

Highly Efficient p-i-n Type Organic Light-emitting Diodes Using Doping of the Transport and Emission Layers

Desta Gebeyehu

Addis Ababa University, Ethiopia, P.O.Box: 1176, Addis Ababa, Ethiopia

E-mail address: dgebeyeh68@gmail.com

ABSTRACT

We demonstrate high-efficiency organic light-emitting diodes (OLEDs) by incorporating a double as well as triple emission layers into *p-i-n*-type device structures based on vacuum deposition technique. The term *p-i-n* means here a layer sequence in the form *p*-doped layer, intrinsic layer and *n*-doped layer. Both predominantly hole transporting material (TCTA) and an exclusively electron transporting host material (TAZ) are doped with the green phosphorescent dye tris(phenylpyridine)iridium [Ir(ppy)₃]. The intrinsic and doped transport and emission layers are formed using a high vacuum controlled co-evaporation deposition technique. As results, high efficient light emission is obtained in double emission system. For double emission system, a power efficiency of 68 lm/W and peak external quantum efficiency of 20 % are achieved at 100 cd/m² and at an operating voltage of 3.0 V. In addition, impressive characteristics of white OLED has been achieved in doped red and green phosphorescent dopants {NPB:Ir(MDQ)₂(acac) and TCTA:Ir(ppy)₃} and blue-fluorescent dye (Spiro-DPVBi). As a result, a power efficiency of 14.4 lm/W is obtained at a driving voltage of 3 volt and a luminance of 1000 cd/m² in stacked white OLEDs.

Key words: *p-i-n* structure, doped charge transport layers, doped emission layers, phosphorescent OLEDs

INTRODUCTION

The reports of Tang and Van Slyke (1987) first and later of Burroughes *et al.* (1990) on electroluminescence from thin organic films made of small-molecular weight molecules and conducting polymers, respectively, opened a new field of research. Solution processed polymer OLEDs provide an attractive alternative to small

molecule devices, mainly due to their significantly reduced production cost. Fabrication of small molecule OLEDs normally requires the use of vacuum deposition techniques which are relatively expensive, especially if large substrates were used. One advantage of using vacuum evaporation processes, however, is that the structuring of the emissive layer is achieved relatively easily with shadow masks. For solution processed polymers the

situation is more complicated to define the required pixel structure in the emissive layer.

The working principle of light emitting diodes is based on the generation of excitons. Excitons are created when electron and hole meet each other in the active layer of the light emitting diode. According to the quantum mechanical rules of the momentum addition (i.e. quantum statistics), 25% of all excitons created in this way were singlets and 75% are triplets. In theoretical physics, a singlet usually refers to a one-dimensional representation (e.g. a particle with a vanishing spin). Whereas, a spin triplet is a set of three quantum states of a system, each with total spin $S=1$. The process of charge injection and recombination in OLEDs (Tang and Van Slyke, 1987) results in the generation of singlets and triplets. Furthermore, high efficiency electro-phosphorescent organic light-emitting diodes using phosphorescent dyes have demonstrated the prospect of obtaining devices with internal quantum efficiencies of 100% through radiative recombination of both singlet and triplet excitons (Baldo *et al.*, 1998).

Most widely used approach to achieve white light is a multilayer structure where simultaneous emission of light from two or more separate emitting layers with different emission colors results in white light. This technique is based on the consecutive deposition or co-evaporation of different emitting materials and control of the exciton recombination zone. In this structure often a higher energy emitting

host (donor) materials is doped with lower energy emitting guest (dye, dopant or acceptor) materials to cause energy transfer from the host to the guest. Thereby, Iridium complexes behave as Red, Green and Blue: RGB guest phosphorescent emitters. Organic light-emitting diodes especially the white OLEDs (Gather *et al.*, 2011) with efficient features such as lightweight, potentially flexible, cheap-to-fabricate, fast response time, wide viewing angle and highly energy-efficient lighting and display devices offer one solution in alternative energy lighting and display applications (Wu *et al.*, 2005).

A great deal of progress has been made in organic electroluminescent (EL) materials and devices in terms of synthesis, development, and application of high mobility electron transport and hole transport materials as well as emission layers with high efficiency emitter dopants as a means to improve OLED performance. Figure 1 shows the principle of operation of multilayer OLEDs. The operation principle of organic light emitting diodes comprises four consecutive fundamental steps: (1) opposite sign charge carrier injection, (2) charge carriers transport, (3) generation of excitons, and (4) radiative exciton decay leading to emission of light. The basic OLED cell structure consists of a stack of thin organic layers sandwiched between a transparent anode and a metallic cathode. The anode injects holes into the first organic layer referred as the "hole injection layer (HIL)", while the cathode injects electrons into its adjacent electron injection

layer (EIL). In addition to the hole injection layer the basic OLED cell structure also comprises a “hole transport layer (HTL)”, an “emissive layer (EML)” and an “electron transport layer (ETL)”. When an appropriate voltage (typically a few volts) is applied to the cell the injected positive and negative charges recombine in the emissive layer to produce light that is electroluminescence (Kido *et al.*, 1995; Baldo *et al.*, 1998).

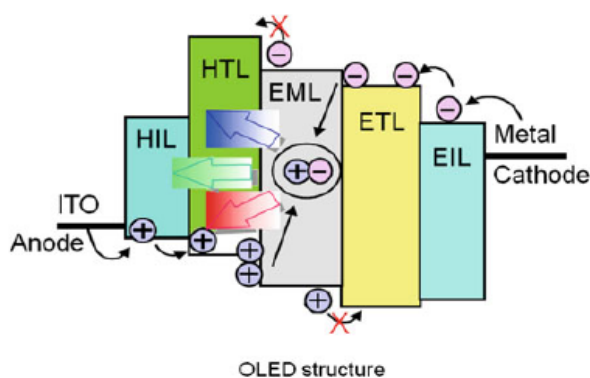


Figure 1: Principle of operation of the multilayer structure OLEDs

Recent reports introduced (Zhou *et al.*, 2001; Zhou *et al.*, 2002) that controlled electrical doping of the transport layers is a key technique for the realization of efficient OLED devices. Thereby, both the p-doped and n-doped regions extend into the bulk of the device. These devices with a doped hole transport layer (HTL) and a doped electron-transport layer (ETL) show remarkably improved properties. Because, the doping of the transport layers leads to (i) thin space charge layers at the contacts and consequently efficient tunneling injection, (ii) to

low voltage drops in the transport layers due to their high ohmic conductivity. Therefore, a high-carrier injection level can be achieved without a matching of the electrode work functions. The objective of this work was to demonstrate high-efficiency organic light-emitting diodes by incorporating a double emission layer (D-EML) or even triple into *p-i-n*-type device structure based on vacuum deposition technique and contribute to a general understanding of the potential applications of the cost-effective OLED lighting and displays.

MATERIALS AND METHODS

Materials are a critical factor for both efficiency and lifetime, the utilization of new materials has allowed revolutionary improvements in OLED efficiency (Pfeiffer *et al.*, 2003; Walzer *et al.*, 2007). Organic light-emitting diodes are ultra thin, large-area light sources made of thin-film organic semiconductors sandwiched between two electrodes and at least one of the two electrodes must be transparent to enable a light emission perpendicular to the substrate. Generally high work function (~ 4.8 eV), low sheet resistant ($> 50 \Omega/\square$) and optically transparent indium tin oxide (ITO) is used as an anode, while the cathode is a low work function metal such as Ca, Mg, Al. Figure 2 shows the organic materials used in this study. State-of-the-art small molecule-based OLEDs consist of various layers, each layer having a distinct functionality. These films are prepared by thermal evaporation in high vacuum or organic vapor

phase deposition. Thus, OLEDs are double charge injection devices, requiring the simultaneous supply of both electrons and holes to the electroluminescent material sandwiched between two electrodes as shown in Figure 1.

The fabrication of OLEDs was described as follows: All OLEDs reported here are fabricated by thermal evaporation of different organic layers onto 25 mm by 25 mm pre-cleaned indium tin oxide (ITO)

coated glass substrates (TFD, Thin Film Devices Inc., Anaheim) $< 50 \Omega/\square$ in an ultrahigh vacuum multi-chamber system at a base pressure of 10^{-8} mbar. That means electron and hole injection, transport, and blocking layers as well as emission layers and 100-nm-thick aluminium cathode layer were deposited on pre-cleaned ITO substrate in high vacuum environment. On the other hand, a 40 nm thick layer of poly (ethylene dioxythiophene):

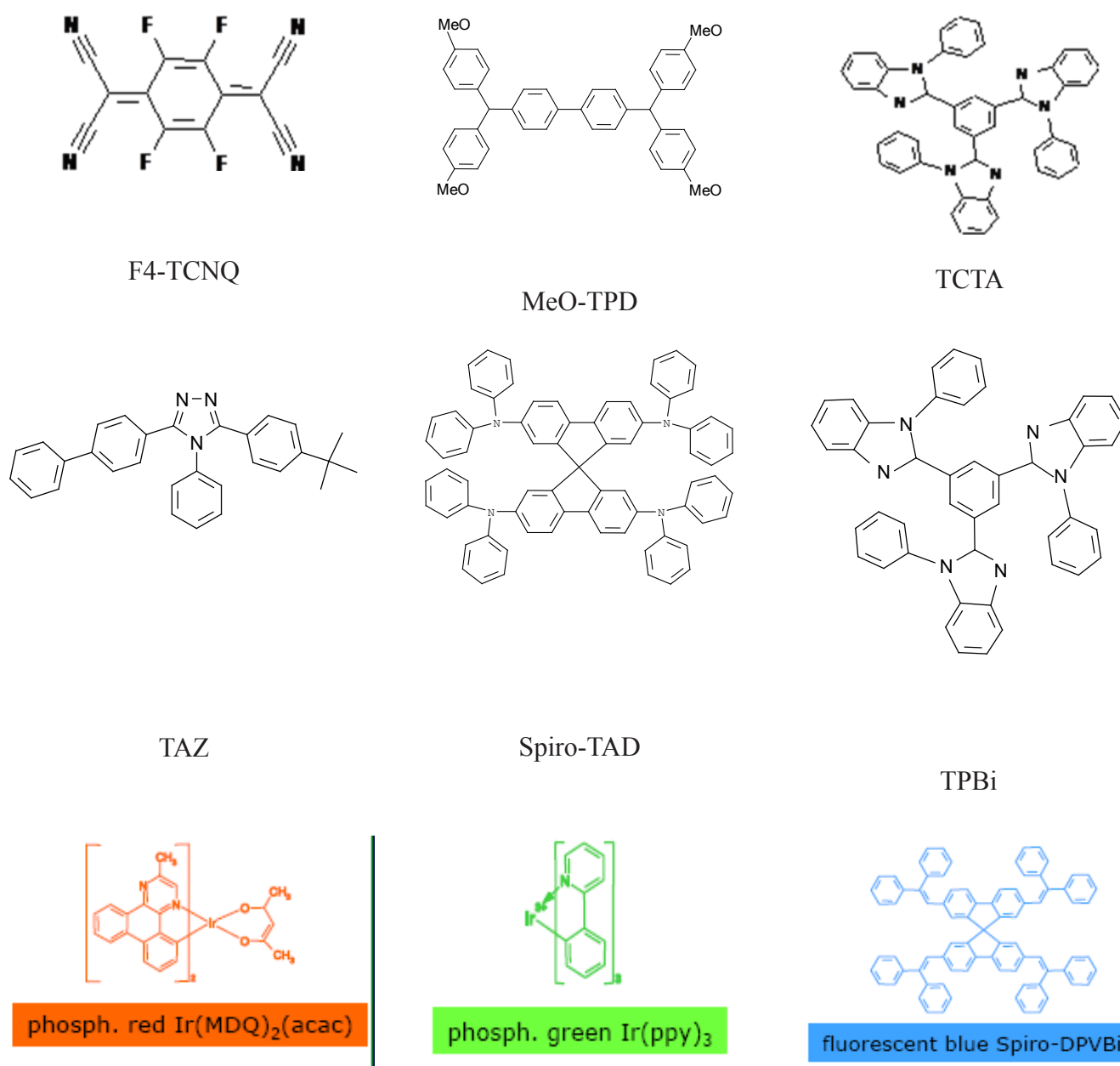


Figure 2: The molecular structures of the materials used in device fabrication of OLEDs

poly(styrene sulfonic acid) (PEDOT:PSS) film was spin-coated on ITO at 3000 rpm and at room temperature under ambient conditions. The evaporation rate of matrix materials and dopant can be controlled independently by measuring them with two separate quartz thickness monitors, allowing the doping ratio to be adjusted. The typical deposition rates are $0.1 \text{ \AA/s} - 1 \text{ \AA/s}$ and 1 nm/s for the different organic materials and metal electrode, respectively. The thickness of the organic and the cathode layers are monitored independently in situ by oscillating quartz thickness monitors.

The active area of the devices defined by the overlap of the ITO and the Al electrodes. The typical active area of OLEDs was 3 mm^2 . The current-voltage (I-V) and luminance-voltage (L-V) characteristics of the OLEDs are simultaneously measured in-situ under vacuum conditions with a Keithley Source Measure Unit SMU236 programmable voltage-current source and a calibrated photodiode, with the luminance (i.e, brightness) obtained by mounting the calibrated silicon photodiode above the OLEDs to detect the light emitted in forward direction through the transparent ITO substrate. The setup is calibrated by comparison with direct luminance measurements using a Minolta CS-100A luminance meter. The quantum efficiency is calculated under the assumptions that the emission pattern is Lambertian and electroluminescence (EL) spectra are angle independent.

RESULTS AND DISCUSSION

Figure 3 shows schematic device structure of D-EML *p-i-n* OLED (a) and fabricated sandwiched green OLED (b). The efficiency of OLEDs is characterized by power efficiency (lm/W) or current efficiency (i.e. candela per ampere, cd/A) and external quantum efficiency (%). Accordingly, the two device structures are shown as follows:

A: ITO/F4-TCNQ: MeO-TPD(1:50, 100 nm)/ Spiro-TAD(10 nm)/ 8.5%Ir(ppy)₃ : TCTA (5 nm)/8.5%Ir(ppy)₃ : TAZ (10 nm) /Bphen(10 nm)/Cs :Bphen (50 nm)/Al(100 nm), and

B: ITO/PEDOT:PSS(40 nm)/F4-TCNQ: MeO-TPD(1:50, 100 nm)/Spiro-TAD(10 nm)/ 8.5%Ir(ppy)₃ : TCTA (5 nm)/8.5%Ir(ppy)₃ : TAZ (10 nm) /Bphen(10 nm)/Cs :Bphen (50 nm)/Al(100 nm).

PEDOT:PSS layer spun on ITO films was used to improve the substrate smoothness, and the other important role was that this film has approximate work function with ITO anode, which would be good for hole injection due to the lower height of injection barrier. Thereby, a maximum external quantum efficiency (EQE) of 20% is obtained with a 40 nm PEDOT:PSS intermediate layer, 5 nm predominantly hole-transporting emission layer with TCTA as a host and a 10 nm predominantly electron-transporting emission layer with TAZ as a host and BPhen for the interlayer at the electron injection side.

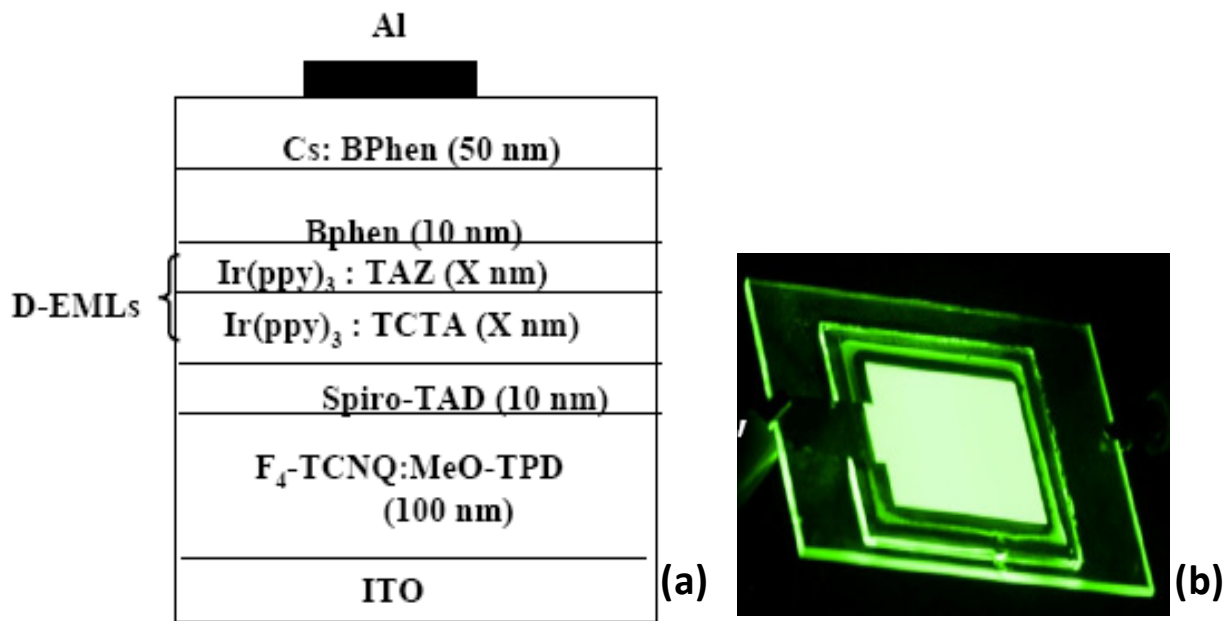


Figure 3: Schematic device structure of D-EML *p-i-n* OLED (a) and fabricated sandwiched green OLED (b). The D-EML system comprising a layer of hole transporting host, TCTA doped with 8 wt.-% of Ir (ppy)₃ and a layer of an electron transporting host like TAZ doped with the same concentration of Ir (ppy)₃.

The resulting current density-voltage and luminance-voltage characteristics of *p-i-n* type phosphorescent double emission layer (D-EML) for devices A and B are presented in Figure 4. As shown in Figure 4(a), both devices exhibited almost the same lower turn-on voltage of 2.4 V for the current. Probably, the turn-on voltage for the current may not be influenced significantly by PEDOT:PSS layer. Because, the turn-on voltage of an OLED is essentially determined by photon energy of the emissive species (emission color) and several additional factors, such as thermal relaxation of energy of excited states (energy for Stokes-shift), effective injection barriers at anode/organic, cathode/organic, and organic/organic interfaces, and potential drops due to charge transport.

Since the voltage-luminance characteristic is one of the most important parameters in evaluating the performance of OLEDs, the luminance of the green-emitting devices is shown as a function of applied bias in Figure 4(b). As it was briefly mentioned above, interfaces generally dominate the driving voltage and much effort had been made to improve interfaces, i.e., reducing the injection barriers in OLEDs for the purpose of lowering the driving voltage, which is directly connected with the increase in power efficiency. Interestingly, both devices (i.e. A and B) are exhibiting extremely low turn-on voltage (2.7 V and 2.8 V, respectively) for the luminance. On the other hand, both devices (i.e. device A and B) showed almost the same luminance of 100 and 1000 cd/m² at a voltage of 2.9 and 3.3 V, respectively. However, the physical reason of it is

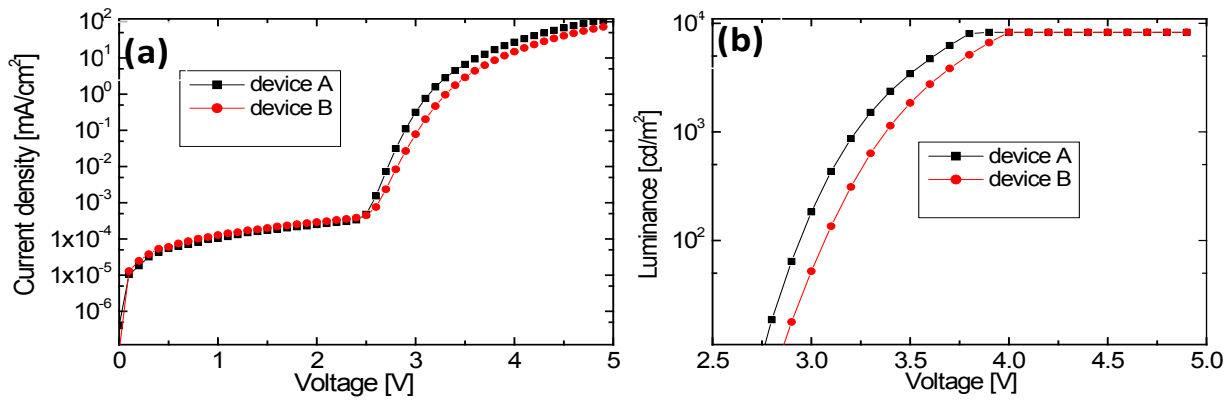


Figure 4: Influence of the electron transporting and hole-blocking capability of TAZ or Bphen on (a) current density-voltage and (b) luminance-voltage characteristics of two similar device structures (i.e. without and with intermediate layer of PEDOT:PSS, see the details in the text) with Spiro-TAD as hole-transporter and electron-blocker layer.

not clear yet. We observed very high luminance at low driving voltage for both devices. As shown in Fig. 4(b), saturated luminances have been observed with increasing driving voltage (> 4 V) for both devices. As can be seen from the device structures, both devices have the same emitter layer thickness (i.e. 5 nm predominantly hole-transporting emission layer with TCTA and 10 nm predominantly electron-transporting emission layer with TAZ, together 15 nm emission layer). Hence, this narrow emitter layer thickness (i.e. 15 nm) may lead to a higher-quenching probability by migrated cesium (Cs) atoms because the Cs atoms are able to diffuse into ease in the organic materials (i.e. emission layers). Furthermore, both devices exhibited the same maximum luminance of 8458 cd/m² at a lower driving voltage (i.e. 4.2 V). The above results confirmed that Spiro-TAD as hole-transporter and electron-blocker, and Bphen, TAZ as electron transporters and hole-

blockers provide nearly complete insulation of the emission layer from the conductive dopants, as well as a confinement of both carriers and excitons in this region. Our results indicate that an enhancement in electron mobility of an electron transporting and hole blocking buffer layer decreases the operating voltage significantly.

The current efficiencies (a) and power efficiencies (b) versus driving voltage characteristics of green emitting *p-i-n* type phosphorescent double emission layer (D-EML) OLED devices are shown in figure 5 below: A power efficiency of 63 lm/W (corresponding to a current efficiency of 58 cd/A) is obtained at 100 cd/m², falling to 53 lm/W (corresponding to a current efficiency of 55 cd/A) at 1000 cd/m² an operating voltage of 3.2 V for a device A. Whereas for the device B, a power efficiency of 68 lm/W (corresponding to a current efficiency of

67 cd/A) is obtained at 100 cd/m² and an operating voltage of 3.0 V, falling to 60 lm/W (corresponding to a current efficiency of 64 cd/A) at 1000 cd/m² and an operating voltage of 3.4 V. It was found that the surface roughness of the ITO glass substrate exerts a considerable influence onto the thin-film properties of the vacuum deposited organic films by inducing thin-film layer in-homogeneities (Yonda *et al.*, 2000) and this could be improved significantly using an intermediate layer of PEDOT:PSS or polymeric smoothing thin-film layer. Hence, device B (with PEDOT:PSS intermediate layer) shows the highest efficiency with a maximum power efficiency of 71 lm/W at a driving voltage of 2.8 V compared to device A (66 lm/W at 2.7 V). The improved performance is believed due to higher work function (Cai *et al.*, 2011), low refractive index, and decreased surface roughness of PEDOT:PSS vs ITO, and to ohmic hole injection from PEDOT:PSS to hole transport layer (i.e. p-MeO-TPD). PEDOT:PSS was used mainly

as a buffer layer between the ITO and the organic layers to improve hole injection or extraction in OLEDs (Cai *et al.*, 2011). Indeed, we have observed high current and power efficiencies at low driving voltages (2.7 V – 3.0 V) for both devices, where the current and power efficiencies are decreased drastically with the increasing driving voltage (> 3.8 V) due to noticeable quenching effects of either triplet-triplet (T-T) annihilation or saturation of the excited state (Baldo *et al.*, 2000; D'Andrade *et al.*, 2001). Our results show significantly improved device efficiencies (i.e. peak external quantum efficiency of 20 % and corresponding current efficiency of 67 cd/A) compared to other reported D-EMLs green phosphorescent OLEDs that show peak external quantum efficiency of about 12.6% and corresponding current efficiency of 44.3 cd/A (Zhou *et al.*, 2002). Moreover, it has been reported that an electrophosphorescent device based on iridium complex with a peak current efficiency of 28.5 cd/A

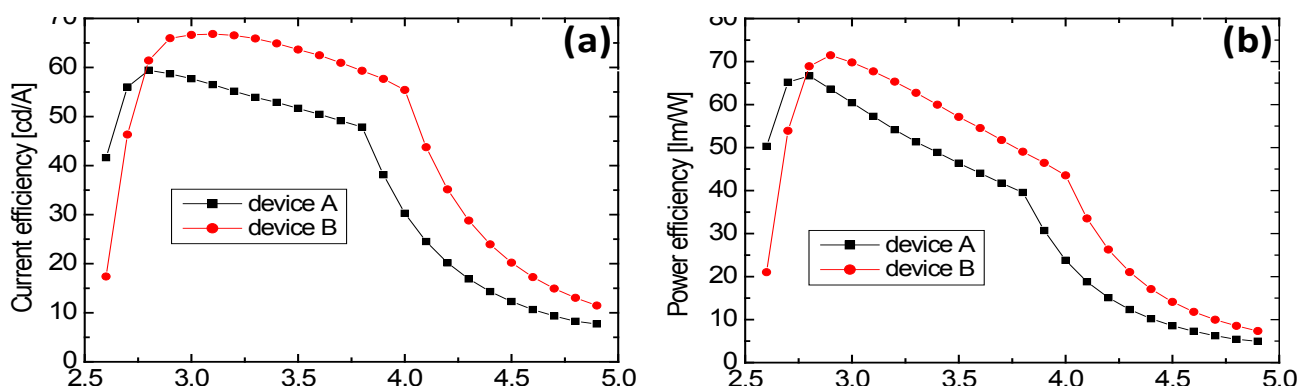


Figure 5: The current efficiencies (a) and power efficiencies (b) versus driving voltage characteristics of the devices A and B with almost similar structures (i.e. without and with PEDOT:PSS intermediate layer, see the details in the text) for a D-EML *p-i-n* OLED.

and a power efficiency of 11.2 lm/W, respectively, at 20 mA/cm² (Zhang *et al.*, 2008).

Most widely used approach to achieve white light is a multilayer structure where simultaneous emission of light from two or more separate emitting layers with different emission colours (Yook *et al.*, 2009) results in white light (Figure 6). This technique is based on the consecutive deposition or co-evaporation of different emitting materials and control of the exciton recombination zone. The interlayer between fluorescent blue-emitting layer and complementary phosphorescent emitting layer plays an important role in the efficiency, brightness, and lifetime since it prevents the single energy transfer from the blue fluorescent emitter to the complementary phosphorescent emitters and minimizes the exchange of energy losses. For this study, mixed interlayer (Schwartz *et al.*, 2006) with hole-predominated material and electron-predominated material (i.e. 3 nm TCTA:TPBi) has been used as an interlayer.

Stacked white OLEDs usually produce higher brightness and efficiency than those of conventional white OLEDs and can be a good candidate as a light source because double or even triple current efficiency can be obtained in such devices as compared to the single emitter device. It is well known that phosphorescent emitter systems show significantly higher quantum efficiency as compared to fluorescent emitters, as they harvest singlet and triplet excitons. Due to this fact, the theoretical limit for the internal quantum efficiency is 100%.

We have successfully demonstrated an efficient OLED by employing two adjacent phosphorescent and fluorescent EMLs. Figure 6 shows schematic diagram of multi-emissive layers type white OLED (a) and fabricated sandwiched white OLED (b) for this device structure. The phosphorescent dopants namely, [Ir(MDQ)₂(acac)] for red, [Ir(ppy)₃] for green and fluorescent dye [Spiro-DPVBi] for blue emissions, are each doped in separate hosts that form a stepped progression of highest occupied and lowest unoccupied molecular orbitals. This structure effectively broadened exciton generation region. The best power efficiency achieved with this approach was 14.4 lm/W at a driving voltage of 3 volt and at a brightness of 1000 cd/m². On the other hand, triplet emitter based p-i-n OLEDs have been reported already, exhibiting peak power efficiency of 11 lm/W at a brightness below 1000 cd/m² (D'Andrade *et al.*, 2003).

Conclusions

A very high-efficiency and low operating voltage p-i-n phosphorescent OLEDs have been demonstrated by doping Ir(ppy)₃ and Ir(MDQ)₂(acac) into both hole transport host and electron transport host. For D-EML green OLED, a luminance of 100 cd/m² is obtained at 3.0 V with a power efficiency of 68 lm/W and an external quantum efficiency of 20 %. Furthermore, for stacked white OLED, a power efficiency of 14.4 lm/W at a brightness of 1000 cd/m² and at a driving voltage of 3 volt was achieved. It is found that the

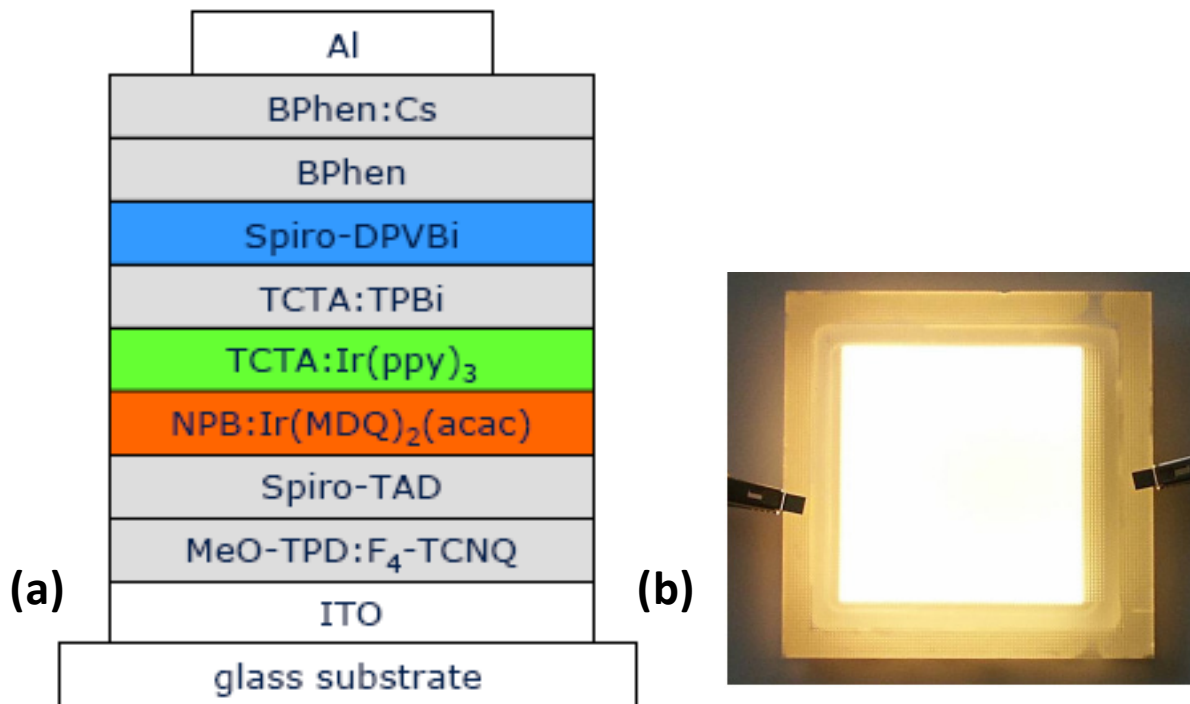


Figure 6: Schematic diagram of multi-emissive layers type white OLED (a) and fabricated sandwiched white OLED (b)

improved efficiency suggests a promising approach for low-power display and solid-state lighting devices. We also plan to achieve devices with lower operating voltage and higher power efficiency by using out-coupling enhancement techniques.

ACKNOWLEDGEMENTS

The author acknowledges the financial support of the German Secretary for Education and Science (BMBF) and Technology University of Dresden, Germany. In addition, the author thanks Prof. K. Leo, and the entire IAPP and NOVALED AG research teams at Technology University of Dresden, Germany for fruitful scientific discussions and continued collaborations.

REFERENCES

- Baldo, M.A., O'Brien, D.F., You, Y., Shoustikov, A., Sibley, S., Thompson, M. E and Forrest S. R. (1998). Highly efficient phosphorescent emission from organic electroluminescent devices. *Nature* **395** (6698):151–154.
- Baldo, M. A., Adachi, C and Forrest, S. R. (2000). Transient analysis of organic electrophosphorescence. II. Transient analysis of triplet-triplet annihilation. *Physical Reviews B* **62**(16):10967–10977.
- Burroughes, J., Bradley, D., Brown, A., Marks, R., Mackey, K., Friend, R., Burn, P and Holmes, A.B. (1990). Light-emitting diodes based on conjugated polymers. *Nature* **347**(6293): 539541.

- Cai, M., Xiao, T., Hellerich, E., Chen, Y., Shinar, R and Shinar, J. (2011). High efficiency solution processed small molecule electrophosphorescent organic light emitting diodes. *Advanced Materials*. **23**: 3590-3596.
- D'Andrade, B. W., Baldo, M. A., Adachi, C., Brooks, J., Thompson, M and Forrest, S. R. (2001). High-efficiency yellow double-doped organic light-emitting devices based on phosphor-sensitized fluorescence. *Applied Physics Letters* **79** (7): 1045-1047.
- D'Andrade, B. W and Forrest, S.R. (2003). Single-dopant p-i-n white organic light emitting devices. *SID Symposium Digest of Technical Papers* 34:967-969.
- Gather, M.C., Kohnen, A and Meerholz, K. (2011). White organic light-emitting diodes. *Advanced Materials* **23**(2):233–248.
- Pfeiffer, M., Leo, K., Zhou, X., Huang, J. S., Hofmann, M., Werner, A., and Blochwitz-Nimoth, J. (2003). Doped Organic Semiconductors: Physics and Application in Light Emitting Diodes. *Organic Electronics* **4**: 89–103.
- Schwartz, G., Fehse, K., Pfeiffer, M., Walzer, K., and Leo, K. (2006). Highly Efficient White Organic Light Emitting Diodes Comprising an Interlayer to Separate Fluorescent and Phosphorescent Regions. *Applied Physics Letters* <http://dx.doi.org/10.1063/1.2338588> **89**, 083509.
- Tang, C.W and Van Slyke, S.A. (1987). Organic electroluminescent diodes. *Applied Physics Letters*. **51** (12):913-915.
- Wu, C.C., Chen, C.W., Lin, C.L and Yang, C.J. (2005). Advanced organic light-emitting devices for enhanced display performances. *Journal of Display Technology* **1** (2): 248-266.
- Yonda, C.H., Mayer, A. B. R and Stolz, U. (2000). Surface roughness effects and their influence on the degradation of light emitting devices. *Journal of Materials Science* **35**: 5645-5651.
- Yook, K.S., Jeon, S.O., Joo, C.W and Lee, J.Y. (2009). Color stability and suppressed efficiency roll-off in white organic light-emitting diodes through management of interlayer and host properties. *Journal of Industrial and Engineering Chemistry* **15** (3):420–422.
- Yook, K.S., Jeon, S.O., Lee, J.Y. Lee K.H., Kwon, Y.S., Yoon, S.S and Yoon, J.H. (2009). High efficiency pure white organic light-emitting diodes using a diphenylaminofluorenebased blue fluorescent material. *Organic Electronics* **10** (7):1378–1381.
- Zhang, L., Chen, P., Li, B., Hong, Z and Liu, S. (2008). Highly efficient electrophosphorescence device based on iridium complexes with high efficiency over a wide range of current densities. *Journal of Physics D: Applied Physics*. **41** (245101):1-6.
- Zhou, X., Pfeiffer, M., Blochwitz, J., Werner, A., Nollau, A., Fritz, T and Leo, K. (2001). Very low-operating voltage organic light-

emitting diodes using a p-doped amorphous hole injection layer. *Applied Physics Letters* **78**(4): 410-412.

Zhou, X., Qin, D. S., Pfeiffer, M., Blochwitz, J., Werner, A., Drechsel, J., Maennig, B and Leo, K. (2002). High efficiency electrophosphorescent organic light-emitting diodes with double light-emitting layers. *Applied Physics Letters* **81**(21): 4070-4072.