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# Organic Light Emitting Diodes Based on Novel Zn and Al Complexes

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## 1. Introduction

Organic light emitting diodes (OLEDs) have gained great interest in the last years due to their potential for future flat panel display and solid state lighting applications. OLEDs are a novel and very attractive class of solid-state light sources, which generate a diffuse, non-glaring illumination with high color rendering. Compared to the other major lighting technologies in the market – incandescent, fluorescent, high intensity discharge (HID) lamps, LED and electroluminescent, OLED technology has the potential of achieving substantial energy and CO<sub>2</sub> savings, without compromising color rendering or switching speed. The unique features of OLED lighting are inspired the imagination of designers who are exploring various OLED applications: windows, curtains, automotive light, decorative lighting and wall papers. The OLED technology is now being commercialized as a multi-billion dollar market. OLEDs are already used in small displays in cellular phones, car stereos, digital cameras, etc. The rapidly growing market for OLED displays and lighting is driving research in both advanced materials and improved manufacturing processes. In spite of the spectacular results achieved, there are still many problems concerning the efficiency, stability and lifetime of OLEDs, materials selection and optimization, encapsulation, uniformity over large areas, manufacturing cost, colour saturation, etc. to be solved.

OLED represents a quite complicated system of many very thin layers of various materials situated between electrode layers (one of which is transparent); this system emits light when placed under electric potential. The type of material used as the light emitter determines the specific characteristics of such devices.

Two types of OLEDs are developed – on the bases of “small” molecules (SM-OLED) (Tang & VanSlyke, 1987) and conjugated polymers (PLED) (Burroughes et al., 1990), oligomers, etc. Potential emitters for SM-OLED are metal complexes from the lanthanide and platinum groups as well as complexes of Al, Zn, Cd, Cu, Be, B with carefully selected ligands from the group of heterocyclic compounds like as hydroxyquinoline, benzoxazole, benzothiazole, triaryl amines, etc. (Petrova & Tomova, 2009). The first generation of efficient devices, pioneered by Tang and Van Slyke from Eastman Kodak (1987), was based on fluorescent

materials. In this case, the emission of light is the result of the recombination of singlet excitons, but the internal quantum efficiency is limited to 25%. The second generation uses phosphorescent materials where all excitons can be converted into emissive triplet state through efficient intersystem crossing (Baldo et al., 1998). Such materials are up to four times more efficient than fluorescent materials.

An important aspect to improve OLEDs performances is suitable selection of materials for functional OLED layers. In this work we have presented our successful decisions for all functional layers – hole transporting, electron transporting, buffer, hole blocking, electroluminescent in the structures of OLEDs. The new examined electroluminescent Zn and Al complexes were synthesized in the Laboratory of Dyes Synthesis at the Department of Applied Organic Chemistry, Faculty of Chemistry, Sofia University "St. Kl. Ohridski".

## 2. OLED structure

The simplest OLED structure is a single layer device architecture, where the organic emitter is deposited between two electrodes and acts as emitter and as charge transport material (holes and electrons) at the same time. If a forward bias voltage is applied to the electrodes of an OLED device as depicted in Fig.1a, electrons from the cathode and holes from the anode are injected into the organic semiconductor. The oppositely charged carriers move towards each other across the organic semiconductor, encounter, recombine to form excitons and some of them decay radiatively. The efficiency of an OLED is determined by the number of charge carriers that are injected and the number of holes and electrons that actually recombine during emission of light. In order to improve the device efficiency, the multi layer OLED architecture was introduced (Fig.1b).

Nowadays devices may have a total of 7–9 layers of active materials: an anode; anode buffer layer (ABL), hole injecting layer (HIL) or electron blocking layer (EBL); hole transporting layer (HTL); emissive layer (EML); electron transporting layer (ETL) or hole blocking layer (HBL), electron injecting layer (EIL); cathode buffer layer (CBL), a cathode and a protective barrier layer (Tomova et al., 2007). Inserting of these layers facilitates charge carrier injection by reducing the respective injection barriers; enhances the recombination of electrons and holes in the emissive layer (due to accumulation of charges in the EL); shifts the recombination area towards the middle of the device and thus prevents the quenching of the excitons at the electrodes.

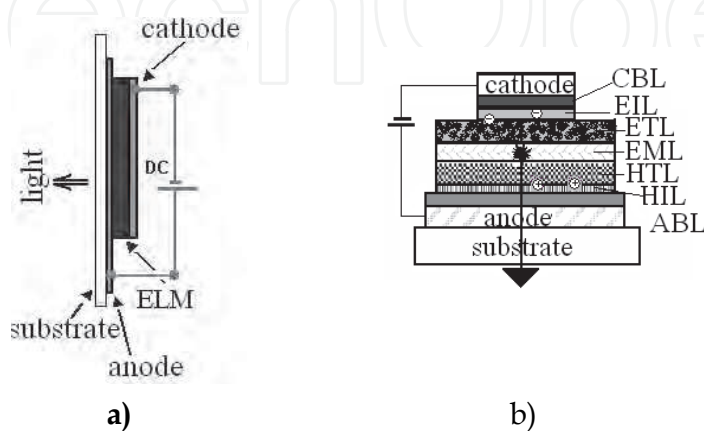


Fig. 1. Structure of: a) monolayer OLED; b) multilayer OLED.

The bilayer OLED consisting of hole transporting layer and emissive layer of different electroluminescent “small” molecular materials is a basic structure in our investigations. They were prepared by thermal evaporation in vacuum better than  $10^{-4}$  Pa at rates 2-5 Å/s on commercial polyethylene terephthalate (PET) flexible substrate, coated with transparent anode of  $\text{In}_2\text{O}_3:\text{SnO}_2$  (ITO - 40  $\Omega/\text{sq}$ ). As cathode was used Al electrode, thermal evaporated in the same vacuum cycle.

We studied the morphology, photoluminescence (PL), electroluminescence (EL) and the performance of the devices measuring the current-voltage (I/V), luminescence-voltage (L/V) and electroluminescence-voltage (EL/V) characteristics. The electroluminescent efficiency ( $\eta_L$ ) was calculated by equation (1) and used for quantifying the properties of the OLEDs.

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

(where  $L$  is the luminescence (in  $\text{cd}/\text{m}^2$ ) and  $I$  is the current density (in  $\text{A}/\text{m}^2$ ) and used for quantifying the properties of the OLEDs.

All measurements were carried out with unpackaged devices with area of  $1\text{cm}^2$ , at room temperature and ambient conditions.

### 3. Hole transporting and buffer layers

The operating mechanisms of OLEDs involve injection of electrons and holes into the organic emitter layers from the electrodes. During recombination, electrons and holes generate molecular excitons (Kido et al., 1998), which result in the emission of light from the emitter layer. Therefore the effective recombination of electrons and holes affects on the electroluminescence efficiency of organic light-emitting diodes. That's why, it is important to balance the number of holes and electrons in EL devices. The mobility of holes in OLED materials used as the hole transport layer (HTL) is some orders of magnitude greater than that of the electrons in the ETL (Zheng et al., 2005). The recombination zone is shifted towards the cathode, which usually leads to a non-radiative loss of energy (Rothberg et al., 1996) and decreasing of an OLED efficiency (Sheats et al., 1996). For that reason, by reducing the mobility of holes in HTL or promoting electron injection into ETL can improve the balance of carriers in OLED. The reducing of holes mobility can be achieved via inserting a proper buffer layer between anode and hole transporting layer. On the other hand introducing of a buffer layer improve the ITO morphology such as inhomogeneity or protrusions, impede the diffusion of indium into the organic layer during device operation, which is correlated with the decay of a device's performance (Schlatmann et al., 1996).

The ITO/organic interface morphology play a key role to stable operation and efficiency of the device. For that reason, a lot of work has been devoted to the anode buffer layers (ABLs) between ITO and the organic material. The introduced buffer layers mainly can be divided in inorganic and organic compounds. Among the reported inorganic anodic buffer layers good inorganic insulators such as transparent metal oxides  $\text{Pr}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{Tb}_4\text{O}_7$ ,  $\text{ZnO}$  (Xu et al., 2001),  $\text{Al}_2\text{O}_3$  (Li et al., 1997; Xu et al., 2001),  $\text{SiO}_2$  (Deng et al., 1999; Xu et al., 2001), silicon nitride  $\text{Si}_3\text{N}_4$  (Jiang et al., 2000; Xu et al., 2001), carbon nitride a-C:N (Reyes et al., 2004), transition metal oxides, also  $\text{V}_2\text{O}_5$ , (Wu et al., 2007; Guo et al., 2005),  $\text{MoO}_x$  (You et al., 2007; Jiang et al., 2007),  $\text{WO}_3$ , (Jiang et al., 2007; Meyer et al., 2007),  $\text{CuO}_x$ , (Hu et al., 2002; Xu et al., 2001),  $\text{NiO}$ , (Chan et al., 2004; Im et al., 2007) and  $\text{Ta}_2\text{O}_5$  (Lu & Yokoyama, 2003), have

attracted much attention due to their capability to lower the hole-injection barrier and improve the interface morphology.

As the organic buffer layers a variety of materials as copper phthalocyanine (Van Slyke et al., 1996; Shi & Tang, 1997; Tadayyon et al., 2004),  $\alpha$ -Septithiophene (Park et al., 2002), Langmuir-Blodgett films of polymethylmethacrylate (Kim et al., 1996), polytetrafluoroethylene (Gao et al., 2003), fluoropolymers (Wang et al., 2006), fluorene-based poly(iminoarylene)s (Jung et al., 2002), conductive polymer such as polythiophene (Arai et al., 1997), poly(3,4-ethylenedioxythiophene) (Carter et al., 1997; Berntsen et al., 1998), and polyaniline (Krag et al., 1996) etc. have been tested.

We explored the effect of *p*-isopropenylcalix[8]arenestyrene copolymer (iPrCS and polycarbonate (PC), as buffer layers in OLED, and the incorporation of TPD with PVK as hole transporting layer.

### 3.1 *p*-Isopropenylcalix[8]arenestyrene copolymer (iPrCS)

The calixarenes are a class of bowl-shaped cyclo-oligomeres obtained via phenol-formaldehyde condensation with a defined upper and lower rim, and a cavity. This speciality enable them to act as host molecules due to their cavities, and allow utilized them as chemical sensors, extractants for radioactive waste processing, materials for non-linear optics, bio-active compounds.

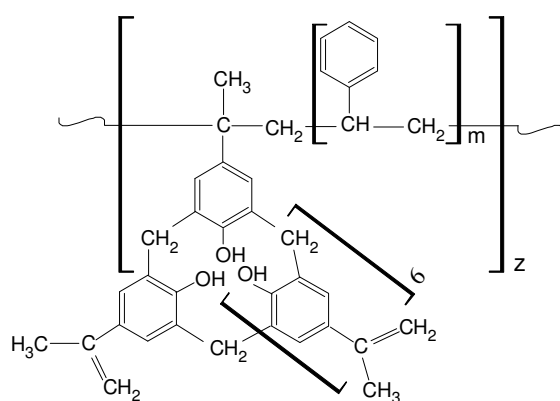


Fig. 2. Chemical structure of the *p*-Isopropenylcalix[8]arenestyrene copolymer used in device fabrication as buffer layer.

In this work, we offer the *p*-Isopropenylcalix[8]arenestyrene copolymer (iPrCS) as a novel anode buffer layer (ABL) for the fabrication of OLED with improved efficiency and life time. The *p*-Isopropenylcalix[8]arenestyrene copolymer (Fig.2) employed (Petrova et al., 2010) for this study was for the first time synthesized according to described procedure (Miloshev & Petrova, 2006), in University of Chemical Technology and Metallurgy, Sofia. Until now the calix[4]arene compounds were used only for design of electroluminescent complexes - for ex. a calix[4]arene [Al I]<sup>3+</sup> complex (Legnani et al., 2004), lanthanide complexes with calix[4]arene derivatives (Wei et al., 2007).

Two types of devices were investigated: ITO/ABL/TPD/Alq<sub>3</sub>/Al, and ITO/TPD/Alq<sub>3</sub>/Al as a reference structure. The buffer layer ( $\delta = 10 - 16$  nm) of iPrCS was deposited on PET/ITO substrates by spin-coating from 0.1 - 0.3% solution in THF at 2000 rpm. N, N'-bis(3-methylphenyl)-N, N'-diphenylbenzidine (TPD) ( $\delta = 30$  nm) as hole transporting and tris(8-hydroxyquinoline) aluminum (Alq<sub>3</sub>,  $\delta = 50, 75$  nm) as electroluminescent and electron

transporting layer were used. TPD, Alq<sub>3</sub> and the Al cathode ( $\delta = 120$  nm) were deposited via thermal evaporation in a vacuum better than  $10^{-4}$  Pa at rates of 2-5 Å/s.

Figure 3 presents typical nonlinear current/voltage (Fig.3a), luminescence/voltage (Fig.3b) and efficiency characteristics (Fig.3c) of ITO/iPrCS<sub>(10-16nm)</sub>/TPD<sub>(30nm)</sub>/Alq<sub>3(50nm)</sub>/Al and ITO/TPD<sub>(30nm)</sub>/Alq<sub>3(50nm)</sub>/Al as a reference structure. It was shown that the turn-on voltage slightly decreased with increasing of the thickness of iPrCS, while the luminescence and efficiency of devices increased and reached maximum values at a thickness of 13 nm. The efficiency of 2 cd/A at 13 nm iPrCS was nearly 80% higher than those of 1.2 cd/A of the reference structure.

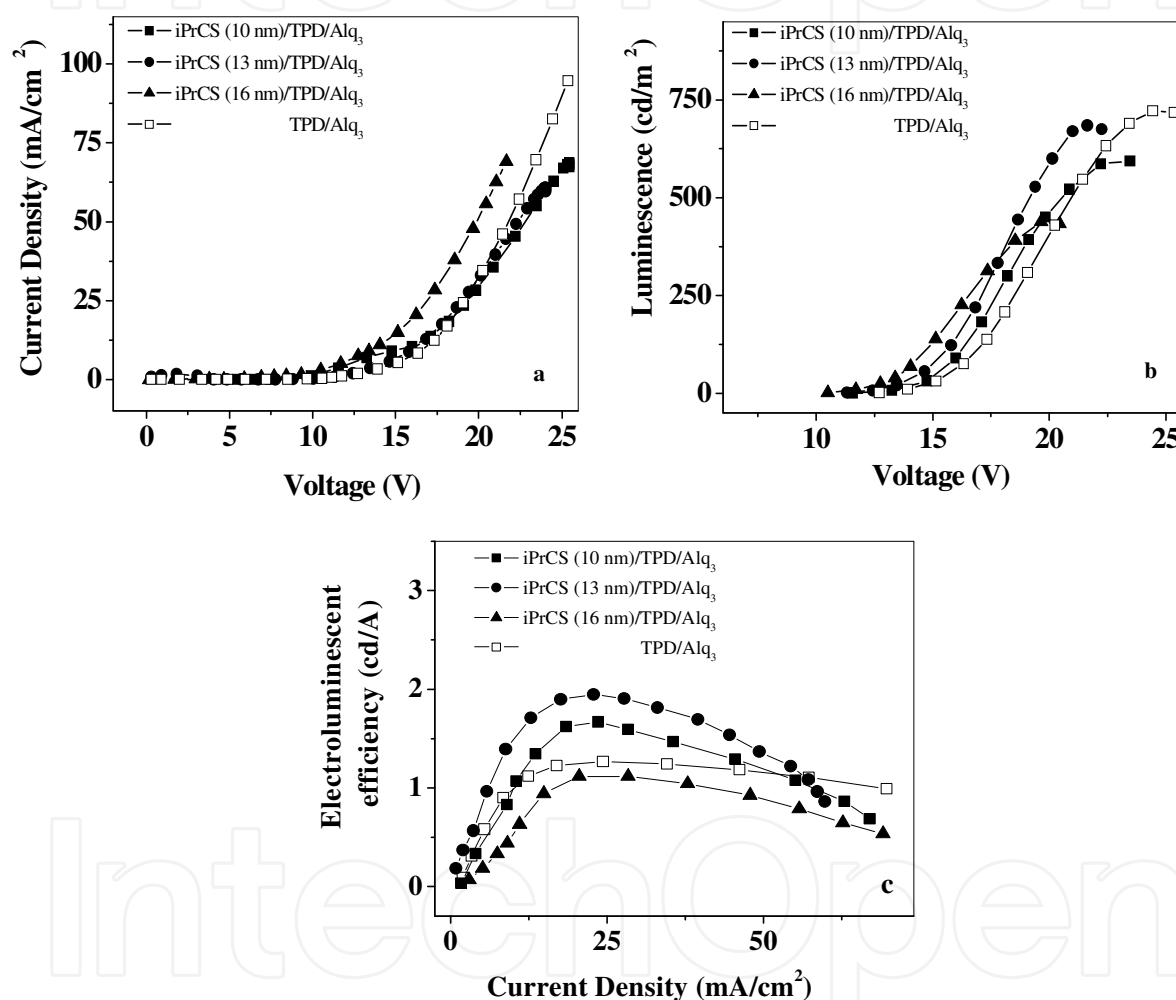


Fig. 3. a) Current/voltage, b) luminescence/voltage and c) efficiency characteristics of ITO/iPrCS/TPD<sub>(30nm)</sub>/Alq<sub>3(50nm)</sub>/Al, and ITO/TPD<sub>(30nm)</sub>/Alq<sub>3(50nm)</sub>/Al.

Effect of the two thicknesses of Alq<sub>3</sub> on the performance of the devices with 13 nm film iPrCS is presented in Fig.4. It was established that the luminescence (Fig.4b) and efficiency (Fig.4c) of the devices with iPrCS were higher compared to the reference structures and that the device with 75 nm emissive layer of Alq<sub>3</sub> showed the best characteristics. The efficiency of 3.04 cd/A at the current density of 20 mA/cm<sup>2</sup> of the device with iPrCS is similar to those of 3.4 cd/A at the same current density, reported by Okamoto for the structure ITO/CF<sub>x</sub>/NPB<sub>(60nm)</sub>/Alq<sub>3(60nm)</sub>/LiF/Al (Okamoto et al., 2006).

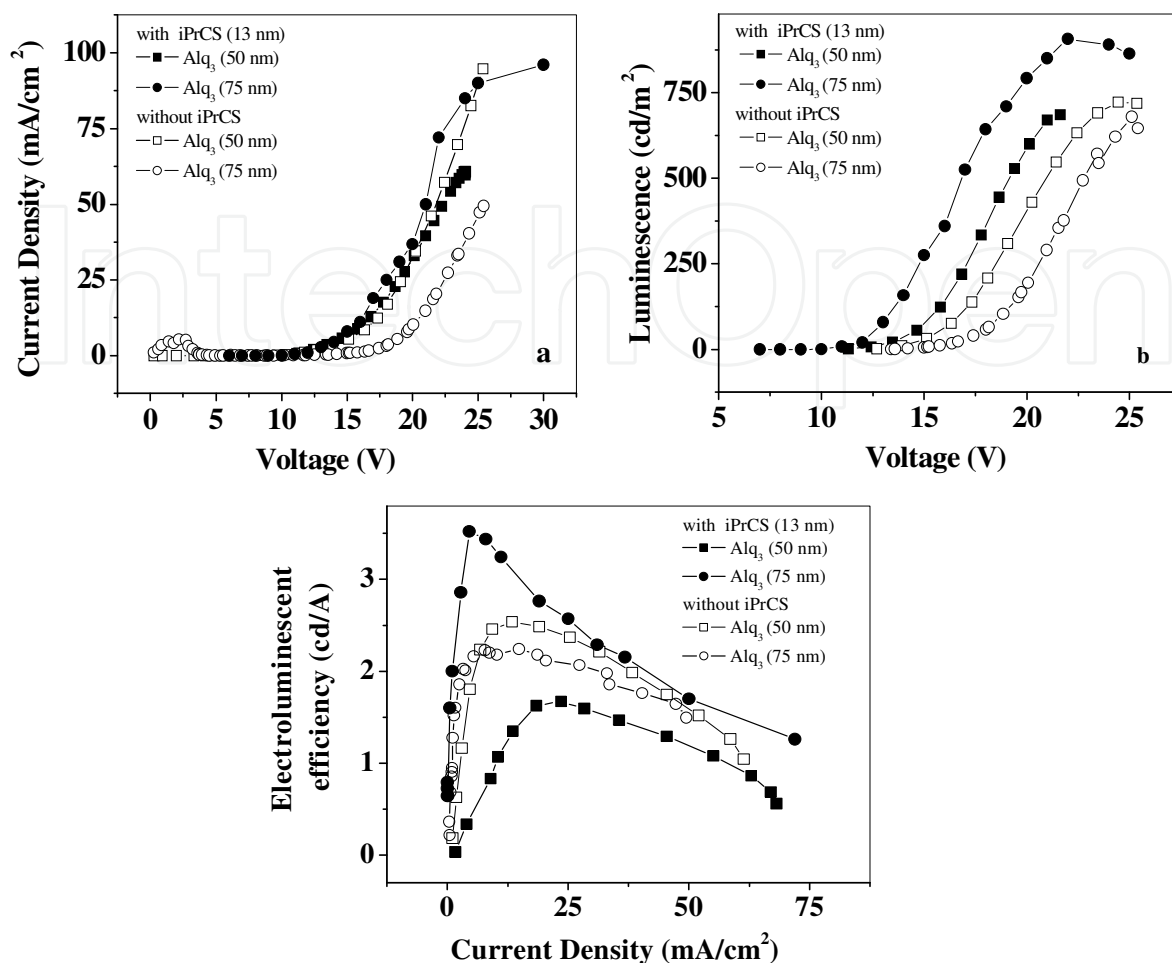


Fig. 4. a) Current/voltage, b) luminescence/voltage and c) efficiency characteristics of ITO/TPD (30nm)/Alq<sub>3</sub> (50, 75nm)/Al with and without iPrCS

It could be supposed that notwithstanding the iPrCS is an insulator, it seems to enhance the hole injection thus improving a hole-electron balance in OLED and makes the tunneling injection in OLED.

## 2.2 Polycarbonate (PC)

The PC is a rigid, transparent and amorphous material with high T<sub>g</sub> 140-155 °C. It possesses excellent dielectric and optical characteristics. The possibility of usage of PC as buffer layer in OLED with ITO/PC/TPD/Alq<sub>3</sub>/Al structure was investigated. The PC layers with thicknesses of 9, 12 and 17 nm were deposited via spin-coating from 0.1%, 0.2% and 0.3% dichloroethane solutions. The basic characteristics of OLED structure with different thickness of PC buffer layer are presented in Fig.5. It was found that inserting of 9 nm buffer layer in OLED devices decreased the turn on voltage from 12.5 to 8 V, and increased the current density from 10 to 24 mA/cm<sup>2</sup> and the luminescence from 220 to 650 cd/m<sup>2</sup> (at 17.5 V) compared to the reference structure. Further increasing of the thickness of PC buffer layer decreases the current density and the luminescence, and shift the turn on voltage toward higher values (Fig.5b), as was established with iPrCS.

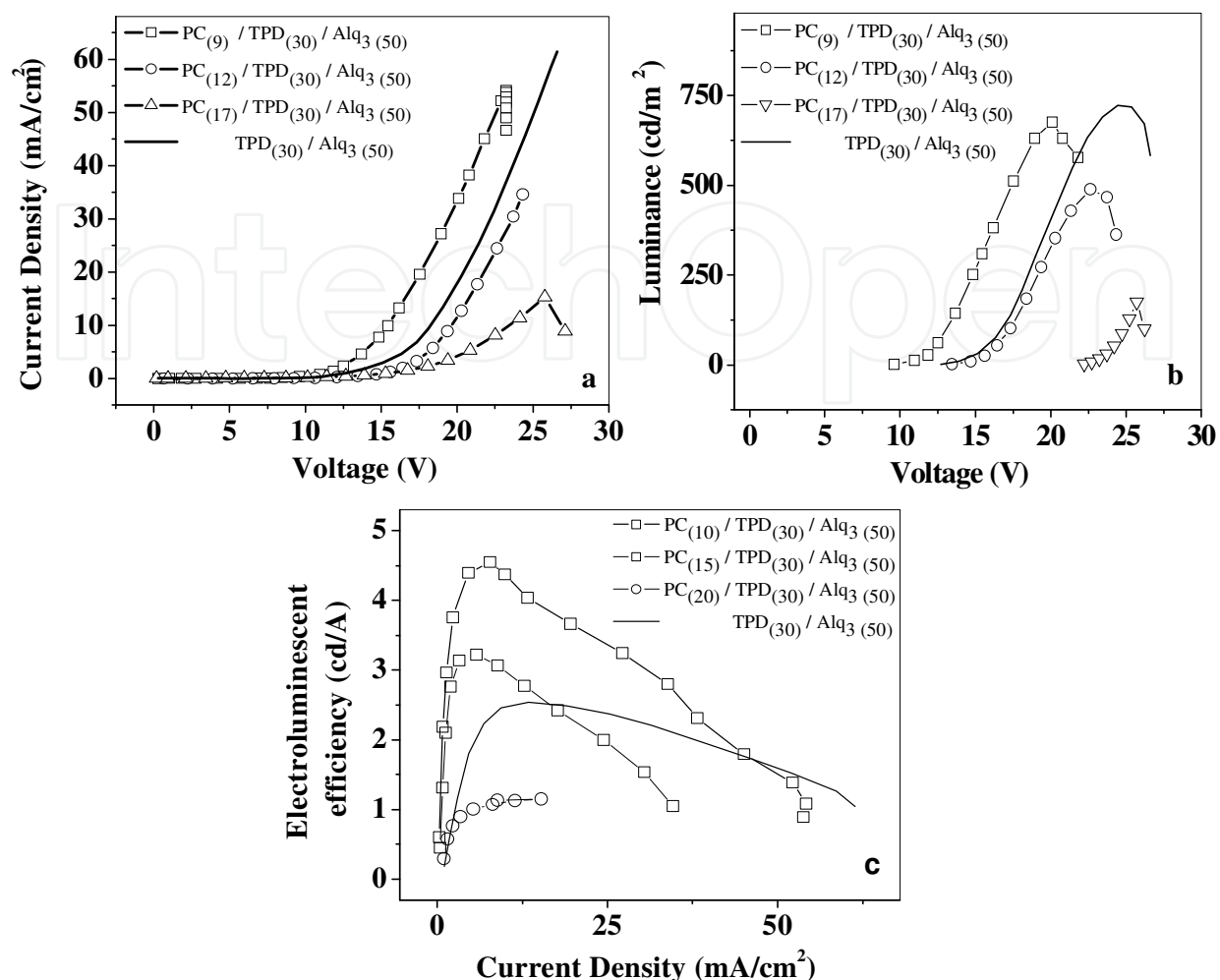


Fig. 5. Current/voltage (5a), luminescence/voltage (5b) and efficiency (5c) for inset legends structures.

The best characteristics – the lowest turn-on voltage, the highest luminescence and the highest efficiency showed OLED with 9 nm PC buffer layer. It should be noted that the efficiency of the device with 9 nm buffer layer is more than 2x higher than that of the reference device. Similar improvement of characteristics of device with 1 nm Teflon buffer layer was observed by Qiu et al. (2002). They supposed that the Teflon layer acts as a stable fence to impede indium diffusion from ITO electrode into the TPD layer and thus enhances the device stability.

It could be supposed that the improvement of EL performance of devices with buffer layers of iPrCS and PC has just the same genesis. Although these compounds are insulators, they seem to enhance the hole injection from anode by tunneling. Thus improving a hole-electron balances in OLED.

We also made attempts to use the PC and iPrCS polymers as a matrix for TPD. In this cases the turn on voltages of the devices with composite buffer layers were lower than that with only PC and iPrCS buffer layers, but unfortunately the luminescence of the devices were significantly reduced and unsatisfactory. The last one makes the application of PC and iPrCS polymers irrelevant as matrix of TPD for OLEDs.

On the results obtained could be concluded that iPrCS and polycarbonate can be successfully use as buffer layers for obtaining of OLED with good performance.

Further devices with the typical hole transporting layers poly(9-vinylcarbazole) (PVK) and N, N'-bis(3-methylphenyl)-N, N'-diphenylbenzidine (TPD) were studied. That's why we investigated the influence of single layer of PVK, TPD, PVK as a buffer layer with respect to TPD and composite layer of PVK:TPD on the performance of the device structure ITO/HTL/Alq<sub>3</sub>/Al. The HTL (31 nm) of PVK and PVK:TPD composite films (10wt% TPD relatively PVK in 0.75% dichloroethane solutions) were deposited by spin-coating.

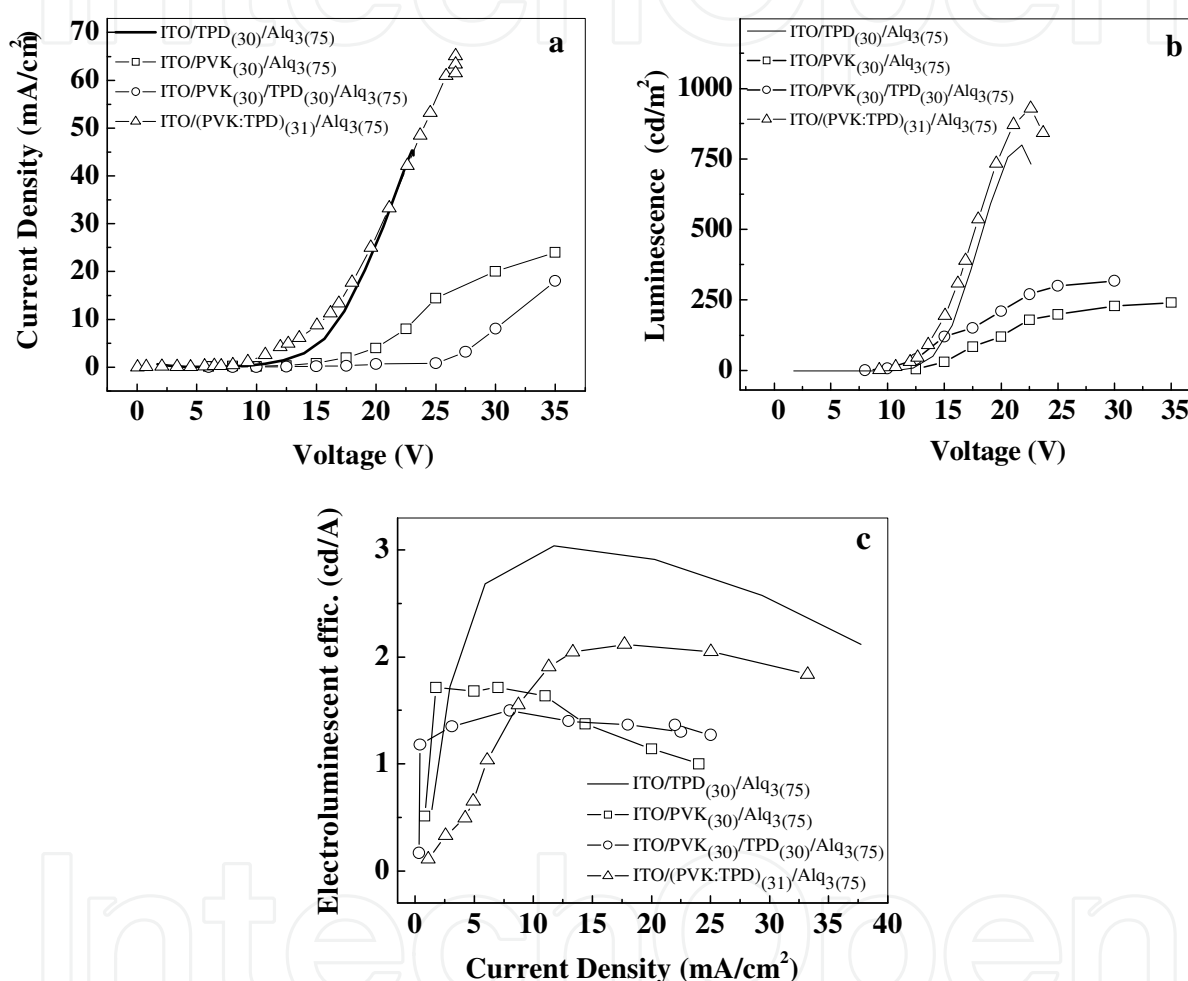


Fig. 6. a) Current/voltage, b) luminescence/voltage and c) efficiency characteristics of devices shown in set.

The optimal I/V, L/V and efficiency characteristics of the devices ITO/PVK/Alq<sub>3</sub>/Al, ITO/PVK/TPD/Alq<sub>3</sub>/Al, ITO/(PVK:TPD)/Alq<sub>3</sub>/Al and ITO/TPD/Alq<sub>3</sub>/Al as reference are presented in Fig.6. It is seen that the I/V and L/V curves for ITO/(PVK:TPD)/Alq<sub>3</sub>/Al and ITO/TPD/Alq<sub>3</sub>/Al structures are almost identical. But it was established that due to the well known trend of TPD thin films to crystallization, the lifetime of the reference device with TPD only is many times shorter than that with composite layer of PVK:TPD. The device structure with only PVK and ITO/PVK/TPD/Alq<sub>3</sub>/Al, showed a decrease in the current density, luminescence and efficiency compared to the reference device. Obviously,

the use of PVK as HTL, or as a buffer layer in respect of TPD HTL in OLEDs is not felicitous, because impedes the charge transfer.

It could be stressed that the devices with PVK:TPD composite layer demonstrates the best characteristics. The involving of TPD in PVK matrix improves the current density, luminescence and luminescent efficiency, reduces the turn-on voltage and increases the lifetime compared to the others devices.

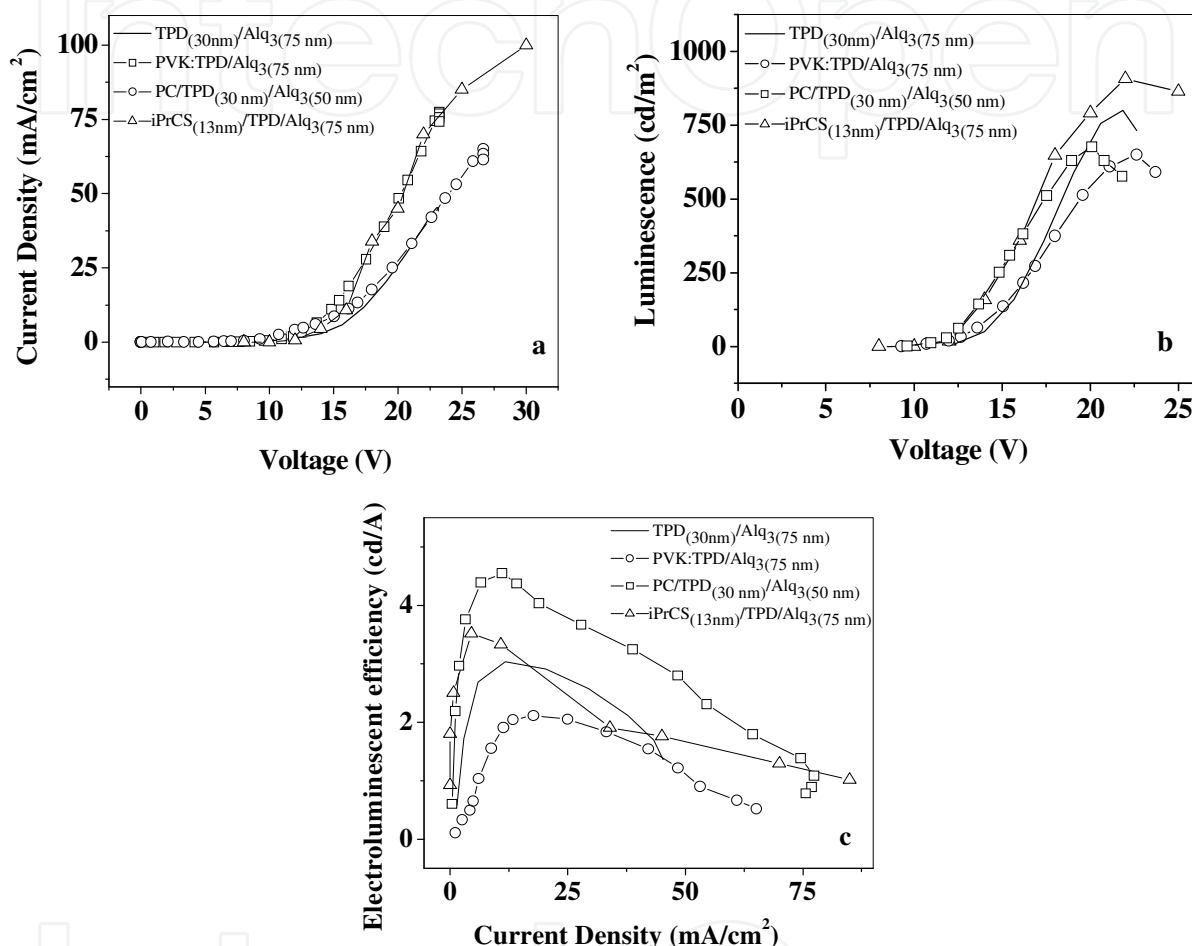


Fig. 7. a) Current/ voltage, b) luminescence/ voltage and c) efficiency characteristics of devices ITO/iPrCS/TPD/Alq<sub>3</sub>/Al, ITO/PC/TPD/Alq<sub>3</sub>/Al, ITO/(PVK:TPD)/Alq<sub>3</sub>/Al and ITO/TPD/Alq<sub>3</sub>/Al shown in set.

The best results obtained for four type devices with different buffer and hole transporting layers are presented in Fig.7. It is clearly seen that inserting of buffer layer caused decreasing of turn on voltage and increasing of current densities, luminescence and efficiency. The best electroluminescence of 570 cd/m<sup>2</sup> at 17.5 V belonged to the device with iPrCS, followed by devices with PC, TPD and PVK:TPD, respectively with 510, 380 and 350 cd/m<sup>2</sup>. At the same time the best efficiency of 3.3 cd/A at 37 mA/cm<sup>2</sup> exhibited device with PC followed by devices with TPD (2.17 cd/A), iPrCS (1.88 cd/A) and PVK:TPD (1.73 cd/A). A comparison of the OLED characteristics for the four devices clearly indicates that the device performance is greatly improved when the ITO surface was covered by polymeric film.

Besides that the efficiency of the devices with composite PVK:TPD layer is not so high, this HTL is most perspective due to the synergistic effect from properties of both components. The incorporation of TPD with PVK offers an attractive route to combine the advantages of easy spin-coating formability of PVK with the better hole transporting properties of TPD. The composite PVK:TPD layers is very reproducible, simplify the obtaining of experimental samples and by reason of that it was used in our basic structure for the study of different electroluminescent compounds as emitting layer in OLEDs.

The efficiency of the OLED is a complexed problem, and depends not only on the energy levels of functional layers of the devices, but also on the interfaces between inorganic electrodes/organic layers. We demonstrate that the thin polymeric films enable to facilitate the transport of carriers and to improve the adhesion and morphology between ITO, and “small” molecular organic layer.

### 2.3 Effect of morphology

The ITO is common known as an excellent electrode, but its morphology can has an affect on the organic layers evaporated on ITO substrate, where the small spikes in the ITO surface can lead to local crystallization of HTL and EL causing a bright white-spot that may increase the leakage and instability of the device.

The surface morphology of the hole transporting and buffer layers were studied by scanning electron microscopy (SEM) and atom force microscopy (AFM).

SEM micrographs of vacuum deposited TPD and spin-coating composite PVK:TPD hole transporting films on PET/ITO substrates are presented in Fig.8 and Fig.9.

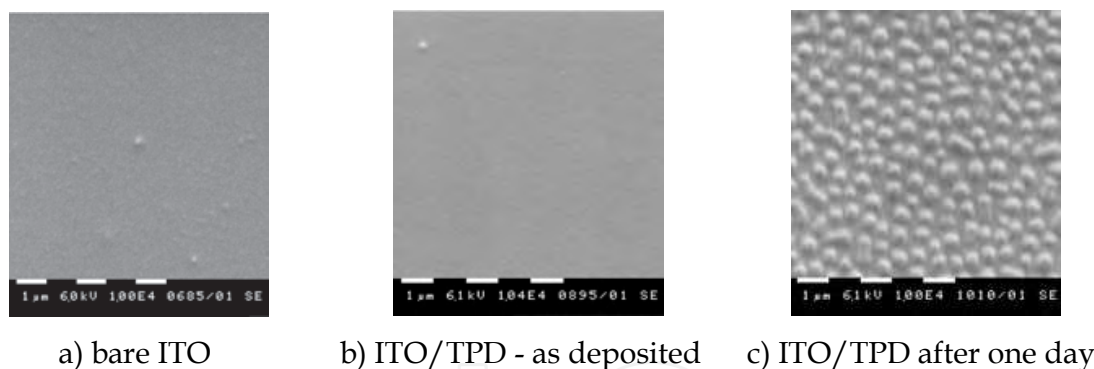


Fig. 8. SEM images of: a) bare ITO on PET substrate; b) as deposited, and c) after one day vacuum deposited 30nm TPD layer on ITO/PET

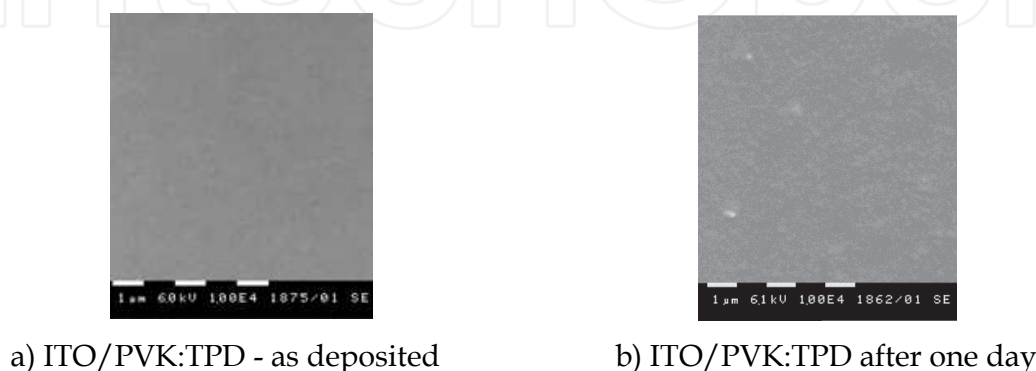


Fig. 9. SEM images of composite PVK:TPD spin-coating deposited layer on ITO/PET

The surface morphology of the developed by us composite films of PVK:TPD (Fig.9.) is very smooth and homogeneous, without any defects and cracks, thus creating a suitable conditions for the condensation of the next electroluminescent layer. The similar is the surface morphology of the vacuum as-deposited TPD films on bare ITO (Fig.9b.), but after 1 day storage at ambient temperature, TPD formed an islands structure with bubbles, which is a prerequisite for recrystallization and oxidation (Fig.8c.). At the same time the surface morphology of PVK:TPD, layers does not show any changes after 1 day storage (Fig.9b.) – better stability of devices with composite PVK:TPD hole transporting layer could be expected. The results of AFM investigations are presented in Fig.10. It is shown that surface of the commercial ITO coated PET substrates is with uniform roughness with some imperfections. The evaporated TPD layer onto this ITO surface makes a granular structure (Fig.10. a, b). The introducing polymer buffer layers covered the ITO pinholes, spikes and other defects, thus leveling its surface (Fig.10. c, e, and g). The amorphous and very smooth surface of spin-coated polymer thin films creates more suitable conditions for vacuum deposition of TPD thin films compared to the bare ITO. As far as TPD layers deposited onto studied buffer coatings are concerned, a quite even granular structure is observed (Fig.10. d, f, h).

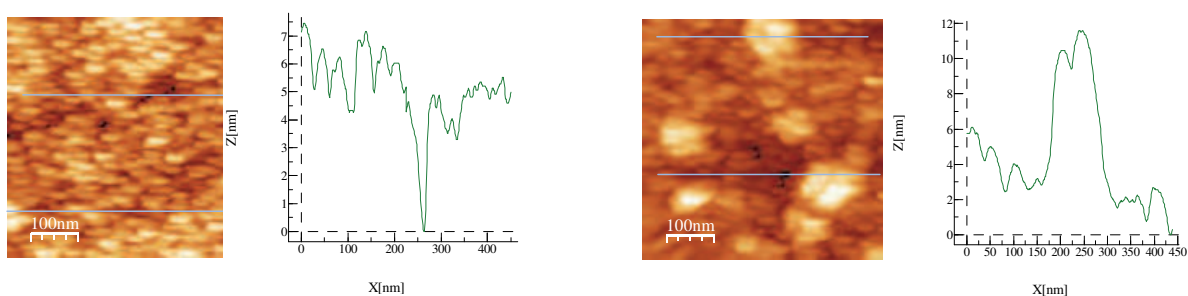
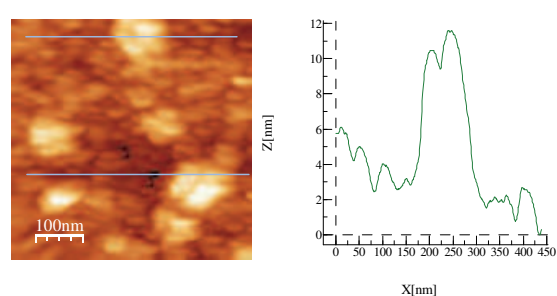


Fig. 10. a) bare ITO surface onto PET substrate.



b) ITO/TPD surface

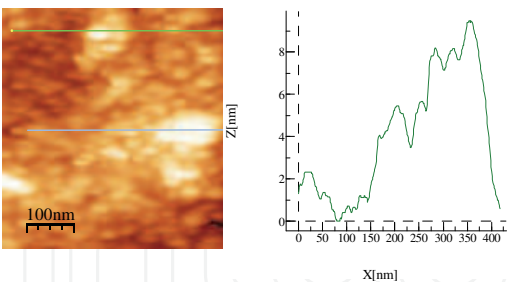
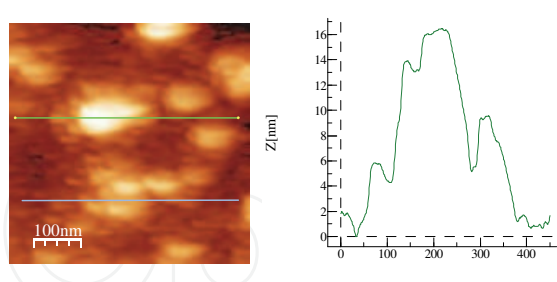


Fig. 10. c) ITO/ iPrCS surface



d) ITO/iPrCS/TPD surface

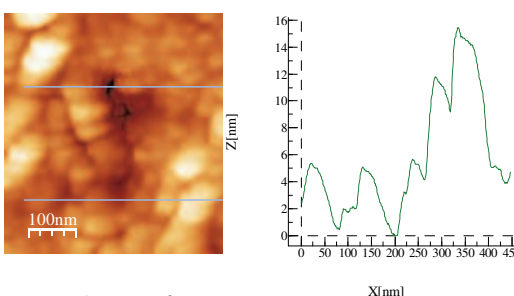
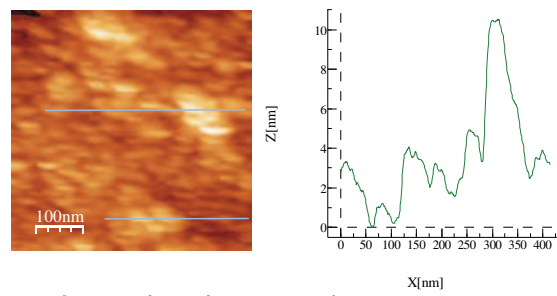


Fig. 10. e) ITO/ PC surface



f) ITO/PC/TPD surface

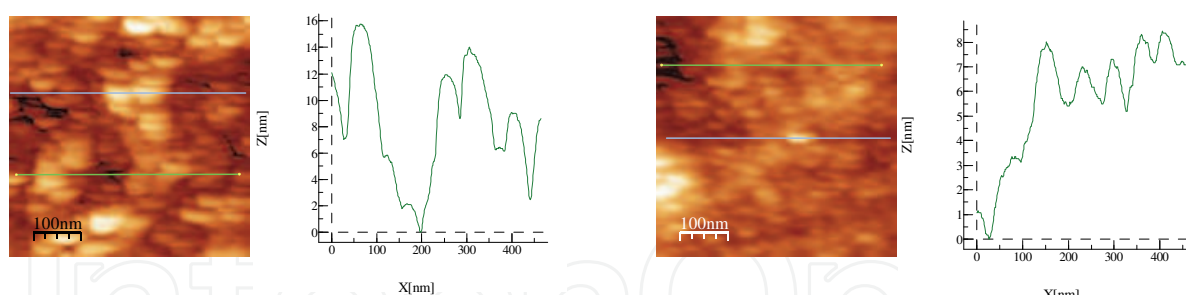


Fig. 10. g) ITO/ PVK surface

h) ITO/PVK/TPD surface

Fig. 10. AFM images and cross-section profiles of the surfaces of a) bare ITO, b) ITO/TPD, c) ITO/iPrCS surface, d) ITO/iPrCS/TPD surface, e) ITO/PC surface, f) ITO/PC/TPD surface, g) ITO/PVK surface, h) ITO/PVK/TPD surface

Unlike the fast recrystallization of TPD layer deposited on bare ITO, the amorphous and homogeneous surface of TPD films deposited on the buffer-coated ITO was very stable. The results obtained show that the polymer modifies successfully the film morphology, thus preventing the recrystallization of hole transporting layer (TPD) and following emissive layer. These results definitely have an effect on the current density and luminance characteristics of the devices. Probably, the higher  $T_g$  of the polymers than that of the TPD, improve the durability of HTL on Joule heat, which arises in OLED operations, thus enable the better performance of OLED.

### 3. Novel Zn complexes

Many organic materials have been synthesized and extended efforts have been made to obtain high performance electroluminescent devices. In spite of the impressive achievements of the last decade, the problem of searching for the new effective luminescent materials with different emission colours is still topical. Metal-chelate compounds are known to yield broad light emission and seem to provide design freedom needed in controlling photo-physical processes in such 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 (Sapochak et al, 2001, 2002; Hamada et al, 1996; Sano et al, 2000; Kim et al, 2007; Rai et al, 2008). Zinc(II) bis[2-(2-hydroxyphenyl) benzothiazole] ( $\text{Zn}(\text{BTz})_2$ ) has been studied as an effective white light emissive and electron transporting material in OLED. Hamada et al. (1996) reported that the device with single-emitting layer of  $\text{Zn}(\text{BTz})_2$  showed a greenish white emission. Later on an efficient white-light-emitting device were developed with electroluminescent layers of  $\text{Zn}(\text{BTz})_2$  doped with red fluorescent dye of 4-dicyanomethylene-2-methyl-6-[2-(2,3,6,7-tetrahydro-1H,5H-benzo[i,j]quinolizin-8-yl)vinyl]-4H-pyran (DCM2) (Lim et al, 2002) or rubrene (Zheng et al, 2005; Wu et al, 2005). Recently Zhu et al. (2007) fabricated white OLED with  $\text{Zn}(\text{BTz})_2$  only as emitter. The obtained white emission is composed of two parts: one is 470 nm, which originates from exciton emission in  $\text{Zn}(\text{BTz})_2$ , the other is 580 nm, which originates from exciplexes formation at the interface of TPD/ $\text{Zn}(\text{BTz})_2$ .

We investigated the new Zn complexes Zinc(II) [2-(2-hydroxyphenyl)benzothiazole] acetylacetonate ( $\text{AcacZnBTz}$ ) and Zinc(II) bis[2-(2-hydroxynaphthyl)benzothiazole]

(Zn(NBTz)<sub>2</sub>), and known Zinc(II) bis[2-(2-hydroxyphenyl)benzothiazole] (Zn(BTz)<sub>2</sub>) (Tomova et al, 2008), and Zinc(II) bis(8-hydroxyquinoline) (Znq<sub>2</sub>) (Fig.11), synthesized by prof. Deligeorgiev as electroluminescent and electron transporting compounds. The basic OLED structure was PET/ITO/(PVK:TPD)/EML/Al.

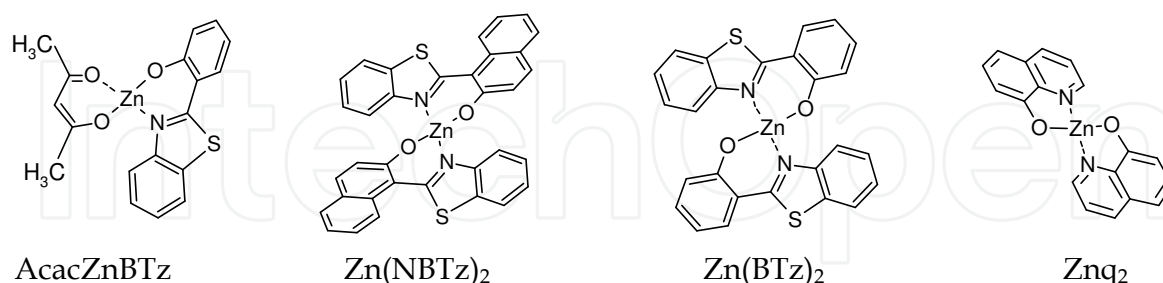


Fig. 11. The chemical structures of used Zn complexes

The absorption and fluorescent (PL) spectra of the complexes were taken using the Spectrofluorimeter Perkin Elmer MPF 44 are presented in Fig.12.

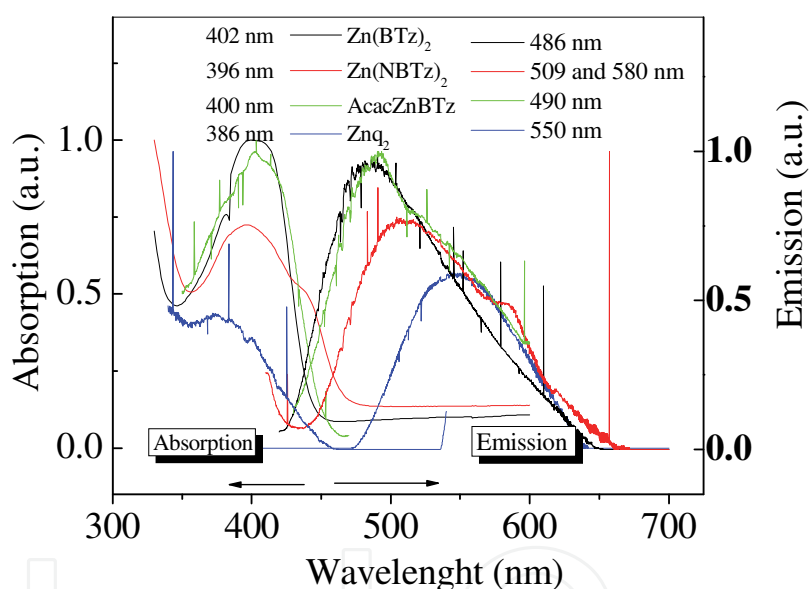


Fig. 12. Absorption and PL emission spectra of 100 nm films of Zn complexes evaporated on glass substrate

The PL peak wavelength of Znq<sub>2</sub> is at 550 nm, of Zn(BTz)<sub>2</sub> at 486 nm, of AcacZnBTz at 490 nm. Zn(NBTz)<sub>2</sub> shows peak at 509 nm and shoulder at 580 nm. The data obtained for PL peaks of Znq<sub>2</sub> and Zn(BTz)<sub>2</sub> are very closed to the results reported by Shukla & Kumar (2010) for Znq<sub>2</sub> (540 nm) and by Qureshi et al. (2005) for Zn(BTz)<sub>2</sub> (485 nm).

The electroluminescent (EL) spectra of devices PET/ITO/(PVK:TPD) (31 nm)/EML (75 nm)/Al, obtained at different voltages by Ocean Optics HR2000+ spectrometer are shown in Fig.13.

It was established that the EL spectra of the complexes with benzthiazole ligand were very similar and exhibited a green electroluminescence around 525 nm. Besides the EL spectra of all four compounds were red shifted, about 10 nm for Znq<sub>2</sub> and 25 - 30 nm of benzthiazole complexes, compared to their corresponding PL spectra. Take into account the fact that the exciton disassociates easily under the excitation of electric field than the light, red shifting of

EL spectra were quite understandable (Wu et al, 2005). The highest EL intensity showed the devices with AcacZnBTz followed by those with Zn(BTz)<sub>2</sub>, Znq<sub>2</sub>, and Zn(NBTz)<sub>2</sub>.

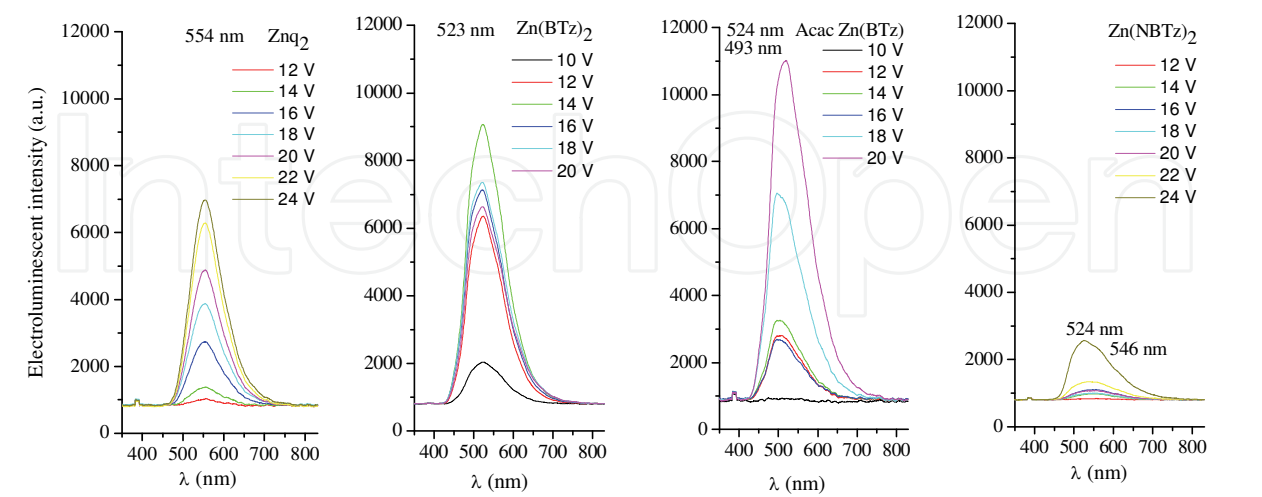


Fig. 13. Electroluminescent spectra of OLEDs with different Zn complexes

The EL peak wavelength of the devices with Znq<sub>2</sub> and Zn(BTz)<sub>2</sub> is the same during the device operation independantly on the working voltage, while EL peak of the devices with AcacZnBTz moves from 493 to 524 nm with increasing the working voltage. Our results were quite different from these obtained by Wu et al. (2005), who showed almost identical EL and PL for Zn(BTz)<sub>2</sub>, and Qureshi et al. (2005) who founded broader EL than PL spectrum AFM images of top surfaces of devices with EML of different Zn complexes are presented in Fig.14.

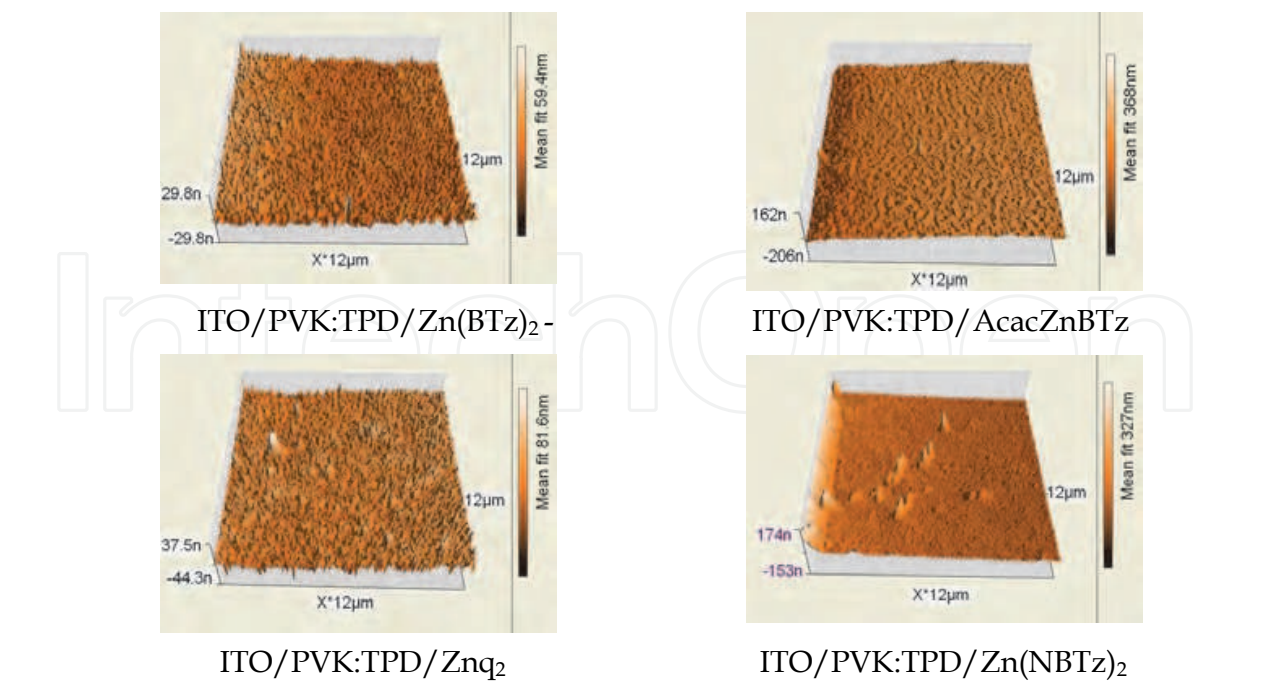


Fig. 14. AFM images of top surfaces of devices with EML of different Zn complexes, performed by “EasyScan 2” produced by “Nanosurf” (Switzerland) on area of 12.5 x 12.5 μm, at measurement mode “scan forward” and Scan mode from down to up.

The AFM images show that evaporated  $\text{Znq}_2$  and  $\text{Zn}(\text{BTz})_2$  compounds, on PET/ITO/PVK:TPD structure, formed similar fine-textured surfaces with root mean square (RMS) roughness respectively 6.88 nm and 4.64 nm. The AcacZnBTz layer made soft outline ridge surface with RMS roughness 20.06 nm.

All three complexes formed smooth and even surfaces requisite for the good performance of OLED on their base. Maybe due to the molecular structure specific of the  $\text{Zn}(\text{NBTz})_2$  the film obtained from it is very flat (RMS roughness 22.82 nm), but with some acicular formations over 150 nm on some areas. Namely these formations are a precondition for the worse EL performance of OLED with electroluminescent layer of  $\text{Zn}(\text{NBTz})_2$ .

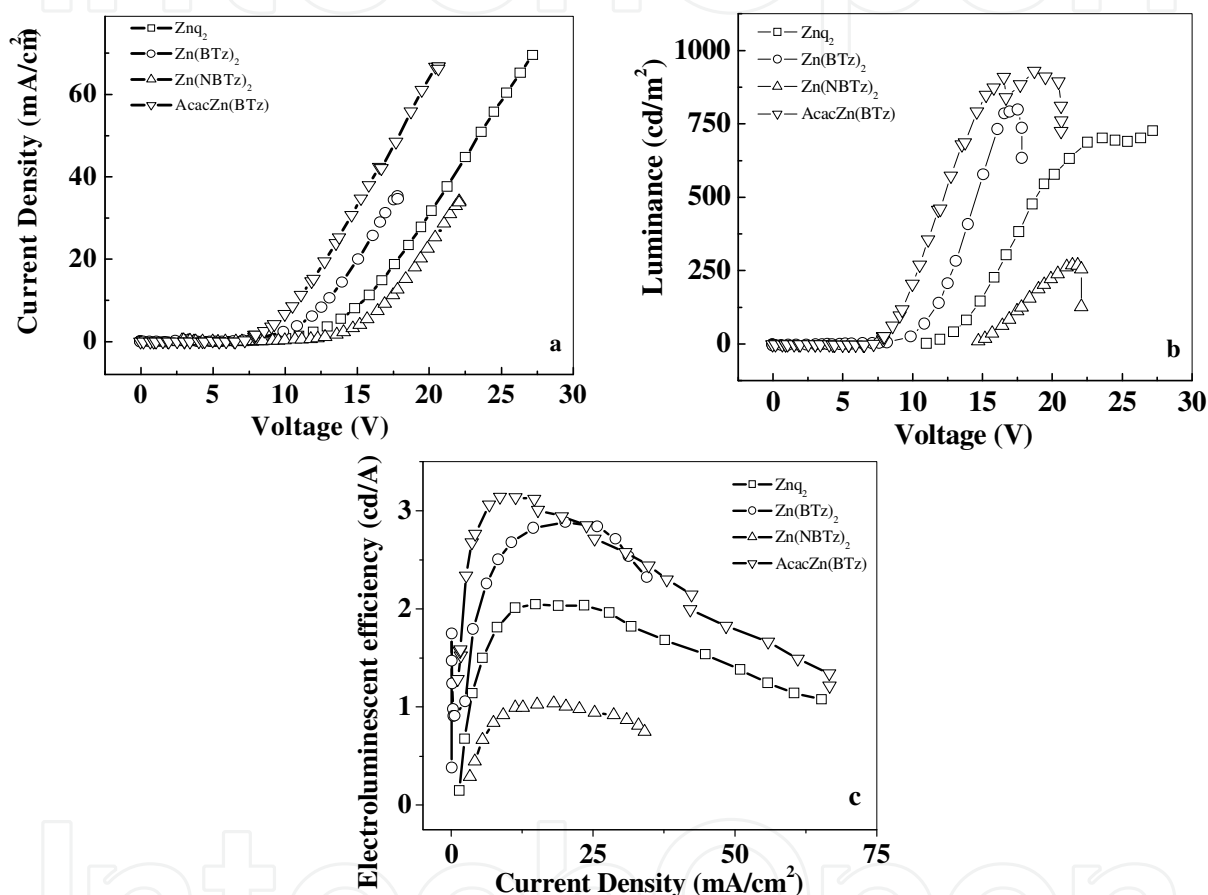


Fig. 15. a) Current/voltage and b) luminescence/voltage characteristics and c) electroluminescent efficiency for devices with different EML (75nm) and HTL of (PVK:TPD) (31nm)

Fig.15. presents the current/voltage, luminance/voltage and efficiency characteristics of four type identical devices with different EML. It was established that the current densities and the luminescence decreased and the turn-on voltage of devices increased in following sequence AcacZnBTz,  $\text{Zn}(\text{BTz})_2$ ,  $\text{Znq}_2$ ,  $\text{Zn}(\text{NBTz})_2$ . Luminescence of the device with AcacZnBTz at 15 V DC was nearly 1.5 and 3 times higher than those by  $\text{Zn}(\text{BTz})_2$  and  $\text{Znq}_2$ , respectively (Fig.15b). At the same time the electroluminescent efficiencies of the devices with AcacZnBTz and  $\text{Zn}(\text{BTz})_2$  were nearly the same (around 3 cd/A) and 1.5 and 3 times higher than that of devices with  $\text{Znq}_2$  and  $\text{Zn}(\text{NBTz})_2$  (Fig.15c).

For OLEDs with similar structures Sano et al. (2000) reported efficiency 1.39 cd/A at luminance 100 cd/m<sup>2</sup> for ITO/TPD/ $\text{Zn}(\text{BTz})_2$ /Mg:In device, Zheng et al. (2005) - 4.05 cd/A

for doped with rubrene  $\text{Zn}(\text{BTz})_2$  white device at maximum luminescence  $4048 \text{ cd/m}^2$  [10] and Rai et al., (2008) -  $1.34 \text{ cd/A}$  for ITO/NPD/ $\text{Zn}(\text{Bpy})_2/\text{Al}$ .

The results presented in this chapter show that the studied Zn complexes with the exception of  $\text{Zn}(\text{NBTz})_2$  can be successfully used as emitters and electron transporting layers for OLED. It could be stressed that the efficiency of the devices with  $\text{Zn}(\text{BTz})_2$  is  $2.9 \text{ cd/A}$  at luminance  $250 \text{ cd/m}^2$  – one of the best reported up to now in the literature for the devices with similar structure. Besides that the devices with new Zn complexes are not optimized, its characteristics are quite promising, especially for  $\text{AcacZnBTz}$  – the highest luminance and the efficiency  $3 \text{ cd/A}$  in the range of  $10 - 30 \text{ mA/cm}^2$ .

#### 4. Aluminum bis(8-hydroxyquinoline)acetylacetonate ( $\text{Alq}_2\text{Acac}$ ) complex

Since Tang and VanSlyke (1987) had developed the first organic light-emitting diode (OLED), Aluminum tris(8-hydroxyquinoline) ( $\text{Alq}_3$ ) has been one of the most successful organic materials ever used as the emitting, electron-transport and host material layer in OLEDs. Numerous derivatives on  $\text{Alq}_3$  structure were prepared and their optical and semiconductor properties were tested.  $\text{Alq}$  complex  $\text{BAq}$  (bis(2-methyl-8-quinolate)4-phenyl-phenolate) was first introduced by Kodak group as a blue-emitting material and mostly used as hole blocking layer (Kwong et al., 2002) and as a blue emitter (Kwong et al., 2005; Iwama et al., 2006; Yu et al., 2007). Hopkins and coworkers (1996) have also obtained blue shifted emission from  $\text{Alq}_3$  derivate via introduction of the strong electron withdrawing  $-\text{SO}_2\text{NR}_2$  group at C-5 of the 8-hydroxyquinoline ligand.

Azenbacher group investigated the role of 5-(arylethynyl)- (Pohl & Anzenbacher, 2005), 5-(aryl)- (Pohl et al., 2004; Montes et al., 2004, 2006; Pérez-Bolívar et al., 2006), and two C4-aryl- (Pérez-Bolívar et al., 2010) substituents on the quinolinolate rings, in  $\text{Alq}_3$  derivatives and their effect on the photophysical properties and electroluminescence. Many methyl-substituted derivatives  $\text{nMeq}_3\text{Al}$  (Kwong et al., 2005; Sapochak et al., 2001; Kido & Iizumi, 1998), phenyl-substituted  $\text{Alpq}_3$  (Tokito et al., 2000), soluble 5-substituted- $\text{Alq}_3$  derivatives (Mishra et al., 2005), aluminum complexes such as  $\text{Alq}_2\text{OR}$  ( $\text{OR}=\text{aryloxy}$  or  $\text{alkoxy}$  ligand) (Lim et al., 2006), have been developed and have been demonstrated to be useful emissive materials or/and hole blocking/electron transporting materials. Ma et al. (2003) have synthesized a new material dinuclear Aluminum 8-hydroxy-quinoline complex ( $\text{DAlq}_3$ ) with two time higher electron mobility than that in  $\text{Alq}_3$ .

Omar et al. (2009) synthesized and investigated new aluminum tris(8-hydroxyquinoline) derivatives, having nitrogen functionalities at position-4 of the quinolate ligand, acting as efficient emitters with higher luminance and external quantum efficiency than the parent  $\text{Alq}_3$  in an identical OLEDs. (The PL and EL emission wavelengths of the new Al complexes can be tunes according to the electronic properties of the substituents at position-4). Bingshe Xu et al. (2008) reported about a mixed-ligand 8-hydroxyquinoline aluminium complex with higher electron mobility and electroluminescent efficiency compared with  $\text{Alq}_3$ .

Here we presented a new Al complex, aiming the development of OLED with improved performance. The novel mixed-ligand Aluminum bis(8-hydroxyquinoline)acetylacetonate ( $\text{Alq}_2\text{Acac}$ ) complex (Fig.16.) was synthesized and its performance as electroluminescent and electron transporting layer for OLED was studied and compared with that of the parent  $\text{Alq}_3$  (Petrova et al., 2009).

To investigate the efficiency of the new Al complex as emitter, the devices ITO/HTL/EML/Al with EML layers of  $\text{Alq}_2\text{Acac}$  or commercial  $\text{Alq}_3$  were fabricated.

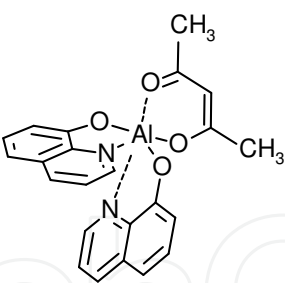


Fig. 16. Structure of Aluminum bis(8-hydroxyquinoline)acetylacetonate (Alq<sub>2</sub>Acac)

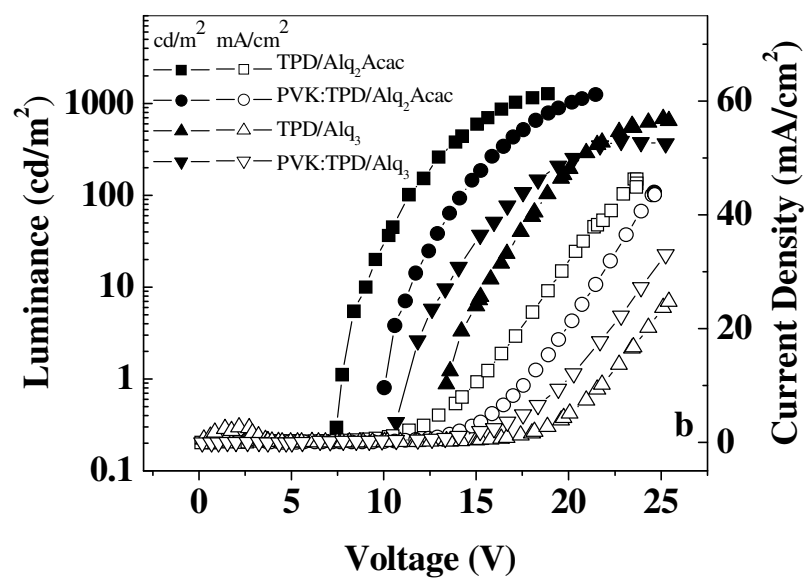


Fig. 17. I/V and L/V characteristics for devices with different HTL<sub>(31 nm)</sub> and EL<sub>(75 nm)</sub>

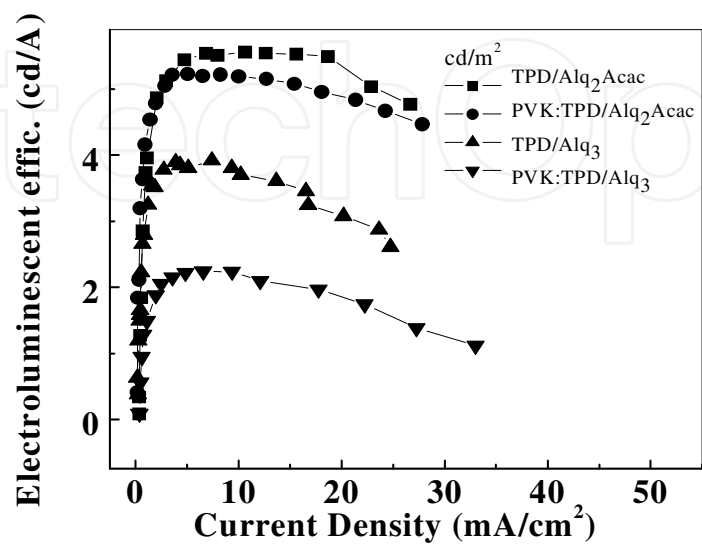


Fig. 18. Electroluminescent efficiency for devices with different HTL<sub>(31 nm)</sub> and EL<sub>(75 nm)</sub>

The current density-voltage and luminescence-voltage characteristics of the studied devices are shown in Fig.17. The I/V curves of the devices with Alq<sub>2</sub>Acac were located in lower voltage region compared to the devices with Alq<sub>3</sub>. The luminescence of the devices with Alq<sub>2</sub>Acac is 2 times higher compared to the similar devices with Alq<sub>3</sub> (Fig.17). The turn-on voltage of the devices with Alq<sub>2</sub>Acac is lower compared to those with Alq<sub>3</sub> especially in the case with TPD hole transporting layer – nearly 2 times.

Bingshe Xu et. al. (2008) reported the electron mobilities in Alq<sub>2</sub>Acac can be determined to be  $2.7\text{--}4.4 \times 10^{-6} \text{ cm}^2/\text{V.s}$  at electric fields ranging between  $1.42 \times 10^6$  and  $2.40 \times 10^6 \text{ V/cm}$ , which is higher than those in Alq<sub>3</sub> published in the literature (Huang et al., 2005; Brütting et al., 2001).

It could be stressed that the efficiency of the devices with Alq<sub>2</sub>Acac are nearly 50 % higher compared to those with Alq<sub>3</sub> with HTL of TPD and about 2 times higher with HTL of PVK:TPD (Fig.18).

The ionization potential (Ip) and the electron affinity (Ea) of Alq<sub>2</sub>Acac and Alq<sub>3</sub> were determined by cyclic voltammetry of 0.001 M solutions of compounds in C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> in presence of 0.1 M tetra-n-butylammonium hexafluorophosphate as supporting electrolyte.

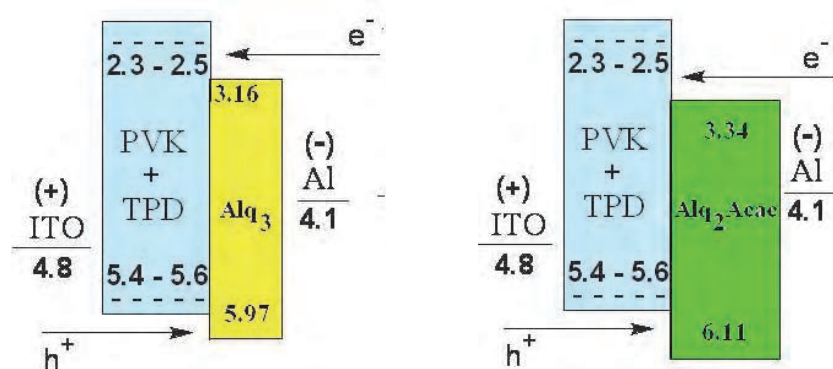


Fig. 19. The energy band diagram of investigated OLEDs

They were: Ip: Alq<sub>2</sub>Acac 6.11 eV and Alq<sub>3</sub> 5.97 eV; Ea: Alq<sub>2</sub>Acac 3.34 eV and Alq<sub>3</sub> 3.16 eV.

The band gaps were nearly equal ( $E_g = 2.77 \text{ eV}$  for Alq<sub>2</sub>Acac and  $2.81 \text{ eV}$  for Alq<sub>3</sub>), that is in agreement with the values of  $2.64 \text{ eV}$  obtained by extrapolation of UV-Vis spectrums to absorption edges (Fig.20). As can be seen in Fig.19, both barriers for electrons and for holes are higher at Alq<sub>2</sub>Acac compared with these of Alq<sub>3</sub>, which explains the better efficiency of devices with Alq<sub>2</sub>Acac.

Our results for the devices ITO/TPD (30nm)/Alq<sub>2</sub>Acac (or Alq<sub>3</sub>) (75nm)/Al are  $5.6 \text{ cd/A}$  for Alq<sub>2</sub>Acac and  $3.9 \text{ cd/A}$  for Alq<sub>3</sub>. Alq<sub>2</sub>Acac based devices performed higher current density and emission efficiency. It indicates that the electron transport of Alq<sub>2</sub>Acac is better than that of Alq<sub>3</sub> after the electron injection from the cathode to the electron transport layer, which is in a good agreement with the actual measurement of mobility. Probably, the molecular mixed-liqand structure of Alq<sub>2</sub>Acac promoted higher electroluminescence efficiency and led to subsequent increase of the device performance.

#### 4.1 Luminescence studies

The absorption and the fluorescent emission spectra of thin layers Alq<sub>2</sub>Acac and Alq<sub>3</sub> are nearly identical see Fig.20. Both complexes emit green light with maximum at 520nm.

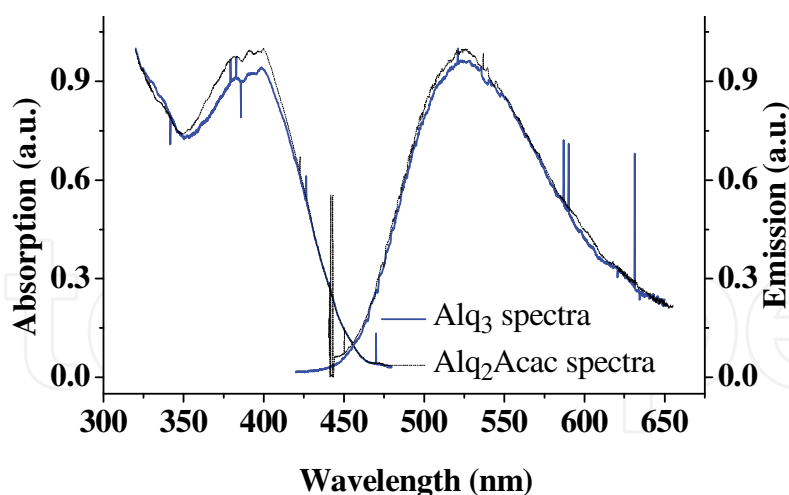


Fig. 20. Absorption and fluorescent emission spectra of Alq<sub>2</sub>Acac and Alq<sub>3</sub> 100 nm layers deposited on glass substrates.

The EL spectra observed at different voltages from the two studied devices ITO/PVK:TPD/Alq<sub>2</sub>Acac and ITO/PVK:TPD/Alq<sub>3</sub> were shown in Fig.21.

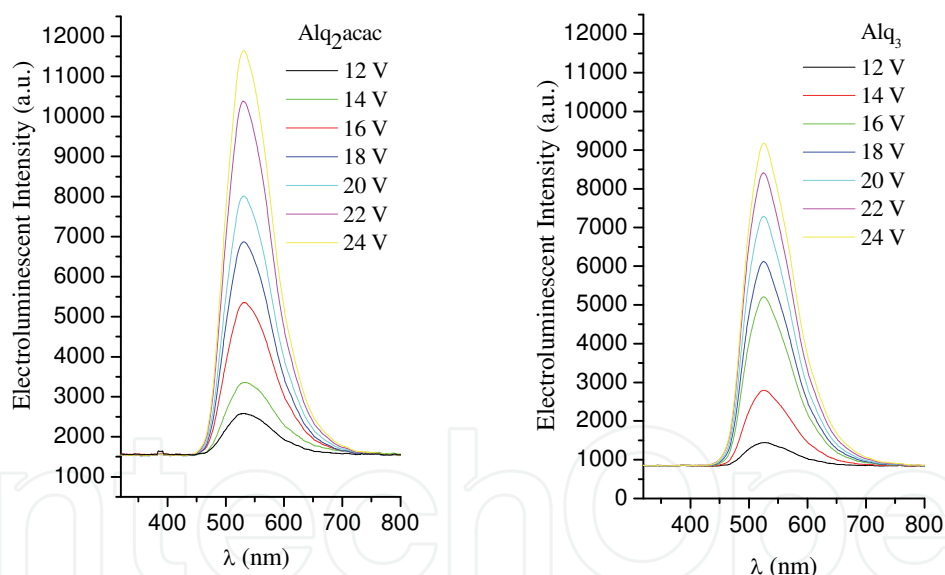


Fig. 21. EL spectra at different voltages of OLED structures ITO/PVK:TPD/Alq<sub>2</sub>Acac and ITO/PVK:TPD/Alq<sub>3</sub>.

The electroluminescence of both devices was similar to the fluorescence. It was established that the Alq<sub>2</sub>Acac emission peak was located at 531 nm, quite close to that of Alq<sub>3</sub> at 525 nm, respectively. As far as concerned to the intensity of the peaks, those of the devices with Alq<sub>2</sub>Acac emitter layers are nearly 2 times higher than that with Alq<sub>3</sub> at the identical experiments. It could be take note of that EL spectra of the two devices (Fig.21a and Fig.21b) are nearly identical like the PL spectra of the corresponding Alq<sub>2</sub>Acac and Alq<sub>3</sub> thin solid films (Fig.20). It is possible, the included in Al complex acetylacetonate ligand does not participate in the  $\pi - \pi^*$  transition of quinolinolato ligands responsible for light emission.

Obviously the replacement of a quinolinolato ligand with an acetylacetonate ligand couldn't tune the emission colour but increase the efficiency of the devices.

## 4.2 Morphology

The performance of OLEDs is greatly influenced by the morphology of organic thin layers. This is due to the important role that morphology of the active organic thin films play in the phenomena that led to light emission. As was mentioned above, strong recrystallization of the TPD layers after 1 day storage at ambient temperature was established. At the same time composite PVK:TPD films remain stable - very smooth and homogeneous without any defects and cracks.

In this part of the work, the surface roughness of organic thin films was investigated via White Light Interferometer (WLI) MicroXAM S/N 8038. The surface relief profiles of the hole transporting layers of TPD and composite films of PVK:TPD were presented in Fig.22, while the surface profiles of the next electroluminescent layers of Alq<sub>2</sub>Acac deposited onto corresponding HTL were presented in Fig.23. The root mean square (RMS) roughness observed of the different samples are:  $2.00 \pm 0.15$  nm for TPD,  $1.65 \pm 0.14$  nm for PVK:TPD,  $2.45 \pm 0.13$  nm for TPD/Alq<sub>2</sub>Acac, and  $2.05 \pm 0.17$  nm for PVK:TPD/Alq<sub>2</sub>Acac. The RMS of PVK:TPD/Alq<sub>3</sub> determined from the surface profile shown in Fig.24 is  $2.20 \pm 0.22$ . Both electroluminescent layers of Alq<sub>3</sub> and Alq<sub>2</sub>Acac deposited on the composite films PVK:TPD show flat and amorphous surfaces which is a prerequisite for good performance of devices.

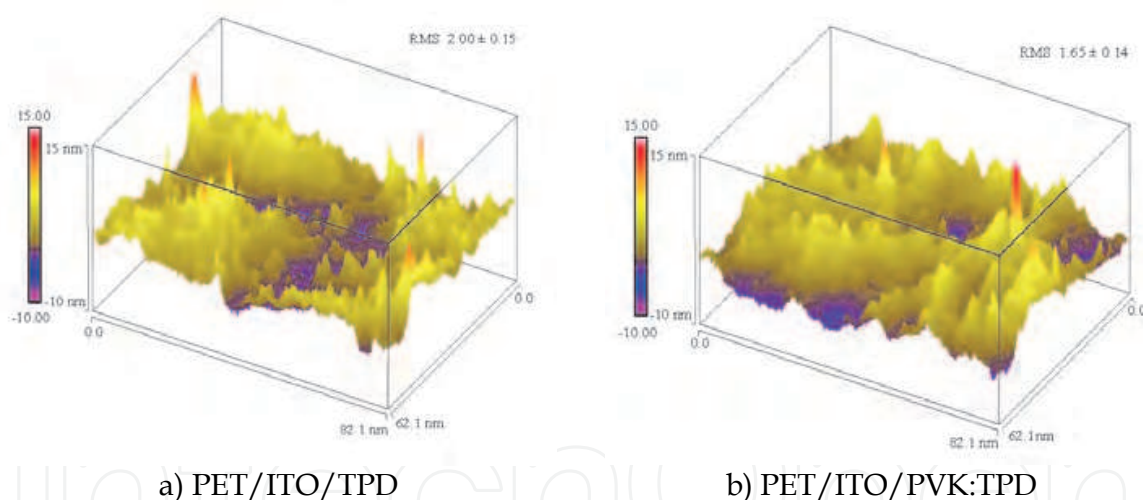


Fig. 22. WLI of: OLED HTL layers of TPD (as deposited), and composite PVK:TPD

The similar is the surface morphology of the vacuum as deposited TPD films. Quantitative values indicate that the flexible acetylacetonate moieties help the formatting of more uniform and planarizing molecular film. The PVK:TPD, PVK:TPD/Alq<sub>3</sub> and PVK:TPD/Alq<sub>2</sub>Acac layers does not show any changes after 1 day storage - better stability of devices with composite PVK:TPD hole transporting layer could be expected.

In conclusion, must to give prominence that the molecular structure of Alq<sub>2</sub>Acac not only promoted the formation of very quantitative thin films, contributing to the high device efficiency, as well as the replacement of quinolinolato ligand with acetylacetonate ligand couldn't tune the emission colour. Alq<sub>3</sub> is still one of the widely-used fundamental materials as emitter and electron transporting layer in OLED due to its excellent thermal stability,

high fluorescence efficiency and relatively good electron mobility. The results obtained show that the change of one 8-hydroxyquinoline ligand with acetylacetonate ligand in the novel complex improves substantially the performance of OLED. Besides that the devices with new Al complex are not optimized, its characteristics are quite promising.

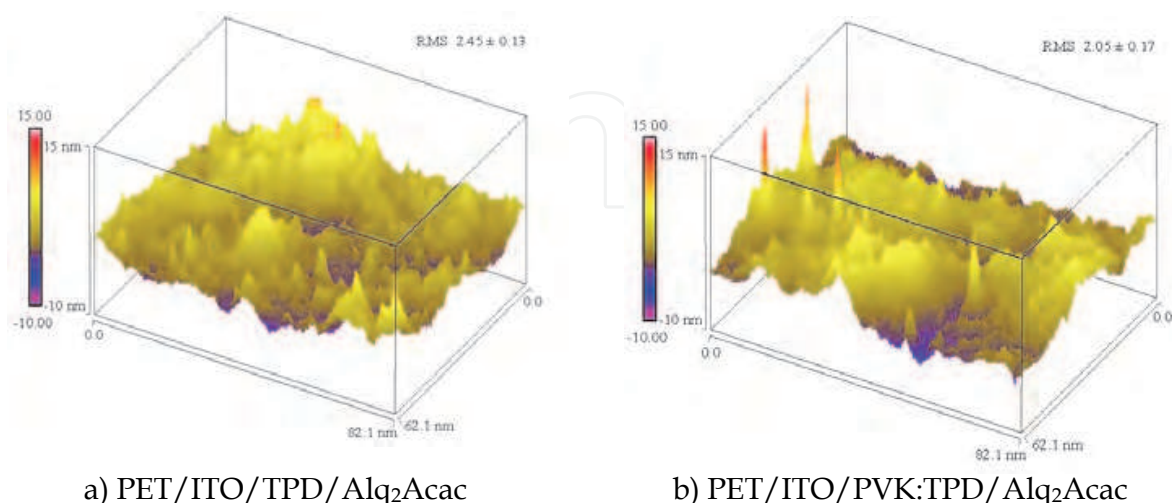


Fig. 23. WLI surface of electroluminescent Alq<sub>2</sub>Acac layer deposited onto HTLs.

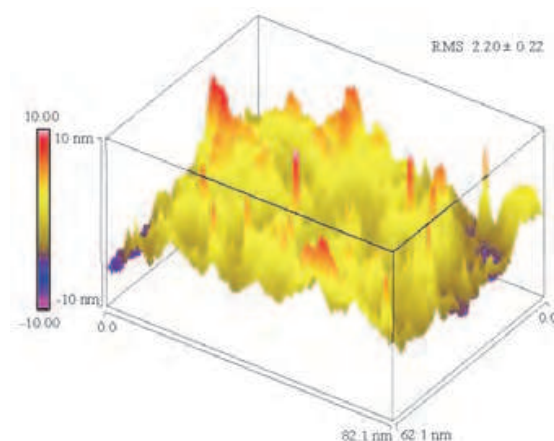


Fig. 24. WLI surface of electroluminescent Alq<sub>3</sub> layer deposited on PET/ITO/PVK:TPD HTL.

## 5. Bathocuproine as hole-blocking layer

In conventional PVK:TPD/Alq<sub>3</sub>/Al OLEDs, the mobility of holes in PVK:TPD is much larger than that of the electrons in Alq<sub>3</sub>. Also, the injection barrier of the anode/PVK:TPD interface is lower than that of the cathode/Alq<sub>3</sub> interface, resulting in the imbalance of holes and electrons in the emitting zone (Brütting et al., 2001; Mück et al., 2000). Therefore, it is necessary to confine the redundant holes in the emitting layer in order to increase the efficiency. Many effective methods have been reported to reduce the hole mobility and improve the balance of holes and electrons in the emitting layer (Troade et al., 2002; Masumoto & Mori, 2008; Mori et al., 2008; Kim et al., 2005).

2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline (bathocuproine, BCP) was used in OLED and organic photovoltaic cell because of its multiple role as hole blocking (Adamovich et al., 2003; Kim et al., 2008; Tomova et al., 2008, 2010), exciton-blocking layer (Zhang et al., 2005; Tripathi et al., 2008; Mori & Kato, 2007; Wu et al., 2003), electron transporting and buffer layer (Wang et al., 2006), or in combination with NPB in (NPB/BCP)<sub>n</sub> (n-number of layers) as hole-trapping layer ( Shi et al., 2006).

In this work we present our results concerning the role of bathocuproine as hole blocking layer in OLED structure: ITO/HTL/EML/HBL/ETL/M. HTL of composite PVK:TPD was spin-coated layer, and HBL, EML and ETL -were thermal evaporated films of BCP and Alq<sub>3</sub>. The absorption and emission photoluminescence spectra of evaporated layers of BCP, Alq<sub>3</sub> and BCP/Alq<sub>3</sub>, measured by Spectrofluorimeter Perkin Elmer MPF 44 are presented in Fig.25.

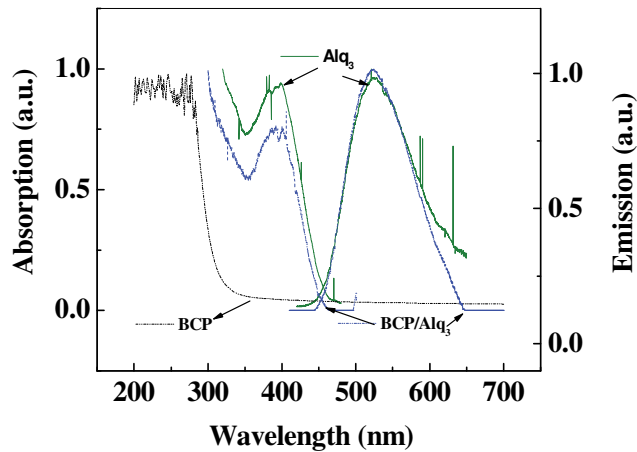


Fig. 25. Absorption and PL emission spectra of thin evaporated films (100 nm) of BCP, Alq<sub>3</sub> and BCP/Alq<sub>3</sub>

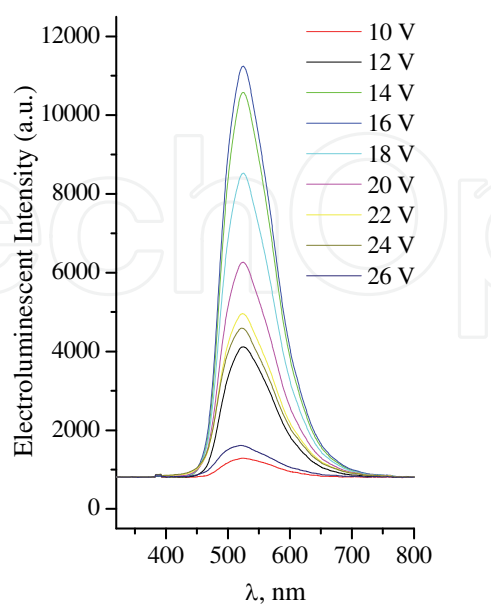


Fig. 26. EL spectra of the ITO/PVK:TPD (31nm)/Alq<sub>3</sub> (40 nm)/BCP (1 nm)/ Alq<sub>3</sub> (15 nm) device at different voltages, were measured on Ocean Optics HR2000+ spectrometer

It is seen that the PL spectra of  $\text{Alq}_3$  and  $\text{BCP}/\text{Alq}_3$  layers are nearly identical with PL peak wavelength at 520 nm. Therefore in these wave length ranges BCP neither absorbs nor radiates and observed fluorescent emission originates from  $\text{Alq}_3$  only. Besides, the EL spectra (Fig.26) observed from the  $\text{ITO}/\text{PVK}:\text{TPD}/\text{Alq}_3(40\text{ nm})/\text{BCP}(1\text{ nm})/\text{Alq}_3(15\text{ nm})$  device at different voltages are quite similar to the fluorescent spectrum of the corresponding  $\text{Alq}_3$  film. The emission peaks were located at 525 nm and are at the same position as the peak of  $\text{Alq}_3$  based structure (presented earlier in this chapter), which also is an evidence that BCP do not participate in the light emission.

Fig.27 presents the current density (Fig.27a) and luminance (Fig.27b) versus voltage, and current and power efficiency versus luminance (Fig.27c) characteristics of the devices  $\text{ITO}/\text{PVK}:\text{TPD}/\text{Alq}_3(40\text{ nm})/\text{BCP}(x\text{ nm})/\text{Alq}_3(15\text{ nm})/\text{Al}$ , where  $x$  is 0; 1; 5 and 15 nm. The I-V curves (Fig.27a) show that insertion of BCP layer decreases the current density and shifts the threshold voltage from 11V to 17V for devices without and with 15 nm BCP. The luminescence initially increases from  $750\text{ cd/m}^2$  to  $1100\text{ cd/m}^2$  for device with 1 nm BCP and then decreases with increasing the thickness of BCP (Fig.27b).

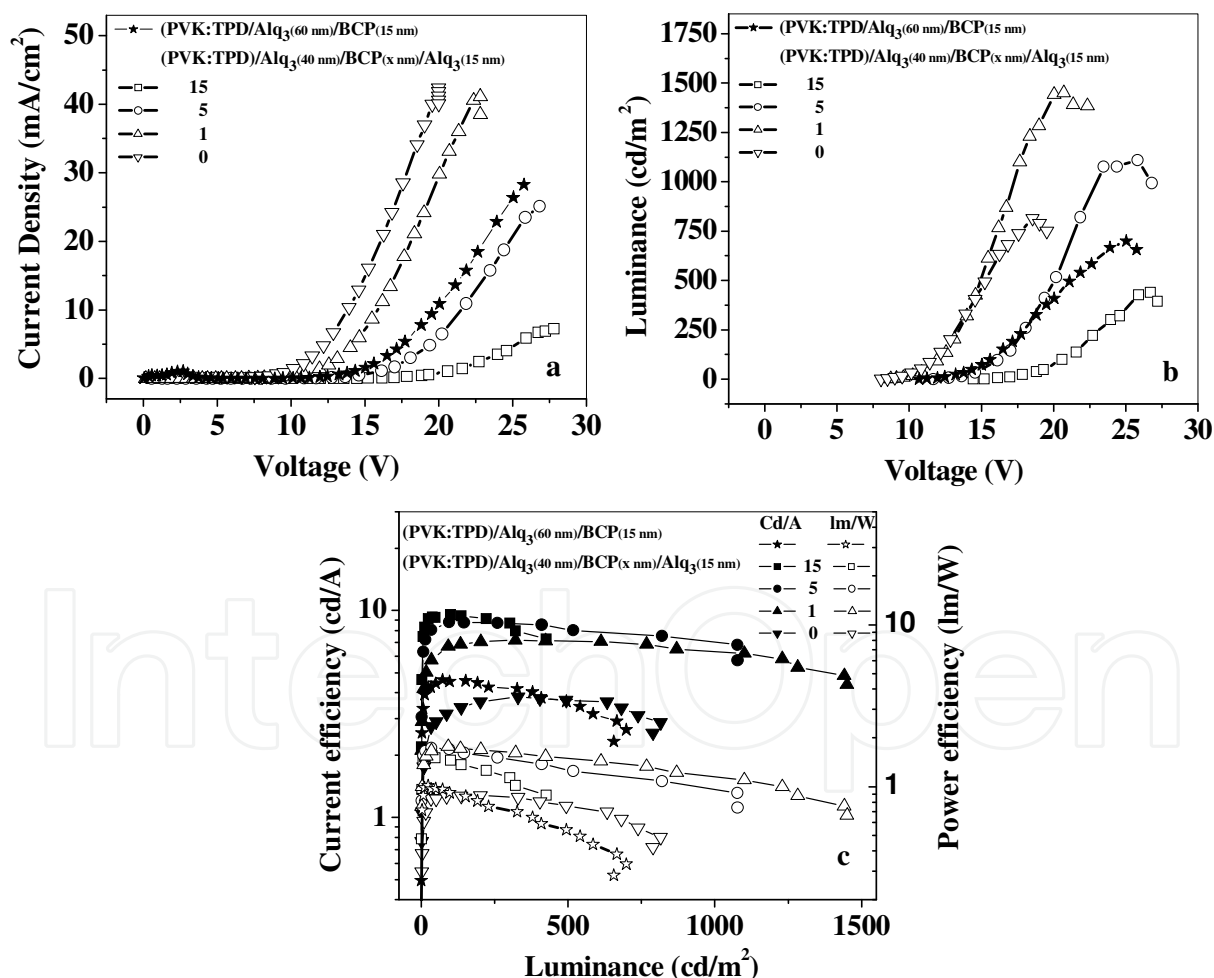


Fig. 27. Current-voltage (I-V) (2a), luminescence-voltage (L-V) (2b), current and power efficiency (2c) curves for devices shown in set

Fig.28 presents the driving voltage and the efficiency at luminance 100 and 200  $\text{cd/m}^2$  in dependence on the thickness of BCP. It is seen that despite of the higher voltage of the

devices with BCP their current efficiency significantly increase from 3.7 to 9.6 cd/A, and power efficiency increase from 0.87 to 1.46 lm/W (at 100 cd/m<sup>2</sup>) for devices without and with 15 nm BCP layer. The beneficial influence of BCP is not only related to the magnitude of the efficiency but also to the broader luminance range which could be seen in Fig.27c. The best characteristics - the lower threshold and working voltage, the highest luminescence and 2 times increased efficiency from 3.7 to 7.1 cd/A and from 0.87 to 1.75 lm/W at 100 cd/m<sup>2</sup> demonstrates device with 1 nm BCP layer compared to the device without BCP.

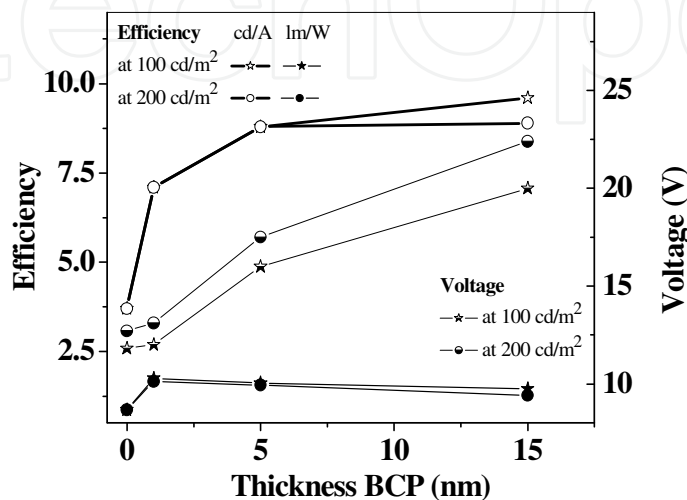


Fig. 28. Current and power efficiency, and voltage v/s thickness of BCP

At first sight increasing of the luminance for device with very thin BCP layer looks strangely, but it can be explain with the island structure of thin layer. On one hand the islands are enough great to confine the holes (due to the high hole barrier from 0.7 eV at the EML/HBL (Fig.29) thus improving the recombination at the EML/BCP interface, but on the other hand they aren't enough dense to cause materially decreasing of the electric field yet.

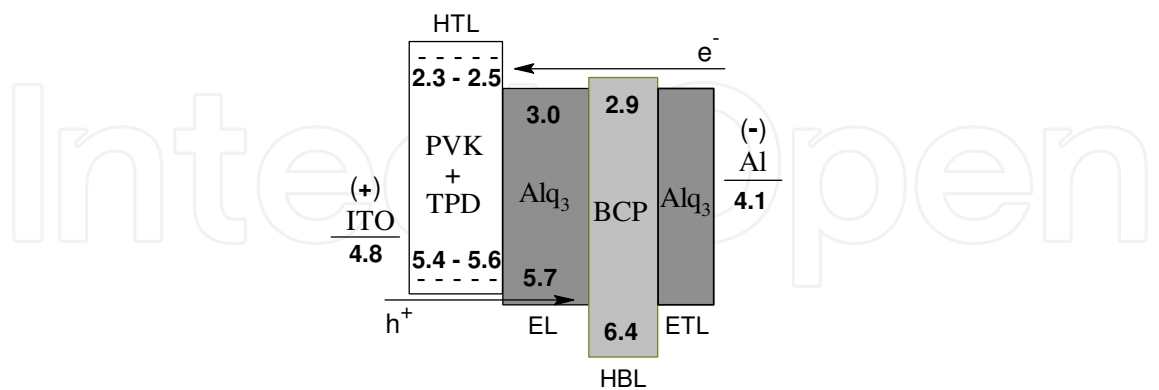


Fig. 29. The energy band diagram of the investigated OLEDs.

Khalifa et al. (2004) estimated that the diffusion length of holes in BCP probably lies in the 15-20 nm range. Thicker BCP layers lead to a decrease of luminance which could be attributed to a decrease of electron density arriving at the Alq<sub>3</sub>/BCP interface and thus to a degradation of the carrier balance. The comparison of the results obtained for devices with BCP/Alq<sub>3</sub> and BCP only, at equal thicknesses of BCP, shows more than 2 times higher

current efficiency and 70-100% higher power efficiency at approximately equal luminance for the devices with Alq<sub>3</sub> as ETL. Obviously this is due to the higher with 0.1 eV LUMO level of BCP than that of Alq<sub>3</sub>, which make the electron injection from Al to BCP more difficult.

The crystallization of organic films in OLEDs is one factor reducing the device performance. It is well known that, because of molecular migration, an evaporated BCP film is immediately crystallized after deposition (Masumoto & Mori, 2008). That's why we investigated the surface relief profiles and roughness, of consequently deposited layers of the device with best performance PVK:TPD/Alq<sub>3</sub> (40nm)/BCP (1nm)/Alq<sub>3</sub> (15nm). The WLI images presented in Fig.30 show flat and amorphous layers structure with nearly the same roughness - RMS  $2.20 \pm 0.22$  nm for PVK:TPD/Alq<sub>3</sub> (40nm), RMS  $2.16 \pm 0.34$  nm for PVK:TPD/Alq<sub>3</sub> (40nm)/BCP (1nm) and RMS  $1.89 \pm 0.22$  nm for PVK:TPD/Alq<sub>3</sub> (40nm)/BCP (1nm)/Alq<sub>3</sub> (15nm). It is a prerequisite for good performance.

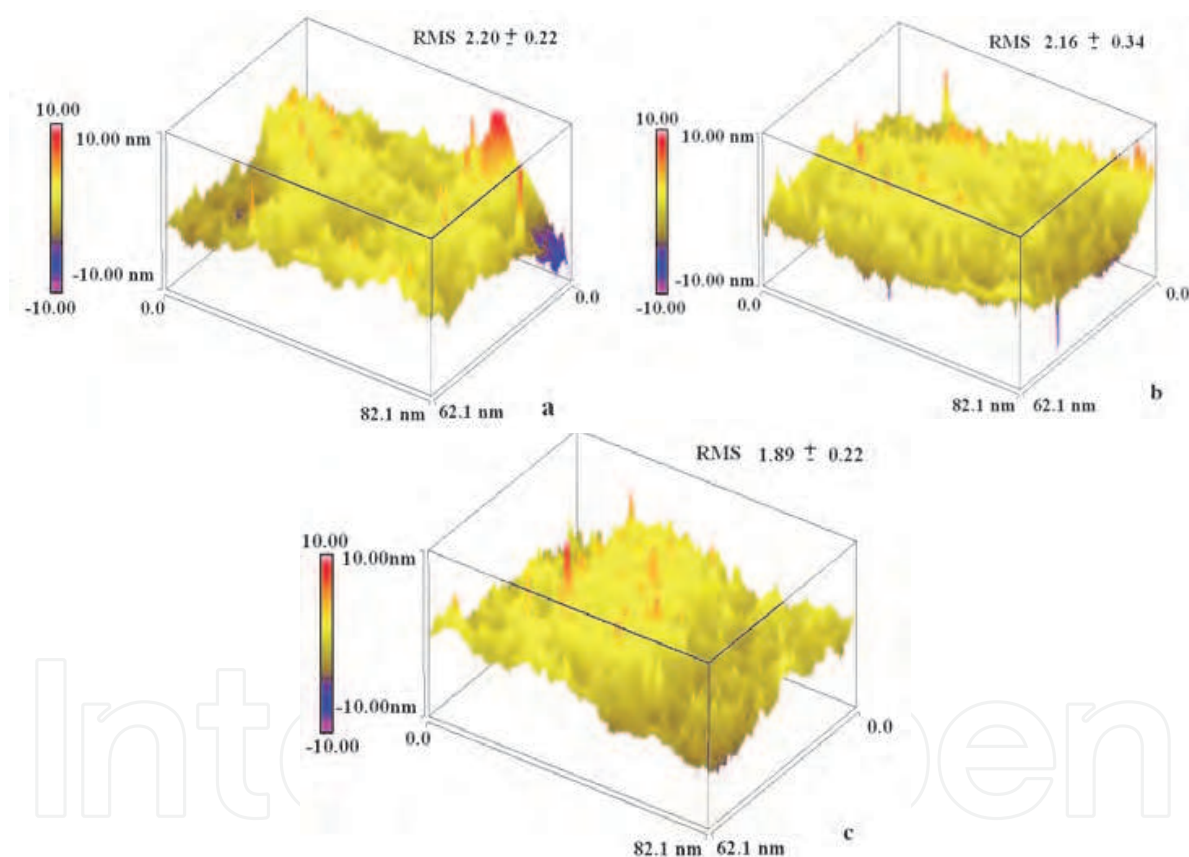


Fig. 30. Surface relief profiles, obtained on White Light Interferometer MicroXAM S/N 8038 of: a) PVK:TPD (31 nm)/Alq<sub>3</sub> (40 nm); b) PVK:TPD/Alq<sub>3</sub> (40 nm)/BCP (1 nm); c) PVK:TPD (31 nm)/Alq<sub>3</sub> (40 nm)/BCP (1 nm)/Alq<sub>3</sub> (15 nm)

Becker et al. (2007) in their research of the influence of thermal annealing of BCP and Alq<sub>3</sub> (used as exciton blocking layers) on characteristics of organic photovoltaics were found that BCP is more susceptible to heat and oxygen than Alq<sub>3</sub>. They observed that visible on a macroscopic level crystals of BCP were appeared at temperature of 100°C while Alq<sub>3</sub> even at 300°C, in open air, formed only minor pinpoint crystals. In our case probably that is the

reason causing the better performance of devices containing additional ETL of Alq<sub>3</sub>. OLED with improved efficiency 4.3 cd/A more than twice that of the undoped OLED (1.8 cd/A) by doping BCP into Alq<sub>3</sub> as an ETL and HBL was fabricated by Wu et al. (2003). Our results for efficiencies from 7.2 up to 9.6 cd/A in dependence on the thickness of BCP are quite promising.

In conclusion it can be said that BCP with its deep HOMO level (6.4 eV) is a good hole blocking layer. The influence of HBL in confining the carriers and excitons was clearly evidenced by a strong increase of the device efficiency. BCP offers possibilities to optimize the architecture of the OLED thus improving significantly the performance of the devices. The better performance of the devices with BCP could be attributed to the improved hole-electron balance.

## 6. Conclusions

On the basis of synthesized novel Zn and Al complexes, successfully chosen functional layers and improved architecture experimental OLEDs with very good characteristics are developed. The results reveal a new approach to the design and preparation of high-performance luminescence materials for the development of full-color flexible displays, new class energy-saving solid state light sources.

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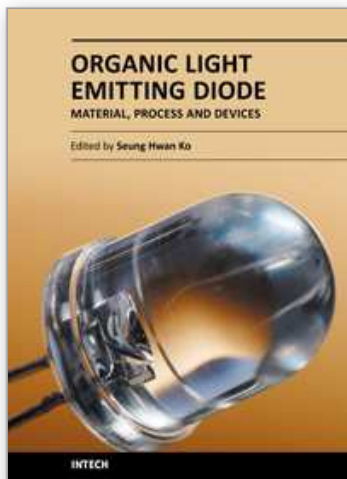
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## **Organic Light Emitting Diode - Material, Process and Devices**

Edited by Prof. Seung Hwan Ko

ISBN 978-953-307-273-9

Hard cover, 322 pages

**Publisher** InTech

**Published online** 27, July, 2011

**Published in print edition** July, 2011

This book contains a collection of latest research developments on Organic light emitting diodes (OLED). It is a promising new research area that has received a lot of attention in recent years. Here you will find interesting reports on cutting-edge science and technology related to materials, fabrication processes, and real device applications of OLEDs. I hope that the book will lead to systematization of OLED study, creation of new research field and further promotion of OLED technology for the bright future of our society.

### **How to reference**

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Petia Klimentova Petrova, Reni Lyubomirova Tomova and Rumiana Toteva Stoycheva-Topalova (2011). Organic Light Emitting Diodes Based on Novel Zn and Al Complexes, Organic Light Emitting Diode - Material, Process and Devices, Prof. Seung Hwan Ko (Ed.), ISBN: 978-953-307-273-9, InTech, Available from: <http://www.intechopen.com/books/organic-light-emitting-diode-material-process-and-devices/organic-light-emitting-diodes-based-on-novel-zn-and-al-complexes>

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