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Highly efficient organic electroluminescent device with modified cathode

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One of the key parameters for high efficiency organic electrophosphorescent light emitting diodes is charge injection into the phosphorescence compound. By introducing a hybrid device architecture, and incorporating electron and hole interfacial layers with lowest unoccupied molecular orbital and highest occupied molecular orbital levels similar to that of the phosphorescence compound, on the cathode and the anode side of the device, respectively, charge injection properties were improved. A green electrophosphorescence device with luminous efficacy of 50 lm/W at luminance efficiency reaching 55 cd/A was demonstrated. © 2006 American Institute of Physics.
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The ability of organic phosphorescence emitters to achieve emission from both singlet and triplet excited states has open the possibility to develop highly efficient organic light emitting diodes (OLEDs) for flat panel displays and solid state lighting applications.¹ The field of organic electronics is divided in two broad categories: thermally deposited small molecules (low molecular weight materials) and solution processed polymer based OLEDs. Of the two, the small molecule technology is the more mature, and has produced high efficiencies up to 77 lm/W for green phosphorescence based OLEDs (PHOLEDs).² This particular device structure consists of several stacked layers, each one optimized to perform functions including charge confinement, electron and hole injection/transport/blocking, and exciton recombination.³ However, such complicated structures do increase fabrication complexity,^{3,4} and may not be suitable for low cost, high volume manufacturing. Thus, there remains interest in investigating solution processed OLEDs as these fabrication techniques are more scalable and have better potential for low cost high volume processing.

However, to achieve the same kind of efficiencies, solution processed approaches will also have to incorporate phosphorescent emitters in place of existing fluorescent emitters while keeping simple device architectures. Although incorporation of phosphorescence emitters into conjugated polymers has been reported to improve device performance for red PHOLEDs, efficiency values are still much lower than those obtained for small molecule based devices. The problem is more severe for blue and green emissions due to luminescence quenching effects caused by the low triplet energy level of the conjugated polymers.⁵ Thus, to minimize quenching effects, large band-gap host materials with higher triplet energy than that of the phosphorescence dye are needed.

Recent work have used nonconjugated polymers, such as poly(*N*-vinylcarbazole) (PVK), as the large band-gap host. This host is then molecularly doped with *N,N'*-diphenyl-*N,N'*-(bis(3-methylphenyl)) - [1,1-biphenyl]-4-4'-diamine (TPD), 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD), and tris(2-(4-tolyl)

phenylpyridine)iridium Ir(mppy)₃, components that serves the purpose of carrier transport and emission. With this composition, a single layer green emitting polymer based PHOLED with luminous efficacy (or power efficiency) of 24 lm/watt at luminance (or current) efficiencies exceeding 30 cd/A was achieved.⁶ The PVK polymer is particularly suitable for a host since it can ensure the confinement of the triplet excited state in the Ir(mppy)₃ guest phosphorescence molecule, and thus prevent luminescence quenching.⁷ In this type of device, good charge balance within the phosphorescence light emitting layer (LEP) has been achieved.^{6,8,9}

We have recently reported further improvement on the performance of molecular doped PHOLEDs by incorporation of a solution processed interfacial layer, based on poly(9,9-dioctyl-fluorene-co-*N*-(4-butylphenyl)-diphenylamine) (TFB) between 3,4-polyethylene dioxathiophene:poly(styrene sulfonate) (PEDOT:PSS) and the LEP.¹⁰ Devices with the TFB interfacial layer show luminous efficacy of 41 lm/W at efficiencies reaching 50 cd/A,¹⁰ exceeding the 31 lm/W reported for a small molecule PHOLED, using 4-4'-*N,N'*-dicarbazole-biphenyl the small molecule derivative of PVK as a host and the same emitter.¹¹

In this letter we demonstrate that further improvement in the device performance was achieved by improving the electron injection properties. This was achieved with a modified cathode. The cathode now consists of interfacial layer specially chosen to enhance electron injection. With this modified cathode, the efficiency of the PHOLED is further enhanced by 25%.

Details about the materials, standard device preparation, and characterization have been published elsewhere.^{10,12} In the present study TFB and PBD were used as hole and electron injecting interfacial layers, respectively. The TFB layer was spin coated inside the glovebox onto the PEDOT:PSS buffer layer from toluene solution and baked at 130 °C for 10 min in a nitrogen environment. Under these conditions an interlayer thickness of around 10 nm was obtained. To achieve the interfacial layer and prevent mixing of the TFB layer with the active organic layer we introduced a washing step using toluene on the TFB layer. This result to a TFB polymer based interfacial layer with a thickness of ≤3 nm. Full details for the improvement on the hole injection properties for organic electronic devices by incorporation of a TFB interfacial layer have been published previously.^{10,13}

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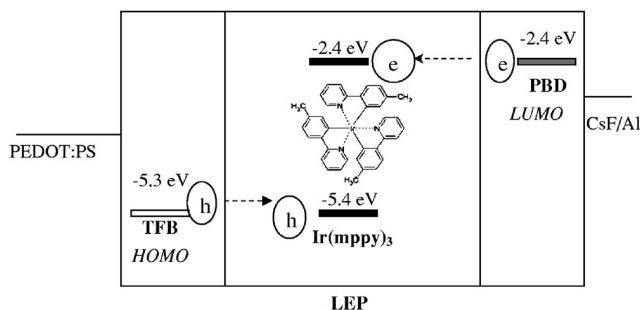


FIG. 1. The device architecture for optimized charge injection, incorporating an electron (PBD) and hole (TFB) interfacial layers. The LUMO energy levels of PBD and the HOMO energy level of TFB are similar to that of the Ir(mppy)₃ phosphorescence compound. The arrows in the scheme indicate the electron/hole injection from the PBD/TFB interfacial layers into Ir(mppy)₃ phosphorescence compound.

The PBD small molecule based electron injected interfacial layer was thermally evaporated at a rate of 0.02 nm/s on the top of LEP inside the glovebox. The same evaporator used to incorporate the CsF/Al and the PBD interfacial layer on the cathode side of our device structure.

The device architectures studied are described as follows. The control device is based on ITO/CH8000 PEDOT:PSS (60 nm)/LEP (70 nm)/CsF (1 nm)/Al (200 nm). First improved device with new cathode incorporates a PBD interfacial layer between the LEP layer and the cathode, indium tin oxide (ITO)/CH8000 PEDOT:PSS (60 nm)/LEP (70 nm)/PBD (3 nm)/CsF (1 nm)/Al (200 nm). Second device architecture further adds the TFB interfacial layer, ITO/CH8000 PEDOT:PSS (60 nm)/TFB (≤ 3 nm)/LEP (70 nm)/PBD (3 nm)/CsF (1 nm)/Al (200 nm). The LEP for all the devices studied contains [61% PVK+24% PBD+9% TPD+6% Ir(mppy)₃].^{6,10} All the device studies were encapsulated with a glass lid and getter. The concentrations are given by weight. Figure 1 shows the device architecture incorporating the interfacial layers and the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energetic levels of the materials involved, as reported in the literature.^{6,10}

An important point to draw from Fig. 1 is that the LUMO level of PBD is well aligned to the LUMO level of Ir(mppy)₃ and PBD in the LEP. The same is true for the HOMO level of TFB being aligned to the HOMO level of TPD and Ir(mppy)₃. This good alignment of energy levels is important to facilitate carrier injection into both the transport molecules and Ir(mppy)₃.

Figure 2 shows the current density-voltage (J - V) properties (upper plot) and the brightness-voltage properties (lower plot) of the devices under study. From the J - V and brightness-voltage characteristics it is clear that the current density and brightness are larger through the whole voltage range for the device incorporated a TFB interfacial layer compared to the control device, and these values increase further when the TFB interfacial layer was added. We have previously reported the effect of a TFB interfacial layer to assist direct hole injection into Ir(mppy)₃ phosphorescence compound.¹⁰ In this case we hypothesize that the large increase in current for the devices incorporating a PBD interfacial layer is due to improved electron injection.

Figure 3 (upper plot) shows the luminance efficiency versus current density and the lower plot shows the luminous

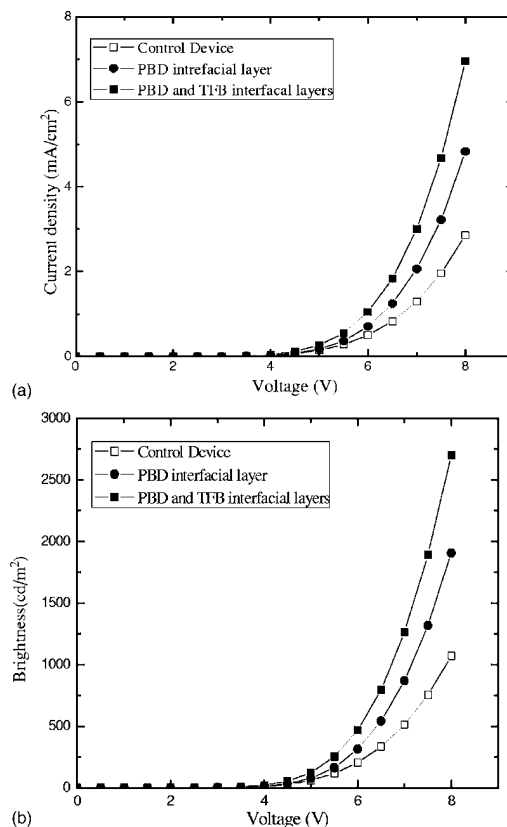


FIG. 2. Upper plot: current density-voltage characteristics. Lower plot: brightness-voltage characteristics of the PHOLEDs under study. The control device is represented with open squares, the devices incorporating a PBD electron injecting interfacial layer represented with solid circles, and the devices incorporating both PBD and TPD electron and hole injecting interfacial layers, respectively, represented with solid squares.

efficacy versus current density for the devices under study. The peak luminous efficacy of the control device (without interfacial layers) was 29 lm/W with a luminance efficiency reaching 40 cd/A. Devices with PBD interfacial layer show an improvement in the device performance, with luminous efficacy of 35 lm/W at luminance efficiencies exceeding 45 cd/A. Since the molecularly doped LEP is charge balanced, incorporation of thicker electron transporting layers (6–10 nm) with hole blocking properties did not improve device efficiency.⁹ When both PBD and TFB interfacial layers were used, the highest peak luminous efficacy of 50 lm/W with luminance efficiencies reaching 55 cd/A was achieved. This improvement is attributed to increased electron injection as discussed further below. This result indicates that in the case of molecularly doped phosphorescence devices using nonconjugated polymers as a host though the control device is charge balanced, efficiencies can still be improved by increasing the number of carriers injected. It should be noted that incorporation of such electron injecting layers can also be done by solution processed techniques.¹⁴

In J/V measurements the improvement in the current density can be related to both injection and bulk transport properties. However, due to the processing conditions used for incorporating the interfacial layers is very unlikely to affect the bulk transport properties. The washing step of the TFB with toluene prevents the mixing of the polymer based interfacial layer with the LEP (Refs. 10 and 13) and the PBD was thermally evaporated on the top of the LEP. Furthermore, the devices were not exposed to air so any additional

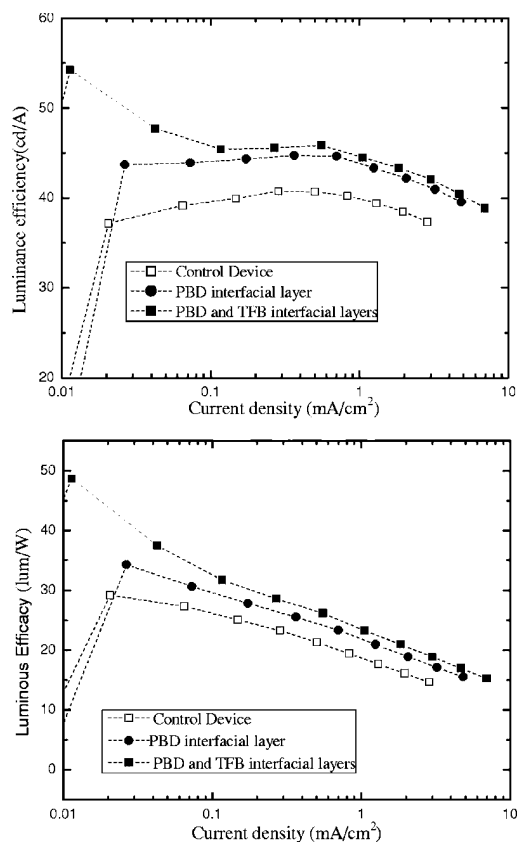


FIG. 3. Upper plot: luminance efficiency-current-density characteristics. Lower plot: luminous-efficacy-current-density characteristics of the PHOLEDs under study. The control device is represented with open squares, the devices incorporating a PBD electron injecting interfacial layer represented with solid circles, and the devices incorporating both PBD and TPD electron and hole injecting layers interfacial, respectively, represented with solid squares.

doping affects due to oxygen can be ruled out. Our results indicate that the increase in the current density and device performance is related to improved injection properties. The improvement on the hole injection properties by TFB assisting direct hole injection to the phosphorescence compound has been presented in details previously.¹⁰

Possible mechanisms responsible for the improvement in electron injection when incorporating a PBD interfacial layer are (1) formation of a dipole layer¹⁴ at the CsF/PBD interface, (2) CsF/PBD doping interactions, or (3) bridging effect due to energy level alignments as seen on the anode side with TFB.¹⁰ Devices with thicker (6–10 nm) PBD layer showed reduced efficiency which is not expected if reason (2) or (3) is valid. In cases where the increase in the electron injection would arise from reason (2) or (3) no reduction in the efficiency should have been observed. CsF/PBD doping interactions should have also been dominant for thicker PBD layers and the bridging effects due to energy level alignment of the LUMO of the PBD and the phosphorescence compound should have also been observed with the thicker PBD layers. Thus the most likely reason for the improved electron injection by incorporation of the PBD interfacial layer on the cathode interface is reason 1 (formation of a dipole layer at the CsF/PBD interface). Optimized charge injection also

plays an important role in the performance of fluorescence based OLEDs. Our approach described here to add interfacial organic layers on the cathode side of the device can be used as a general method to improve electron injection in organic electroluminescence devices.

These results also show that complicated multilayer PHOLED structures may not be necessary to obtain good efficiencies. Even when incorporation of thick transport/blocking layers into these complicated multilayer structures improves the luminance efficiency, the cost in operating voltage increase may be too high. We have demonstrated here that the increase in efficiency can be achieved even with simple structures that control charge balance and injection. Incorporation of interfacial layers can alternatively be described as a method of conditioning interfaces within organic electronic devices.¹³

In conclusion, we have described a novel device architecture incorporating hole injecting interfacial layer with its HOMO level aligning with that of the phosphorescent dyes and the electron injecting interfacial layer with its LUMO level aligning to that of the phosphorescence dye. This simpler hybrid device architecture simplifies the fabrication process, reduce the manufacture cost, and increase device efficiency while maintaining or even lowering the device operating voltage. By improving charge injection, a solution processed green PHOLED with luminous efficacy of 50 lm/W at luminance efficiency reaching 55 cd/A was achieved.

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