

EMISSION CHARACTERISTICS OF ORGANIC LIGHT-EMITTING DIODES WITH A HETEROSTRUCTURE OF DYE DOPED POLY(*N*-VINYLCARBAZOLE)/TRIS(8-HYDROXYQUINOLINE) ALUMINUM*

Yong Qiu**, De-qiang Zhang and Yan Shao

Department of Chemistry, Tsinghua University, Beijing 100084, China

Abstract Organic electroluminescent diodes with a heterostructure of 9,10-bis(phenylethynyl) anthracene (BPEA) doped poly(*N*-vinylcarbazole) (PVK)/tris(8-hydroxyquinoline)aluminum (Alq₃) have been fabricated. The electroluminescence (EL) both from BPEA and Alq₃ were observed when the Alq₃ layer is thin enough. With increasing thickness of the Alq₃ layer, the relative emission intensity of BPEA is gradually decreased. For the thin Alq₃ layer structure, the light emission of Alq₃ becomes more dominant as the applied voltage increases. It is proposed that the electron-hole recombination takes place in both PVK and Alq₃ films. The field-induced quenching theory has also been applied to explain the change of the EL spectra with applied voltage.

Keywords Electroluminescence, Poly(*N*-vinylcarbazole), Electron transport, Hole transport

INTRODUCTION

In the past decade, organic light-emitting diodes (OLEDs) have attracted much interest due to their unique merits such as low drive voltage, easy fabrication, full color emission^[1-6]. Since the lifetime of the device has been greatly improved to over ten thousand hours in the past few years, this technology has reached practical application stage. Although numerous advances have been made in the field of OLEDs, especially in the development of new electroluminescent (EL) materials, the operation mechanism for charge carrier transport, electron hole recombination as well as the shift of the exciton still remains poorly understood. Such an understanding is of great significance, since it has been recognized that controlling the movement of the charge carriers and the location of the carrier recombination are crucial for obtaining high-performance OLEDs.

For a typical OLED, holes are injected from the anode film (indium-tin-oxide, ITO) into hole transport material and the electrons are injected from the cathode film into the electron transport material. The radiative recombination of the injected holes and electrons leads to light emission. It is obvious that the carrier recombination is critical in an OLED. The recombination region is determined by a few factors, such as the film thickness, the bias voltage, the barrier height at the interface as well as the charge transport properties of the materials.

Tang *et al.*^[1] have demonstrated that in diamine/tris(8-hydroxyquinoline)aluminum (Alq₃) devices, the carrier recombination is confined to the Alq₃ layer near the diamine layer and only the light emission from Alq₃ was observed. Alq₃ is known to be both an excellent electron transport

* This work was supported by the National Natural Science Foundation of China (No. 59790050-08) and the Youth Foundation of Tsinghua University.

** Corresponding author: Yong Qiu (邱勇), E-mail: qiuym@mails.tsinghua.edu.cn

Received March 20, 1998

material and an efficient light-emitting material. In the double-layer devices with Alq_3 as the electron transport material, the electron-hole recombination always occurs in the Alq_3 layer and the green light emitted from Alq_3 is observed. For the structure diamine derivative (TPD)/ Alq_3 , when a 1,2,4-triazole derivative was inserted between the TPD and Alq_3 layers to slow down hole migration to the Alq_3 layer, carrier recombination occurs in the TPD^[6]. However, In the poly(*p*-phenylene vinylene) (PPV)/ Alq_3 diodes, simultaneous observation of EL emission from both PPV and Alq_3 was recently reported^[7]. Among the polymers employed in the fabrication of OLEDs, poly(*N*-vinylcarbazole) (PVK) was considered to be a good hole transport material with good stability. In order to tune the emission color by doping the PVK with dye molecules, a third blocking layer was needed between the Alq_3 layer and the PVK layer^[7, 8]. The inserted layer blocks the hole transport, resulting in the electron-hole recombination occurring in the PVK layer.

In this paper, we report that in the dye doped PVK/ Alq_3 devices without a blocking layer, when the Alq_3 layer is thin enough, the light emission from both the PVK layer and Alq_3 was simultaneously observed. The fluorescent dye 9,10-bis(phenylethynyl)anthracene (BPEA) was chosen as the dopant due to its highly fluorescent efficiency. The EL spectrum as a function of the thickness of the Alq_3 layer and the applied voltage has been investigated. An explanation of the experimental results is also presented.

EXPERIMENTAL

Our organic light-emitting diodes consist of an ITO coated glass substrate, a hole transport layer of PVK containing BPEA, an electron transport layer of Alq_3 and an cathode of Mg:Ag in 10:1 atomic ratio. The schematic diagram and the structure of the used molecules are shown in Fig. 1. The ITO glass substrate was first cleaned by sequential heating in a detergent, rinsing in deionized water, ultrasonic cleaning in acetone and isopropanol. Both PVK and BPEA were dissolved in 1,2-dichloroethane. The dye doped polymer thin film was formed by spin-coating the solution of PVK and BPEA, the concentration of BPEA in PVK was about 2 wt%. The thickness of the polymer layer was estimated to be about 50 nm. The Alq_3 film was formed by thermal evaporation under a vacuum of 2×10^{-5} Torr, and the deposition rate was 0.2~0.3 nm/s, as measured by a quartz crystal thickness monitor. Under the same vacuum condition, the alloy cathode was deposited on the organic layer by coevaporation from two separate sources. The active area of the EL cell was about 0.28 cm².

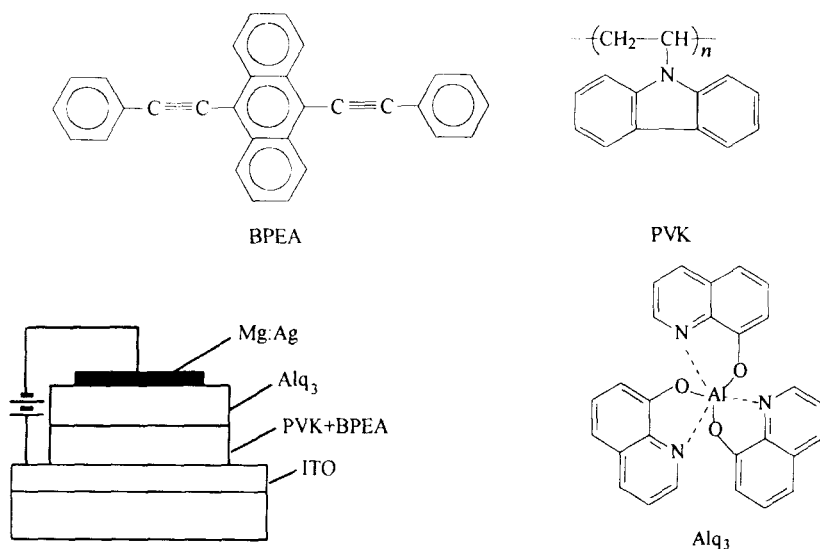


Fig. 1 Schematic diagram of the device and the molecular structures of the materials

The EL spectra were measured with a linear CCD (Charge Coupled Devices) spectrometer, which was calibrated with a standard lamp. All the measurements were carried out directly in air at room temperature without any post-treatment to the devices. The absorption and photoluminescence spectra of BPEA doped PVK film and Alq₃ film, both deposited on the slide substrates without the ITO film by spin-coating and vacuum evaporation, respectively, were measured (Fig. 2). Since the Alq₃ emission spectrum overlapped with the BPEA absorption spectrum slightly, the radiative migration and radiationless electronic energy transfer from Alq₃ to BPEA is not important, although it cannot be excluded.

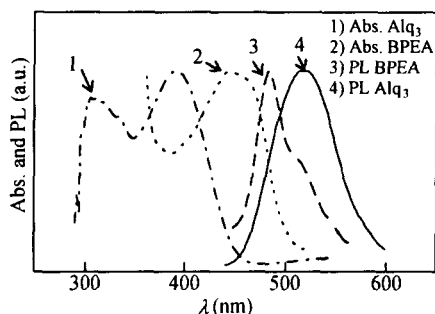


Fig. 2 Normalized absorption (ABS) and photoluminescence (PL) spectra of Alq₃ film and BPEA doped in PVK film

RESULTS AND DISCUSSION

Figure 3 exhibits the current-voltage (I-V) and luminance-voltage (B-V) characteristics of the devices under a forward bias with positive charge on the ITO electrode. With increasing thickness of the Alq₃ layer, the turn-on voltage of the EL emission in the devices increases. This is because the onset of the EL emission of OLEDs is determined by the electric-field strength. The best luminous efficiency was found to be 1.0 lm/W in the BPEA doped PVK/50 nm Alq₃ structure.

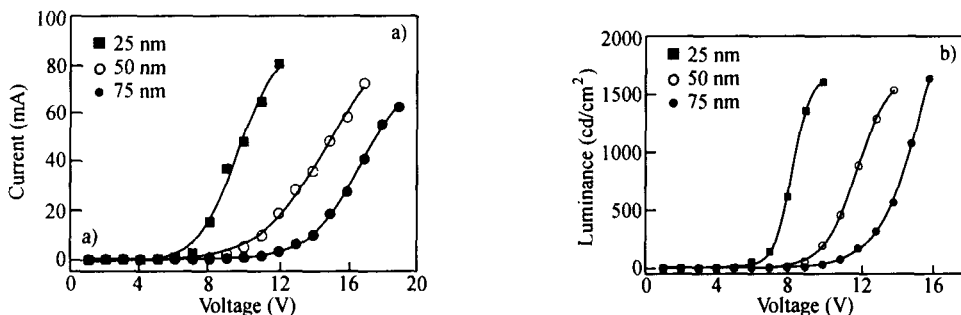


Fig. 3 Current-voltage a) and luminance-voltage b) curves of the BPEA doped PVK/Alq₃ devices with different Alq₃ thickness: 25 nm (square), 50 nm (open circle), 75 nm (solid circle)

Figure 4 shows that the EL spectra of the devices with the thickness of the Alq₃ layer varying from 25 nm to 75 nm.

In the case of a thin Alq₃ layer, two emission peaks, which are located at 490 nm and 520 nm, were observed in the EL spectra (Fig. 4). Since the photoluminescence spectra of BPEA and Alq₃ exhibit emission peaks at 490 nm and 520 nm, respectively (Fig. 2), it is reasonable to ascribe the two emission peaks in the EL spectra to be due to BPEA and Alq₃, respectively. It can be concluded that the EL spectra come from both the Alq₃ layer and the PVK layer. When the thickness of the Alq₃ layer increases, the 490 nm peak decreases correspondingly (Fig. 4). For the

device with Alq₃ layer of 75 nm, only one peak at 530 nm was observed in the EL spectrum (Fig. 4). The shift of the Alq₃ emission towards longer wavelength with increasing Alq₃ layer thickness is due to the interference phenomenon of emission in front of a reflecting mirror^[1].

In the devices with the structure PVK/Alq₃, the emission color could be tuned by doping the polymer layer, but a third layer was needed to block the hole transport^[7]. It is, to the best of our knowledge, the first time that direct light emission was observed from the PVK layer without a third blocking layer. One possible explanation is that the exciton transport from Alq₃ layer into the PVK layer leads to the excitation of BPEA molecules. Recently, Wu *et al.*^[9] reported the simultaneous appearance of light emission from both the electron transport layer and the hole transport layer in the structure of poly(*p*-phenyl vinylene)(PPV)/Alq₃. They concluded that excitons are formed in the Alq₃ film, far from the PPV/Alq₃ interface, and the exciton diffusion from Alq₃ into PPV is responsible for the excitation of PPV molecules, since the dependence of the EL spectra on the layer thickness and its independence on bias are observed^[9]. In our work, the similar dependence of the EL spectra on the Alq₃ layer thickness is found, however, the EL spectra are also found to be a function of the voltage (Fig. 5).

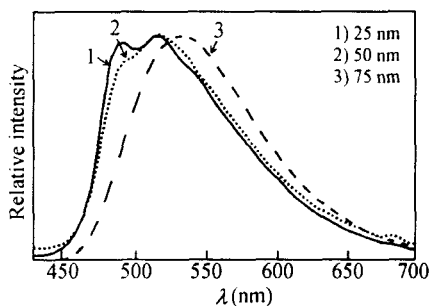


Fig. 4 Normalized EL spectra of the BPEA doped PVK/Alq₃ devices with different Alq₃ thickness: 25 nm (solid line), 50 nm (dotted line) and 75 nm (dashed line)

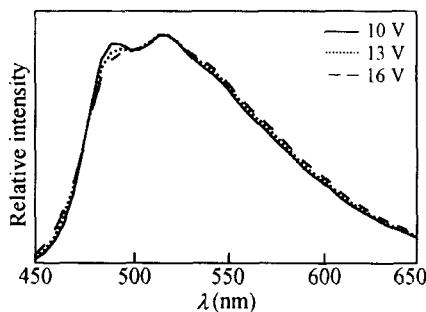


Fig. 5 Normalized EL spectra of the BPEA doped PVK/Alq₃ devices driven by different voltages: 10 V (solid line), 13 V (dotted line), 16 V (dashed line)

Figure 5 exhibits the dependence of the EL spectrum upon the applied voltages. For the thin Alq₃ layer structure, with increasing bias voltage, the peak intensity at 490 nm decreases with respect to that at 520 nm, indicating that the relative contribution to the light emission from the doped dye molecules becomes smaller. Thus, the exciton shift mechanism is not applicable in our case since excitons are neutral and its movement should not be affected by the electric field. In addition, PVK and BPEA have larger exciton energies than that of Alq₃, thus the excitons created within the Alq₃ layer do not have the ability to migrate into PVK layer^[10]. Suzuki *et al.*^[11, 12] have also shown that for the two-layer coumarin 6 (C6) doped polymer/Alq₃ films, the exciton diffusion from Alq₃ to C6 layer does not exist, although in a vacuum deposited Alq₃ film doped with C6, efficient energy transfer from the host Alq₃ to the doped C6 molecules was confirmed^[2]. One of the plausible reasons is that the exciton diffusion across an interface is prevented by the presence of nonradiative recombination centers at the interface^[12].

We hold that the hole-electron recombination and the subsequent exciton formation takes place both in PVK and Alq₃ layers and results in the respective emission. In the case of a thin Alq₃ layer, some electrons enter the PVK layer and recombine with holes near the PVK/Alq₃ interface. A schematic energy diagram is shown in Fig. 6. The energy barrier for electron transport is 1.2 eV, while the barrier for hole transport is 0.3 eV. Obviously, PVK blocks electrons more efficiently than Alq₃ blocks holes. Thus, the fact that the EL intensity from BPEA decreases correspondingly as the thickness of the Alq₃ layer increases can be explained by the decay of electron flux with

distance from the Alq₃/cathode, causing less exciton formation in the PVK layer. Suzuki *et al.*^[13] have also demonstrated that in the OLEDs with the structure poly(methylphenylsilane)/dye doped poly(styrene)/Alq₃, the emission from the dye dopants originates from the direct charge-carrier recombination. This result is also consistent with the work of Jordan *et al.*^[14]. They demonstrated that for the structure TPD/2-naphthyl-4,5-bis(4-methoxyphenyl)-1,3-oxazole (NAPOXA)/Alq₃, recombination takes place both in NAPOXA and Alq₃ layers and the relative amount of formed excitons in NAPOXA or Alq₃ is determined by the NAPOXA layer thickness. A similar result has also been obtained by Mori *et al.*^[15].

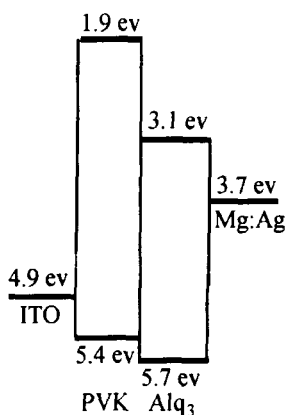


Fig. 6 The energy diagram of the device

The dependence of color change of the OLEDs on voltage can be explained in terms of different mechanisms^[16~18]. In our case, however, we argue that the rate of hole injection into Alq₃ across the interface increases as the applied voltage increases. This enables more efficient hole-electron recombination in the Alq₃ layer and results in fewer electrons entering the PVK layer from the Alq₃ film, causing the overall recombination zone to move to the cathode. Another origin of the change in the EL spectra with bias voltages might be associated with the electric-field-induced dissociation of the excitons. The dissociation of the singlet excitons caused by the electric field leads to the formation of electron-hole pair or charge transfer state^[19]. It is possible that the electric-field-induced quenching efficiency of BPEA is larger than that of Alq₃, resulting in the decrease of BPEA emission intensity with respect to Alq₃.

The excitation process of the BPEA dopant is not apparent at present. However, two plausible mechanisms can be presented. First, the BPEA molecules are excited *via* Förster-type energy transfer from the host PVK excitons, while the latter generated by the recombination of holes with electrons injected from Alq₃; second, the charge carrier recombination occurs on BPEA molecules and results in the formation of excitons of BPEA.

Summarizing, double-layered OLEDs with the structure BPEA doped PVK/Alq₃ were fabricated. It is the first time that EL emission was observed from both the dye dopant and the Alq₃ without a third blocking layer for the same device structure. It appears that the electron-hole recombination zone can extend over different layers, depending on the energy barriers at the interface, the active layer thickness as well as the bias voltages. The dependence of the EL spectra on the Alq₃ layer thickness has been explained in terms of the existence of electron-hole recombination both in the Alq₃ and PVK layers. The change of the EL spectra with bias voltages has also been discussed.

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