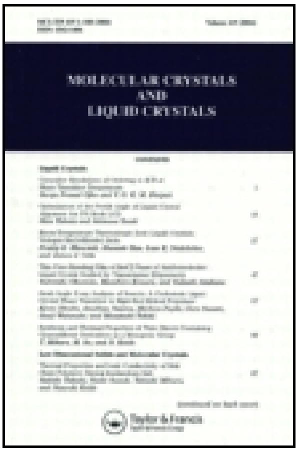

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High Molecular Weight PVK as an Interlayer in Green Phosphorescent OLEDs

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High Molecular Weight PVK as an Interlayer in Green Phosphorescent OLEDs

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Performance of high molecular weight polyvinylcarbazole (PVK) ($M_n = 1{,}100{,}000$) as an interlayer has been demonstrated in the green phosphorescent organic light emitting devices (PHOLEDs) using solution process. The PVK interlayer on the surface of PEDOT:PSS has a good film uniformity characteristic with homogenous low dissolution, thereby improving the charge injection in the emissive layer effectively. The performance of high molecular weight PVK interlayer was compared with the poly(2,7-(9,9-di-n-octylfluorene)-alt-(1,4-phenylene-((4-sec-butylphenyl)imino)-1,4-phenylene)) (TFB) interlayer. The maximum current and power efficiency values of 23.1cd/A, 9.8 lm/W were demonstrated using a PVK interlayer in the green PHOLED. The effect of high molecular weight PVK interlayer and the device structure by solution processing are provided with efficient and simple manufacturing.

Keywords Phosphorescent organic light-emitting diode; high molecular weight PVK; hole transfer materials

Introduction

Solution-processable phosphorescent organic light emitting diodes (PHOLEDs) are of increasing interest, owing to their low cost fabrication, flexibility, and higher quantum efficiency for flat-panel displays and solid-state lighting [1, 2]. The fundamental requirement for efficient operation and high luminance at low current density for PHOLEDs are realized by balanced carrier injection/extraction from the electrodes into the emitting layer. The poly(3,4-ethylenedioxythiophene)-poly(4-stylenesurfonate) (PEDOT:PSS) layer has already been proven successfully as an efficient hole-injection layer [3, 4]. However, it still does not provide a full ohmic contact to the number of OLEDs. Despite its effectiveness, further insertion of thin interlayer between PEDOT:PSS and emissive layer could improve the device efficiency and lifetime. To enhance the hole injection in the devices, several conjugated and non-conjugated polymeric materials as an interlayer have been tried so far [5, 6]. Conjugated polymers such as poly(p-phenylene vinylene) (PPV), poly(9,9′-dioctylfluorene-alt-benzothiadiazole) [7], poly[9.9-dioctylfluorene-co-(bis-N,N′-(3-carboxyphenyl)-bis-N,N′-phenylbenzidine)] (BFA) [8], poly(2,7-(9,9-di-n-octylfluorene)-alt-(1,4-phenylene-((4-sec-butylphenyl)imino)-1,4-phenylene)) (TFB) [9] have been used to improve the device efficiency. However, their disadvantages confined them to use in the practical purposes. For instance, PPV needs additional thermal

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*Corresponding author. E-mail: jhkwon@khu.ac.kr conversion step; TFB has dissolution issues during EML coating. Also, TFB's low triplet energy (2.2–2.3) causes quenching in the green PHOLEDs. In general, conjugated polymers are difficult to use in the printing process and in removing the undesired material from the substrates due to their solubility issues in several organic solvents [9]. However, non-conjugated polymers [10, 11] such as polyvinylcarbazole (PVK) [12], have hole transport chemical units attributing to improve hole injection has been used widely. PVK is comprised of a linear chain of repeated vinyl polymers with pendant carbazole side groups, arranged randomly around the same chain [13]. Morphologically, its amorphous nature may cause distortion in molecular packing due to lack of stereoregularity [14]. Therefore, use of high molecular weight PVK interlayer is advantageous as it forms the dense film and provides a good preservation characteristic during coating of an emissive layer [9]. It can bring its active group closer to each other thus making easy interaction between the π-electron systems of the large pendant groups, thereby minimizing the free energy on the surface.

In this work, performance of the green devices with a high molecular weight PVK (M_n = 1,100,000) as an interlayer has been demonstrated. To the best of our knowledge, high molecular weight PVK as an interlayer has never been implemented in solution processed PHOLEDs. For this, we have employed 1:1 mixture of 4,4′,4″-tris(N-carbazolyl)-tri-phenylamine (TCTA) and 2,2′,2″-(1,3,5-phenylene)tris(1-phenyl-1H-benzimidazole (TPBI) as the host materials blended with a dopant, tris(2-(4-toltyl)phenylpyridine) iridium ($Ir(mppy)_3$) emitting green phosphorescent light. The high molecular weight PVK as a hole transport layer shows good solubility and stability in the chlorobenzene solvent, uniform film growth characteristics without any crystallization issues, and hole transporting properties. The multilayered green electrophosphorescent OLEDs shows a luminance of 20720 cd/m^2 at 11.6V and luminous efficiency of 21.1 cd/A and 9.3 lm/W at 7.8V are demonstrated.

Experimental

OLED Fabrication

OLED devices were fabricated on the indium-tinoxide (ITO) glass having an emission area of 2 mm×2 mm with a sheet resistance of 12Ω/square. A line pattern of ITO was formed using photolithography process. Before coating with organic layers, the patterned ITO glass was cleaned by sonification in the isopropyl alcohol (IPA) and rinsed in deionized water. It was finally irradiated in a UV-ozone chamber. A 45 nm of poly(ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was spin coated on the ITO substrates and then dried using a hot plate at 120°C for 20 min to remove the solvent. A 20 nm thick high molecular weight PVK as an hole transport layer was later spin-coated on the PEDOT:PSS layer. For complete dissolution of high molecular weight PVK, 0.375 wt.% optimized value of PVK was dissolved in chlorobenzene. After spin coating, it was then baked at 120°C for 20 minutes. For TFB, 0.5 wt% in toluene (thickness of about 30 nm) was spin coated and later dried at 180°C for 30 min on a hot plate. A 20 nm thick emissive host system i.e. TCTA and TPBI (1:1) mixture was doped with 13wt% of $Ir(mppy)_3$ in 1,2-dichlorobenzene was later spin-coated on the interlayer. The spin-coated emissive layer was then baked on a hot plate at 120°C for 10 min. The spin coating and baking process were carried out in a glove box with nitrogen ambient. Subsequently, 30 nm TPBI was deposited in an organic chamber using vacuum thermal evaporation at a base pressure of 10^{-7} Torr, while LiF (1 nm) and Al (100 nm) were deposited in an adjacent metal chamber without breaking the system vacuum.

Measurements

The current density-voltage (J-V) and luminance-voltage (L-V) characteristics of the fabricated OLEDs were measured using a Keithley SMU 2635 and Konika Minolta CS-100A. Also, the electroluminescence (EL) spectra and CIE color coordinates were obtained using a Konika Minolta CS-1000A spectro-radiometer. Atomic force microscopy was carried out using a Park system (XE-100).

Results and Discussion

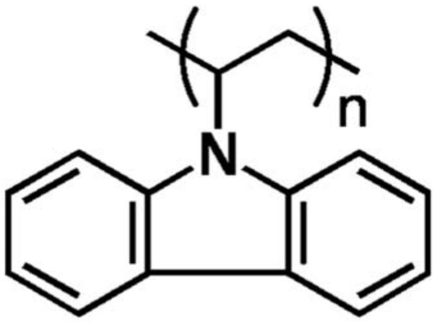
Figure 1(a) and 1(b) shows molecular structure of PVK and TFB. Figure 1(c) shows the energy band diagram of the devices. For comparison, PVK and TFB polymeric materials are employed as an interlayer in the soluble green phosphorescent OLED. TFB and PVK can effectively block the electrons at the interlayer/EML interface, which helps to enhance the electron-hole radiative recombination.

A series of solution processed devices were fabricated by using a host/guest blend system and evaluated in terms of their J-V and L-V output characteristics. The Devices A and B were fabricated using TFB and PVK interlayer, respectively. These devices were fabricated on ITO with a multilayered structure of ITO/PEDOT:PSS (35 nm)/PVK or TFB (20 nm)/ TCTA +TPBI(1:1):Ir(mppy)$_3$(35 nm)/TPBI (30 nm)/LiF(1 nm)/Al(100 nm). The dopant concentration is optimized with 13 wt% for each device in similar experimental conditions. Here PEDOT:PSS improves the hole injection in Device A as its HOMO level is 5.2 eV which is close to HOMO of TFB (5.3 eV). However, PVK HOMO level is much lower than that of PEDOT:PSS layer. Therefore, hole injection to PVK interlayer is not perfectly favorable. The operating conditions and characteristics of both the devices with fixed concentration ranges are compared and summarized in Table 1.

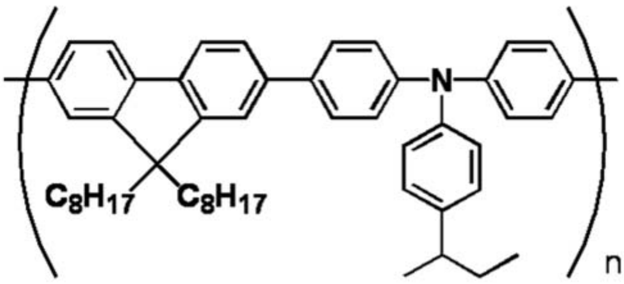
Figure 2 shows the current density-voltage (J-V) and luminance-voltage (L-V) characteristics of Device A and B. The Device A exhibited turn-on voltage of 3.0 V, which is similar to Device B. Devices A has almost same driving voltages compared to Device B. It was observed that driving voltages to reach 1000 cd/m^2 were found to be 7.6 and 7.8 V for the Devices A and B. Figure 2 also shows L-V characteristics, exhibiting maximum brightness of 12530 cd/m^2 at 11.2 V for Device A, and 20720 cd/m^2 at 11.6 V for Device B, respectively.

Table 1. A summary of device performance in Device A and B

	Device A (TFB)	Device B (PVK)
Turn-on voltage (at 1 cd/m^2)	3.0 V	3.0 V
Operating voltage (1000 cd/m^2)	7.6 V	7.8 V
Efficiency (1000 cd/m^2)	12.2 cd/A	21.1 cd/A
	5.1 lm/W	9.3 lm/W
Efficiency (Maximum)	12.3 cd/A	23.1 cd/A
	5.1 lm/W	9.8 lm/W
CIE (x,y) (1000 cd/m^2)	(0.31, 0.60)	(0.31, 0.61)



(a) Polyvinylcarbazole (PVK)



(b) Poly(2,7-(9,9-di-n-octylfluorene)-alt-(1,4-phenylene-((4-sec-butylphenyl)imino)-1,4-phenylene)) (TFB)

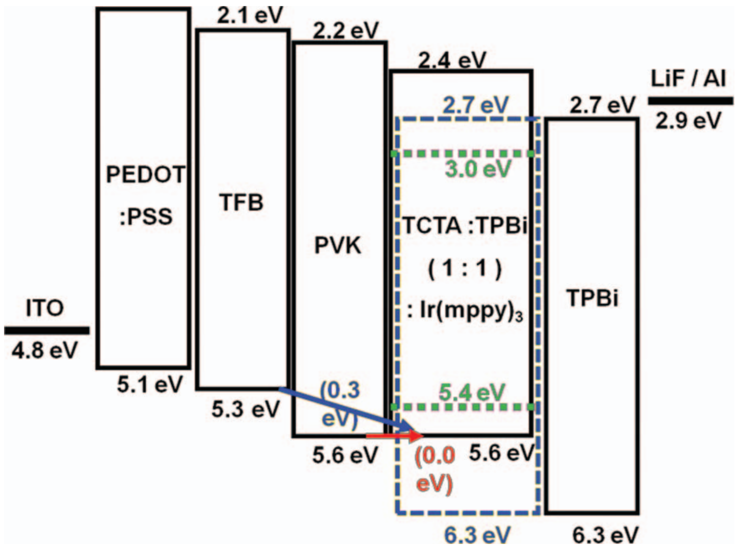


Figure 1. (a) Molecular structure of PVK and (b) TFB. (c) Device structure and energy band diagram of the devices using interlayer.

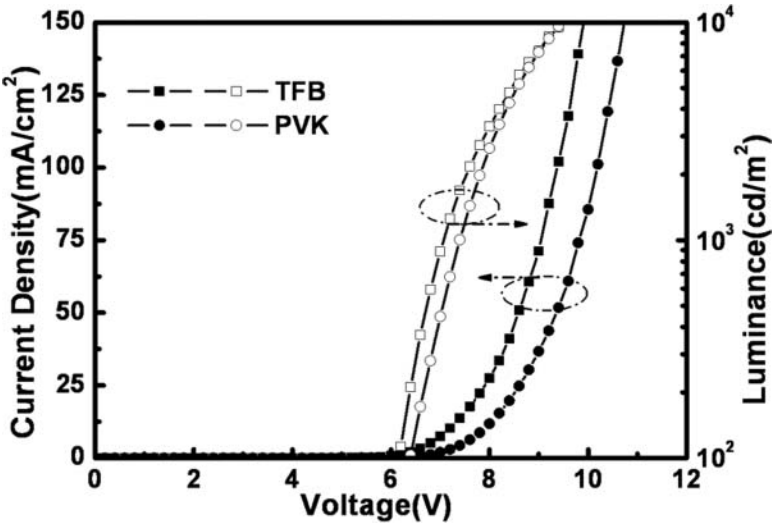


Figure 2. Luminance and current density as a function of voltage in Devices A and B.

The current and power efficiencies of the devices A and B are depicted in Figure 3 and Table 1. At a given constant luminance of 1000 cd/m^2, the current and power efficiencies of these devices were 21.1 cd/A and 9.3 lm/W for Device A, and 12.2 cd/A and 5.1 lm/W for Device B. Furthermore, the maximum current and power efficiencies obtained were 23.1 cd/A and 9.8 lm/W for Device A and 12.3 cd/A, and 5.1 lm/W for Device B.

Figure 4 shows the EL spectra of the Devices A and B exhibiting emissions in the green regions. It indicates complete energy transfer from the host materials to the guest

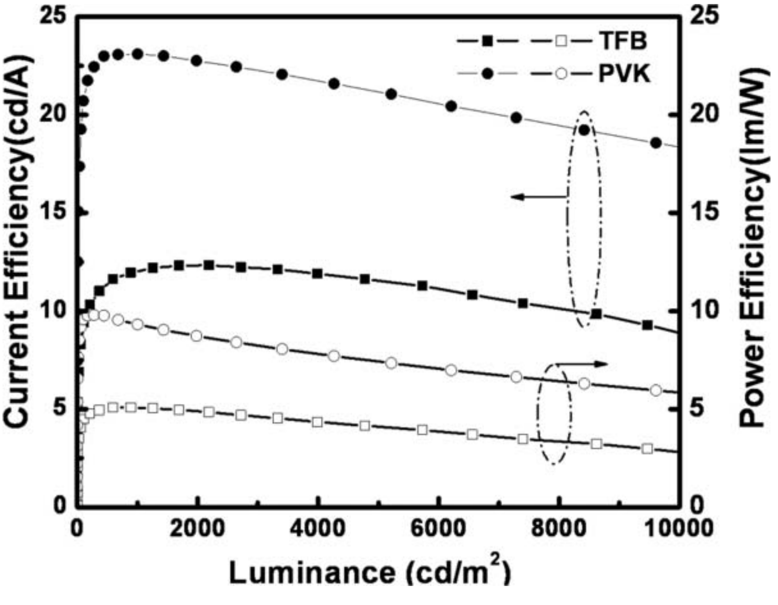


Figure 3. Current and power efficiency versus luminance in Devices A and B.

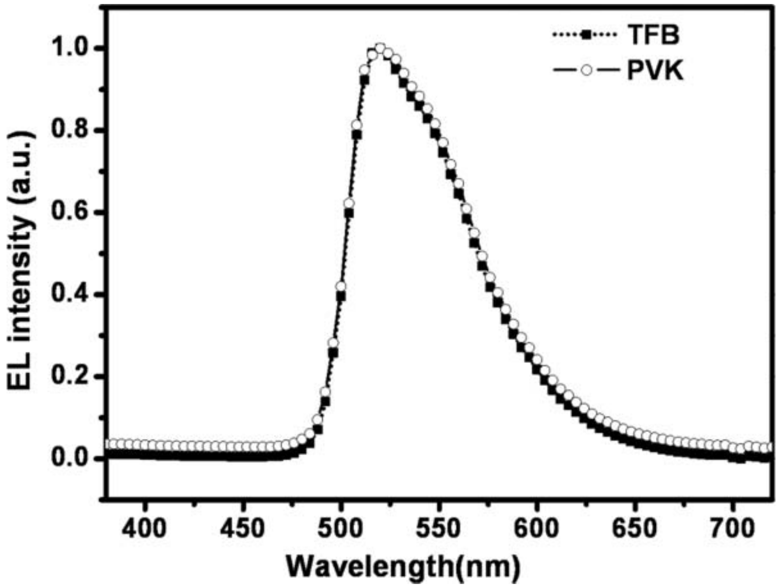


Figure 4. Electroluminescence spectra of Devices A and B.

due to confinement of triplet excitons at Ir(mppy)$_3$ dopant molecule. The EL spectral peaks and CIE$_{xy}$ coordinates of all the devices are summarized in Table 1. At 1000 cd/m^2, the EL spectral peaks and CIE$_{xy}$ coordinates of the Devices A and B were 520 nm/(0.31,0.60). The EL spectrum of each device does not change significantly with the applied voltage. It is manifested that phosphorescence photoluminescence quantum efficiency at high doping concentration tends to reduce inevitably due to self quenching or triplet-triplet annihilation by dopant molecules.

In order to investigate the stability and morphology of PVK film, atomic force microscopy (AFM) was done. The topographies of the AFM images were investigated on a 2 μm×2 μm area. Figure 5(a) and (b) shows the AFM morphology of PVK and PVK after dissolution with EML solvent. The RMS values of spin-coated films consisting of PVK and PVK after dissolution with EML solvent (as the same process of EML coating) were found at 2.2 and 4.9 Å, respectively. The AFM images of the PVK with and without solvent washing shows the uniform and homogeneous film formation characteristics with their RMS roughness under 5 Å. Figure 5 (c) and (d) also shows the AFM images only TFB and TFB after dissolution with EML solvent. Their RMS values were found at 6.7 and 14.8 Å, respectively. These unlike RMS values are attributed to the solvent diffusion during the process of spin coating. Therefore, the good surface characteristics of spin-coated PVK film are well suited for use as an interlayer due to its greater stability against solvents. This indicates that PVK helps in forming the densely packed structure in the soluble devices.

To quantify the dissolution issue of interlayer in the emissive layer solvent, thick TFB and PVK interlayers of approximately 70 nm were spin coated on glass substrates and dried on hot plate at 180°C for 30 min. When EML solvent chlorobenzene was spin coated over interlayers, and baked at 120°C for 10 min., it was found that thickness of TFB was reduced about 22–25 nm compared to 8–10 nm of high molecular weight PVK. This proves stability of high molecular weight PVK layer for improving the device performance of green PHOLEDs.

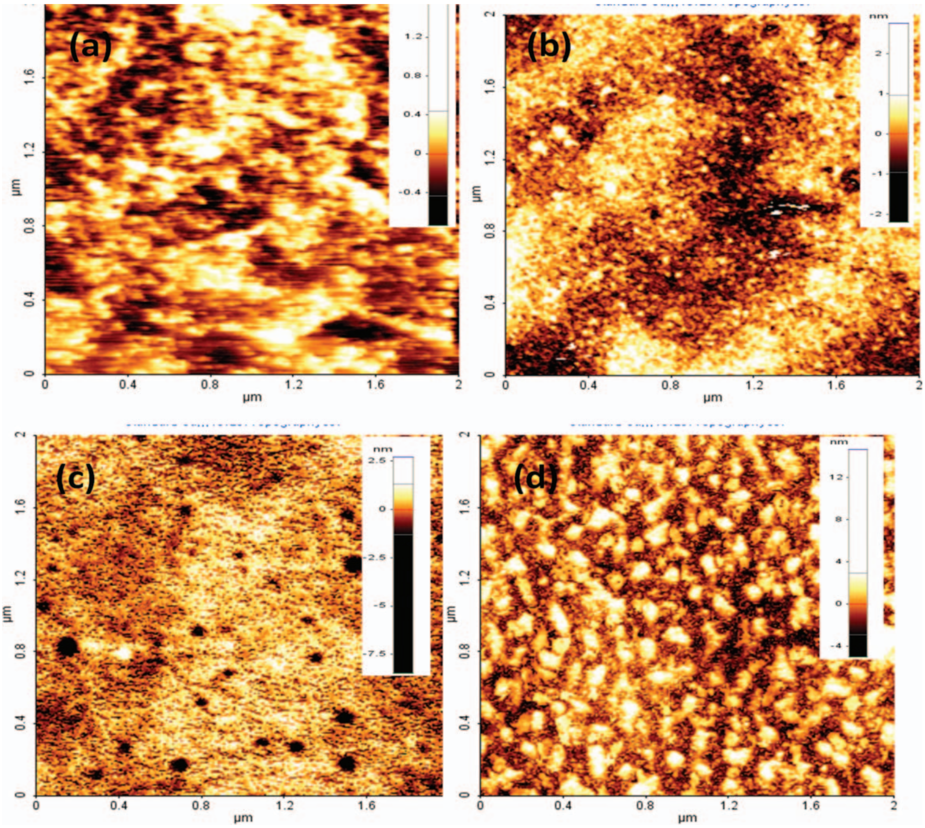


Figure 5. AFM images of (a) PVK (b) solvent washed PVK film (c) TFB (d) solvent washed TFB film.

Indeed high molecular weight PVK deposited by spin coating have brought the electron/hole charge carriers injection and transport effectively. The HOMO value of PVK (5.6 eV) [9] is close to a HOMO level of TCTA (5.7 eV) of emissive layer which facilitates hole injection effectively. While TFB has to overcome a barrier due to its low value of HOMO energy level (5.3 eV). From the interlayer, injected holes are trapped at the HOMO of dopant having a HOMO energy level of 5.4 eV. Also triplet energy of PVK is about 2.5 eV which is higher than that of TFB (2.2 eV), therefore triplet energy confinement from Ir(mppy)$_3$ (2.4eV) to PVK is better compared to TFB. Thus improved device efficiency can be seen in the PVK type of device. The reduced light emission in TFB interlayer type of device is obviously due to triplet exciton quenching in the PHOLEDs.

Conclusions

In summary, we have demonstrated the performance of high molecular weight PVK as an interlayer in multilayered green phosphorescent devices using spin-coating technique. Optimized concentration of high molecular weight PVK has a good solubility in chlorobenzene, which allows solution processing for the formation of the stable interlayer over PEDOT:PSS. The uniform deposition of PVK interlayer allows the efficient carrier transfer between PEDOT:PSS buffer layer and emissive layer. The results show that efficiency in the interlayer type of devices depends not only on the energy levels of the materials but also on surface interaction of each layer.

Acknowledgment

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