Highly efficient phosphorescent polymer OLEDs fabricated by screen printing


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Abstract

We demonstrate the use of screen printing in the fabrication of highly efficient phosphorescent polymer organic light-emitting devices (OLEDs) based on a green-emitting Ir(ppy)$_3$ and a host polymer PVK. We incorporate PBD in the polymer host as an electron-transporting dopant and α-NPD as a hole-transporting dopant. The best screen-printed single-layer device exhibits very high peak luminous efficiency of 63 cd/A at a relatively high operating voltage of 17.1 V at the luminance of 650 cd/m$^2$. We observed the highest luminance of 21,000 cd/m$^2$ at 35 V. Due to the high operating voltage, despite of the high peak luminous efficiency the peak power efficiency was found to be 12.2 lm/W at the luminance of 470 cd/m$^2$ (15.9 V).

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1. Introduction

Intense research efforts are being devoted on organic light-emitting devices (OLEDs) due to their potential applications in flat panel displays and solid state lighting. Among the two different kinds of OLEDs which are small-molecule OLEDs and polymer OLEDs, the polymer OLEDs are known to have an advantage of their compatibility with solution processing. Since Baldo et al. [1] first demonstrated efficient OLEDs based on phosphorescent emitters in 1998, the phosphorescent OLEDs have attracted much attention due to their high efficiency. Because phosphorescent OLEDs can utilize all the injected charge carriers for emission unlike fluorescent OLEDs (25% theoretically), they normally exhibit much higher luminous and power efficiencies.

For the phosphorescent emitter, we have chosen a green-emitting Ir(ppy)$_3$, which is commercially available and most widely used one. For the preparation of phosphorescent polymer OLEDs, the commonly used practice is to blend a low molecular weight phosphorescent dye with a properly chosen polymer matrix. Since a polymer host with a triplet state energy above that of the phosphorescent dye is required to guarantee the confinement of the triplet excited state on the guest, large band gap polymers such as poly(N-vinyl carbazole) (PVK; polymer host in this study) are commonly utilized for the purpose. It is well-known fact that the electron-transporting properties of PVK are poor. In order to improve the properties, it has been reported in the literature that the electron-transporting materials such as 2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) have been blended with PVK to insure better efficiencies and low driving voltages [2–4].

On the other hand, Yang et al. [4] reported that by introducing hole-transporting TPD molecules in PVK the driving voltage of polymer OLEDs could be decreased. In this study, we have chosen α-NPD as the hole-transporting molecules instead of TPD based on the fact that hole injection barrier from PEDOT/PSS to α-NPD is lower than that to TPD. Makinen et al. [5] showed that hole injection barrier from PEDOT/PSS to α-NPD was 0.51 eV while to TPD was 0.58 eV.

In the present work, we demonstrate the implementation of screen printing technology in the fabrication of single-layer phosphorescent polymer OLEDs. Screen printing is a commonly used industrial technique for fast, inexpensive deposition of dye films over large areas. In addition, screen printing allows patterning to easily define which areas of the substrate receive deposition. This is important, for instance, for fabricating a flat panel displays that is integrated onto a substrate containing other electronic devices. In the industrial processes, films fabricated with screen printing usually have a thickness greater than 0.5 μm. The use of screen printing to fabricate a polymer layer with a thickness less than 100 nm, serving as the hole transport layer in an OLED, has been first demonstrated [6]. Birnstock et al. [7] reported that they have fabricated high-efficiency OLEDs on basis of conjugated polymers, in which both polymer layers (PEDOT and emitting polymer layers) were screen printed. For their devices, single-layer red- or green-emitting polyfluorene derivative (PF) was used and luminance of 10,000 cd/m$^2$ at 8 V and peak efficiencies exceeding 10 cd/A for green devices.

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In this study, we report single-layer phosphorescent polymer OLED fabricated by screen printing technique. The single emitting layer in the device is composed of PVK as a host polymer, PBD as an electron-transporting molecule, \( \alpha \)-NPD as a hole-transporting molecule, and Ir(ppy)\(_3\) as a phosphorescent dopant. To our knowledge, the polymer OLED device reported in this study is not only one of few OLED devices fabricated by screen printing technique but also the first phosphorescent device via screen printing technique.

2. Experimental

ITO glasses of a nominal sheet resistance of 30 \( \Omega / \square \) were ultrasonically cleaned, followed by rinsing with deionized water, trichloroethylene, acetone, and methanol. The ITO glasses were then treated by oxygen plasma at 100 W for 5 min. Poly(3,4-ethylenedioxy thiophene) (PEDOT:PSS) (Baytron P, AI 4083) was spin-coated onto pre-cleaned and plasma-treated ITO glasses, yielding a layer with a thickness of 40 nm. The PEDOT:PSS layer was then baked at 120 \( ^\circ \)C for 10 min. On top of the PEDOT:PSS layer, single emissive layer was subsequently screen-printed using a semi-automatic commercial screen printing machine. For the screen printing, a 400 mesh screen composed of stainless steel fabric of which the diameter was 23 \( \mu \)m and the opening size was 41 \( \mu \)m was utilized.

In order to ensure 100 nm thick polymer layer as the result of screen printing, the printing ink should have a viscosity less than 2.4 cp. Using PVK polymer of average molecular weight 1,100,000, the weight of PVK should be strictly controlled less than 2.4 cp. The inset shows that a PVK thin film of a thickness of 100 nm can be printed using a 2.4 cp viscous solution obtained with a PVK content of 11.

<table>
<thead>
<tr>
<th>( \text{Ir(ppy)}_3 ) concentrations (%)</th>
<th>Max. brightness (cd/m(^2)) at voltage (V)</th>
<th>Volatges at current density of 150 (mA/cm(^2))</th>
<th>Max. luminous efficiency (cd/A) at voltage (V)</th>
<th>Max. power efficiency (lm/W) at voltage (V)</th>
</tr>
</thead>
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<td>48.4 (21.8)</td>
<td>0.1 (14.1)</td>
<td>0.024 (13.0)</td>
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<td>30.1 (15.3)</td>
<td>6.58 (13.3)</td>
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<td>2.4</td>
<td>4900 (33.0)</td>
<td>11.9 (18.0)</td>
<td>2.12 (16.8)</td>
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</tr>
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<td>3.6</td>
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<td>63.2 (17.1)</td>
<td>12.2 (15.9)</td>
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<td>10,500 (27.5)</td>
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<td>6.1</td>
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<td>8000 (33.7)</td>
<td>12.2 (18.9)</td>
<td>2.19 (16.0)</td>
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</table>

3. Results and discussion

In order to find an optimal Ir(ppy)\(_3\) doping concentration, we have fabricated single-layer devices with seven different Ir(ppy)\(_3\) doping concentrations from 0% to 8% as shown in Table 1. The device without Ir(ppy)\(_3\) dopant showed very weak blue emission which was responsible for PVK or \( \alpha \)-NPD. With 1.2% doping of Ir(ppy)\(_3\), EL spectra were observed green emission solely from the phosphorescent dopant even at the low doping concentration. The same observation has been reported by Noh et al. [8]. This indicates that the singlet energy transfer is almost complete at the low doping concentration. The result is consistent with the homogeneous dispersion of the dopant with large Förster radius [8]. The maximum peak luminous and power efficiencies were obtained at 3.6% doping of Ir(ppy)\(_3\). The maximum brightness was measured to be over 20,000 cd/m\(^2\) and peak luminous efficiency was found 63.2 cd/A with the brightness of 650 cd/m\(^2\) at 17.1 V. Increasing the doping concentration further, the brightness and efficiencies were found to decrease. It should be mentioned here that the solubility of the phosphorescent dopant, Ir(ppy)\(_3\) in chlorobenzene solvent used in this study was low and the dopant was not dissolved in the solvent completely at concentrations higher than 4.8%. We could attribute the cause of decrease in performance at higher dopant concentrations to the incomplete dissolution of the dopant in the printing solution. One more thing to note from Table 1 is the fact that the driving voltages for the current density of 150 mA/cm\(^2\) could be lowered with increasing Ir(ppy)\(_3\) concentration above 3.6%. This observation is similar to what has been reported in the literature [2,4,8]. This implies that Ir(ppy)\(_3\) itself can participate in charge transport, especially by hopping of holes at higher concentrations.

Fig. 2 shows that EL spectra of the Ir(ppy)\(_3\)-doped devices (3.6%) obtained at different operating voltages. In the voltage range measured, no emission except from Ir(ppy)\(_3\) was found. As shown in the inset of Fig. 2, the devices fabricated by screen printing method have a single emitting layer on top of the hole injection layer PEDOT:PSS. The single emitting layer is composed of PVK as a host polymer, PBD as an electron-transporting molecule, \( \alpha \)-NPD as a...
hole-transporting molecule, and Ir(ppy)₃ as a phosphorescent dopant. The effect of co-doping of PBD and α-NPD on the performance of devices have been reported in the literature [2,4,9,10].

As shown in Fig. 3, the current–voltage characteristics tend to shift to higher voltages with increasing concentration of Ir(ppy)₃. From 1.2% to 3.6% doping concentration of Ir(ppy)₃, the voltage gradually increases at a constant current density. However, the voltage drops significantly to an even lower value at 4.8% concentration than that at 1.2% concentration. It means that at low doping concentrations Ir(ppy)₃ acts as a carrier trap while at high doping concentration Ir(ppy)₃ affects the carrier transport favorably. Indeed, from the highest occupied molecular orbital (HOMO) energy of Ir(ppy)₃ and PVK at −5.4 eV and −5.8 eV, respectively, it is evident that the dopant will constitute a hole trap with an energy depth of 0.4 eV. In addition, since the lowest unoccupied molecular orbital (LUMO) energies of Ir(ppy)₃, and PVK are −2.4 and −2.2 eV, the dopant should form an electron trap as well. Due to these carrier traps, we consider that the increase in the dopant concentration should cause the increase in voltage at the low doping concentrations. At higher doping concentration, however, the direct hopping should cause the increase in voltage at the low doping concentrations. At higher doping concentration, however, the direct hopping traps, we consider that the increase in the dopant concentration should cause the increase in voltage as the result. It should be noted that the decrease in voltage at the higher concentration was so significant unlike the results reported in the literature [2]. We attribute the fact to the over-saturated Ir(ppy)₃ guest in PVK host beyond 4.8% doping concentration. Since the drying of chlorobenzene solvent after the screen printing of solution is much slower than that after spin coating, the phase separation in the resulting thin film should be more vulnerable to occur in case of the screen printing. In fact, the higher concentration of Ir(ppy)₃ at the surface of the resulting film was found for the screen printing. We think that this phase separation effect of Ir(ppy)₃ around cathode also could cause the noticeable decrease in voltage at the higher Ir(ppy)₃ concentration.

The relatively higher driving voltage could be reduced by annealing the screen-printed polymer film at around 80 °C before the deposition of the cathode. It has been reported in the literature [2] that the reduction in the driving voltage is due to the less severe build-up of a space-charge field in the annealed devices. The report has also revealed that the efficiency of the devices was significantly improved. From the report, the luminescence efficiency of the devices that have undergone annealing was about 20% higher than that of devices without thermal treatment, and at the same time the driving voltage for a certain current density decreased by about 12% [2].

Figs. 3 and 4 show the voltage-brightness and the current-efficiencies properties of the screen-printed devices with a few different Ir(ppy)₃ doping concentrations. The peak luminous efficiency is 63 cd/A at a current density of 1 mA/cm², a voltage of 17.1 V and a brightness of 650 cd/m². The luminous efficiency of the screen-printed single-layer phosphorescent polymer devices is comparable to the best value of spin-coated single-layer phosphorescent polymer OLEDs in the literature [3]. Moreover, the maximum power efficiency is 12.2 lm/W, with a current density of 0.76 mA/cm², a voltage of 15.9 V and a brightness of 470 cd/m². The operating voltages for 100, 1000, 10,000 cd/m² are 11.8, 19.0, 30.5 V, respectively. These performance results are comparable to those of devices fabricated by spin coating reported in the literature [2–4,8,11–14].

It should be mentioned here that the aforementioned performance was measured with the one of the four devices of which the emitting area was 1.2 mm × 1.2 mm (Fig. 5b) in the total screen-printed area was 2.5 cm × 2.5 cm (Fig. 5a). In Fig. 5a, the two parallel ITO lines are shown below the screen-printed area. Due to the low viscosity of the printing ink, the ink tended to spread easily on the surface and the edges after the screen printing were seen somewhat blurred as the result. The test devices were then completed with the vacuum evaporation of the two parallel LiF(1 nm)/Al cathode lines (width 1.2 mm) perpendicular to the ITO lines. We have also fabricated larger screen-printed devices of which the total emitting area was 4 cm × 4 cm with nine 1.2 × 1.2 cm pixels of same size (Fig. 5c). At this point of research, even though we have not measured the lifetime of the devices yet, the stability of the devices seems not to be quite different to that of the devices fabricated by the spin coating.

Finally, in that screen printing is a simple and cheap wet processing technique under ambient environment, we would like to note that the screen printing technique is a useful way to fabricated single-layer phosphorescent polymer OLEDs.

4. Conclusion

We successfully fabricated single-layer phosphorescent polymer OLEDs by screen printing with a high luminous efficiency over 60 cd/A at the luminance of 650 cd/m². The highest luminance of 21,000 cd/m² was measured for a device with 3.6% Ir(ppy)₃ concentration at 35 V. The single emitting layer in the devices is composed of PVK as a host polymer, PBD as an electron-transporting molecule, α-NPD as a hole-transporting molecule, and Ir(ppy)₃ as a phosphorescent dopant. To our knowledge, the polymer OLED device reported in this study is not only one of few OLED devices fabricated by screen printing technique but also the first phosphorescent device via screen printing technique.
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References


Fig. 5. Photographs showing (a) the screen-printed area on the patterned ITO substrate, (b) the EL emission from a small pixel, and (c) the EL emission from a larger device.