

Charge carriers bulk recombination instead of electroplex emission after their tunneling through hole-blocking layer in OLEDs

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Abstract. Charge carriers bulk recombination instead of forming electroplex after their tunneling through a hole-blocking layer, i.e. 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), in organic electroluminescence (EL) device ITO/poly-(N-vinyl-carbazole)(PVK)/BCP/tris(8-hydroxyquinoline) aluminum (Alq₃)/Al is reported. By changing the thickness of BCP layer, one can find that high electric fields enhance the tunneling process of holes accumulated at the PVK/BCP interface into BCP layer instead of forming “electroplex emission” as reported earlier in literatures. Our experimental data show that charge carriers bulk recombination takes place in both PVK layer and BCP layer, and even in Alq₃ layer when BCP layer is thin enough. Further, it is suggested that PVK is the origin of the emission shoulder at 595 nm in the EL spectra of trilayer device ITO/PVK/BCP/Alq₃/Al.

PACS. 73.20.-r Electron states at surfaces and interfaces – 73.40.-c Electronic transport in interface structures – 74.78.Fk Multilayers, superlattices, heterostructures – 77.84.Jd Polymers; organic compounds

1 Introduction

Extensive studies have been made on organic light-emitting diodes (OLEDs) in view of both academic interest and practical application. In both layered and single-film structures, the key device processes, charge recombination and charge separation, occur at the heterojunction between the two components [1,2]. A thorough understanding of the organic-organic interface is therefore of crucial importance. Recently, a number of papers appeared showing EL spectra of OLEDs to differ substantially from the photoluminescence (PL) spectra of their component materials [3–15]. The EL spectra show often up as red-shifted broad bands which have been mostly assigned as emission from exciplexes formed at the solid interface between a hole-transporting layer (HTL) and an electron-transporting layer (ETL). The materials of the former act as molecular electron donors (D) and the latter as molecular electron acceptors (A). Exciplex formation is favored where there is significant spatial overlap between the lowest unoccupied molecular orbitals (LUMOs) of the constituent species [16], which is clearly the case for conjugated organics, whose LUMOs are highly delocalized π orbitals. However, electroplex is particular emission species and it distinguishes from exciplex in that electroplex only occurs under high electric fields but exci-

plex occurs under both photoexcitation and high electric fields. Wang et al. [17–19] reported that a new emission shoulder at 595 nm was found in the EL spectra of device made of PVK:BCP (1:1 in weight) blend, and he designed it is from “electroplex emission” that occurred between PVK and BCP molecules, and white light emission has been observed by making good use of this kind of “electroplex emission” at the PVK/BCP interface [17]. In his papers, however, he seldom mentioned the thickness of organic layers in the devices. As we know, the EL spectra of bilayer or multi-layer devices usually depend on both the thickness of the organic layers and the bias voltages.

Therefore, in order to get more insight into the nature of the charge carriers recombination process under high electric fields at the organic-organic interfaces with high charge carriers injection barriers, in this paper, we choose PVK, BCP and Alq₃ to demonstrate the influence of BCP on EL spectra of trilayer device ITO/PVK/BCP/Alq₃/Al, and the origin of the new emission at around 595 nm in the EL spectra of ITO/PVK/BCP/Alq₃/Al is discussed in detail.

2 Experimental

In our experiments, PVK firstly is dissolved in chloroform solution with a concentration of 10 mg/ml, and then is

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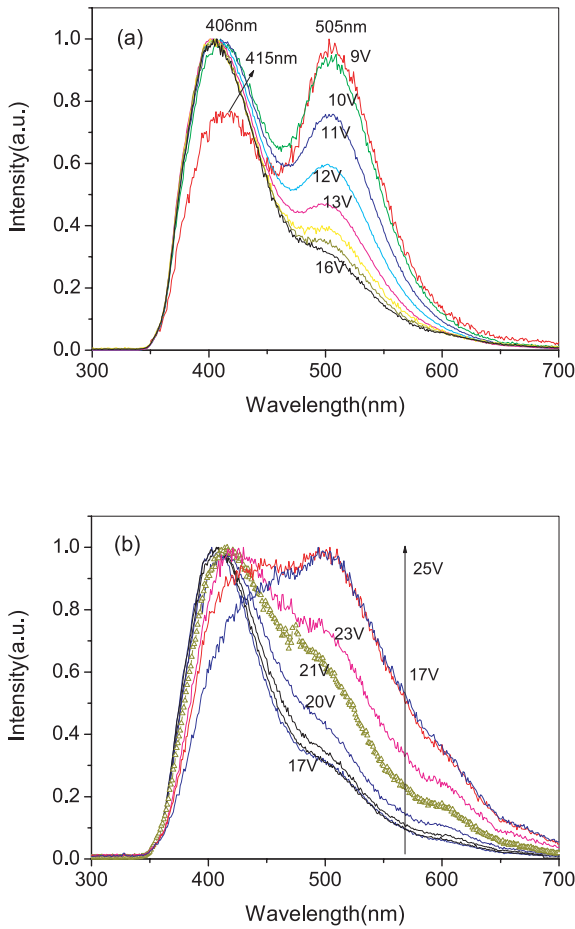


Fig. 1. Normalized EL spectra of device ITO/PVK/BCP(10 nm)/Alq₃(10 nm)/Al at different applied voltages. (a) Applied voltages from 9 V to 16 V; (b) applied voltages from 17 V to 25 V.

spin-coated onto the ITO substrate (sheet resistance of 80 Ω /square) which was thoroughly cleaned by scrubbing, ultrasonic and irradiation in a UV-ozone chamber. Alq₃ and BCP films are deposited by thermal evaporation at a rate of 0.1 nm/s under high vacuum of 2×10^{-6} Torr. The thickness of PVK layer (about 80 nm) is measured with an XP-2 surface profilometer. The EL and PL spectra are measured with Spex Fluorolog-3 spectrometer at room temperature in air.

3 Results and discussions

The normalized EL spectra of device ITO/PVK/BCP(10 nm)/Alq₃(10 nm)/Al are shown in Figure 1a (from 9 V to 16 V) and Figure 1b (from 17 V to 25 V). From Figures 1a and 1b, we can see that the EL spectra mainly consist of two maximum emissions at around 410 nm (exciton emission from PVK) and 505 nm (it is related to excimer emission from BCP [20]). The emission at 505 nm is dominant at lower applied voltages but later emission from PVK dominates under higher electric fields, and then the emission at 505 nm gets more and

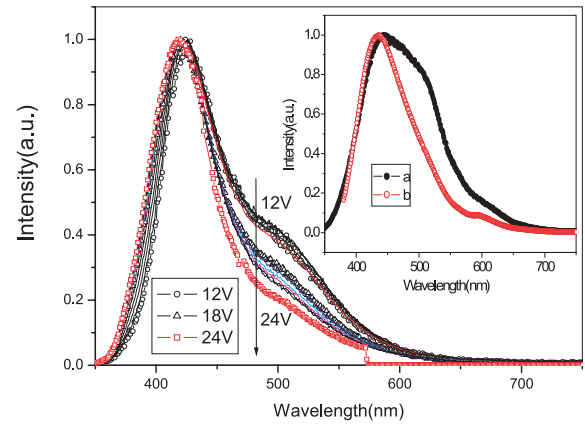


Fig. 2. Normalized EL spectra of device ITO/PVK/BCP(30 nm)/Alq₃(10 nm)/Al at different applied voltages. The inset shows the normalized EL spectra of devices (a) ITO/PVK/ZnSe(120 nm)/Alq₃(15 nm)/Al and (b) ITO/PVK/ZnSe(100 nm)/Alq₃(15 nm)/Al.

more intense again for further increasing applied voltages and, in sequence, the spectrum gets much broader. One may notice that both emission from Alq₃ excitons (peak at 520 nm) and a shoulder around 595 nm appear and get stronger under high electric fields, in the meantime, the relative intensity of exciton emission of PVK decreases. From here, one can see that recombination zone moves to Alq₃ layer. By only increasing BCP film to 30 nm and keeping others constant, no emission from Alq₃ layer is observed any more, as shown in Figure 2. The relative emission intensity of BCP to PVK decreases with increasing applied voltages. Except for a 6 nm blue-shift of PVK emission, the emission shoulder at about 595 nm is not visible any more even under high electric fields. Under almost the same electric fields, why there is no emission at 595 nm from the latter device? Therefore, it is natural and reasonable for one to doubt that the emission at 595 nm originates from electroplex emission cross the PVK/BCP interface. From Figure 1, one can see holes accumulated at the BCP/PVK interface tunnel through BCP layer and recombine with electrons in Alq₃ layer under high electric fields.

In order to confirm if the BCP is necessary for the emission at 595 nm, further, we substitute BCP with an inorganic semiconductor, zinc selenide (ZnSe), to do the same experiments and made device ITO/PVK/ZnSe(100 nm)/Alq₃(15 nm)/Al, in which ZnSe film is fabricated by electron-beam evaporation [21]. As shown by the inset in Figure 2, an emission shoulder at about 595 nm is observed in its EL spectra. By only increasing ZnSe film to 120 nm and keeping the thickness of other layers constant, the emission from ZnSe intensifies and the emission shoulder at 595 nm is not so obviously as before. Because the difference of conduction band of ZnSe and HOMO of PVK is only 1.4 eV (see the inset in Fig. 3), the emission around 595 nm could not be from any “electroplex emission” occurred at the PVK/ZnSe interface. Therefore, based on above experimental results

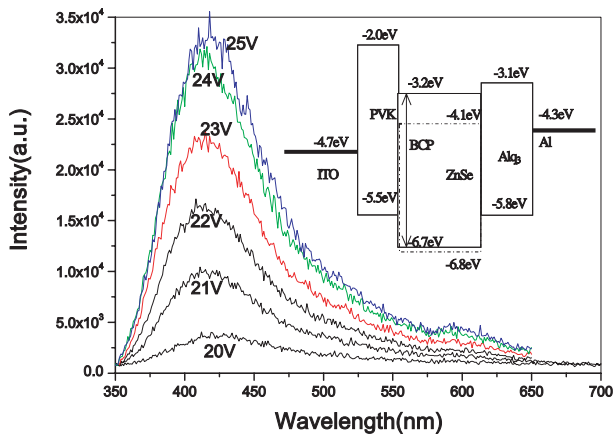


Fig. 3. EL spectra of device ITO/PVK(120 nm)/Al at different applied voltages. The inset shows the energy diagram of trilayer device ITO/PVK/BCP(ZnSe)/Alq₃/Al.

a conclusion can be drawn that the emission shoulder at 595 nm is not from BCP, and it should be related with PVK.

Actually, Hu et al. [15] reported that there is an emission shoulder at around 595 nm from pure PVK film under high electric fields. Therefore, we made single-layer device ITO/PVK/Al and the emission shoulder at 595 nm really appears under a certain applied voltage, as shown in Figure 3. Furthermore, we fabricated device ITO/PVK(100 nm)/BCP(10 nm)/Alq₃(15 nm)/Al, the normalized EL spectrum of this trilayer device at 31 V is shown in Figure 4, as well as the normalized EL spectrum of single-layer device ITO/PVK(120 nm)/Al at 25 V. From this figure, one can see that the relative intensities of shoulder emission at 595 nm are almost the same in these two EL spectra except for ca.12 nm red-shift of the peak emission for the trilayer device. Therefore, we believe that the emission shoulder at 595 nm in the EL spectra of ITO/PVK/BCP/Alq₃/Al is from PVK layer instead of “electroplex emission” occurred across the PVK/BCP interface.

The energy diagram of ITO/PVK/BCP(ZnSe)/Alq₃/Al is also shown by the inset in Figure 3, the holes and electrons injection barriers concurrently increase to 1.2 eV at PVK/BCP interface after inserting BCP layer, therefore, holes (electrons) will be blocked by BCP (PVK) and accumulate on opposite sides at the PVK/BCP interface. In this way, recombination region usually occurs in both sides near the PVK/BCP interface, that’s the reason why we can see two emission peaks around 410 nm and 505 nm. The amount of electrons and holes accumulated at the interface increases with applied voltage, sequentially the electric field in the bulk redistributes and the electric field in PVK layer gets higher than that in BCP layer, in this way, the recombination region moves back to BCP layer again, therefore, emission from BCP intensifies again. During this process, the increment of electric field in BCP layer will make its holes mobility to increase dramatically and holes accumulated at PVK/BCP interface can transport through the BCP layer and then recombine

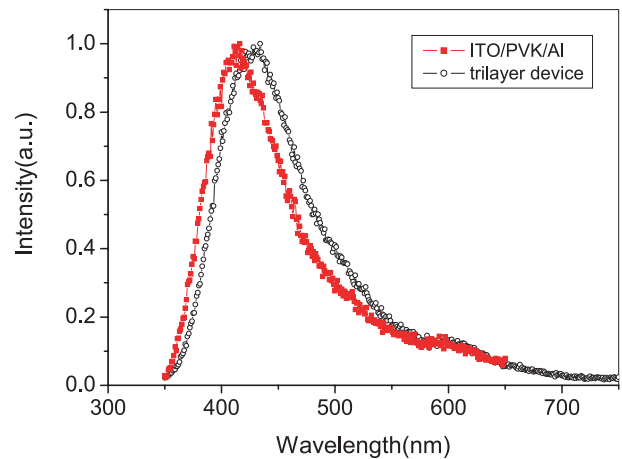


Fig. 4. Normalized EL spectra of trilayer device ITO/PVK/(100 nm)/BCP(10 nm)/Alq₃(15 nm)/Al at 31 V and single-layer device ITO/PVK(120 nm)/Al at 25 V. One can see that the relative intensities of emission at 595 nm are almost the same for these two EL spectra.

with electrons in Alq₃ layer, competing with bulk exciton emissions in both PVK layer and BCP layer. For a thicker BCP layer, electric field redistributes in the device bulk and, holes cannot efficiently tunnel BCP layer any more, therefore only bulk charge recombination (excitons emission) in both PVK layer and BCP layer can be observed, and the relative emission intensity from BCP decreases with increasing the applied voltages since the recombination region moves to the PVK layer.

4 Conclusion

In summary, the influence of BCP on the EL of trilayer device ITO/PVK/BCP/Alq₃/Al is discussed. Under high electric fields, the tunneling process of holes accumulated at the PVK/BCP interface will be enhanced and injected into BCP layer instead of forming electroplex emission across the PVK/BCP interface. Therefore, the EL spectrum of the device consists of emissions from both PVK layer and BCP layer. Further, if BCP layer is thin enough, the EL spectrum is the superposition of charge carriers bulk recombination in PVK layer, BCP layer and Alq₃ layer as the result of holes tunneling through BCP layer. Also, our experimental results suggest that the emission shoulder at 595 nm is from PVK.

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