Improved characteristics of polymer light-emitting diode based on poly(alkylfluorene) with functional layer fabricated by contact printing method

H Kajii, K Mizuno and Y Ohmori

Graduate School of Engineering, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan

E-mail: kajii@oled.eei.eng.osaka-u.ac.jp

Abstract. In the organic light-emitting diode, the multilayer structure is useful to achieve the effective carrier injection and transport, and improve the emission efficiency. The characteristics of the polymer light-emitting device with a functional layer by contact printing method are investigated. Hole transport material, the guest and electron transport material are mixed at each layer with the same host. Poly(9,9-dioctylfluorene) (F8) and Tris[1-phenylisoquinolinato-C2,N]iridium(III) (Ir(piq)3) are used as the host and guest materials. We focused on the effects of a functional layer with 1,3,5-Tris (1-phenyl-1H-benzimidazol-2-yl)benzene(TPBi) as the electron transport material doped in F8. For a non-heterostructure device with F8:TPBi functional layer, electrons are injected from the cathode interface to TPBi and transported through F8. TPBi acts as the effective hole blocking and electron transport layer as TPBi is mixed in F8 at the cathode side. Non-heterostructure device exhibits improved emission efficiency and lower driving voltage.

1. Introduction
In organic semiconductors, π-conjugated polymers, being quasi-one-dimensional macromolecular electronic systems, offer a number of unique properties. Blue polymer light-emitting diodes utilizing poly(alkylfluorene) have been demonstrated for the first time [1]. Fluorene-type polymers have emerged as an important class of conducting polymers due to their efficient emission, high stabilities and relatively high mobilities [2-4]. Fluorene-type polymers also have the potential for full-color emission via energy transfer to longer wavelength emitters in blends with other fluorescent and phosphorescent dyes [5].

Employing phosphorescent materials yields high efficiencies because breaking the spin conservation rule allows both singlet and triplet excitons to contribute to emission. A specific class of organic light-emitting diodes (OLEDs) has achieved high luminescence efficiency using the phosphorescent emission from a triplet state of Ir complexes [6,7]. Employing solution process of organic materials is useful for OLEDs fabrication, and allows for the possibility of low cost mass production and for making high-sized screens.

In the OLEDs, the multilayer structure is useful to achieve the effective carrier injection and transport, and to improve emission efficiency. We investigated the characteristics of the polymer light-emitting diode (PLED) based on poly(alkylfluorene) with a functional layer by contact printing method.
2. Materials and Methods

The glass substrate was degreased with solvents and cleaned in a UV ozone chamber. To reduce the possibility of electrical shorts within the PLEDs, a 40-nm-thick poly(ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) hole-injection layer was spin-coated on an indium tin oxide (ITO)-coated glass substrate. Poly(9,9-dioctylfluorene) (F8) and tris[1-phenyliso quinolinato-C2,N]iridium(III) (Ir(piq)_3) were used as the host and the guest materials. The doping concentration of Ir(piq)_3 was fixed at 3 wt.% relative to F8. Hole transport material, guest and electron transport material were mixed at each layer with the same host. To improve carrier balance, a hole transport material of 4,4',4''-Tri(9-carbazoyl)triphenylamine (TCTA) are blended into an emissive layer. 1,3,5-Tris (1-phenyl-1H-benzimidazol-2-yl)benzene (TPBi) was used as the electron transporting material.

The emissive layers (EMLs) were fabricated by spin-coating method into 50 or 70 nm-thick layers on PEDOT:PSS layer. The concentration of the EML of F8:TCTA:TPBi:Ir(piq)_3 was 100:50:40:3 wt.%.

A TPBi layer was fabricated by organic molecular beam deposition on the EML to form the device at a background pressure of about 10^{-5} Pa. The cathode consisting of CsF (2 nm)/Mg:Ag/Ag or MoOx (5 nm)/Ag and Al anode were deposited in vacuum at a chamber base pressure of about 10^{-4} Pa. The active area was 4 mm^2.

The absolute photoluminescence quantum yields (PLQYs) were measured using an absolute PL quantum yield measurement system (HAMAMATSU, Quantaures-QY). The film for the PL QY measurement was formed on quartz glass substrate. The electroluminescence (EL) spectra were measured using a photonic multichannel spectral analyzer (Hamamatsu Photonics, PMA-11). The current density-voltage-luminance (J-V-L) characteristics were obtained using a digital sourcemeter (Keithley2400), and a luminance meter (Minolta LS-100). Impedance spectroscopy measurements were carried out using a Solatron 1260 impedance analyzer with a 1296 dielectric interface. The typical AC oscillation amplitude was 100 mV.

3. Results and Discussion

A multilayer approach to fabricating active layers helps to improve PLED performance. We focused on the improved characteristics of a non-heterostructure PLED with a functional layer based on TPBi doped in F8. The device structures are as follows:

- device A: ITO/PEDOT:PSS/F8:TCTA:Ir(piq)_3 (70 nm)/CsF/Mg:Ag/Ag,
- device B: ITO/PEDOT:PSS/F8: TCTA:TPBi:Ir(piq)_3 (70 nm)/CsF/Mg:Ag/Ag,
- device C: ITO/PEDOT:PSS/F8:TCTA: Ir(piq)_3 (50 nm)/F8:TPBi (20 nm)/CsF/Mg:Ag/Ag,
- device D: ITO/PEDOT:PSS/F8:TCTA: Ir(piq)_3 (50 nm)/TPBi (20 nm)/CsF/Mg:Ag/Ag.

For device C, a F8:TPBi layer, deposited on a poly(dimethysiloxane) stamp, was transferred to the EML using contact printing [8]. For comparison, device D with TPBi as a hole-blocking layer was fabricated.

![Figure 1](image-url)  
**Figure 1.** (a) J-V-L and (b) current efficiency–current density characteristics of devices A, B, C and D. The inset of Fig. 2b shows typical EL spectrum of device C.
PLQY of an EML is one of the important factors to achieve the high efficiency. The energy transfer between other host materials and Ir(piq)$_3$, mainly occurred via the triplet state of host materials and the metal ligand charge transfer (MLCT) state of Ir(piq)$_3$. The excited energy state also transferred from the singlet state of host materials to the singlet MLCT state, and then transferred to the triplet (MLCT) state via intersystem crossing. PLQYs of F8:TCTA:Ir(piq)$_3$ and F8:TCTA:TPBi:Ir(piq)$_3$ films were estimated to be 40 and 41%. PLQY of EML in device B was almost the same as those in devices A, C and D. All devices exhibited red emission based on Ir(piq)$_3$, as shown in the inset of Fig. 1b.

Figure 1 shows the current density-luminance-applied voltage (J-V-L) characteristics – current density characteristics of devices A, B, C and D. Devices C and D showed increased luminance and current efficiency, as compared to devices A and B. For device C, the maximum luminance of approximately 10,000 cd/m$^2$ was obtained. Devices A and C showed lower driving voltage than devices B and D.

We fabricated four types of hole-only devices A$_h$, B$_h$, C$_h$ and D$_h$ with MoOx/Ag cathode instead of CsF/Mg:Ag/Ag to understand hole injection and transport. Hole current of device B was markedly lower than those of devices A$_h$, C$_h$ and D$_h$, as shown in Fig. 2a. Hole currents of devices C$_h$ and D$_h$ were also slightly decreased, compared to device A. This result suggested that TPBi acts as the hole blocking as TPBi has the lowest unoccupied molecular orbital (LUMO) level lower than other materials which results in higher driving voltage for device B.

In order to estimate the effect of electron injection and transport, current density-voltage characteristics of four types of electron-only devices A$_e$, B$_e$, C$_e$ and D$_e$ with Al anode instead of ITO/PEDOT:PSS are given in Fig. 2b. Electron current of device D$_e$ was markedly lower than those of devices A$_e$, B$_e$ and C$_e$, which results in higher driving voltage for device D.

The fundamental properties of devices are mostly investigated under DC operation. The $J$–$V$ characteristics represent the overall result of injection and transport of carriers through the organic layers and electrodes. From the view of carrier transport dynamics, impedance spectroscopy is an effective method to study transport dynamics in the devices [9-12]. To further understand the factors affecting the electrical properties due to TPBi, these behaviors of the electrical properties of the devices were analyzed using impedance spectroscopy measurements. Figure 3 shows the Bode plot of the imaginary part of the modulus in devices A, B and C. The peak frequencies of the Bode-plot show the reciprocal value of the relaxation times. For all devices, the relaxation times of the emission layer increased with increasing voltage. The peak shift to a higher frequency is related to the decrease in resistance of the organic layers. Compared to devices B and C, an additional peak for device A was
observed at high frequencies. This result suggested that for device A, CsF induces transient accumulation of electrons at the F8/electrode interface. For the devices B and C with mixed F8 and TPBi, electrons are injected from the cathode interface to TPBi and transported through F8. Electron transport ability of F8 is better than that of TPBi. For device C, F8:TPBi layer acts as hole blocking and electron transport layer, which results in improved carrier balance.

4. Conclusions

We investigated the characteristics of the polymer light-emitting devices with functional layers by contact printing method. We focused on the effects of the F8:TPBi functional layer. Non-heterostructure device showed the maximum luminance of approximately 10,000 cd/m$^2$. For the non-heterostructure device with a F8:TPBi functional layer, electrons are injected from the cathode interface to TPBi and transported through F8. TPBi acts as the effective hole blocking and electron transport layer as TPBi is mixed in F8 at the cathode side. Non-heterostructure device exhibited improved emission efficiency and lower driving voltage owing to improved carrier balance and transport.

Acknowledgements

Part of this work was supported by Grant-in-Aid for Scientific Research, from the Ministry of Education, Culture, Sports, Science and Technology, Japan. This research was also partially supported financially by a Grant in Aid of Special Coordination Funds for Promoting Science and Technology.

References

[1] Ohmori Y, Uchida M, Muro K and Yoshino K 1991 Jpn. J. Appl. Phys. 30 L1941-L1943
[2] Kajii H, Koiwai K, Hirose Y and Ohmori Y 2010 Org. Electron. 11 509-513
[3] Koiwai K, Kajii H and Ohmori Y 2011 Synth. Met. 161 2107-2112
[4] Tanaka H, Kajii H and Ohmori Y 2015 Synth. Met. 203 10-15
[5] Hino Y, Kajii H and Ohmori Y 2006 Thin Solid Films 499 359-363
[6] Baldo M A, Lamansky S, Burrows P E, Thompson M E and Forrest S R 1999 Appl. Phys. Lett. 75 4-6
[7] Adachi C, Baldo M A, Forrest S R and Thompson M E 2000 Appl. Phys. Lett. 77 904-906
[8] Takakuwa A, Misaki M, Yoshida Y and Yase K 2009 Thin Solid Films 518 555-558
[9] Meier M, Karg S and Riess W 1997 J. Appl. Phys. 82 1961-1966
[10] Scherbel J, Nguyen P H, Paasch G, Brüttng W and Schwoerer M 1998 J. Appl. Phys. 83 5045-5055
[11] Okachi T, Nagase T, Kobayashi T and Naito H 2008 Thin Solid Films 517 1327-1330
[12] Yamamoto T, Kajii H and Ohmori Y 2014 Org. Electron. 15 1077-1082

Figure 3. Bode-plot of the imaginary part of the modulus in (a) device A, (b) device B and (c) device C.