would be desirable for this application. As a white emitting material, it should have a broad photoluminescence(PL) spectrum to display all of the RGB components.

Zn(BOX)₂ and Zn(BTZ)₂ were reported to have broad PL spectra and to emit a white luminescence.⁵⁻⁷⁾ In this study these compounds were synthesized as emitting materials for the application to OELD. Their PL and EL properties were studied and electrochemical properties were particularly examined. The electrochemical properties studied herein revealed a valuable information about the band gap and emitting colors of these compounds. The electrochemical studies of the emitting materials are important to investigate the light-emitting

mechanisms and to study the relationship with electroluminescent features such as driving voltage and luminous efficiency.⁸⁾ Understanding the emitting mechanisms can further contribute to the design and development of highly efficient emitting materials.

EXPERIMENTAL

Zn(BOX)₂ and Zn(BTZ)₂ were prepared according to the procedure reported by Nakamura, et al. with some modification. The ¹H NMR and FT-IR spectra of Zn(BOX)₂ and Zn(BTZ)₂ synthesized herein were identical to the spectra of those complexes reported in the reference.⁷⁾

(1) Synthesis of Zn(BOX)₂ [where BOX = the anion of 2-(2-hydroxyphenyl)benzoxazole]

A solution of Zn(CH₃COO)₂ (0.50g, 2.6mmol) in 25mL of methanol was slowly added to a stirred methanol solution (100mL) of 2-(2-hydroxyphenyl)benzoxazole (1.1g, 5.2mmol) at 50°C. Addition of zinc acetate solution resulted in immediate precipitation. The mixture was stirred for 2h at 50°C. The resulting solid was filtered, washed 3 times with 15mL of water and 1mL of cold methanol, and dried under vacuum. (1.2g, 95%) The pale yellow powder of Zn(BOX)₂ showed green-blue luminescence under the UV light and its PL was further investigated, *vide infra*.

(2) Synthesis of Zn(BTZ)₂ [where BTZ = the anion of 2-(2-hydroxyphenyl)benzothiazole]

A solution of Zn(CH₃COO)₂ (0.41g, 2.2mmol) in 20mL of methanol was slowly added to a stirred methanol solution (100mL) of 2-(2-hydroxyphenyl)benzothiazole (1.0g, 4.4mmol) at 50°C. Treatment of solution mixture with 1M NaOH aqueous solution to make the solution pH about 7~8 resulted in the yellow-green

precipitate. The mixture was stirred continuously for 3h at 50°C. The resulting solid was filtered, washed 3 times with 15mL of water and 1mL of cold methanol, and dried under vacuum. (0.88g, 77%) The powder of Zn(BTZ)₂ showed green-white luminescence under the UV light and its PL was further investigated, *vide infra*.

Electrochemical measurements were performed using cyclic voltammetry at room temperature with 3 electrodes (Ag/Ag⁺ (0.1M AgNO₃) as a reference electrode, Pt wire as a counter electrode and ITO (indium tin oxide) or Al electrode as a working electrode). The constant scan rate was 100~20 mV/sec in 0.1M tetrabutylammonium perchlorate (Bu₄NClO₄) with acetonitrile.

RESULTS AND DISCUSSION

The molecular structures of two metal-chelate complexes prepared in this study were shown in Fig. 1. These metal-chelate complexes were characterized by FT-IR, ¹H-NMR, UV-VIS and photoluminescence (PL) spectra. The spectral data were identical to the reported ones.

The spectra featuring the absorption and photoluminescence of two metal-chelate complexes were shown in Fig. 2.

The PL peaks of Zn(BOX)₂ and Zn(BTZ)₂

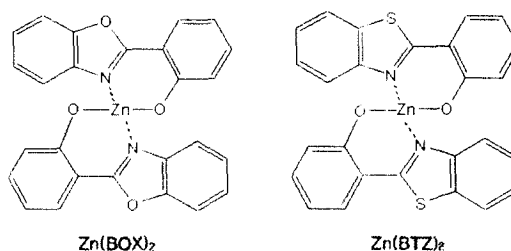


Fig. 1. Molecular structures of Zn(BOX)₂ and Zn(BTZ)₂

were observed at the wavelength of 471nm and 497nm, respectively. The PL spectra of these complexes showed broad emission with a half-spectral bandwidth of more than 100nm. Their peak-wavelengths of 471nm and 497nm were in the green-blue region.

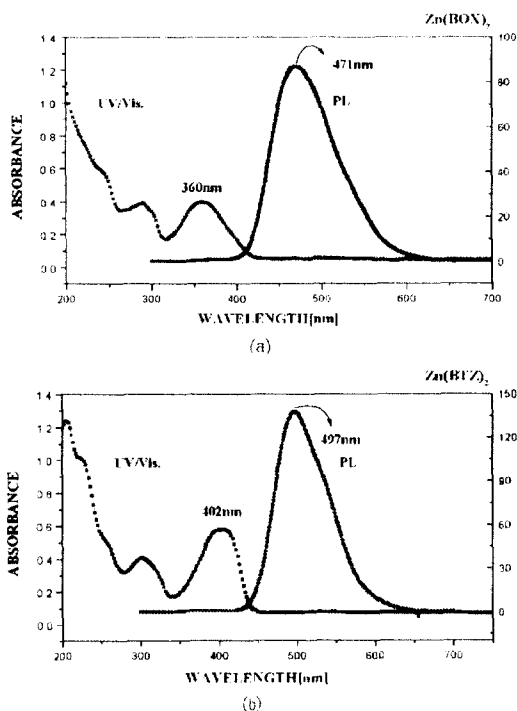


Fig. 2. (a) The UV and PL spectrum of Zn(BOX)₂
 (b) The UV and PL spectrum of Zn(BTZ)₂

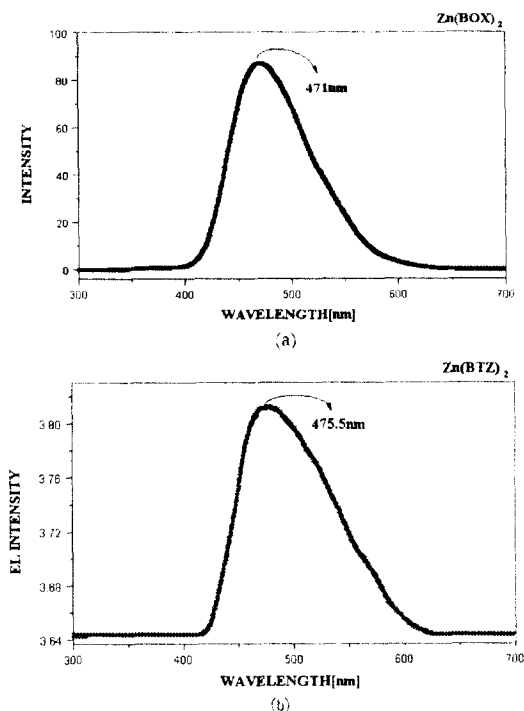


Fig. 3. (a) The EL spectrum of Zn(BOX)₂
 (b) The EL spectrum of Zn(BTZ)₂

Fig. 3 shows the electroluminescence(EL) spectra of Zn(BOX)₂ and Zn(BTZ)₂. The EL spectra of Zn(BOX)₂ and Zn(BTZ)₂ displayed electroluminescence with maximum emission at 461nm and 475.5nm, respectively, which were similar to those of the PL spectra. This indicates that the EL actually originated from the emitting layer of the complexes. Their emission was not white because their half-spectral band width values were insufficient to include RGB components in the EL spectra, where the wavelength is in the green-blue region. The maximum luminances of Zn(BOX)₂ and Zn(BTZ)₂ were 97cd/m² and 420cd/m², respectively. Further details on electroluminescent characteristics of these metal-chelates will be published elsewhere.

The electrochemical gap(E_g), electron affinity(EA) and ionization potential(IP) of the films containing these complexes were investigated using cyclic voltammetry(CV) and UV-VIS absorption spectra. To transpose the measured redox behavior into estimates for the ionization potential(IP) and electron affinity(EA), it is necessary to obtain the electrochemical potentials relative to the vacuum level, where IP and EA are also defined. An empirical relationship has been proposed by Bredas et al.⁸⁾

$$IP = E_{onset}^{ox} + 4.8 ; EA = E_{onset}^{re} + 4.8$$

The voltammograms measured for Zn(BOX)₂ and Zn(BTZ)₂ are shown in Fig. 4. It was found that the films of these two complexes can be both irreversibly oxidized and reduced. The oxidation onset potential and the reduction onset potential of Zn(BOX)₂ were then measured to be +0.70V and -2.15V about the SCE electrode which yields IP=5.50eV, EA=2.65eV and E_g= 2.85eV (432nm) in 0.1M Bu₄NClO₄ with acetonitrile at 100mV/sec. The optical gap for Zn(BOX)₂, taken as the absorption edge was found to be E_g = 2.95eV (417nm) in UV-Vis spectra of Fig. 2. The oxidation onset potential and the reduction onset potential of Zn(BTZ)₂ were then measured to be +0.95V and -1.86V about the SCE electrode which yields IP=

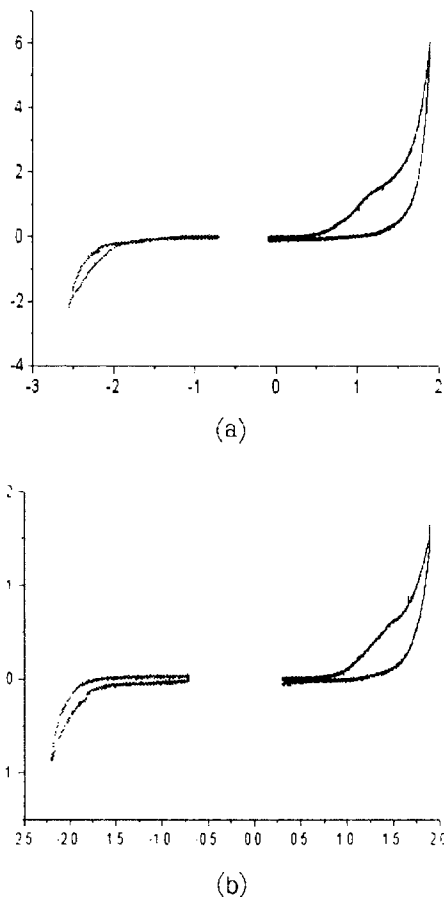


Fig. 4. (a) The Cyclic voltammogram of Zn(BOX)₂
(b) The Cyclic voltammogram of Zn(BTZ)₂

5.75eV, EA=2.94eV and $E_g=2.81\text{eV}$ (438nm) in 0.1M Bu₄NClO₄ with acetonitrile at 100mV/sec. The optical gap for Zn(BTZ)₂, taken as the absorption edge was found to be $E_g=2.80\text{eV}$ (440nm) in UV-Vis spectra of Fig. 2. According to UV-VIS measurements, the $\pi-\pi^*$ band gap (E_g) for Zn(BOX)₂ and Zn(BTZ)₂ films corresponds to the extrapolated absorption edge. The absorption edge obtained by UV-VIS measurements was in good agreement with the band gap obtained by the electrochemical measurement.

CONCLUSION

For the application to organic electroluminescent devices as white-emitting materials, two metal-chelate complexes such as Zn(BOX)₂ and Zn(BTZ)₂ were synthesized and their electroluminescent characteristics were investigated. Electron affinity(EA) and ionization potential(IP) of these materials were also measured by cyclic voltammetry(CV). It was found that these metal-chelate complexes show the greenish blue emission, where this is not enough for the white light emission. It was also found that IP of Zn(BTZ)₂ was higher than that of Zn(BOX)₂ even though the E_g of these two metal-chelates were almost the same.

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