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Comparative study of electroluminescent Zn metal–chelate complexes with mixed ligands

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In this work the results from a comparative study of electroluminescent and photophysical properties of four Zn chelate complexes based on benzothiazoles and quinolines ligands (zinc bis-[8-hydroxyquinoline], zinc [8-hydroxyquinoline] acetylacetonate, zinc bis[2-(2-hydroxyphenyl) benzothiazole], zinc 2-(2-hydroxyphenyl) benzothiazole acetylacetonate), and their application in Organic Lght-emitting Diodes (OLED) are presented. The absorption, photoluminescence spectra and morphology of thin films of Zn complexes were investigated. The luminance-voltage (L-V) characteristics, efficiencies and electroluminescences of the diodes based on bilayer structure ITO/HTL/Zn complex/Al were determined.

***Keywords*:** OLED, Zn complex, Znq_2, Znq acac, $Zn(BTz)_2$, ZnBTz acac

INTRODUCTION

Organic light-emitting diodes (OLEDs) have attracted great interest in the last years due to their potential applications as the future generation flat panel displays and solid-state light sources. Blue, green, and red light-emitting materials with standard color and high efficiency are necessary for full color displays. Since the first Tang's report [1] of the light-emitting diode based on Aluminum tris-(8-hydroxyquinoline), a variety of organic materials have been synthesized and studied, and extended efforts have been made to obtain high performance electroluminescent devices. Among these materials, Zn complexes have been especially important because of the simplicity in synthesis procedures and wide spectral response. Extensive research work is going on in various laboratories to synthesize new Zn complexes containing new ligands to produce a number of novel luminescent Zn complexes as emitters and electron transporters [2-8]. Zinc bis-(8-hydroxyquinoline) (Znq_2) has been investigated as an electroluminescent [3] and electron transporting material [4] in vapor deposited [3, 9] or Langmuir-Blodgett films [10]. Zinc bis[2-(2-hydroxyphenyl) benzothiazole] ($Zn(BTz)_2$) has been studied as an effective white light emissive and electron transporting material in OLED. Hamada et al. reported that $Zn(BTz)_2$ was a new white-light emitting material, but the device with single-emitting layer of $Zn(BTz)_2$ showed a greenish white emission [4]. Recently Zhu *et al.* fabricated white OLED with $Zn(BTz)_2$ only as emitter [11]. White emission is composed of two parts: one is at 470 nm, which originates from exciton emission in $Zn(BTz)_2$, the other is at 580 nm, which originates from exciplexes formation at the interface of TPD/$Zn(BTz)_2$.

The aim of this paper is to make a comparative study of the performance of OLEDs based on Zinc bis-[8-hydroxyquinoline] (Znq_2), Zinc [8-hydroxyquinoline] acetylacetonate (Znq acac), Zinc bis[2-(2-hydroxyphenyl) benzothiazole] ($Zn(BTz)_2$), and Zinc 2-(2-hydroxyphenyl) benzothiazole acetylacetonate (ZnBTz acac).

EXPERIMENTAL

We investigated the electroluminescent devices with conventional structure: ITO/HTL/EL/M, where ITO is a transparent anode of In_2O_3:SnO_2, HTL – a hole-transporting layer, EL is electroluminescent layer (75 nm) of Zn complex and M - a metallic Al cathode (120 nm). Devices with area 1 cm^2 were prepared on commercial polyethylene terephtalate (PET) substrates coated with ITO (40 Ω/sq). The HTL (31 nm) of PVK : TPD_x (x = 10 w% relative to PVK) composite films were prepared by spin-coating from 0.75% solution in dichloroethane at 2000 rpm. The layers of Zn

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complexes and metal cathode were deposited by thermal evaporation in vacuum better than 10^{-4} Pa at rates 2-5 A/s. ITO covered PET substrate, PVK and TPD were purchased from Aldrich. The four investigated Zn complexes (Fig. 1) were synthesized in the Laboratory of Dyes Synthesis at the Department of Applied Organic Chemistry, Faculty of Chemistry, Sofia University "St. Kl. Ohridski".

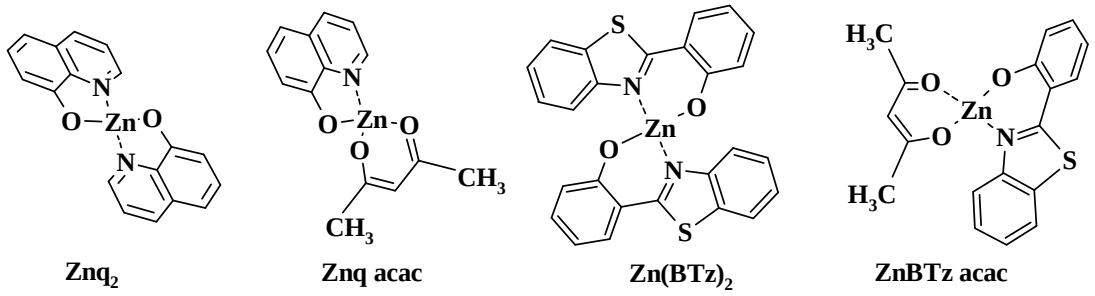


Fig. 1. Chemical structures of the investigated Zn complexes.

All measurements were performed with unpackaged devices at room temperature and under ambient atmosphere. The absorption and fluorescent (PlS) spectra of the complexes were taken using the Spectrofluorimeter Perkin Elmer MPF 44 and the electroluminescent spectra (ElS) by Ocean Optics HR2000+ spectrometer. The current-voltage (I-V) and luminance–voltage (L–V) characteristics were measured by programmable with Labview power supply. The luminescence (L) was measured in DC (direct current) mode and the light output was detected using a calibrated Hamamatsu silicon photodiode S2281-01. The electroluminescent efficiency (η_L) was calculated by equation (1) and used for quantifying the properties of the OLEDs.

$$\eta_L = L/I \qquad (1)$$

where L is the luminescence (in cd/m^2) and I is the current density (in A/m^2))

The surface morphology of the electroluminescent layers was studied with a AFM "EasyScan 2" produced by "Nanosurf" (Switzerland) on area of 12.5 x 12.5 μm, at measurement mode "scan forward" and Scan mode from down to up.

RESULTS AND DISCUSSION

Morphology

The results of AFM investigations are presented in Fig. 2**.** The AFM images show that the evaporated Znq_2, Znq acac and $Zn(BTz)_2$ compounds on the PET/ITO/PVK:TPD structure, formed amorphous, homogeneous and very smooth surfaces with root mean square (RMS) roughness 6.88 nm, 7.52 nm and 4.64 nm, respectively. The ZnBTz acac layer made soft outline ridge surface with RMS roughness 20.06 nm. The formed from all of complexes flat film surfaces are a prerequisite for a good performance of devices on their base.

Electrical measurements

Fig. 3. presents the luminance/voltage and efficiency characteristics of four identical devices with different EL. The highest luminescence showed the device with ZnBTz acac as EL followed by that with $Zn(BTz)_2$, Znq acac and Znq_2 (Fig. 3a). The luminescence of the device with Znq acac at 15 V DC is nearly 1.5, 2.4 and 3 times higher than those by $Zn(BTz)_2$, Znq acac and Znq_2, respectively.

At the same time the electroluminescent efficiencies of the devices with ZnBTz acac and $Zn(BTz)_2$ are nearly the same (around 3 cd/A) and 1. 5 times higher than that of devices with Znq_2 and Znq acac (Fig. 3b) which are 2 and 1.8 cd/A, respectively. The higher luminance and efficiency of the devices based on Zn hydroxyphenyl benzothiazole complexes indicate better electron transport properties of these complexes than Znq_2 and Znq acac.

For OLEDs with similar structures Sano *et al.* reported in [5] efficiency of 1.39 cd/A at luminance 100 cd/m^2 for ITO/TPD/$Zn(BTz)_2$/Mg:In device, Zheng *et al.* - 4.05 cd/A for doped with rubrene $Zn(BTz)_2$ white device at maximum luminescence

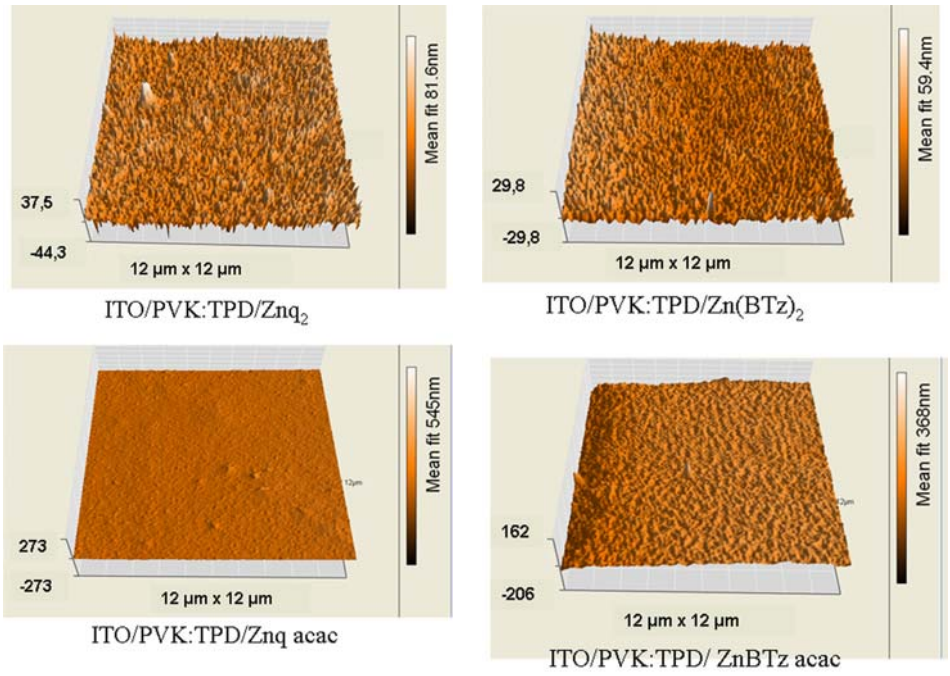


Fig. 2. AFM images of the top surfaces of layers from different Zn complexes.

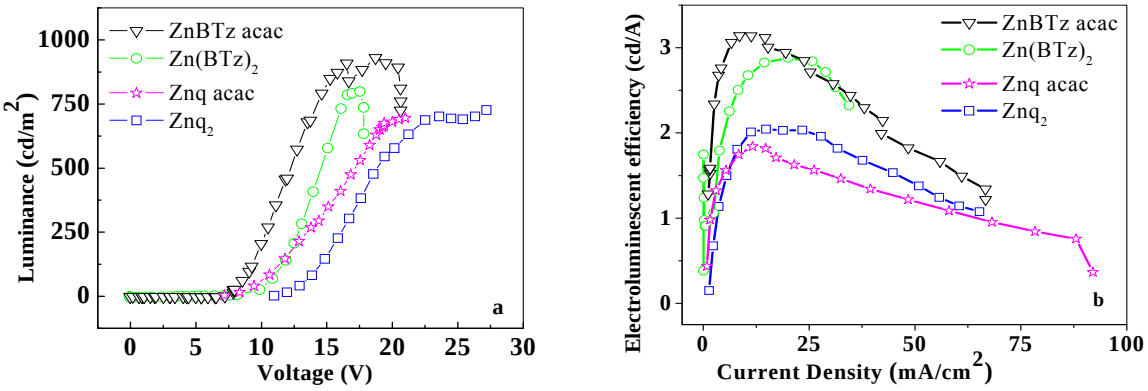


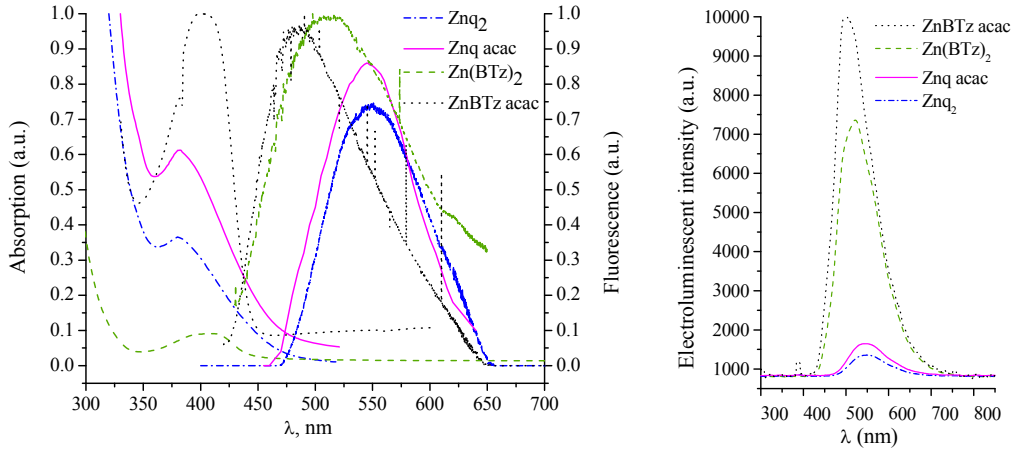
Fig. 3. a) Luminescence / voltage characteristics (L-V) and **b)** electroluminescent efficiency (η_L) for devices ITO/PVK:TPD /Zn complex /Al with different EL.

4048 cd/m^2 [12] and Rai *et al.* - 1.34 cd/A for ITO/NPD/Zn(Bpy)q/Al [8]. It could be stressed here that the efficiency of the devices with $Zn(BTz)_2$ is 3.9 cd/A at luminance 250 cd/m^2 and 2.9 cd/A at luminance 100 cd/m^2 – one of the best reported in the literature up to now for devices with similar structure. Although the devices with new Zn complexes are not optimized, its characteristics are quite promising, especially for ZnBTz acac – the highest luminance and the efficiency 3 cd/A in the range of 10 – 30 mA/cm^2. The results presented in this paper show that the studied mixed-ligands Zn complexes can be successfully used as emitters and electron transporting layers in OLED.

Luminescence studies

Absorption and fluorescent spectra of thin 100 nm layers of the investigated Zn complexes deposited on glass substrates, as well as their electroluminescent spectra obtained from OLED with stricture ITO/HTL/EL/M are presented in Fig. 4.

As can be seen in Fig. 4a, absorption and fluorescent emission spectra of Znq acac and Znq_2



a) **b**

Fig.4. a) Absorption and fluorescent emission spectra of 100 nm layers from different Zn complexes, deposited on glass substrates and **b)** electroluminescent spectra at 16 V of OLED devices ITO/PVK:TPD /Zn complex /Al with different Zn complexes as EL.

are nearly identical. The absorption bands of the both Zn complexes are at 381 nm corresponding to the zinc quinolinolate moiety attributable to the π-π^* transition. Both complexes emit green-yelow light with maximum emission at 545 nm wavelength for Znq acac and 540 nm for Znq_2. The absorptions of $Zn(BTz)_2$ and ZnBTz acac are similar at 406 and 402 nm, respectively, but the fluorescent spectrum of $Zn(BTz)_2$ at 512 nm is slightly red shifted in respect to this of ZnBTz acac at 486 nm and fluorescences are in green range. The data obtained for PL bands of Znq_2 and $Zn(BTz)_2$ are very closed to the results reported by Shukla & Kumar [13] for Znq_2 (540 nm) and by Qureshi *et al.* [14**]** for $Zn(BTz)_2$ (485 nm).

It was established that, the electroluminescent wavelength of devices (Fig. 4b) is very close to the photoluminescent wavelengths. The EL spectra of the complexes with benzthiazole ligand are very similar and exhibited a green electroluminescence at 500 nm of ZnBTz acac and 520 nm of $Zn(BTz)_2$ nm, while the EL spectra of the hydroxyquinoline based devices are almost identical with green-yellow emission at 546 nm of Znq acac and 550 nm of Znq_2. It is seen that in mixed-ligands complexes the acetylacetonate ligand reveals withdrawing effect leads to weak blue shifting of emitting light. Besides, the EL spectra of all four compounds were negligible red shifted compared to their corresponding PL spectra. Take into account the fact that the exciton disassociates easier under the excitation of electric field than the light, red shifting of EL spectra were quite understandable (Wu *et al.* [15**]**). Our results were quite different from these obtained by Wu *et al.* [15**]**, who showed almost identical EL and PL for $Zn(BTz)_2$, and Qureshi *et al.* [14**]** who founded broader EL than PL spectrum.

Obviously the included acetylacetonate ligand in Zn complexes couldn't tune the emission colour but increase the luminance intensity of the devices. It can be supposed that the included in Zn complexes acetylacetonate ligand does not participate in the π - π^* transition of aromatic ligands responsible for light emission.

CONCLUSION

In summary, a comparative study of novel Zn complexes as electroluminescent and electron transporting layers in OLEDs was carry out. The investigated Zn complexes formated very quantitative thin films, contributing to the high device efficiency, The devices with acetylacetonate complexes show higher luminance compared to these with known Znq_2 and $Zn(BTz)_2$. The replacement of one aromatic ligand with acetylacetonate in the mixed complexes improves substantially the performance of OLED without significant alteration of the color emission. The best performance shows the device with novel ZnBTz acac used.

It was established that the novel Zn complexes are very promising materials for practical application in OLEDs as electron transporting and emitting layers.

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СРАВНИТЕЛНО ИЗСЛЕДВАНЕ НА ЕЛЕКТРОЛУМИНЕСЦЕНТНИ Zn МЕТАЛ-ХЕЛАТНИ КОМПЛЕКСИ СЪС СМЕСЕНИ ЛИГАНДИ

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(Резюме)

В работата са представени резултатите от едно сравнително изследване на електролуминесцентните и фотофизичните свойства на четири цинкови хелатни комплекса, базирани на бензотиазолни и хинолонови лиганди (цинков бис(8-хидроксихинолин), ацетилацетонатен цинков 8-хидроксихинолин, цинков бис[2-(2-хидроксифенил) бензотиазол], ацетилацетонатен цинков 2-(2-хидроксифенил) бензотиазол) и тяхното приложение в OLED. Изследвани са абсорбцията, фотолуминесцентните спектри и морфологията на тънки филми от цинковите комплекси. Определени са характеристиките луминесценция / напрежение, ефективностите и електролуминесценциите на ITO/HTL/Zn complexes/Al диодите.