

INFLUENCE OF TETRABUTYLAMMONIUM HEXAFLUOROPHOSPHATE (TBAPF₆) DOPING ON THE PERFORMANCE OF POLYMER LIGHT EMITTING DIODES (PLEDs) BASED ON PVK:PBD BLEND FILMS

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ABSTRACT

The effect of tetrabutylammonium hexafluorophosphate (TBAPF₆) doping on the electrical and electroluminescence properties of single-layer polymer light emitting diodes (PLEDs) with ITO/PVK:PBD/Al structure were investigated where indium tin oxide (ITO) was used as anode, poly(9-vinylcarbazole) (PVK) as polymeric host, 2-(4-biphenyl)-5-phenyl-1,3,4-oxadiazole (PBD) as electron-transporting molecule and aluminium (Al) as cathode. The emitting layers were spin-coated onto the ITO-coated glass substrates. It was found that the doped devices underwent transition at the first voltage scan where the current increased drastically at certain voltage. After the transition, the threshold voltage for current injection as well as the light emission decreased significantly as compared to undoped device. The turn on voltage of the doped device was 5 V. The significant improvement was attributed to the reduction of both electron and hole injection energy barriers caused by accumulation of ionic species at the interface. In conclusion, doping of TBAPF₆ has been shown to be a valuable approach to reduce the turn-on voltage and increase the EL intensity of PLEDs.

INTRODUCTION

Organic light emitting diodes (OLEDs) using either small molecules or polymers, have attracted considerable interest due to their easy processability, flexibility, low cost, low operating voltages, wide viewing angles, tunability of the color emission, fast response time, and ease of forming large area [1-2]. Generally, OLED is a thin film device in which the emitting organic material is sandwiched between two electrodes. It will emit light when current is passed through it.

Commercial applications of OLEDs require maximum brightness, high power efficiency, and extended lifetimes. To meet these requirements, light emission at low turn on voltage is necessary since high operating voltage will shorten the device lifetime due to thermal aging and impurity diffusion under high electric field [3-4]. One of the approaches to reduce the turn on voltage is by insertion of a buffer layer at the interface between electrode layer (cathode and anode) and organic layer [5-7]. However, this

method may increase the production cost due to additional step in manufacturing process. It has also been reported that the incorporation of ionic species either inorganic or organic salt in OLEDs greatly enhances the charge injection [8-14]. Even so, the turn on voltage for those devices stays quite large (>10 V).

The present work reports on the influence of doping of TBAPF₆ on the electrical and electroluminescence properties of single layer PLED based on PVK:PBD blend films. In contrast to the undoped device, the doped devices that underwent transition at first voltage scan required significantly lower driving voltage and exhibited higher EL intensity. A relatively low turn on voltage of 5 V has been achieved. Ionic space charge effect was proposed to explain the significant improvement of the doped device.

EXPERIMENTAL METHOD

The host polymer PVK, having a high weight-average molecular weight of 1,100,000 g/mole, electron-transporting molecule, PBD, and organic salt, TBAPF₆ were all purchased from Aldrich Chemical Company. All materials were used as received without further purification.

The PLED with ITO/PVK:PBD:TBAPF₆(10:10:1)/Al structure was fabricated as shown in Figure 1. The ITO-coated glass substrates were etched and patterned to serve as anode. The substrates were cleaned with 2-propanol and acetone in an ultrasonic bath each for 15 minutes. PVK:PBD:TBAPF₆ in weight ratio of 10:10:1 were dissolved in 1,2-dichloroethane solution with total solid concentrations of 15 mg/mL. The solutions were then spin-coated onto the ITO surface with a typical spinning speed and time at 2000 rpm and 40 s, respectively. The polymer film thickness was 90 ± 5 nm as determined by examination of a cross section with a scanning electron microscope. Lastly, 150-nm aluminium was deposited as cathode by using electron gun evaporation technique. The emitting area was 0.07 cm². Besides, a ITO/PVK:PBD(10:10)/Al PLED with the same thickness was also made for comparison.

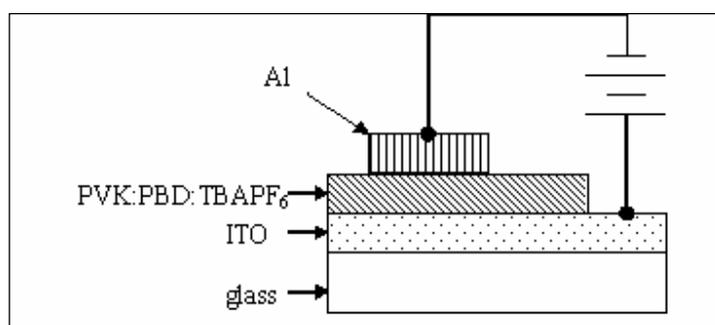


Figure 1: A PLED with ITO/PVK:PBD:TBAPF₆(10:10:1)/Al structure

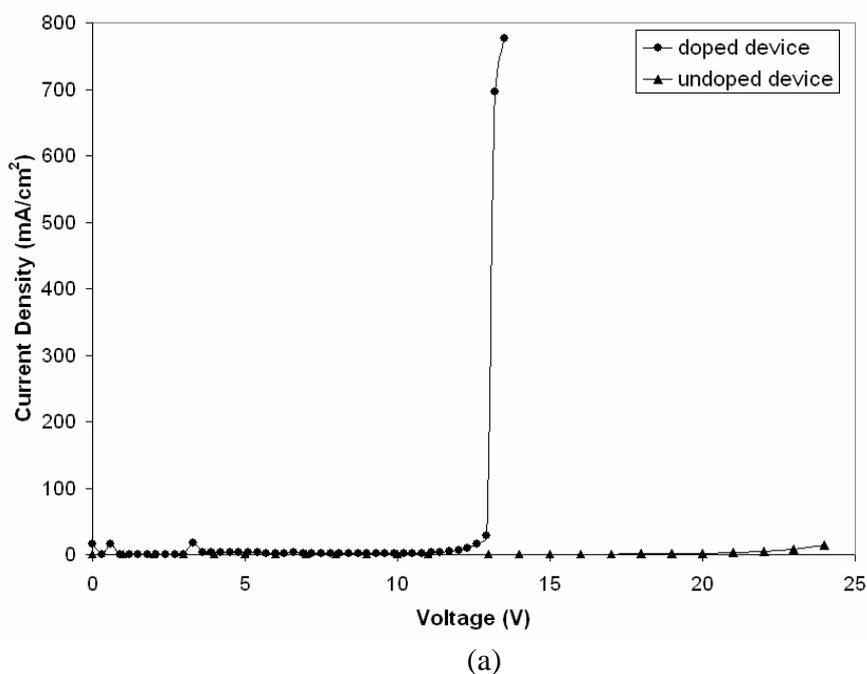
Keithley 238 source measurement unit was used to measure the electrical characteristics of the devices. The EL intensity was obtained with Ocean Optic HR2000 spectrometer.

All polymer thin films preparations and measurements were carried out at room temperature in air.

RESULTS AND DISCUSSION

Figure 2 (a) shows the current density-voltage (J-V) measurements of the devices at the first voltage scan. It was found that the current density of doped device increased drastically at applied voltage of 13 V, but not for undoped device. A unique change in the emission state was observed in this transition [13]. Multiple bright green points of light appeared at the emission area and spread quickly with applied voltage. The applied voltage was turned-off as soon as the EL extended to whole emission area. The start up of current in the first voltage scan could be attributed to the predominant contribution of ionic current. This is expected as due to the polarization of ions in organic layer to build up ions alignment near the electrodes [9-14]. After undergoing transition, the doped device exhibited a lower threshold voltage for current injection as compared to the undoped device as shown in Figure 2 (b).

Figure 3 gives the EL intensity-voltage (L-V) property of the altered doped device. The EL intensity of undoped device was very low and could not be detected due the detection limit of the equipment. The turn-on voltage is defined as the voltage applied on device when EL intensity reaches 1 cd/m^2 . A relatively low turn on voltage of 5 V was obtained from the doped device as compared to the reported organic salt-doped devices [9-14].



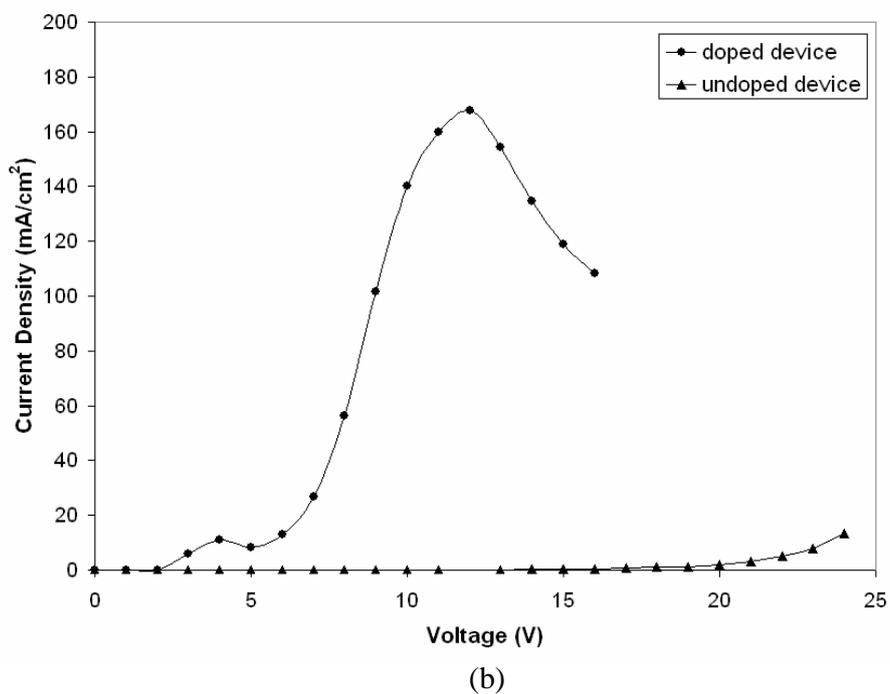


Figure 2: Current density-voltage (J-V) characteristics of doped device and undoped device for (a) the first voltage scan and (b) second voltage scan

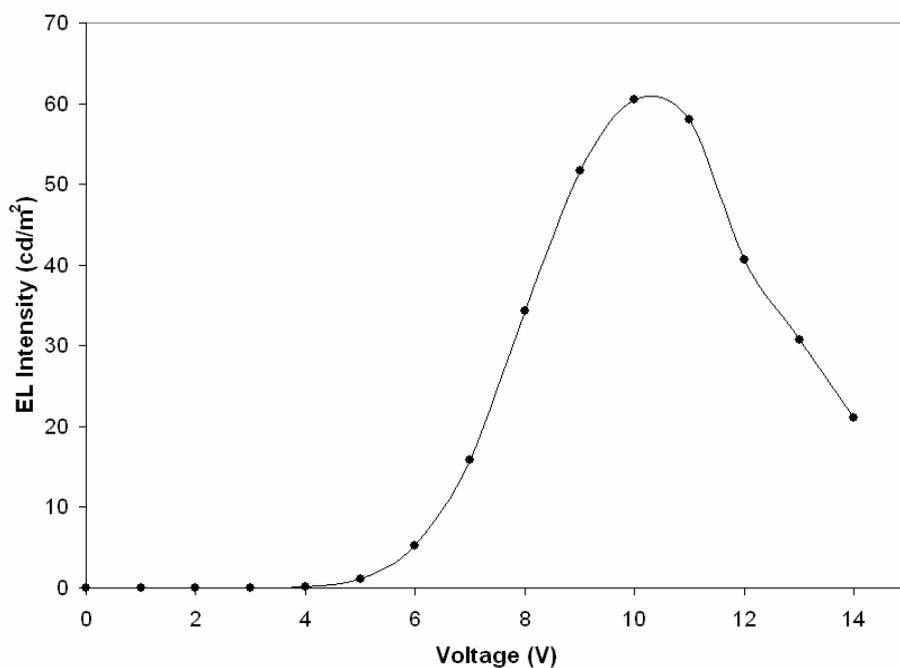
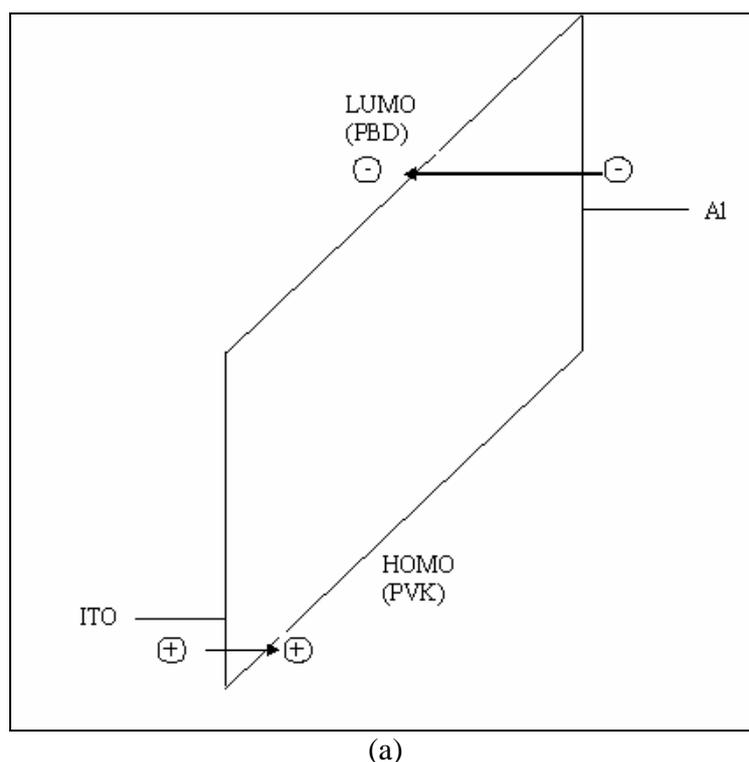


Figure 3: EL intensity-voltage (L-V) characteristics of altered doped device

These experimental results proved the strong influence of TBAPF₆ doping on the properties of single-layer PLEDs. Without doping, electrons and holes need to overcome a big injection barrier before they are able to tunnel into the polymer layer (Figure 4a). Ionic space charge effect and Fowler-Nordheim tunneling injection were used to explain the mechanism of charge injection at the polymer-electrode interface of the doped device [12]. When the doped device was biased with a sufficiently voltage at the first scan, the ions moved under the influence of the electric field to their corresponding electrodes. At the ITO anode contact, the accumulation of separated negative PF₆⁻ ions can assist hole injection from ITO to the polymer layer. At the same time, the accumulation of the positive TBA⁺ ions near the cathode aids the injection of electrons from the Al cathode to the polymer layer by reducing the tunneling barrier of the cathode interface. Since the barrier injection of electron is much higher than the hole injection (1.7 eV > 0.8 eV) [15], the enhanced current density and EL intensity in the doped devices undoubtedly indicate the enhancement of electron injection is by far dominant than hole injection.



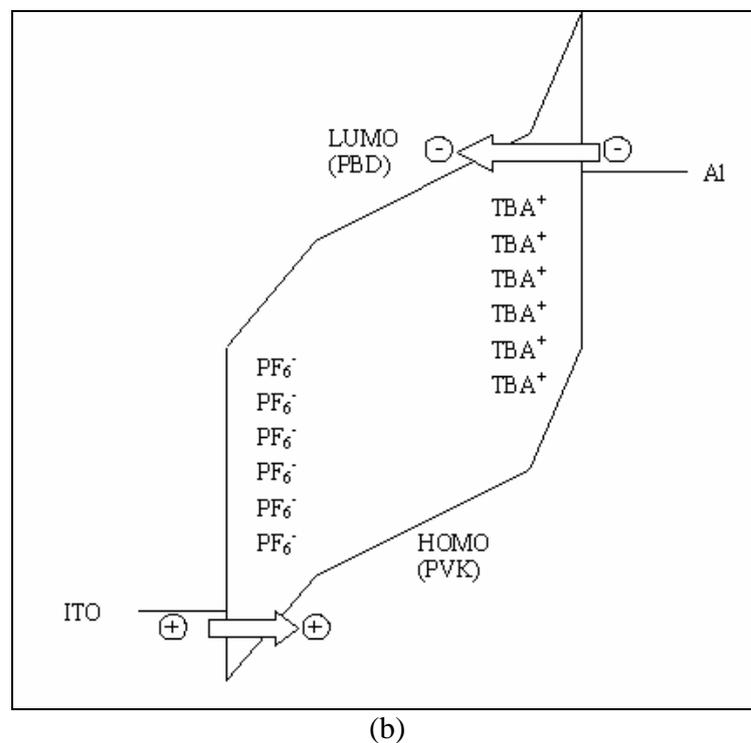


Figure 4: Schematic band diagrams for (a) undoped device and (b) doped device operating in forward bias.

CONCLUSION

The effect of TBAPF₆ doping on the electrical and electroluminescence properties of ITO/PVK:PBD/Al single-layer PLED have been examined. The doped devices that underwent transition at first voltage scan required significantly lower driving voltage and exhibited higher EL intensity compared with undoped devices. The turn on voltage of the doped device was 5 V. The significant improvement was attributed to the reduction of both electron and hole energy barriers caused by accumulation of ionic species at the interface. The operation mechanism has been illustrated comprehensively with energy schematic diagram. Therefore, TBAPF₆ doping has been shown to be a valuable approach to reduce the turn-on voltage and increase the EL intensity of OLEDs.

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