

Synthesis and Characterization of Crosslinked Hole Transporting Polymers for Organic Light Emitting Diodes

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Introduction

Impressive scientific and technological progress has recently been achieved in the area of multilayer organic light-emitting diodes (OLEDs).¹ Typical small-molecule hole transporting layers (HTLs) are triarylamine-based materials such as TPA or TPD (Figure 1), which are known to have appreciable hole transporting and electron blocking / exciton blocking capacity because of their relatively high-lying lowest unoccupied molecular orbital (LUMO) levels and large highest occupied molecular orbital (HOMO)-LUMO gaps.¹ Multilayer polymer-based LEDs (PLEDs) have several advantages compared to the small-molecule counterparts in the aspect of low cost, large-area and flexible display, but they are far more challenging to fabricate due to the risk of partial dissolution of a previous layer while depositing the next layer by solution processes.

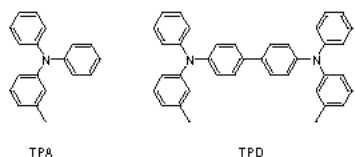


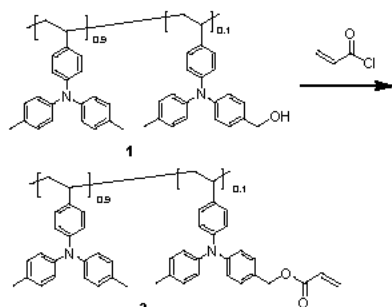
Figure 1. Chemical structures of small-molecule HTL materials

Poly(3,4-ethylene dioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) is the best-known polymer HTL, and has been shown to significantly enhance PLED anode hole injection and thus the device efficiency. However, it has serious drawbacks such as the ITO anode corrosion and poor surface energy match with aromatic emissive layers (EMLs).^{2,3}

In this study, we synthesized solution processible and crosslinkable polymeric TPA for HTL which also overcomes the drawbacks of PEDOT-PSS such as ITO corrosion. We prepared vinyl derivatives of TPA and TPD to make linear poly(vinyl-TPA) or poly(vinyl-TPD) bearing thermally crosslinkable substituent such as acrylate, and fabricated multilayer PLEDs by spin-coating and subsequent crosslinking of poly(vinyl-TPA) or poly(vinyl-TPD), prior to spin-coating of EML. Therefore, this paper describes the preparation of TPA networks as an insoluble HTL in PLED and the device performance results.

Experimental

Synthesis. The representative crosslinkable poly(vinyl-TPA) was synthesized as Scheme 1. For the synthesis of polymer 1, respective



Scheme 1. Representative synthesis of crosslinkable poly(vinyl-TPA) derivatives

monomers were prepared according to ref.⁴ which were subject to radical polymerization with AIBN, and the resulting polymer 1 was transformed to crosslinkable polymer 2 by introducing acryloyl chloride. Differential scanning calorimetry results of 2 showed exothermic peak only during the 1st heating, which results from vinyl polymerization of acrylate; it was also confirmed by insoluble nature of 2 after curing at 160°C for 1hr.

PLED Device Fabrication. PLED devices were fabricated using new TPA hole transporting layers, and PLEDs based on PEDOT-PSS were also fabricated as controls. The device structure is ITO / crosslinked TPA / PF9B (45nm) / LiF (1nm) / Al (200nm), and the control device is ITO / PEDOT-PSS / PF9B (45nm) / LiF (1nm) / Al (200nm). ITO was freshly treated by UV-ozone just before device fabrication. Polymeric TPA solution in chlorobenzene was spin-coated on ITO glass, and subsequently cured to crosslink at 190°C for 1hr in nitrogen atmosphere. Poly(9,9-dihexylfluorene-co-benzothiadiazole) (PF9B) solution in toluene was spin-coated on cured HTL as emissive layer, followed by vapor deposition of LiF and Al as cathode. The control device was also fabricated as above except that PEDOT-PSS was used for HTL.

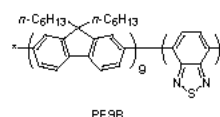


Figure 2. Chemical structure of PF9B ($\lambda_{ex} = 540\text{nm}$)

Results and discussion

The device efficiency using new polymeric crosslinked HTL (TPA device) compared with PEDOT-PSS as HTL (PEDOT device) is shown in Figure 3. External quantum efficiency of TPA device is 0.37% with 40nm thick crosslinked TPA polymer HTL, almost twice as high compared with 0.23% for the PEDOT device with 40nm thick PEDOT-PSS. But the turn-on voltages of TPA devices were about 13V that is higher than 7V of PEDOT device. Lower turn-on voltage of PEDOT devices comes from the conducting nature of PEDOT-PSS as compared with polymeric TPA layer.

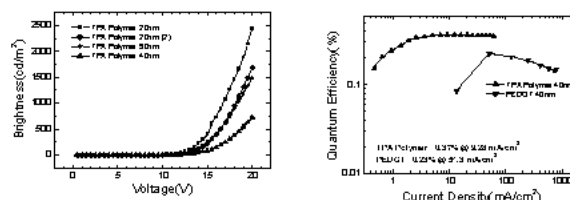


Figure 3. Device performances; TPA Polymer indicates device composed of crosslinked 2 as HTL, and PEDOT indicates control device composed of PEDOT-PSS as HTL

Conclusions

We prepared crosslinkable polymer HTL containing TPA for solution-processible PLEDs. Using PF9B as EML, the external quantum efficiency was higher for the crosslinked TPA-polymer HTL, as compared with conventional PEDOT-PSS HTL.

Acknowledgment

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References

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