The Effect of Controlled Dopant Concentration on the Performance of Blue Polymer Light-emitting Diodes

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Received December 24, 2010; Accepted February 17, 2011; Published Online February 23, 2011

The performance of a blue polymer light-emitting diodes (PLED) was significantly improved by doping a controlled amount (≤1%) of a hole transport molecule N,N′-bis-(1-naphthyl)-N,N′-diphenyl-1,1′-biphenyl-4,4′-diamine (NPB) into the emitting layer. Hole carrier mobility of the blue emitting polymer, BP105 (trade name of The Dow Chemicals Co.), increased from 5.27 × 10⁻⁷ cm²/Vs of the pristine BP105 to 1.80 × 10⁻⁶ cm²/Vs with the addition of 1% NPB in BP105. The enhanced carrier mobility greatly promoted performance of a blue PLED device with a device structure of ITO/PEDOT:PSS/BP105+x% NPB/LiF/Ca/Al. Luminance increased from 573 cd/m² to 2,720 cd/m² at 6V and efficiency increased from 1.1 lm/W to 1.6 lm/W at 1,000 cd/m² with 1% NPB in BP105. The most important improvement was an increase in the lifetime of the blue device from 80 to 120 hours at an initial luminance of 400 cd/m². We found that by choosing the appropriate dopant with good energy alignment and controlled dopant concentration, the performance of a blue PLED device could be greatly improved.

Keywords: PLED; NPB; Mobility; Lifetime.

INTRODUCTION

Organic light-emitting diodes have been studied intensively for their potential applications in flat panel displays since the early discovery of small molecule organic light-emitting diodes (OLED) and polymer light-emitting diodes (PLED). Given the ease of processing, much research effort has focused on PLED for its applications in large size display panels. However, with a simple bi-layer device structure, the high turn-on voltage and a short lifetime have always been problems for the blue PLED devices. Many approaches have been conducted to improve performance of the PLED devices such as modification of device structures, molecular structure modification of emitting polymers, and optimization of the processing parameters. In addition to the above methods, blending of different molecules into the emitting layer for different purposes has also shown efficacy for property modification of PLED devices. The blending of sensitizers with the emitting polymers has selectively altered the color of the emission light of the devices. Unfortunately, operational voltage of the devices has increased because of luminescence quenching by the emitting polymers and also due to carrier trapping of the sensitizers. The blending of inorganic salt with the emitting layer lowered the turn-on voltage of the devices through modification of the tunneling barrier in the metal-polymer-metal junction, but also induced a rough emitting layer surface by increasing an amount of inorganic salt that was not favorable to the operation lifetime of devices. The blending of metal nanoparticles improved the lifetime of the PLED devices via a quenching of the triplet states of the emitting polymers. However, turn-on voltage increased with more

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than 30 ppm of these nanoparticles in the emitting layer. In comparison with the blending of inorganic compounds with emitting polymers, the blending of organic hole transport molecules with the emitting polymers improved the efficiency of the PLED devices by balancing the carrier mobility of the emitting polymers. However, a bathochromic shift of the emission light occurred very often because of an aggregation of the dopant molecules with emitting polymers. Additionally, the operational voltage was increased because of carrier trapping by the large amount of dopant molecules. It seems that performance optimization of PLED devices, especially blue PLED devices, requires a balanced of properties such as the following:

1. a good energy alignment between different functional layers such as the hole injection layer and the emitting layer
2. a lower operation voltage through enhanced and balanced carrier mobility
3. a stable emission spectrum in a wide luminance intensity

In this study, we presented our results on the performance improvement of a blue PLED device fabricated by blending a controlled amount of NPB to the BP105 emitting polymer. A controlled amount of NPB not only lowered the operation voltage of the blue PLED device, but also increased device efficiency and prolonged device lifetime. Additionally, the emission spectrum was also very stable across a wide range of emission intensities. We measured mobility of the blue emitting polymer and its blends with NPB were measured by TOF technique. The TOF samples were about 1 µm thick. The device without NPB in BP105 is treated as the standard device throughout this paper.

RESULTS AND DISCUSSION

The device structure and energy diagram of the device are shown in Fig. 2. BP105 had a very low HOMO value (-5.8 eV), which created a large energy gap (0.6 eV) between the hole injection material, PEDOT:PSS, and the emitting polymer, BP105. The inappropriate energy alignment resulted in a large energy barrier for hole carriers to transport. Fig. 3a
showed results of current density vs. applied voltage for the blue devices with different concentrations of NPB.

Current density was enhanced by the addition of NPB. Current density for the pristine BP105 device was 23.9 mA/cm$^2$ at 6 volts and the current flow increased dramatically to 72.9 mA/cm$^2$ at 6 volts with addition of only 0.5% NPB to the BP105. The current density was further increased to 308 mA/cm$^2$ at 3% NPB, which was more than twelve times than that of pristine BP105. Evidently, the addition of NPB improved the current injection from PEDOT:PSS to the emitting layer. Monkman$^{23}$ demonstrated that doping the Ir complex to the polyfluorene emitting polymer could reduce the turn-on voltage because the Ir complex altered the potential barrier between the hole injection layer and the host polymer. The Ir complex also increased the free electron density and enhanced mobility by reducing the energy of the electron trap. As mentioned earlier, a 0.6 eV energy gap existed between the PEDOT:PSS and the pristine BP105, which created a barrier for hole to inject from PEDOT:PSS to the emitting layer. With the addition of NPB, hole carriers were able to transport between the PEDOT:PSS and the NPB because the NPB had a HOMO of 5.5 eV that was closer to the HOMO of PEDOT:PSS (5.2 eV) than that of the BP105 (5.8 eV). In other words, the blending of NPB to BP-105 assisted the energy level alignment between the anode and the emitting polymer that resulted in better carrier injection from the anode.

The current density of a device is enhanced not only by an improved energy level alignment, but also by improved carrier transport in the emitting polymer. The addition of a controlled amount of NPB to BP105 greatly improved the hole mobility of BP105. Fig. 4 shows the hole mobility of BP105 at different concentrations of NPB.

The measurement of hole mobility using time of flight technique obeyed the Poole-Frenkel form,

$$\mu = \mu_0 \exp(\beta \sqrt{E})$$

where $\mu_0$ is the zero field mobility and $\beta$ is the Poole-Frenkel factor. Hole mobility of BP105 was increased almost one order of magnitude with an NPB concentration of less than 1%. It decreased in a very sensitive manner when NPB concentration was increased to 3% although it remained higher than that of pristine BP105. It is well known that mobility in organic thin film can be affected by both trapping properties and disorder induced by additives. For high concentration additives, disorder properties play a very important role. However, for a low additive concen-

![Energy Diagram and Device Structure](image_url)
tration, trapping is probably more important than disorder properties. Stolka\textsuperscript{24} proposed a model for carrier transport between different compositions of dopant in an inert (no interaction or reaction) host system. At a very low concentration of additives, transport is dominated by the slow release of charges from the additive sites acting as traps for the carrier transport. Carrier mobility becomes smaller under such condition. As the concentration of additive is increased to a certain level (depending upon materials), the transport is dominated by hopping via the additives. Carrier mobility can be higher or lower depending upon the mobility and energy level of the additives. In the present study, we found that NPB did not act as carrier traps to reduce the carrier mobility in BP105 and NPB blends. Instead, mobility increased at a lower NPB concentration. Zero field mobility ($\mu_0$) increased from $5.27 \times 10^{-7}$ cm$^2$/Vs for pristine BP105 to $1.8 \times 10^{-6}$ cm$^2$/Vs for 1.0% NPB in BP105, which implied an increased carrier concentration, as when BP105 is blended with NPB. The increased carrier mobility at low NPB concentration had probably originated from the increased carrier concentration that overwhelmed the minor trapping effect induced by NPB. As the NPB concentration increased to 3% NPB, molecular disorder became dominant and carrier mobility decreased.

Researchers\textsuperscript{25-27} have shown the appearance of a shoulder on the main emission peak results mainly from an enhanced molecular order structure that is induced by molecular aggregation of the emitting polymers such as BP105. As the concentration of NPB in BP105 was increased, as shown in Fig. 5a, the shoulder peak at 490 nm decreased. Evidently, an elevated NPB concentration created a less-ordered structure in BP105 and resulted in decreased mobility at 3% NPB concentration. Both improved energy level alignment and carrier mobility contributed to the increased current density. This improvement resulted in lower operation voltage as seen in Fig. 3b. The pristine BP105 device had a luminance of 1,000 cd/m$^2$ at 6.7 volts; upon blending with NPB, operation voltage at 1,000 cd/m$^2$ quickly dropped to 5.1 volts with 1% NPB in BP105. Because of the improvement in current density, a blue device with very high luminance was fabricated with a ITO/ PEDOT:PSS/BP105+1%NPB/LiF/Ca/Al structure and a maximum luminance that reached 56,040 cd/m$^2$.

The efficiency of PLED devices could be improved by blending hole transport molecules\textsuperscript{21,22} into an emitting polymer. In most cases, the current density of the PLED devices was decreased because of the hole trapping effect,
which resulted in either higher turn-on, or operation voltage. In another case, the turn-on voltage of the device was improved, but current efficiency dropped and the color coordinate showed a red shift. As a result of the reduction in the operation voltage for BP105 and NPB blends, both current efficiency and power efficiency were increased. As seen in Fig. 6a, power efficiency increased 70% at 10,000 cd/m² from 0.65 lm/W for a BP105 device to 1.1 lm/W with 1% NPB in BP105. We observed very little current efficiency declined when the luminance was increased for the BP105 and NPB blends, as shown in Fig. 6b. Evidently, the addition of NPB to BP105 balanced the hole and electron mobility in the BP105 and NPB blends and resulted in very stable efficiency performance for different degrees of luminance. In addition, the CIE coordinate of the BP105 and 1% NPB blend device was also very stable at (0.16, 0.23) as shown in Fig. 5b. The emission spectrum was very stable between 6,000 cd/m² and 40,000 cd/m².

Addition of NPB to BP105 not only enhanced hole mobility and current density of the blue device, but also prevented the blue device from failure at higher current flow. We observed an increase in current density at device breakdown (Jmax) with an improvement from 1.75 A/cm² for BP105 to 3.6 A/cm² with 1% NPB in BP105 (Fig. 3a). It seemed that space charge limited current (SCLC) of the standard BP105 device was increased for BP105 blended with NPB. All the enhanced performance from NPB in BP105 improved the lifetime of the BP105 and NPB blends. Fig. 7 shows the lifetime performance of the blue devices at 400 cd/m² under DC driving condition. Operation lifetime for the BP105 device was about 80 hours at 400 cd/m², which was prolonged to 120 hours as we blended 1% NPB in BP105 - a 50% increase over the standard device.

CONCLUSIONS

We demonstrated an improved blue PLED device by blending 1% of NPB with BP105. Maximum luminance of the blended device reached 56,040 cd/m². In the present study, a controlled amount of NPB did not behave as a hole-trapping site, instead it enhanced the hole transport property of BP105. NPB not only increased the hole mobility of BP105, but it also improved both the current density and the power efficiency of the blue device. In addition, the lifetime was increased by a factor of 50% when using this method.
ACKNOWLEDGEMENT

The authors are grateful to the RiTdisplay Corp. for supplying the blue emitting polymer - BP105. Financial support from National Science Council under project number NSC 98-2113-M-030-002-MY3 also is appreciated.

REFERENCES