

Organic light-emitting diode with 20 lm/W efficiency using a triphenyldiamine side-group polymer as the hole transport layer

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We have used triphenyldiamine side-group polymers as hole transport layers in multilayer organic light-emitting diodes using 8-hydroxyquinoline aluminum (Alq₃) as an emission layer. The device efficiency systematically increases as the ionization potential of the hole transport layer is shifted further from the work function of the indium–tin–oxide anode. We attribute this trend to better balance of hole and electron charges in the device. An optimized device consisting of a fluorinated version of the polymer as the hole transport layer, quinacridone doped Al as the emission layer, and a LiF/Al cathode results in a peak external luminous efficiency of 20 lm/W. © 1999 American Institute of Physics. [S0003-6951(99)02421-3]

Research interest in organic light-emitting diodes (OLEDs)^{1,2} continues to grow as their performance approaches a commercially viable level for applications such as low-cost, flat-panel displays. In order to be useful, these devices must have high brightness and efficiency, while requiring a low operating voltage. Multilayer devices consisting of thermally deposited hole transport layer (HTL) and emission layers have been shown to have high performance and good operational stability.^{3,4} The HTL typically consists of a triphenyldiamine (TPD) or similar compound which is known to have high hole mobility. TPD also has an ionization potential (IP) which is well positioned between the work function of indium–tin–oxide (ITO) (~4.7 eV) and the IP of many emission materials. Initial studies addressing the effects of varying the IP of the HTL on the device performance have led to differing results.^{5,6} However, more recent studies have shown that the device quantum efficiency increases as the difference between the IP of the HTL and the emission layer is decreased.^{7,8} These studies have generally been done using thermally deposited small-molecule hole transport materials. One disadvantage to this approach is that the morphological properties of the HTL film are affected by the particular molecular design. Possible crystallization of the hole transport material and poor interfacial contact with the ITO anode result in decreased device performance. In this study, we use a series of functionalized polymers with TPD derivative side groups as the HTL. The IP of these polymers can be controlled to provide a systematic way to investigate the importance of the IP of the HTL to the device performance while maintaining a consistent film morphology.

The IP of TPD has been measured to be 5.38 eV using ultraviolet photoelectron spectroscopy.⁹ This value can be

systematically decreased (shifted toward the vacuum level) by adding an electron-donating moiety, such as *p*-OCH₃, or increased (shifted further from the vacuum level) by adding an electron-withdrawing moiety, such as *m*-F. This principle is demonstrated by the three polymer TPD derivatives shown in Fig. 1, P1–P3, that have an IP that ranges from 5.06 to 5.56 eV. In this study, we used polymers P1–P3 as the HTL in double-layer OLEDs with a thermally evaporated emission layer of either pure 8-hydroxyquinoline aluminum (Alq₃) (IP=5.93 eV), or Alq₃ doped with quinacridone.

The details of the synthesis of polymers P1–P3 are given

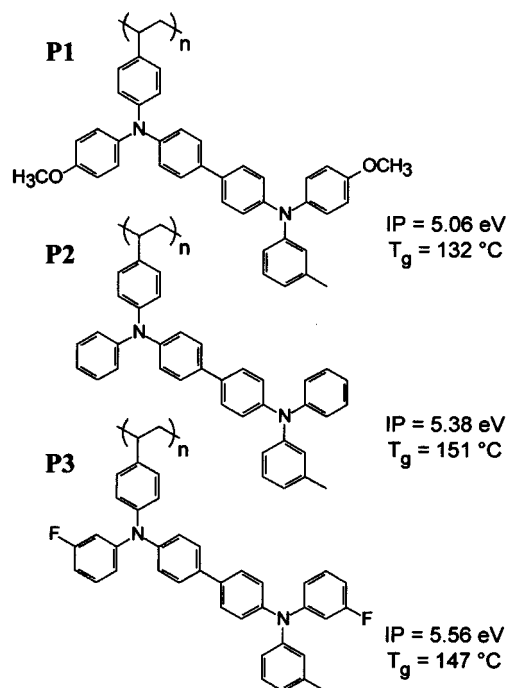


FIG. 1. TPD derivative hole transport polymers used in this study.

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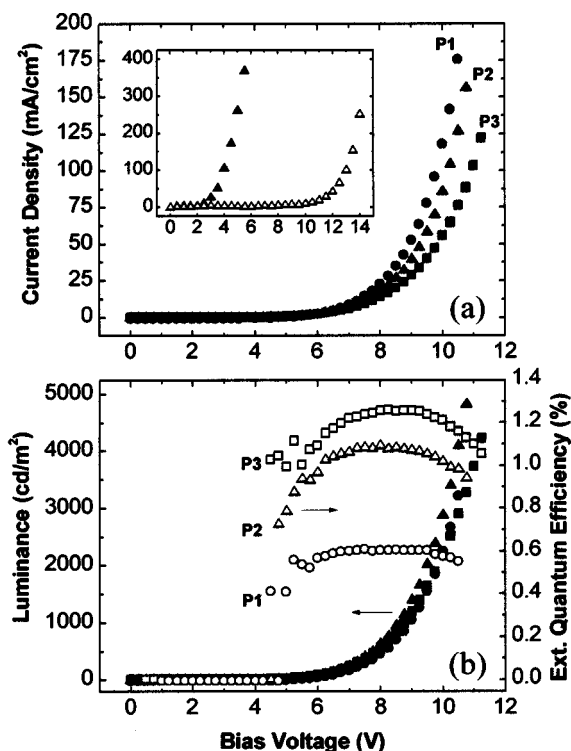


FIG. 2. (a) Current density (mA/cm²) vs applied voltage (V) for ITO/polymer 40 nm/Alq₃ 60 nm/Mg 150 nm devices where polymer=P1 (●), P2 (▲), and P3 (■). (Inset) Current density (mA/cm²) vs applied voltage (V) for ITO/small-molecule TPD 90 nm/Al 150 nm (open) and ITO/polymer P2 90 nm/Al 150 nm (closed) devices. (b) Luminance (cd/m²) (closed) and external quantum efficiency (% photons/electron) (open) vs applied voltage (V) for devices in (a).

elsewhere.¹⁰ Alq₃, quinacridone, and TPD were obtained commercially (Aldrich) and purified by sublimation techniques. OLEDs were fabricated on ITO coated glass substrates (Donnelly Corp.) with a nominal surface resistance of 20 Ω/sq. The hole transport polymer films were spin coated from dichloroethane solutions to a thickness of 40 nm. Emission layers consisting of either pure Alq₃ or Alq₃ doped with quinacridone (0.5% by weight) were thermally deposited to a thickness of 60 nm. Either Mg (150 nm) or a bilayer of LiF (0.8 nm)/Al (150 nm) was thermally deposited as the top cathode. Details of the device fabrication and characterization are given elsewhere.³ Single-layer devices with a thickness of 90 nm were fabricated by either thermal deposition of small-molecule TPD or spin coating of polymer P2 onto ITO substrates followed by deposition of an Al cathode. All thermal depositions were done in a small bell jar (diameter=25 cm) with a source-to-sample distance of 17 cm and a fixed sample holder. The IP of the polymers P1–P3 was estimated to be the same as that of thermally deposited films of the small molecule analogues (TPD, *m*-F–TPD, *p*-OCH₃–TPD) measured via ultraviolet photoelectron spectroscopy.⁹

To compare the current-injection and transport properties of spin-coated polymer TPD (P2) versus thermally evaporated, small-molecule TPD, we prepared single-layer devices on ITO with an aluminum cathode. The inset to Fig. 2 shows that the turn-on voltage for the polymer P2 device is approximately 8 V lower than for the small-molecule TPD device. We attribute this to a difference in the interfacial

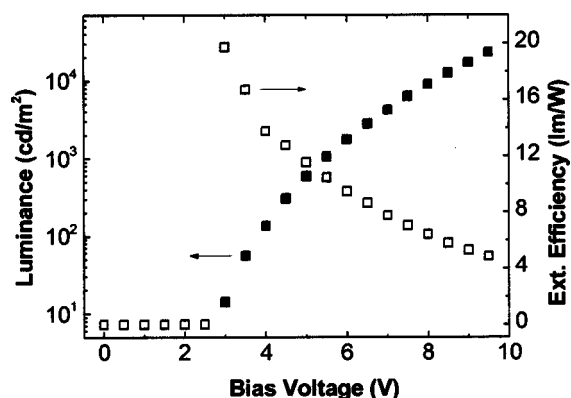


FIG. 3. Luminance (cd/m²) (closed) and external luminous efficiency (lm/W) (open) vs applied voltage (V) for ITO/polymer P3 40 nm/Alq₃:quinacridone (0.5% by weight) 60 nm/LiF 0.8 nm/Al 150 nm device.

contact with ITO. Spin coating of the polymer provides better contact with the rough ITO surface (2–3 nm rms). This results in low interfacial resistance and a low operating voltage when polymers P1–P3 are used as the HTL in an OLED. We emphasize that our deposition chamber has a small source-to-sample distance and a fixed, nonrotating sample holder; more sophisticated deposition systems are likely to yield better film coverage. However, these data illustrate the importance of the morphology at the organic–ITO interface for hole injection into the OLED.

Figure 2 shows current density, luminance, and external quantum efficiency versus applied voltage for double-layer OLEDs using polymers P1–P3 as the HTL, Alq₃ as the emission layer, and Mg as a cathode. The emission spectra of the three devices were identical and exhibited the characteristic Alq₃ emission peak at approximately 525 nm. Figure 2(a) shows that the operating voltage required to drive a given current increases as the IP of the HTL is increased. Figure 2(b) shows that the external quantum efficiency increases as the IP of the HTL is increased. The OLED is most efficient when the IP of the HTL is shifted away from the work function of ITO and closer to the IP of the Alq₃ emission layer. These same trends were also seen in optimized devices which included doping the Alq₃ emission layer with quinacridone and replacing the Mg cathode with a bilayer LiF/Al cathode.³ Figure 3 shows the luminance and luminous efficiency versus applied voltage for an optimized device using polymer P3 as the HTL. At an applied voltage of 3.0 V, the luminance is 15 cd/m², and the luminous efficiency is 20 lm/W (corresponding to approximately 4.5% external quantum efficiency). At an applied voltage of 4.0 V, the luminance is 135 cd/m², and the luminous efficiency is 14 lm/W.

We find that the most likely explanation for the trend in the OLED efficiencies is that increasing the IP of the HTL reduces the rate of hole injection from the ITO anode and creates a better balance between the number of holes and electrons in the device. The trend in the operating-voltages shown in Fig. 2(a) demonstrates that the number of injected majority carriers, generally thought to be holes, decreases as the IP of the HTL is increased. Another possible explanation for the trend in the efficiencies is that a “cross reaction” occurs at the interface between the HTL and the emission layer to produce luminescence. Electrogenerated chemilumi-

nescence experiments carried out in solution between positively charged TPD molecules and negatively charged Alq₃ molecules have been shown to produce Alq₃ luminescence.⁹ The efficiency of this luminescence was shown to increase as the IP of the TPD derivative was increased, resulting from the increased driving force of the reaction. However, we do not attribute the trend in the OLED efficiencies to this mechanism. Complimentary results show that devices in which a layer of thermally evaporated *p*-OCH₃-TPD, corresponding to polymer P1, has been inserted between the hole transport polymer P3 and the emission layer do not result in a decreased efficiency, as would be expected if the cross-reaction mechanism is important in the device operation. Therefore, we conclude that the cross reaction is not the dominant mechanism of light emission in these devices. We also consider that the hole mobilities of the three polymer P1–P3 may differ because of additional dipole disorder introduced by the side groups. However, it has been shown that the OLED quantum efficiency is independent of the HTL mobility.⁸ Finally, it has been shown that exciplex formation between the HTL and the emission layer reduces the device efficiency,⁶ however we find no evidence of exciplex emission in these devices.

Due to the high glass-transition temperature of polymer P1–P3, which ranges from 132 to 151 °C, we expect these devices to have good thermal stability. However, as reported elsewhere, the device lifetimes correlate more strongly with the IP of the HTL than with its glass-transition temperature.¹⁰ The device lifetime decreases as the IP of the HTL is increased. For small molecules, this has been explained by crystallization at the interface between the ITO and the HTL as a result of joule heat that is produced as charges are injected across a larger energetic barrier.¹¹ Thus, there is an intrinsic tradeoff between the efficiency and the lifetime in these double-layer OLEDs. Preliminary results

indicate that this problem can be overcome by using multiple hole-transport layers to create a staircase of energetic levels between the ITO and the Alq₃ layer.

In summary, we have used TPD derivative side-group polymers to fabricate smooth, pinhole free films on ITO substrates for use as hole transport layers in OLEDs. An optimized device structure exhibits a peak luminous efficiency of 20 lm/W. We find that the OLED efficiency increases as the IP of the HTL is shifted further from the work function of the ITO. We attribute this trend to better balance of hole and electron charges in the device.

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