

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 $\text{Ir}(\text{ppy})_3$ 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/m². We observed the highest luminance of 21,000 Cd/m² at 35V. 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/m² (15.9 V).

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 lightening. 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 luminous and power efficiencies. Since phosphorescent OLEDs can utilize all the injected charge carriers for emission theoretically unlike fluorescent OLEDs, they normally exhibit much higher efficiencies.

2. Experimental

ITO glasses of a nominal sheet resistance of 30 Ω/\square were ultrasonically cleaned, followed by rinsing with deionized water, trichloroethylene, acetone and methanol. The ITO glasses were then treated by oxygen plasma at 100W for 5 minutes. Poly(3,4-ethylenedioxy thiophene) doped with poly(styrene sulfonate) (PEDOT:PSS) (Baytron P, AI 4083) was spin-coated onto pre-cleaned and plasma-treated ITO glasses, yielding a layer with a thickness of 40nm. The PEDOT:PSS layer was then baked at 120°C for 10 minutes. 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 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 11 mg per 1 ml of chlorobenzene solvent. As shown in Fig. 1, by changing the polymer content the viscosity of printing ink can be varied from 0 to more than 30 cp and the thickness of resulting PVK layer can also be controlled by varying viscosity. Beside the polymer, small molecular dopants of PBD, α -NPD, and $\text{Ir}(\text{ppy})_3$ were found not to change the viscosity noticeably.

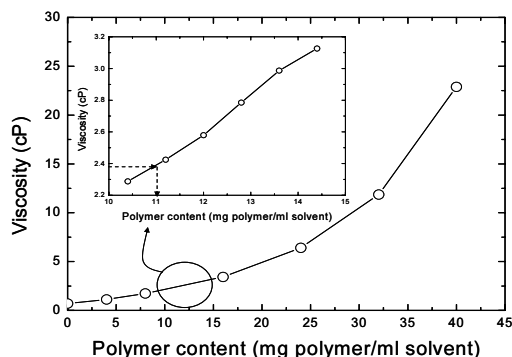


Fig. 1. The viscosity of printing ink with a function of polymer (PVK) content.

3. Results and discussion

concentration, we have fabricated single-layer devices with 7 different Ir(ppy)₃ doping concentrations from 0 to 8% as shown in Table 1.

Ir(ppy) ₃ Concentrations [%]	Max. Brightness [cd/m ²] at voltage [V]	Voltages at current density of 150 [mA/cm ²]	Max. luminous efficiency [cd/A] at voltage [V]	Max power efficiency [lm/W] at voltage [V]
0	48.4 (21.8 V)	-	0.1 (14.1 V)	0.024 (13.0 V)
1.2	9,800 (30.6 V)	28	30.1 (15.3 V)	6.58 (13.3 V)
2.4	4,900 (33.0 V)	31	11.9 (18.0 V)	2.12 (16.8 V)
3.6	20,700 (34.7 V)	33	63.2 (17.1 V)	12.2 (15.9 V)
4.8	10,500 (27.5 V)	26	20.2 (13.6 V)	5.03 (11.7 V)
6.1	7,900 (29.8 V)	27	9.45 (15.2 V)	2.18 (12.2 V)
8.0	8,900 (33.7 V)	28	12.2 (18.9 V)	2.19 (16.0 V)

Table 1. Effect of Ir(ppy)₃ concentration on performance of P-OLED

The device without Ir(ppy)₃ dopant showed very weak blue emission which was responsible for PVK or α -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 Y.-Y. 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/m² and peak luminous efficiency was found 63.2 cd/A with the brightness of 650 cd/m² 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/cm² 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, α -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].

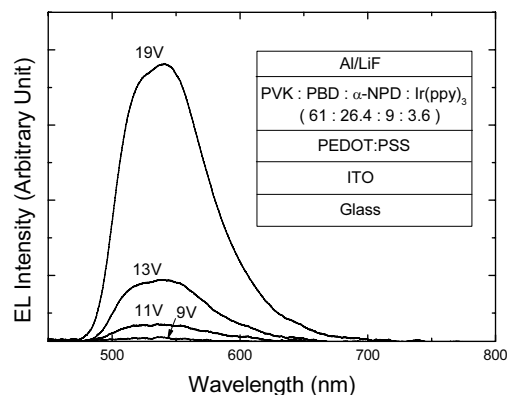


Fig. 2 EL spectra of the Ir(ppy)₃-doped devices (3.6%)

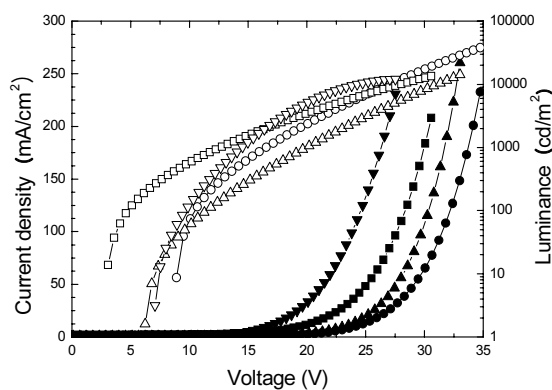


Fig. 3. C-V-L characteristics of the screen-printed single-layer OLEDs. Solid symbols represent C-V curves and open symbols represent L-V curves. Among the four different symbols, the triangular symbol represents the performance of the best device with a Ir(ppy)_3 doping concentration of 3.6%.

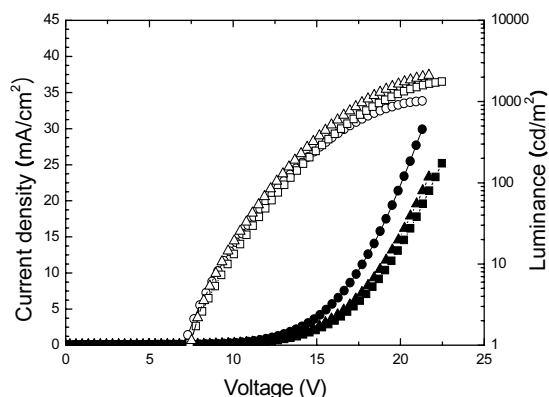


Fig. 4. C-V-L characteristics of the screen-printed single-layer OLEDs. Ir(piq)_2 doping concentration of 6.1%.

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 eV 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 of carriers between Ir(ppy)_3 could have facilitated to lower the 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].

Figure 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/cm^2 , a voltage of 17.1 V and a brightness of 650 cd/m^2 . 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/cm^2 , a voltage of 15.9 V

and a brightness of 470 cd/m². The operating voltages for 100, 1,000, 10,000 cd/m² are 11.8, 19.0, 30.5 V, respectively. These performances are comparable to those of devices fabricated by spin coating reported in the literature [2-4,8,11-14]. Furthermore we tried red, blue phosphorescent pattern using screen-printing process. Fig. 5 shows these screen printed PL images.

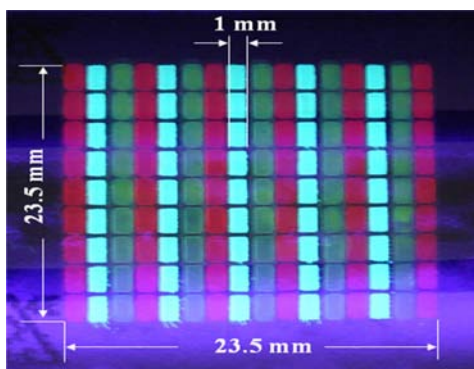


Fig. 5. Red(Ir(piq)₂), green(Ir(ppy)₃), and blue(FIrpic) Phosphorescent PL image.

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 fabricate single-layer phosphorescent polymer OLEDs.

4. Summary

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 35V. 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.

5. References

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