Electrophosphorescent devices from a poly(9-vinylcarbazole)/tris(2-phenylpyridine)iridium(III) bilayer with a concentration gradient

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Electrophosphorescence and the dynamics of charge carrier recombination in poly(9-vinylcarbazole) (PVK)/tris(2-phenylpyridine)iridium [Ir-(ppy)$_3$] bilayer electroluminescence devices were investigated. Because the second layer [Ir-(ppy)$_3$] is spin cast from a solvent that slightly swells the PVK layer, the two layers are partially intermixed at the bilayer interface. Indium tin oxide (ITO)/3,4-polyethylenedioxythiophene-polystyrenesulfonate (PEDOT)/[PVK/Ir(ppy)$_3$] bilayer/2,9-dimethyl-4,7-diphenyl-1, 10-phenanthroline (BCP)/Ca/Al ultilayer devices showed similar emission intensity and color quality to those of the PVK:Ir(ppy)$_3$ blended device. However, turn-on and driving voltage were decreased dramatically compared with those of the ITO/PEDOT/PVK:Ir(ppy)$_3$ blend/BCP/Ca/Al. © *2007 American Institute of Physics.*
[DOI: 10.1063/1.2432271]

Molecular semiconductors are fascinating candidates for emitting materials used in light-emitting diodes (LEDs).[1,2] Research on LEDs has focused on the improvement of the emission efficiency through the development of high efficiency fluorescent materials and the use of original device architectures. By utilizing triplet-based emitting centers in organic LEDs, and thereby capturing both singlet and triplet excited states, the internal quantum efficiency can be increased to 100%.[3,4] Highly efficient electrophosphorescent LEDs realized via doping blue to red emissive phosphorescent dyes in a low molecular weight organic host have been reported.[5,6]

Electrophosphorescent LEDs based on polymers as the host materials are an important development as they can be fabricated at room temperature by processing the materials from solution.[7,8] To date, a hole transporting polymer, poly (*N*-vinyl carbazole)(PVK), has been used as the host, and a phosphorescent material is molecularly doped into the polymer. PVK has chemical compatibility with phosphorescent dyes and its photoluminescent spectrum is coincident with the absorption band of phosphorescent materials. However, polymer electrophosphorescent LEDs with PVK as a host material show lower quantum efficiencies than LEDs consisting of small organic molecules as the host for the same phosphorescent dopant. In addition, the driving voltage of the devices is extremely high, as PVK is a good hole-only conductor. In the case of devices utilizing an iridium complex doped into a blend of PVK with 2-tert-butylphenyl-5-biphenyl-1,3,4-oxadiazol (PBD), transport of both electrons and holes is improved due to the balanced carrier injection, but the driving voltage of the devices remains high.

In previous works, we found that PVK acts as an efficient energy donor that provides the emitting polymer with sufficient excitation energy in a PVK (host)/poly(9,9′-dihexylfluorene-2,7-divinylene-*m*-phenylenevinylene-*stat*-*p*-phenylenevinylene) (guest) bilayer structured polymer LED with a concentration gradient.[9,10] Although our group tried to prepare a PVK/Ir(ppy)$_3$ bilayer structure by solution process the solvent for the upper layer (dichloroethane) dissolved the bottom layer, which destroys bilayer structure.[11]

In the present letter, PVK/Ir(ppy)$_3$ bilayers with a concentration gradient were prepared by spin coating. Trichloroethylene (TCE) solvent, which can cause swelling of PVK film, was employed as second layer solvent. From photoluminescence (PL) of bilayer film, we can observe similar color quality compared to blended system. In addition, we fabricated bilayer polymer electroluminescence (EL) devices with PVK as a hole transporting layer as well as the host material and Ir(ppy)$_3$ as an emitting layer anticipating efficient energy transfer from PVK to Ir(ppy)$_3$ around the intermixed region. PVK matrix EL devices have the disadvantage of slightly high turn-on and driving voltages. Hence, we attempted to reduce turn-on and driving voltages through a PVK/Ir(ppy)$_3$ bilayer system with a concentration gradient via balanced charge injection. These EL devices (indium tin oxide (ITO)/3,4-polyethylenedioxythiophene-polystyrenesulfonate (PEDOT)/[PVK/Ir(ppy)$_3$] bilayer/2,9-dimethyl-4,7-diphenyl-1, 10-phenanthroline (BCP)/Ca/Al) are also expected to show high quantum efficiency compared with a binary-blend system composed of ITO/PEDOT/[PVK:Ir(ppy)$_3$9:1 weight ratio]/BCP/Ca/Al.

PVK (average M_w: 1 000 000) was purchased from Aldrich Chem. Co., and Ir(ppy)$_3$, the emitting organic material, was synthesized by scheme.[12] EL devices having a PVK/Ir(ppy)$_3$ bilayer with a concentration gradient were prepared according to the following method (Fig. 1). PVK and Ir(ppy)$_3$ were dissolved in monochlorobenzene and TCE, respectively. The PVK dissolved in monochlorobenzene was spin coated on PEDOT precoated-ITO coated glass. Then,

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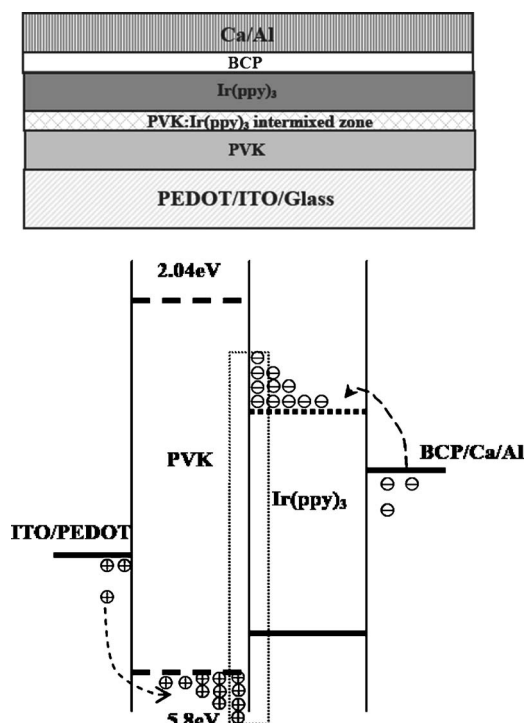b)Electronic mail: jhqkr76@kaist.ac.kr

FIG. 1. (Top) Schematic diagram of the proposed device structure with PVK/Ir(ppy)$_3$ bilayer. (Bottom) Band gap diagram of the bilayer device.

FIG. 2. PL spectra of Ir(ppy)$_3$, Ir(ppy)$_3$:PVK blend, and Ir(ppy)$_3$/PVK bilayer film excited 340 nm. Inset: Normalized absorbance (Abs) and the PL spectra of PVK and Ir(ppy)$_3$: (a) Abs of Ir(ppy)$_3$, (b) Abs of PVK, (c) PL of PVK, and (d) PL of Ir(ppy)$_3$.

after baking the polymer at 100 °C for 2 h, Ir(ppy)$_3$ dissolved in TCE was spin coated on top of the PVK film. The thickness of the PVK and Ir(ppy)$_3$ was, respectively, investigated by alpha step. PVK:Ir(ppy)$_3$ (9:1 weight ratio) was dissolved and completely mixed in dichloroethane and a blend film of 110 nm thickness was prepared for comparison with the bilayer film with a concentration gradient. Finally a hole blocking layer of BCP (20 nm) and a Ca/Al cathode (150 nm) were thermally evaporated in vacuum under a pressure of about 1×10^{-6} Torr. Polymer film thickness was controlled by the solution concentration and the rate of the spin coater. The electrical and luminescent characteristics of the devices were analyzed using a current/voltage source measurement unit (Keithley 236) and a calibrated silicon photodiode.

The inset of Fig. 2 shows the absorption and PL spectra of Ir(ppy)$_3$, and the PL spectrum of neat PVK film. The emission spectrum of PVK peaking at $\lambda_{max}=400$ nm shows a large spectral overlap with the metal-ligand charge transfer absorption band of Ir(ppy)$_3$. As such, efficient energy transfer is expected. Gao *et al.* showed that a bilayer polymer light-emitting polymer [PVK/poly(2-dodecyl-*p*-phenylene)(C120-PPP)] can emit blue or white exciplex emission, depending on the solvent used in the fabrication of the C120-PPP second layer.[13] Ma *et al.* employed a sequential spin coating method to prepare a bilayer structure in which the interface layer is eliminated by interlayer mixing.[14] However, when the same solvent is used to prepare the bilayer film, the bottom layer may be destroyed by the solvent of the upper layer, resulting in poor film quality.

In the present study, PVK is partially swelled in TCE, the dopant layer solvent. TCE, used for spin casting of Ir(ppy)$_3$ on PVK, cannot dissolve PVK film but instead causes the PVK film to swell. As a result, the bilayer interface has a mixed state of PVK molecules and Ir(ppy)$_3$ mol-

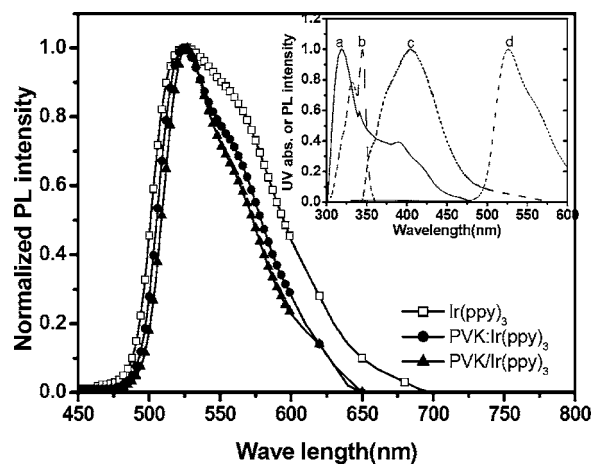ecules as well as good film quality. Figure 2 shows the normalized PL spectra of the blended film of two materials and the bilayer film [PVK60 nm/Ir(ppy)$_3$ 50 nm] as excitation at a wavelength of 340 nm, where the absorption of the host PVK is dominant. Emission from PVK was mostly quenched in the case of the bilayer system. From the PL characteristics, we can predict Föster-type and Dexter-type energy transfers from PVK to Ir(ppy)$_3$. More importantly, the PVK/Ir(ppy)$_3$ bilayer film as well as PVK:Ir(ppy)$_3$ blended film (9:1 by w/w) showed narrower emission bands than that of the neat Ir(ppy)$_3$ film. These PL characteristics indicate that the intermixed region has well dispersed Ir(ppy)$_3$ molecules in PVK.

In order to confirm whether the intermixed zone leads to a concentration gradient of the donor and acceptor material in the bilayer, the depth profiles of the films were studied by recording the Ir concentration from the PVK layer to the Ir(ppy)$_3$ layer with Auger spectroscopy in combination with ion-beam milling. Notably Ir(ppy)$_3$ contains iridium, which can be detected with Auger spectroscopy. From the Ir signal, we can therefore make a qualitative statement of the Ir(ppy)$_3$ content in the bilayer film. Figure 3 show the peak-to-peak Auger signal of the two different bilayer films [PVK100 nm/Ir(ppy)$_3$ 100 nm] as a function of depth in the films. When acetonitrile (nonsolvent for PVK) is used to prepare the bilayer film, the Ir signal is zero while the tested
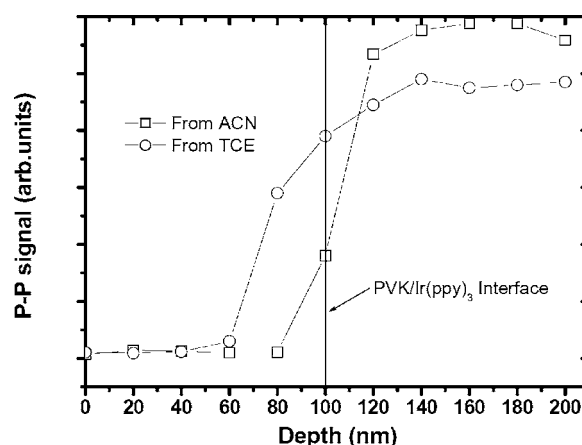

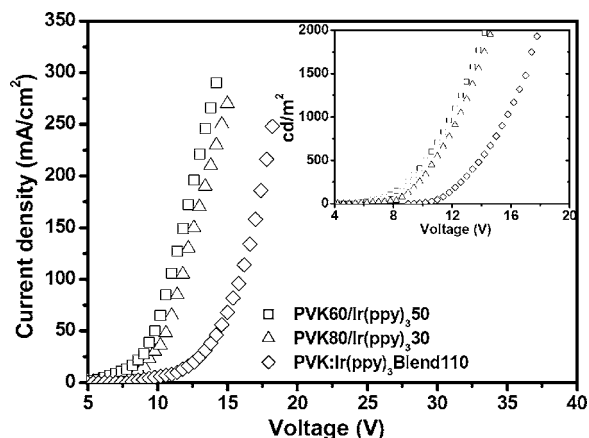FIG. 3. Depth profiles of PVK/Ir(ppy)$_3$ bilayers (from ACN and TCE).

FIG. 4. Current density vs voltage and luminescence vs voltage characteristics for the EL devices of the ITO/PEDOT/ [PVK:Ir(ppy)$_3$ blend]/BCP/Ca/Al, ITO/PEDOT/[PVK60/ Ir(ppy)$_3$50 bilayer]/BCP/Ca/Al, and ITO/PEDOT/[PVK80/ Ir(ppy)$_3$30 bilayer]/BCP/Ca/Al structures.

surface is within the PVK layer and shows a sharp increase in the vicinity of the interface between the PVK and Ir(ppy)$_3$. In the case of bilayer film with concentration gradient, the Ir signal appears at roughly 80 nm from the bottom.

Figure 1 illustrated the expected concentration gradient of injected electrons developed in the bilayer; the electron concentration is highest at the top of the bilayer and decreases towards the PVK layer, resulting in electron confinement at the diffuse interface of the two layers. The injected electrons will accumulate in the diffuse interlayer region due to the high lowest unoccupied molecular orbital (LUMO) level of PVK, thus providing more opportunities for the electrons and holes to recombine with each other. In addition, between the excitons formed on the PVK and Ir(ppy)$_3$ molecules, those formed on the PVK molecules in the interlayer region can act as Förster-type energy donors, as indicated by the PL observations. More importantly, the accumulation of electrons by PVK and holes by BCP in the diffuse interfacial zone favors exciton formation.

Typical current-voltage characteristics of the devices of the bilayer system and blended system are shown in Fig. 4. In this figure, we observe that the PVK/Ir(ppy)$_3$ bilayer device has higher current density than the PVK:Ir(ppy)$_3$ blended system at the same voltage. It is thought that more electrons are readily injected from Ca/Al cathode into the emitting layer in the bilayer system because the energy state of LUMO of the Ir(ppy)$_3$ ($\sim$−2.11) is lower than that of the PVK ($\sim$−2.04). The PVK layer serves as not only a hole transporting layer but also as an electron blocking layer. Hence, more carrier recombination occurs and excitons can be generated at the interface of PVK/Ir(ppy)$_3$. The inset of Fig. 4 shows the luminescence versus voltage characteristics of PVK/Ir(ppy)$_3$. The bilayer device shows increased luminescence compared with that of the PVK:Ir(ppy)$_3$ blended system. The bilayer EL device shows enhanced luminescence and lower turn-on and driving voltage compared with the blended EL device. Thus, the problem of high working voltage in the PVK matrix EL system can be solved.

In conclusion, we have demonstrated the use of PVK/Ir(ppy)$_3$ bilayer structured-electrophosphorescent LEDs with a concentration gradient. By utilizing a bilayer structure with concentration gradient, brighter electroluminescence and lower driving voltage compared with those of a general PVK:Ir(ppy)$_3$ blended device have been attained.

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