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Organic light-emitting diodes based on new n-doped electron transport layer

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ABSTRACT

Organic light-emitting diodes with 8-hydroxy-quinolinato lithium doped 4′7-diphyenyl-1, 10-phenanthroline as electron transport layer (ETL), and etrafluro-tetracyano-quinodimethane doped 4,4′,4″-tris(3-methylphenylphenylamono) triphenylamine as hole transport layer (HTL) are demonstrated. The conductivity of carrier transport layers with different doping concentration is examined by hole-only and electron-only devices. Compared with the referenced device (without doping), the current efficiency and power efficiency of the p–i–n device are enhanced by approximately 51% and 89%, respectively. This improvement is attributed to the improved conductivity of the transport layers and the efficient charge balance in the emission zone.

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1. Introduction

Since the discovery of organic light-emitting devices (OLEDs), there has been a considerable interest in developing OLEDs with high efficiency for display applications [1]. In order to lower driving voltage and enhance power efficiency, it is critical to enhance the carrier injection from the electrode to the transporting layer and to increase the transport conductivity [2,3]. The hole injection can be improved by increasing the work function of ITO with different surface treatments such as O_2 plasma or UV–ozone treatment of ITO surface [4]. It can also be enhanced by introducing hole injection layer (HIL), such as copper phthalocyanine (CuPc) [5], starburst polyamines [6], polymeric PEDT:PSS [7] and 4,4′,4″-tris(*N*-(2-naphthyl)-*N*-phenylamino)triphenylamine (2-TNATA) between the ITO/hole transport layer (HTL) interface.

Recently, the p-doping of HTL has drawn a lot of attentions because of its ability to enhance hole injection and lower driving voltages in OLEDs. The p-doping HTL is typically made by co-evaporating the hole transporting materials with a strong electron acceptor like tetrafluro-tetracyano-quinodimethane (F_4-TCNQ) [8], or oxidants like $SbCl_5$ [9], $FeCl_3$ [10] and iodine [11]. p-Doping can also achieve ohmic conductivity to reduce driving voltage of device and the proper control of doping levels can also lead to efficient carrier injection by tunnelling [12].

However, organic molecules are known to be poor in electron injection and transport compared with that of hole. Many attempts have been made to improve the electron injection and transport, including using low work function metals [1,13–15] as cathode, or inserting a thin interlayer between cathode and electron transporting layer [16–20] to enhance electron injection. Great efforts have been made to enhance the electron conductivity [21–24]. Kido and Matsumoto [22] reported the improved electron transport by doping Li into tris(8-hydroxyquinoline) aluminum (Alq_3). Fong et al. [21] also demonstrated that the device performance was enhanced significantly by doping 4′7-diphyenyl-1, 10-phenanthroline (Bphen) into Alq_3 as a cohost electron transport layer (c-ETL). However, few studies have been reported about using lithium quinolinato complex such as 8-hydroxy-quinolinato lithium (Liq) as an electron injection layer [25], and no work has yet been reported about using Liq-doped BPhen as electron transport layer (ETL).

In this paper, we have demonstrated a device with an new n-doping (33 wt.% Liq:BPhen) layer as ETL and p-type (*m*-MTDATA:*x* wt.% F_4-TCNQ) layer as HTL. Here, 33 wt.% Liq is chosen due to the fact that the device with the doping ratio of 33 wt.% Liq demonstrates the best current density vs voltage (*J*–*V*) curve among all the electron only devices. Using this method, we obtained a sig-

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nificant improvement in the device performance as compared with the referenced device.

2. Experiments

The structure of the complete devices fabricated in this work is as follows:

ITO/*m*-MTDATA:*x* wt.% F_4-TCNQ (40 nm)/NPB (10 nm)/Alq_3 (20 nm)/ BPhen:*y* wt.% Liq (50 nm)/LiF (1 nm)/ Al (130 nm).
Device A (referenced device): $x = 0$, $y = 0$; *Device B*: $x = 0$, $y = 33$; *Device C*: $x = 0.3$, $y = 33$; *Device D*: $x = 2$, $y = 33$; *Device E*: $x = 4$, $y = 33$.

In the devices, 4,4′,4″-tris(3-methylphenylphenylamono) triphenylamine (*m*-MTDATA):*x* wt.% etrafluro-tetracyano-quinodimethane (F_4-TCNQ)and Bphen:*y* wt.% Liq are used as p-doping HTL and n-doping (ETL), respectively. *N*,*N*′-diphenyl-*N*, *N*′-bis(1,1′-biphenyl)-4,4′-diamine (NPB) and Alq_3 are used as interlayer and emission layer (EML), respectively, while LiF and Al are used as electron injection layer and cathode, respectively. The active area of the devices defined by the overlap of the ITO and the Al electrodes is about 5 mm × 5 mm.

The devices were fabricated as follows: Glass coated with ITO (with a sheet resistance of 20 Ω/square) was used as starting substrate. Prior to the organic films being deposited, the substrates were initially scrubbed in a detergent solution. They were then immersed sequentially in a heated ultrasonic bath of de-ionized water for 15 min. Finally, the substrates were blown dry with nitrogen gas and then treated by UV–ozone for 10 min prior to use before it was loaded into an evaporation system. First, a 40 nm-thick *m*-MTDATA:F4-TCNQ HIL was co- deposited onto the ITO. Secondly, a 10 nm-thick layer of NPB was deposited onto the HIL as a hole HTL. Thirdly, a 20 nm-thick Alq_3 as EML was deposited onto the HTL. Then, a 50 nm-thick BPhen:Liq ETL was co-deposited on the EML. In the co-deposition process, organic sources were independently controlled. The deposition rates for the co-deposition layer were monitored using two independent quartz sensors. Finally, a shadow mask was used to define the cathode consisting of 130 nm-thick Al. All the layers (organic layers, and Al electrode) of the devices were fabricated by conventional thermal evaporation in a high vacuum chamber with a base pressure of 1×10^{-5} Torr. The deposition rate was maintained at 0.5 ± 0.2 Å/s for the organic materials, 0.1 Å/s for LiF and 5 ± 2 Å/s for Al.

Using the same methods as above, a series of hole-only devices in which the current consists mainly of the holes and electron-only devices in which the current consists mainly of the electrons were fabricated. These devices have the following structures:

Hole-only devices:ITO/*m*-MTDATA:*x* wt.% F4-TCNQ (40 nm)/NPB (10 nm)/Al (130 nm). *Device H1*: $x = 0$; *Device H2*: $x = 0.3$; *Device H3*: $x = 2$; *Device H4*: $x = 4$.
Electron-only devices:ITO/BCP (5 nm)/BPhen:*y* wt.% Liq (50 nm)/Al (130 nm). *Device E1*: $y = 0$; *Device E2*: $y = 17$; *Device E3*: $y = 33$; *Device E4*: $y = 50$.

The current vs voltage (*I*–*V*) and luminance characteristics were measured by computer controlled programmable Keithley 2400dc Source Meter and Minolta LS-110 luminance meter. All measurements were carried out at room temperature and under ambient conditions without any protective coating. Molecular structures of the organic materials used in this study are shown in Fig. 1.

3. Results and discussion

Fig. 2 and 3 show the *J*–*V*, current efficiency vs current density and power efficiencies vs current density characteristics of the

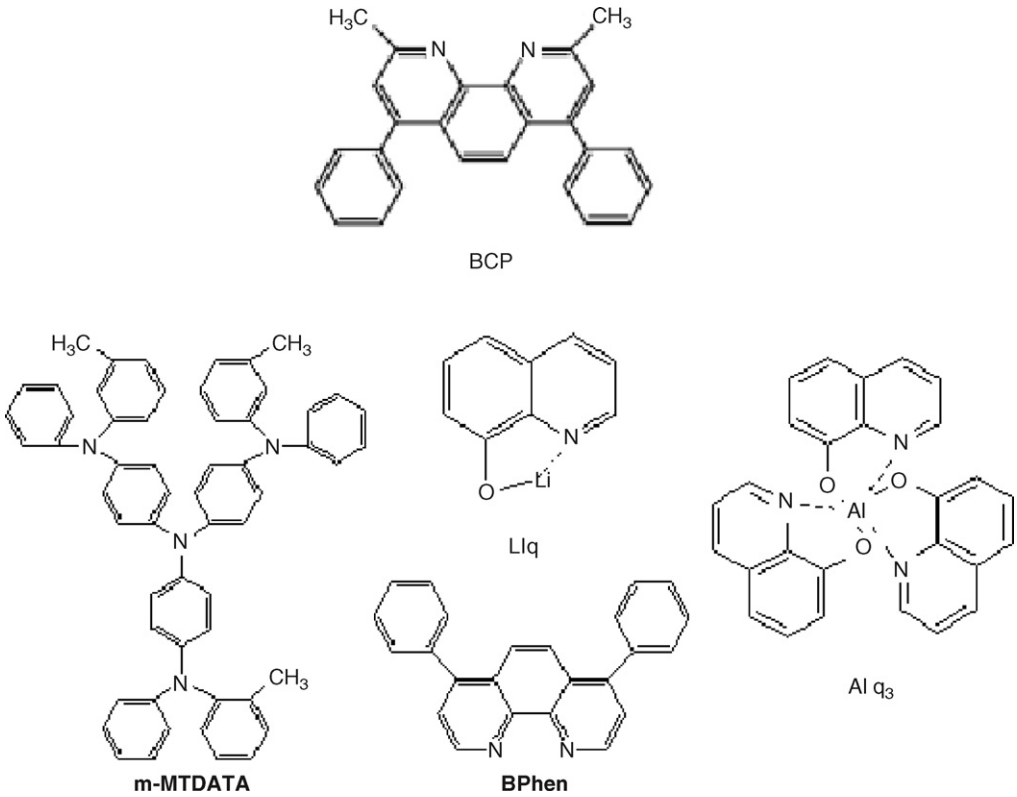

Fig. 1. Molecular structures of main materials used.

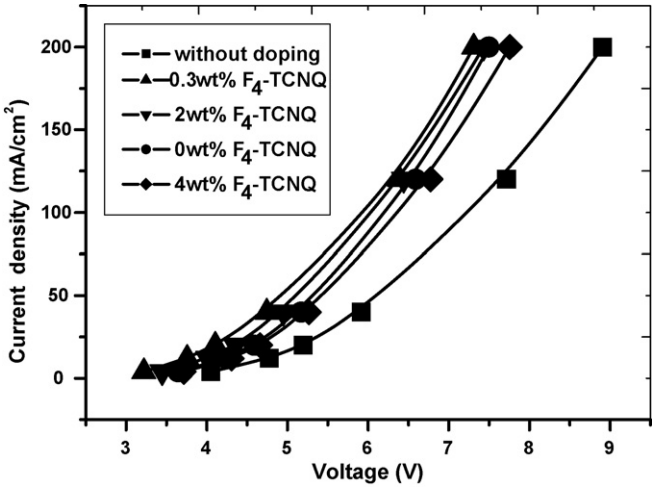

Fig. 2. Current density vs voltage characteristics of the complete devices.

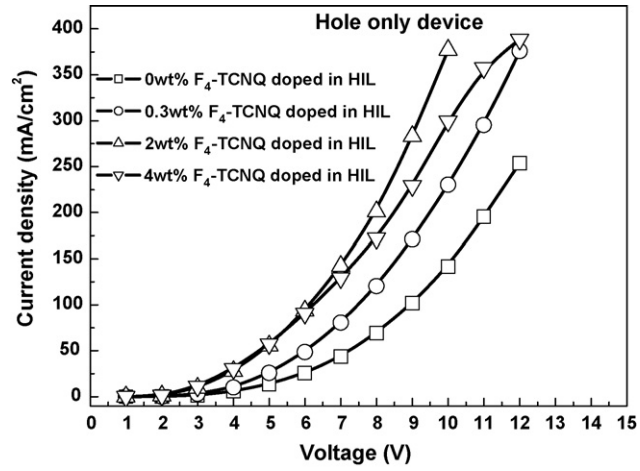

Fig. 4. Current density vs voltage characteristics of hole-only devices with 0 wt.%, 0.3 wt.%, 2 wt.% and 4 wt.% F_4-TCNQ doped into *m*-MTDATA.

complete devices, respectively. Shown are results for *Device B, C, D, E* with different weight ratios of F_4-TCNQ (0 wt.%, 0.3 wt.%, 2 wt.%, 4 wt.%) to *m*-MTDATA and Liq (33 wt.%) to Bphen, compared to a referenced *Device A* with an undoped *m*-MTDATA HIL and Bphen ETL. In Fig. 2, one can see that already slight doping HIL (0.3 wt.% F_4-TCNQ) strikingly decreases the driving voltage and that heavy doping (2 wt.%) leads to a further improvement.

In Fig. 3, it can be seen that the current and power efficiencies of doping Devices (*Devices B, C, D, E*) are considerably improved as compared to *Device A*. However, the maximum value of current and power efficiencies are obtained in the *Device C* with the doping ratio of F4-TCNQ (0.3 wt.%) into *m*-MTDATA and Liq (33 wt.%) into Bphen. At 20 mA/cm^2, one can see that the highest current efficiency and power efficiency of *Device C* are 5.9 cd/A and 4.51 lm/W, respectively, which have been improved by approximately 51%, and 89%, respectively as compared to those (3.92 cd/A, 2.38 lm/W) of *Device A*. At the same time, the driving voltage of *Device C* at 20 mA/cm^2 is 4.1 V, which is reduced by 29%, compared to that (5.31 V) of *Device A*. This significant enhancement in the device performance is attributed to the improved transport conductivity of both p-doped HTL and n-doped ETL at a particular doping concentration of F_4-TCNQ into *m*-MTDATA and Liq into Bphen. As a result, the high carrier balance is reached in the emission zone, which leads to the enhanced current and power efficiency at low driving voltage.

Superior performances of *Device C* are attributed to the high hole injection ability of p-doping HIL, the high electron mobility of n-doping ETL, and the high carrier balance for hole and electron in the emission zone. For the study of carrier injection and balance, a series of hole-only devices and electron-only devices, which have been described in experimental part, are fabricated.

Figs. 4 and 5 show the *J–V* characteristics of hole-only and electron-only devices. As can be seen that the *J–V* characteristics of hole-only devices are strongly dependent on the doping ratio of the hole transport layer. At the same voltage, the current density increases along with the increase in doping ratio. The highest current density is observed at the doping ratio of 2 wt.% F_4-TCNQ. The driving voltage of *Device H2*, *H3* and *H4* at 100 mA/cm^2 is 7.5 V, 6.1 V and 6.3 V respectively, reduced by 18%, 33% and 31%, respectively, compared with that (9.1 V) of the undoped *Device H1*.

This is expected and is a result of an electron transfer from the highest occupied molecular orbitals (HOMO) of the matrix *m*-MTDATA to the lowest unoccupied molecular orbitals (LUMO) of the dopant F_4-TCNQ. The HOMO level (5.11 eV) of *m*-MTDATA and LUMO level (5.24 eV) of F_4-TCNQ have close energetic positions,

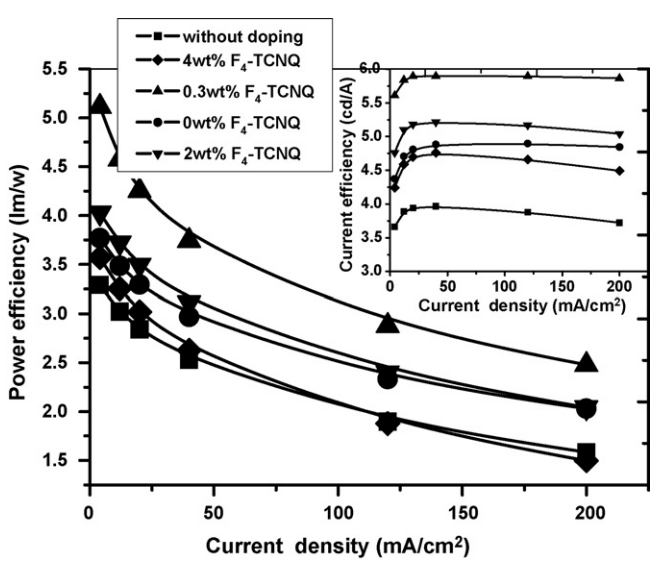

Fig. 3. Power efficiency vs current density characteristics of the complete devices. Inset: Current efficiency – current density characteristics of the complete devices.

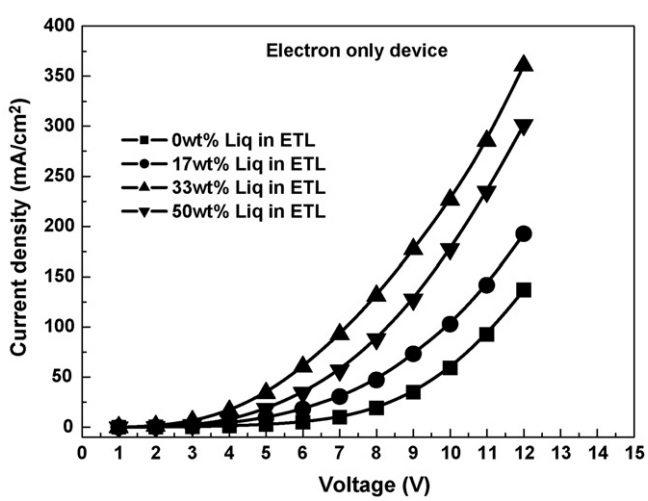

Fig. 5. Current density vs voltage characteristics of electron-only devices of 0 wt.%, 17 wt.%, 33 wt.% and 50 wt.% Liq doped into BPhen.

making a charge transfer an energetically favorable process, since it is known that upon negative charging the LUMO of TCNQ-type molecules is additionally lowered by 0.3–0.5 eV due to renormalization of orbital energy [26]. The electron transfer results in an increased concentration of charge carriers in the bulk of the HTL which increases the conductivity of the film and reduces ohmic losses in the HTL during device operation. Through the process of increased bulk conductivity, current density is expected to increase with increased dopant concentration. However, our devices demonstrate reduced performance at a concentration of 4 wt.% F_4-TCNQ to *m*-MTDATA. It is likely that because of the heavy doping F_4-TCNQ molecules saturate the film and escape to the HIL (*m*-MTDATA:F_4-TCNQ)/HTL (NPB) interface. This thin film of F_4-TCNQ creates a dipole barrier at the interface with HTL which increases the necessary driving voltage of the device. In addition, there might be an accumulation of positive space charge at the interface with the HTL, leading to reduced hole transport. It has also been suggested that a contact of electrical dopant molecules with the emissive layer can reduce device efficiency through better formation of an exciplex [27], which decays non-radiatively. The HTL of NPB is also functioned as blocking layer to prevent such quenching. However, it is possible that a high concentration of F_4-TCNQ at HTL interface may lead to significant diffusion of the dopant through the HTL into EML and cause EL quenching in the emissive region in Alq_3.

In electron-only devices, a thin layer of BCP is used to prevent holes from entering the ETL because of its high HOMO level (6.7 eV) [28]. An increase in current density is seen when a small doping concentration of the Liq (17 wt.%) is introduced into the Bphen layer, compared with the undoped device. As can be seen that the *J–V* characteristics of electron-only devices are strongly dependent on the doping ratio of the electron transport layer. At the same voltage, the current density increases along with the increase in doping ratio. The highest current density is observed at the doping ratio of 33 wt.% Liq. The driving voltage of *Device E2*, *E3* and *E4* at 100 mA/cm^2 is 9.9 V, 7.1 V and 8.3 V, respectively, reduced by 11%, 36% and 25%, respectively, compared with that (11.1 V) of the undoped *Device E1*.

These *J–V* characteristics of electron-only devices suggest that a certain doping ratio of Liq to Bphen can improve the electron transport ability of the co-deposited layer. The advantage of using BPhen:Liq as ETL can be explained by electron hopping exchange alongwith their LUMO. In a single host device, electrons hop along the LUMO in BPhen. Since the LUMO–LUMO difference between BPhen (3.0 eV) [29] and Liq (3.1 eV) [28] is neglectable, subject to their similar LUMO. Transport manifolds alongwith their LUMO are expected to exhibit a certain extent of overlap after a mixing ratio goes beyond 17 wt.%. Therefore, it's likely that a large energetic disorder between Bphen and Liq contributes to electron hopping, implying that electron hopping among BPhen and Liq sites is favorable [29]. Therefore, the high electron conductivity of BPhen:Liq may be originated from short hopping length for electron transport, compared to the pure BPhen HTL. However, the current conduction is reduced slightly as the doping ratio further increases to 50 wt.%. This result may be attributed to the effect of carrier quench and generation of defects. The detailed reasons are possibly the same as that of the heavy doping concentration of F_4-TCNQ into *m*-MTDATA in the hole-only devices.

As we know, the power efficiency depends on carrier injection and transport, while current efficiency not only relies on the carrier injection, but also on the carrier balance. In order to further find the reason for the best performance in *Device C*, a series of *J–V* characteristics of all hole-only devices are compared with that of each electron-only device, which is shown in Fig. 6. It can be found

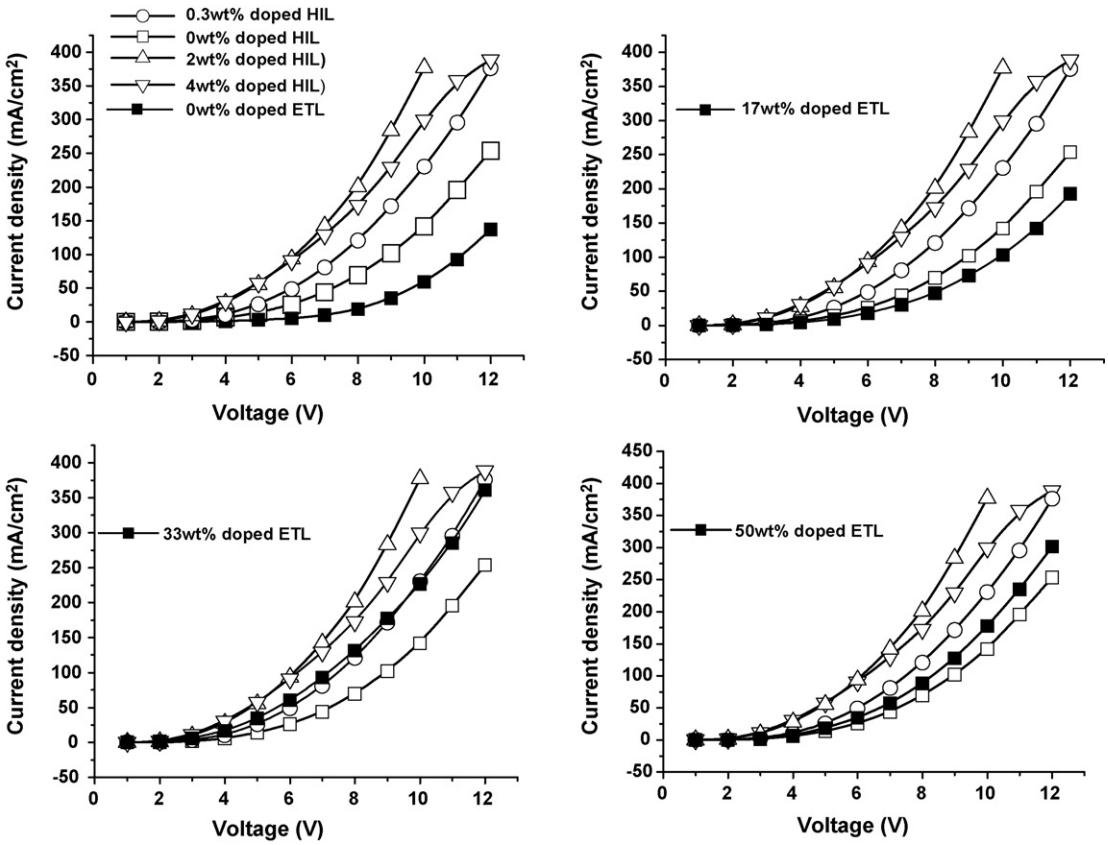

Fig. 6. Comparison of current density vs voltage characteristics of *Device E3* (*x* wt.% Liq:BPhen) with all hole-only devices, *x* = 0, 17, 33, 50.

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from Fig. 6 that the *J–V* curve of 0.3 wt.% F_4-TCNQ:*m*-MTDATA is very close to that of 33 wt.% Liq:BPhen, indicating that electrons and holes have a good balance. That is to say, the complete *Device C*, which has the best performance, has a good carrier balance. Thus, a conclusion can be made that the enhancement in the device performances is the result of an efficient charge balance in the emission layer caused by conductivity improvement in transport layers.

For the stability of the devices, we have known that in un-doping devices, such as *Device A*, the number of holes is much more than electrons. So, a surplus of holes at the NPB/Alq_3 interface increases the probability that Alq_3 cations are formed, which are known to be unstable [30] and lead to rapid device degradation. However, in this paper, we introduce a p–i–n devices with a novel n-doping (33 wt.% Liq:BPhen) layer as ETL and a p-doped (0 wt.%, 0.3 wt.%, 2 wt.% and 4 wt.% F_4-TCNQ:*m*-MTDATA) layer as HTL, in which the holes and electrons have a good balance seen from Fig. 6, leading to the decrease in surplus of holes. So, we can predict that the complete *Device C* should have a good lifetime.

4. Conclusion

A good carrier balance is considered to be one of the most important factors in getting an excellent performance in OLEDs. In this paper, the p–i–n devices with a novel n-doping (33 wt.% Liq:BPhen) layer as ETL and a p-doped (0 wt.%, 0.3 wt.%, 2 wt.% and 4 wt.% F_4-TCNQ:*m*-MTDATA) layer as HTL is fabricated. We have demonstrated the high current efficiency of 5.90 cd/A, power efficiency of 4.51 lm/W, and a driving voltage of 4.10 V at a current density of 20 mA/cm^2 in Alq_3 based p–i–n OLEDs. The *J–V* comparison between electron-only and hole-only devices has been presented to find the reason for the significant improvement in performance and come to a conclusion that an effective carrier balance is achieved due to the enhanced conductivity of doped transport layers, leading to the enhanced efficiency in our devices.

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