

Photo-Crosslinkable Hole Transport Material for Efficient Solution Processed Light Emitting Diode

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Keywords: Organic light-emitting diode (OLED), Photo-crosslinkable HTM, Red phosphorescent OLED

1 ABSTRACT

We investigated new crosslinkable hole transport materials (HTMs) for efficient solution-processed OLEDs. Especially, we developed the intrinsically photo-crosslinkable HTMs by adding nitrene type photo-crosslinking agent. Finally, we compared the device performances of those prepared with HTMs having semi-IPN composition as we reported before.[1]

2 INTRODUCTION

Organic light emitting devices (OLEDs) have attracted a lot of attention in recent decades due to their advantages such as vivid colors for the clear images, extremely high contrast ratio, wide viewing angle, design freedom due to its flexibility, etc. However, vacuum thermal deposition process, a current mass production method, has limitation in producing large area and high-resolution displays, which also result in low production yields as well as high production costs which may cause enormous difficulties in low cost manufacturing. Therefore, in order to improve those points, we are developing solution processed OLED to realize a large area as well as high-resolution devices as a low-cost processing. Unfortunately, solution processed OLEDs must avoid interface mixing during continuous wet processes because it affects the device performances such as device efficiency as well as operational lifetime.[2] Therefore, to protect such intermixing behavior, it is necessary to apply cross-linkable materials or the materials showing orthogonality of solubility against the next materials for wet process. However, when we crosslink the material after deposition, the carrier mobility is severely lowered, resulting in charge imbalance, resulting in deteriorated performances of devices.

In order to solve this problem, we need to blend high mobility materials inside such crosslinked network. As a result, we could obtain improved device performances, but intermixing issue cannot be excluded due to the linear polymers blended inside such crosslinked HTL system. Therefore, in this study, we investigated the possibility to use an intrinsically crosslinked HTL by adding crosslinking agent into the TFB and poly TPD, with high hole mobility.[3]

3 EXPERIMENT

The indium tin oxide (ITO) substrate with a 9 mm² emission area was used to make a solution processed OLED device. The substrates were cleaned with acetone and isopropyl alcohol for 20 min each by sonication and then treated with UV-ozone for 10 min. PEDOT: PSS (Heraeus ClevisTM P VP CH 8000) as a hole injection layer was spin coated under ambient conditions and immediately afterwards the substrate was transferred to an N₂ filled glove box and annealed at 150 °C for 20 minutes. HTM was spin casted and crosslinked by using HTM solution with a photo-crosslinking agent (PXA) of about 5 wt. % proportion. For a photo-crosslinking process, we pre-annealed the HTL at 80 degrees for 10 minutes and then photo-crosslinked by exposure under deep ultraviolet light (wavelength 254 nm) condition at a dose of about 300 mJ/cm². In the case of HTM requiring thermal crosslinking, the annealing was performed at 100 °C for 10 minutes (soft baking) and then at 220 °C for 30 minutes (hard baking) to give TX-HTM (thermally crosslinkable – HTM). The EML (emission layer) was prepared by spin-coating of EML solution with red host (RH) doped with 5% of red dopant (RD) and annealing at 80 °C for 10 minutes inside glove box. The electron transport layer was thermally deposited at a rate of 0.5 Å / s under typical vacuum conditions, and LiF and Al were also thermally deposited at 0.3 Å / s and 3 Å / s under typical vacuum conditions.

The following device structures are used for this study
Device A: ITO / PEDOT: PSS (40 nm) / **TX-HTM** : TFB (20%, 20 nm) / RH: RD (5%, 30 nm) / TPBI (40 nm) / LiF (1 nm) / Al (100 nm)
Device B: ITO / PEDOT: PSS (40 nm) / **TFB** : PXA (PX-TFB, 5%, 20 nm) / RH: RD (5%, 30 nm) / TPBI (40 nm) / LiF (1 nm) / Al (100 nm)
Device C: ITO / PEDOT: PSS (40 nm) / **TX-HTM** : Poly-TPD (20%, 20 nm) / RH: RD (5%, 30 nm) / TPBI (40 nm) / LiF (1 nm) / Al (100 nm)
Device D: ITO / PEDOT: PSS (40 nm) / **Poly-TPD** : PXA (PX-poly-TPD, 5%, 20 nm) / RH: RD (5%, 30 nm) / TPBI (40 nm) / LiF (1 nm) / Al (100 nm)

4 RESULTS

Fig 1 (a) shows the energy level diagram of the materials used in this study device. Fig 1 (b) shows the device structure. In this study, TFB and Poly-TPD materials were blended with TX-HTM, a thermally crosslinkable material, and FPA, a photo-crosslinking agent (PXA), was used when TFB and Poly-TPD were used alone. Fig 2 shows the UV-vis absorption spectra of TFB, Poly-TPD films after crosslinking. Especially, we inspected those spectra before and after rinsing to estimate the degree of crosslinking. In other words, after rinsing with chlorobenzene, at least 98% and 95% of each HTM remains unchanged, indicating good solvent resistance of HTM. Fig. 3(a) shows the J - V and L - V characteristics of fabricated red PHOLEDs and the representative results are summarized in Table 1. At a given constant voltage of 6.0 V, current density values of 1.50, 0.29, 2.56, and 19.03 mA/cm² are observed in the fabricated Devices A, B, C, and D, respectively. The driving voltage to reach 1000 cd/m² is 6.5, 7.5, 6.5, and 6 V for the Devices A, B, C, and D, respectively (Table 1). The relatively high turn-on voltages of 4, 4.5, 3.5, and 2.5 V were observed for the Devices A, B, C, and D, respectively. Probably, the moderate current density could be obtained from the semi-interpenetrating network (semi-IPN) by blending of TX-HTM and linear polymers (TFB and poly-TPD). Very interestingly, the current density is seriously reduced when we photo-crosslinked the TFB polymers (PX-TFB). In contrast, it increased dramatically when we photo-cured the poly-TPD. Especially, the Device D with poly-TPD showed the greatest current density at the observed driving voltage region and the operating voltage at 1000 cd/m² of brightness was observed to be ~6V, which is the lowest among the devices fabricated in this study. This means that the photo-crosslinked poly-TPD may have significantly higher hole mobility behavior compared to other materials while photo-crosslinked TFB polymers showed serious exciton quenching as well as mobility drop after crosslinking reaction. Because of this reason, we need to differentiate the optimal thickness for poly-TPD for the final device. Anyhow, from the same device structure as described above, the current and power efficiency characteristics of fabricated PHOLEDs obtained as shown in Fig. 3(b), The representative characteristics are also summarized in Table 1. At a given constant luminance of 1000 cd/m², the current and power efficiencies are 16.33 cd/A and 7.89 lm/W for the Device A, 10.49 cd/A and 4.39 lm/W for the Device B, 12.65 cd/A and 6.11 lm/W for the Device C, 7.24 cd/A and 3.79 lm/W for the Device D, respectively. These efficiency data correspond to 11.30, 7.17, 9.68, and 5.31 % external quantum efficiencies of PHOLEDs A, B, C and D, respectively. The maximum current and power efficiencies are 16.52 cd/A and 9.09 lm/W for the Device A, 10.97 cd/A and 5.30 lm/W for the Device B, 13.48 cd/A

and 10.08 lm/W for the Device C, 9.24 cd/A and 11.61 lm/W for the Device D, respectively. The color coordinates at 1,000 cd/m² were (0.64, 0.36), (0.64, 0.36), (0.65, 0.35), (0.65, 0.35) for Devices A, B, C, D, respectively.

5 CONCLUSIONS

Crosslinking is essential to increase efficiency by preventing intermixing in multilayer solution-processed OLEDs. However, in general, crosslinking seriously deteriorates charge mobility. However, semi-interpenetrating polymer network (semi-IPN) approach can be used to overcome those issues. Nevertheless, intermixing is still a concern due to non-crosslinked linear hole transport polymers (~ 20%) can be dissolved during the successive wet processes. Therefore, we developed a photo crosslinked HTM by using well-known linear hole transport polymers showing high hole mobility values. As a result, we found that the photo-crosslinked poly-TPD shows very low operating voltage behavior although its efficiency values should be improved by device optimization.

REFERENCES

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ACKNOWLEDGEMENTS

This research was supported by the Ministry of Trade, Industry and Energy (MOTIE, Korea) under Industrial Technology Innovation Program. No. 10067715, "Development of crosslinkable organic materials for highly efficient multistacked OLEDs fabricated by continuous printing process" also, we were supported by the BK21 Plus Program (Future-oriented innovative brain raising type, 21A20130000018) funded by the Ministry of Education (MOE, Korea) and National Research Foundation of Korea (NRF).

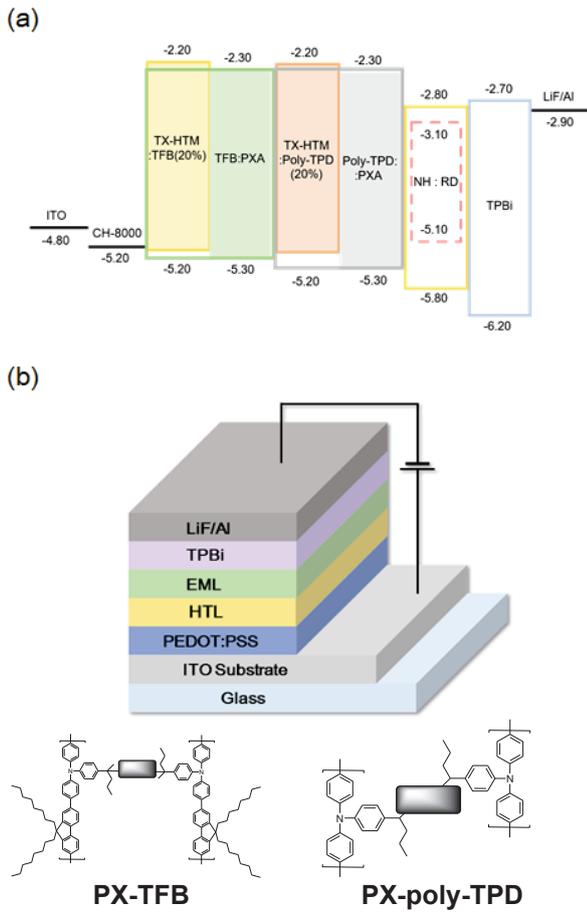


Fig. 1 (a) Energy level diagram and (b) multi-stacked device structure of the OLEDs prepared in this study.

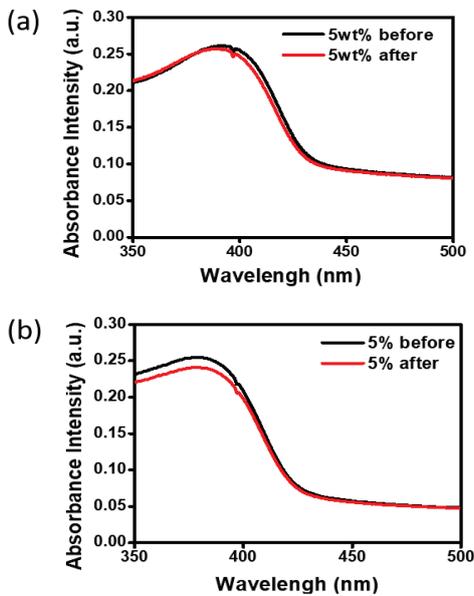


Fig. 2 (a) UV-vis spectra of crosslinked TFB before and after rinsing and (b) poly-TPD before and after rinsing.

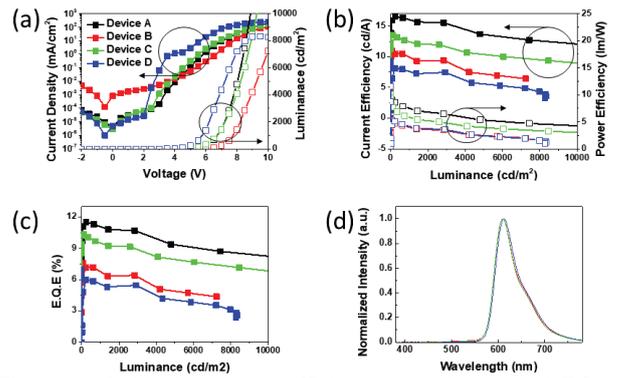


Fig. 3 (a) J-V-L (b) current efficiency - luminance (c) EQE - luminance (d) normalized EL (electroluminescent) spectra (at a brightness of 1000 cd/m²) of the solution processed red PHOLEDs.

Table 1. Summary of device characteristics

	Device A	Device B	Device C	Device D
Turn-on voltage (1 cd/m ²)	3.5 V	4V	3.5V	2.5V
Operating voltage (1,000 cd/m ²)	6.5V	7.5V	6.5V	6V
Efficiency (1,000 cd/m ²)	16.33 cd/A 7.89 lm/W	10.49 cd/A 4.39 lm/W	12.65 cd/A 6.11 lm/W	7.24 cd/A 6.94 lm/W
Efficiency (Max)	16.52 cd/A 9.09 lm/W	10.97 cd/A 5.30 lm/W	13.48 cd/A 10.08 lm/W	9.24 cd/A 11.61 lm/W
CIE(x,y) (1,000 cd/m ²)	(0.64, 0.36)	(0.64, 0.36)	(0.65, 0.35)	(0.65, 0.35)
E.Q.E (1,000 cd/m ²)	11.30%	7.17%	9.68%	5.31%