ELSEVIER

**DECLARATION OF RACHEL GARLAND**

I, Rachel Garland, am over twenty-one (21) years of age. I have never been convicted of a felony, and I am fully competent to make this declaration. I declare the following to be true to the best of my knowledge, information and belief:

1. I am Senior Publisher, Materials Science for Elsevier Limited ("Elsevier").

2. Elsevier is a neutral third party in this dispute.

3. I am not being compensated for this declaration.

4. Among my responsibilities as Senior Publisher, Materials Science I act as a custodian of certain records for Elsevier.

5. I make this declaration based on my personal knowledge and information contained in the business records of Elsevier.

6. As part of its ordinary course of business, Elsevier, publishes and makes available technical articles. These publications are made available for public download through Elsevier's digital library, ScienceDirect.

7. It is the regular practice of Elsevier to publish articles and other writings including article abstracts and make them available to the public through ScienceDirect. Elsevier maintains copies of publications in the ordinary course of its regularly conducted activities.

8. The article below has been attached as Exhibit A to this declaration:

9. I obtained a copy of Exhibit A through ScienceDirect, where it is maintained in the ordinary course of Elsevier's business. Exhibit A is a true and correct copy of the Exhibit, as it existed on or about November 8, 2024.

10. The article and abstract from Science Direct shows the date of publication for the first online version. Science Direct populates this information using persistent publication metadata that is embedded in the articles metadata. Once this publication metadata has been first calculated it is not changed.

11. J. Ma, et. Al., "Organic light-emitting diodes based on new n-doped electron transport layer" was published in Synthetic Metals, Vol. 158, Issues 21-24 and was available

online on August 29, 2008. The article is currently available for public download from the Elsevier digital library, Science Direct.

12. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with the knowledge that willful false statements and the like are punishable by fine or imprisonment, or both, under 18 U.S.C. § 1001.

I declare under penalty of perjury that the foregoing statements are true and correct.

**Date**
**11th November 2024**

_____

**Signature**

_____

# EXHIBIT A

ScienceDirect

Synthetic Metals

Volume 158, Issues 21–24, December 2008, Pages 810-814

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

J.W. Ma [a], Wei Xu [a], X.Y. Jiang [a], Z.L. Zhang [a b]

[a] Department of Materials Science, Shanghai University, Jiading 201800, Shanghai, PR China

[b] Key Laboratory of Advanced Display and System Applications, Ministry of Education, Shanghai University, Shanghai 200072, PR China

Received 11 March 2008, Accepted 14 May 2008, Available online 29 August 2008.

What do these dates mean?

Show less

Outline | Share Cite

https://doi.org/10.1016/j.synthmet.2008.05.009

Get rights and content

## 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.

Reading Assistant Alpha Powered by GenAI

*Answers are AI-generated and may vary in quality. Learn more.*

Ask about this publication

Get answer

Find answers across publications ↗



## Keywords

Organic light-emitting diodes; Doping concentration; Carrier transport; Conductivity

## 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], [14], [15] as cathode, or inserting a thin interlayer between cathode and electron transporting layer [16], [17], [18], [19], [20] to enhance electron injection. Great efforts have been made to enhance the electron conductivity [21], [22], [23], [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 significant 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 $1\times10^{-5}$ 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.

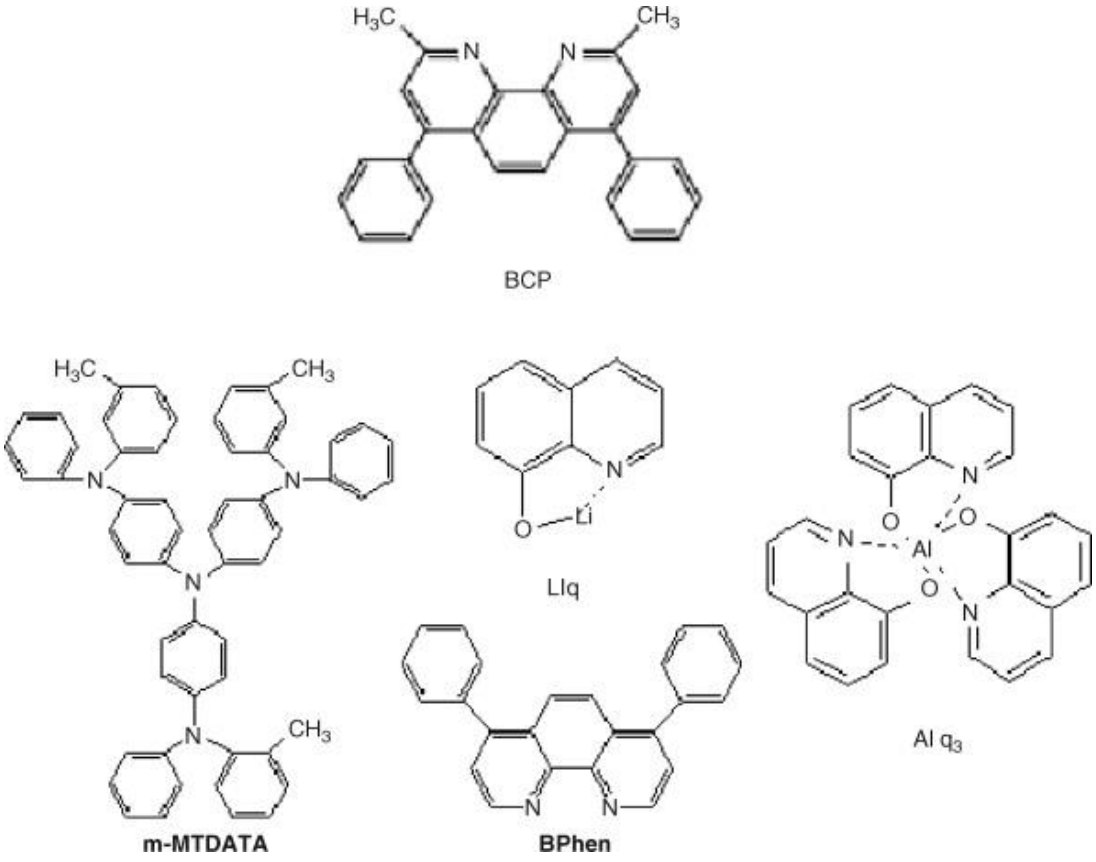
Using the same methods as above, a series of hole-only devices in which the current consists mainly of the holes and electron-only devices in which the current consists mainly of the electrons were

fabricated. These devices have the following structures:

Hole-only devices:ITO/*m*-MTDATA:*x*wt.% F4-TCNQ (40nm)/NPB (10nm)/Al (130nm). *Device H1*: *x*=0; *Device H2*: *x*=0.3; *Device H3*: *x*=2; *Device H4*: *x*=4.

Electron-only devices:ITO/BCP (5nm)/BPhen:*y*wt.% Liq (50nm)/Al (130nm). *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.



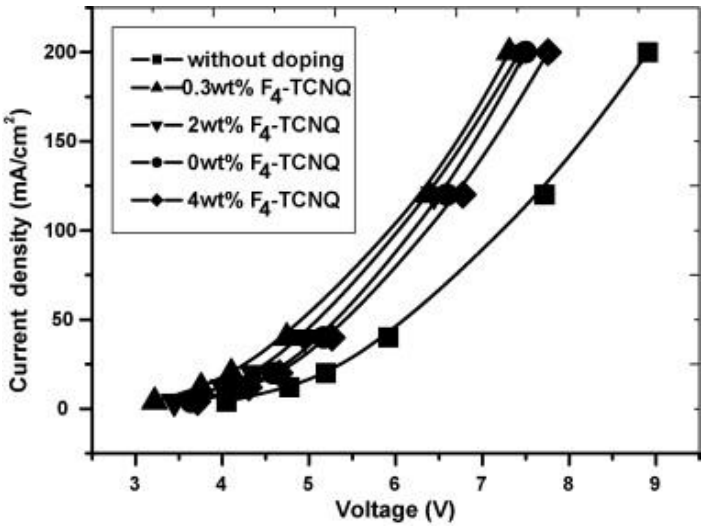

Download: Download full-size image

Fig. 1. Molecular structures of main materials used.

## 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 complete devices, respectively. Shown are results for *Device B, C, D, E* with different weight ratios of $F_4$-TCNQ (0wt.%, 0.3wt.%, 2wt.%, 4wt.%) to *m*-MTDATA and Liq (33wt.%) to Bphen, compared to a referenced *Device A* with an undoped *m*-MTDATA HIL and Bphen

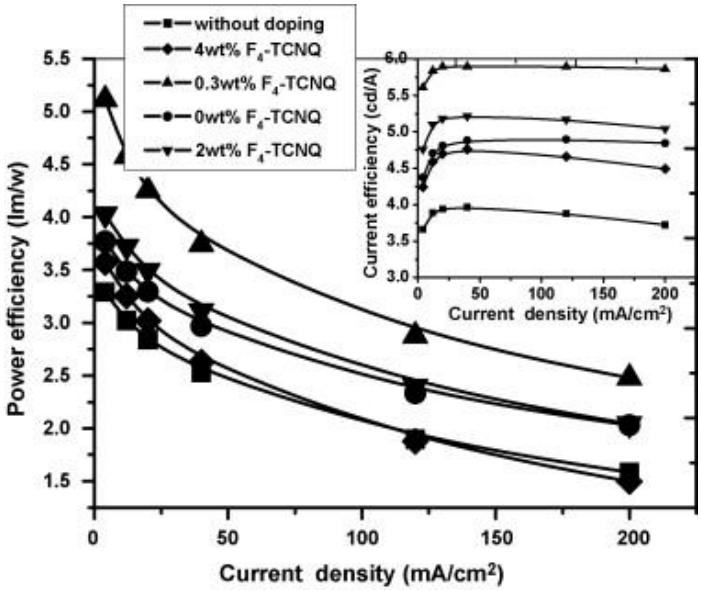
ETL. In Fig. 2, one can see that already slight doping HIL (0.3 wt.% $F_4$-TCNQ) strikingly decreases the driving voltage and that heavy doping (2 wt.%) leads to a further improvement.




Download: Download full-size image

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

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.

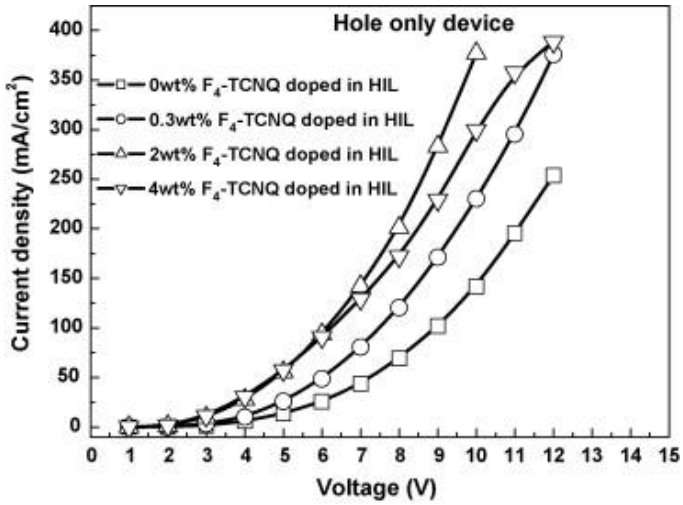



Download: Download full-size image

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

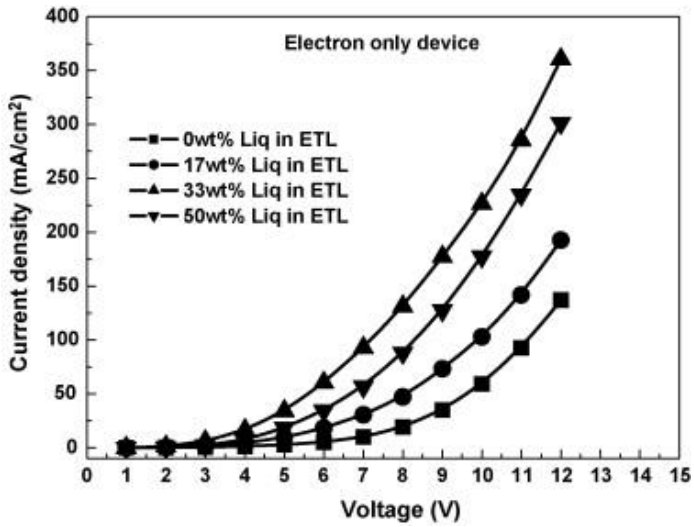
Superior performances of *Device C* are attributed to the high hole injection ability of p-doping HIL, the high electron mobility of n-doping ETL, and the high carrier balance for hole and electron in the emission zone. For the study of carrier injection and balance, a series of hole-only devices and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

Fig. 4, Fig. 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*.




Download: Download full-size image

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.




Download: Download full-size image

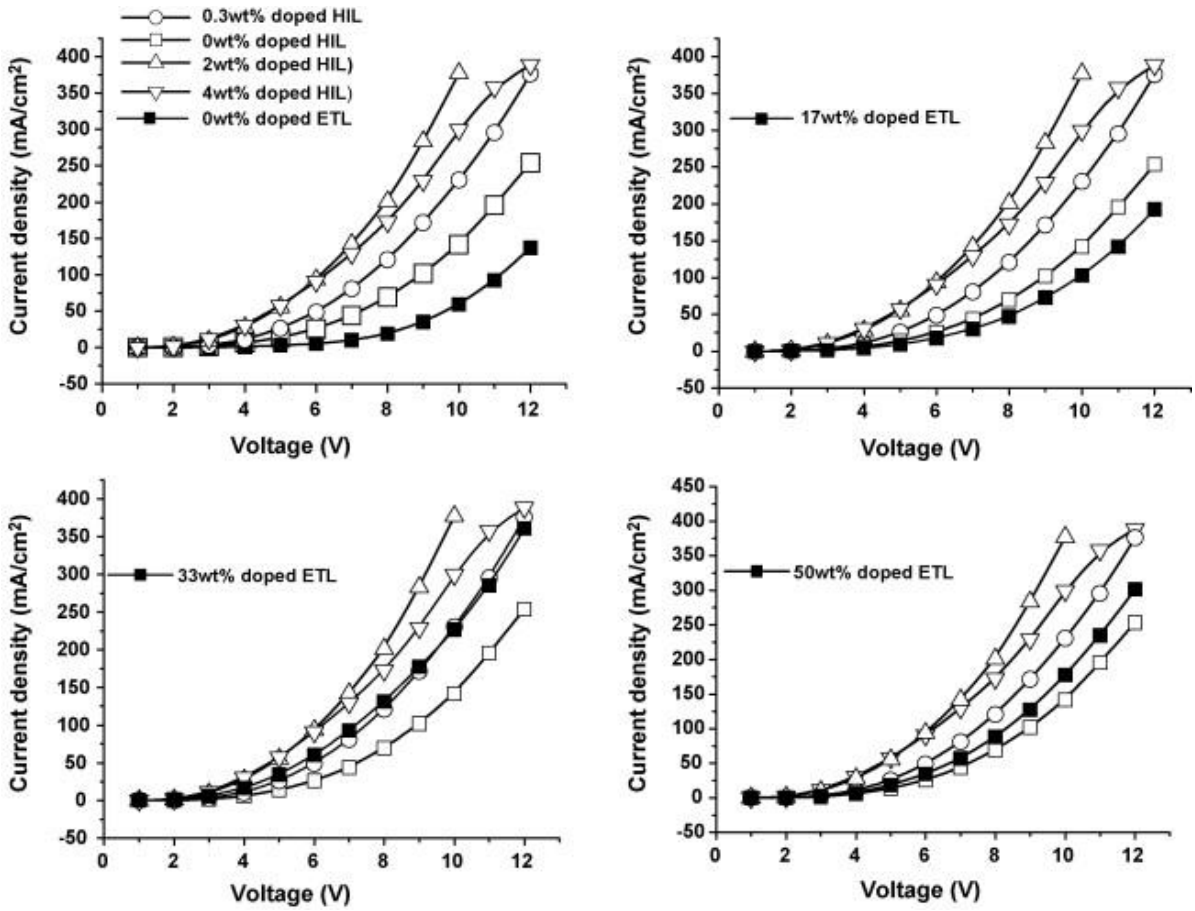
Fig. 5. Current density vs voltage characteristics of electron-only devices of 0 wt.%, 17 wt.%, 33 wt.% and 50 wt.% Liq doped into BPhen.

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, 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 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.




Download: Download full-size image

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.

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 (33wt.% Liq:BPhen) layer as ETL and a p-doped (0wt.%, 0.3wt.%, 2wt.% and 4wt.% $F_4$-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 (33wt.% Liq:BPhen) layer as ETL and a p-doped (0wt.%, 0.3wt.%, 2wt.% and 4wt.% $F_4$-TCNQ:*m*-MTDATA) layer as HTL is fabricated. We have demonstrated the high current efficiency of 5.90cd/A, power efficiency of 4.51lm/W, and a driving voltage of 4.10V at a current density of 20mA/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.

## Acknowledgement

The authors acknowledge the financial support given by The National Natural Science Foundation of China (90201034, 60477014, 60577041), 973 project no. (2002CB613400).

Recommended articles

## References

[1] C.W. Tang, S.A. Vanslyke
Appl. Phys. Lett., 51 (12) (1987), pp. 913-915
View in Scopus ↗

[2] J. Huang, M. Pfeiffer, A. Werner, J. Blochwitz, K. Leo, S. Liu
Appl. Phys. Lett., 80 (1) (2002), pp. 139-141
View in Scopus ↗

[3] J.S. Kim, M. Granstrom, R.H. Friend, N. Johansson, W.R. Salaneek, R. Daik, W.J. Feast, F. Cacialli
J. Appl. Phys., 84 (12) (1998), pp. 6859-6870
View in Scopus ↗

[4] M.G. Mason, L.S. Hung, C.W. Tang, S.T. Lee, K.W. Wong, M. Wang
J. Appl. Phys., 86 (3) (1999), pp. 1688-1692
View in Scopus ↗

[5] S.A. VanSlyke, C.H. Chen, C.W. Tang
Appl. Phys. Lett., 69 (15) (1996), pp. 2160-2162
View in Scopus ↗

[6] Y. Yang, A.H. Heeger
Appl. Phys. Lett., 64 (10) (1994), pp. 1245-1247
View in Scopus ↗

[7] T. Grandlund, L.A.A. Pettersson, O. Inganas
J. Appl. Phys., 89 (11) (2001), pp. 5897-5902

[8] J. Blochwitz, M. Pfeiffer, T. Fritz, K. Leo
Appl. Phys. Lett., 73 (6) (1998), pp. 729-731
View in Scopus ↗

[9] C. Ganzoring, M. Fujihira, Improved drive voltages of organic electroluminescent devices with an efficient p-type aromatic diamine hole-injection layer, Appl. Phys. Lett. 77 (25) 4211–4213.
Google Scholar ↗

[10] D.B. Romero, M. Schaer, L. Zuppiroli, B. Cesar, B. Francois
Appl. Phys. Lett., 67 (12) (1995), pp. 1659-1661
View in Scopus ↗

[11] F. Huang, A.G. MacDiamid, B.R. Hsieh
Appl. Phys. Lett., 71 (17) (1997), pp. 2415-2417
View in Scopus ↗

[12] M. Pfeiffer, A. Beyer, T. Fritz, K. Leo
Appl. Phys. Lett., 73 (22) (1998), pp. 3202-3204
View in Scopus ↗

[13] A.R. Brown, D.D.C. Bradley, J.H. Burroughes, R.H. Friend, N.C. Greenham, P.L. Burn, A.B. Holmes, A. Kraft
Appl. Phys. Lett., 61 (23) (1992), pp. 2793-2795
View in Scopus ↗

[14] I.D. Parker
J. Appl. Phys., 75 (3) (1994), pp. 1656-1666
View in Scopus ↗

[15] T. Wakimoto, Y. Fukuda, K. Nagayama, A. Yokoi, H. Nakada, M. Tsuchida
IEEE Trans. Electron Devices, 44 (8) (1997), pp. 1245-1248
View in Scopus ↗

[16] L.S. Hung, C.W. Tang, M.G. Mason
Appl. Phys. Lett., 70 (2) (1997), pp. 152-154
View in Scopus ↗

[17] J. Kido, Y. Lizumi
Appl. Phys. Lett., 73 (19) (1998), pp. 2721-2723
View in Scopus ↗

[18] C. Ganzorig, M. Fujihara
Appl. Phys. Lett., 77 (25) (2000), pp. 4211-4213
View in Scopus ↗

[19] P. Piromreun, H. Oh, Y. Shen, G. Malliaras, J.C. Scott, P.J. Brock
Appl. Phys. Lett., 77 (15) (2000), pp. 2403-2405
View in Scopus ↗

[20] Y. Kim, H. Park, J. Kim
Appl. Phys. Lett., 69 (5) (1996), pp. 599-601

View in Scopus ↗

[21] H.H. Fong, W.C.H. Choy, K.N. Hui, Y.J. Liang
Appl. Phys. Lett., 88 (2006), p. 113510

[22] J. Kido, T. Matsumoto
Appl. Phys. Lett., 73 (20) (1998), pp. 2866-2868
View in Scopus ↗

[23] G. He, M. Pfeiffer, K. Leo, M. Hofmann, J. Birnstock, R. Pudzich, J. Salbeck
Appl. Phys. Lett., 85 (17) (2004), pp. 3911-3913
View in Scopus ↗

[24] G. He, O. Schneider, D. Qin, X. Zhou, M. Pfeiffer, K. Leo
Appl. Phys. Lett., 95 (10) (2004), pp. 5773-5777
View in Scopus ↗

[25] X. Zheng, Y Wu, R. Sun, W. Zhu, X. Jiang, Z. Zhang, S. Xu
Thin Solid Films, 478 (2) (2005), pp. 252-255
View PDF View article View in Scopus ↗

[26] M. Pope, C.E. Swenberg
Electronic Processes in Organic Crystals and Polymers
Oxford University Press, Oxford (1999)
pp. 200
Google Scholar ↗

[27] X. Zhou, J. Blochwitz, M. Pfeiffer, A. Nollau, T. Fritz, K. Leo
Adv. Funct. Mater., 11 (2001), p. 310
View in Scopus ↗

[28] Jun Ho Kim, Eun Jung Nam, Soo Yeon Hong, Bong Ok Kim, Sung Min Kim, Seung Soo Yoon, Jung Ha Suh, Yunkyung Ha, Young Kwan Kim
Mater. Sci. Eng., C 24 (2004), pp. 167-171

[29] S. Naka, H. Okada, H. Onnagawa, T. Tsutsui
Appl. Phys. Lett., 76 (2) (2000), pp. 197-199
View in Scopus ↗

[30] H. Aziz, Z.D. Popovic, N.-X. Hu, A.-M. Hor, G. Xu
Science, 283 (1999), p. 1900
View in Scopus ↗

## Cited by (12)

Room-temperature interface state analysis of Au/Poly(4-vinyl phenol)/p-Si structure

2009, Synthetic Metals

Show abstract

Improved Thermal Stability and Operational Lifetime of Blue Fluorescent Organic Light-Emitting Diodes by Using a Mixed-Electron Transporting Layer ↗

2022, ACS Materials Letters

A Series of Lithium Pyridyl Phenolate Complexes with a Pendant Pyridyl Group for Electron-Injection Layers in Organic Light-Emitting Devices ↗

2017, ACS Applied Materials and Interfaces

Effect of doping of 8-hydroxyquinolinatolithium on electron transport in tris(8-hydroxyquinolinato)aluminum ↗

2011, Journal of Applied Physics

Spectroelectrochemical and photovoltaic characterization of a solution-processable n-and-p type dopable pyrrole-bearing conjugated polymer ↗

2010, Macromolecular Chemistry and Physics

One polymer for all: Benzotriazole containing donor-acceptor type polymer as a multi-purpose material ↗

2009, Chemical Communications

View all citing articles on Scopus ↗

View Abstract

Copyright © 2008 Elsevier B.V. All rights reserved.

ELSEVIER

All content on this site: Copyright © 2024 Elsevier B.V., its licensors, and contributors. All rights are reserved, including those for text and data mining, AI training, and similar technologies. For all open access content, the Creative Commons licensing terms apply.

RELX™



SDC EX. 1036 - 17/22

Synthetic Metals 158 (2008) 810–814

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet

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

J.W. Ma[a,*], Wei Xu[a], X.Y. Jiang[a], Z.L. Zhang[a,b]

[a] Department of Materials Science, Shanghai University, Jiading 201800, Shanghai, PR China
[b] Key Laboratory of Advanced Display and System Applications, Ministry of Education, Shanghai University, Shanghai 200072, PR China

ARTICLE INFO

*Article history:*
Received 11 March 2008
Accepted 14 May 2008
Available online 29 August 2008

*Keywords:*
Organic light-emitting diodes
Doping concentration
Carrier transport
Conductivity

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.

© 2008 Elsevier B.V. All rights reserved.

## 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-

* Corresponding author. Tel.: +86 21 69980357.
*E-mail address:* majunwei250802944@163.com (J.W. Ma).

0379-6779/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.synthmet.2008.05.009

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 $1 \times 10^{-5}$ Torr. The deposition rate was maintained at $0.5 \pm 0.2$ Å/s for the organic materials, 0.1 Å/s for LiF and $5 \pm 2$ 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

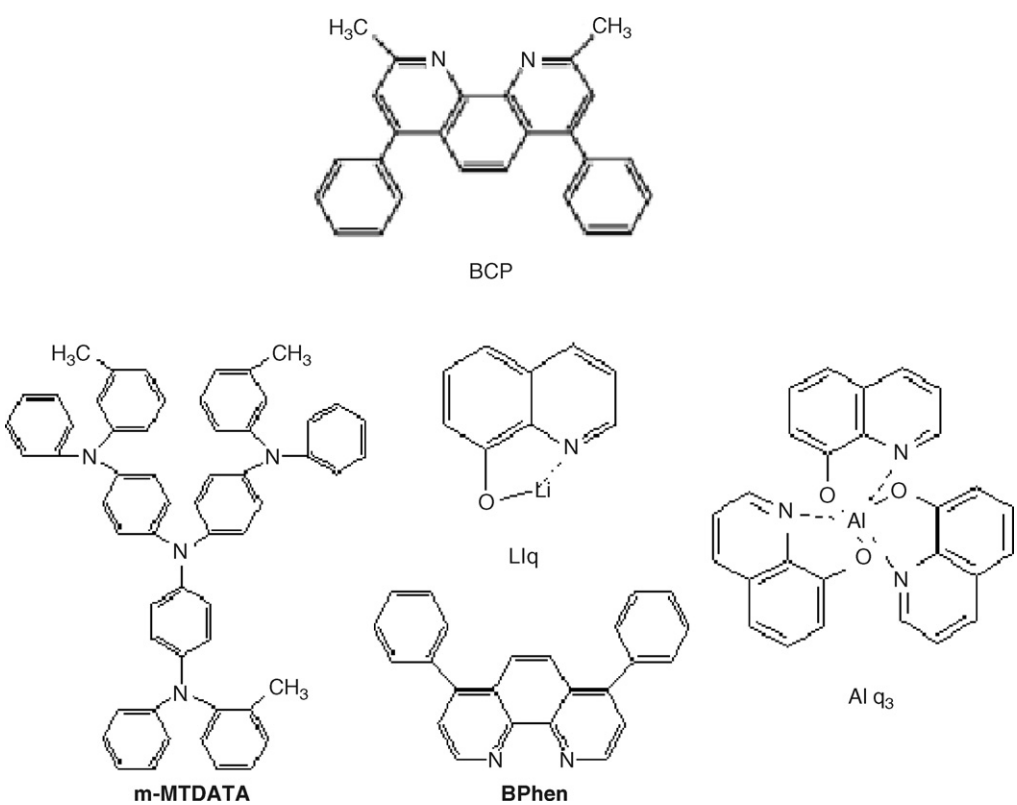



**Fig. 1.** Molecular structures of main materials used.

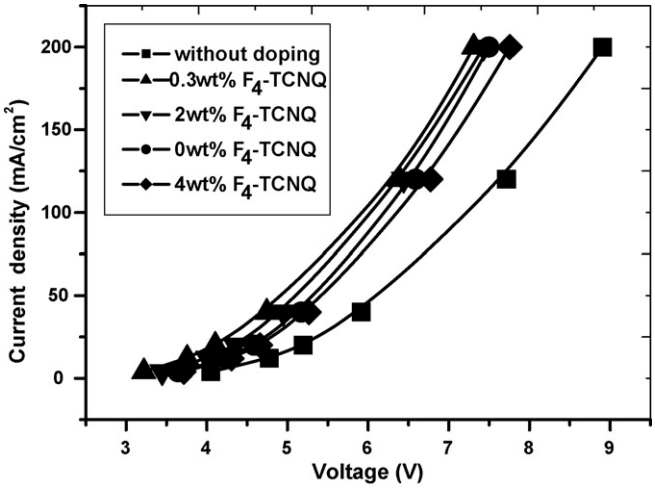



**Fig. 2.** Current density vs voltage characteristics of the complete devices.

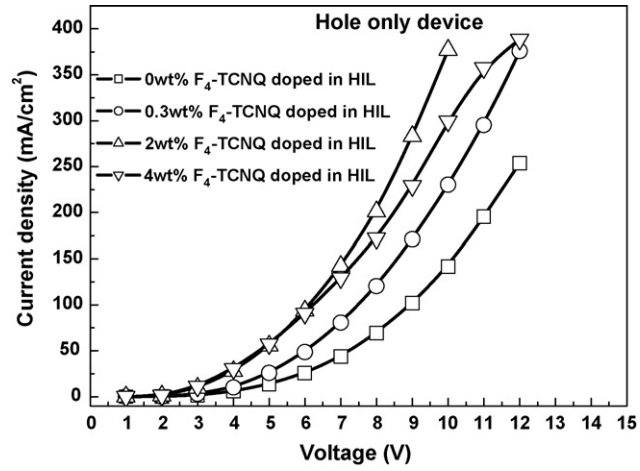



**Fig. 4.** Current density vs voltage characteristics of hole-only devices with 0 wt.%, 0.3 wt.%, 2 wt.% and 4 wt.% $F_4$-TCNQ doped into *m*-MTDATA.

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,

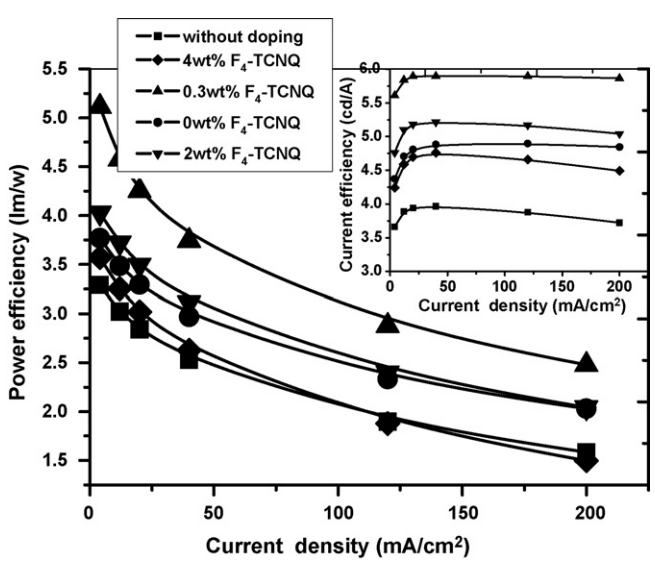



**Fig. 3.** Power efficiency vs current density characteristics of the complete devices. Inset: Current efficiency – current density characteristics of the complete devices.

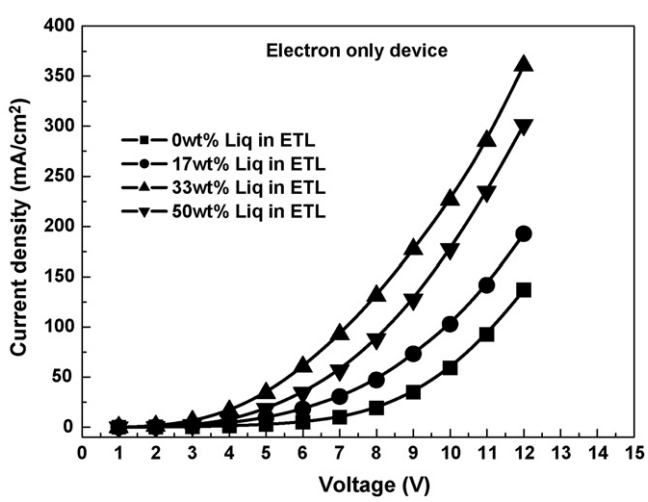



**Fig. 5.** Current density vs voltage characteristics of electron-only devices of 0 wt.%, 17 wt.%, 33 wt.% and 50 wt.% Liq doped into BPhen.

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

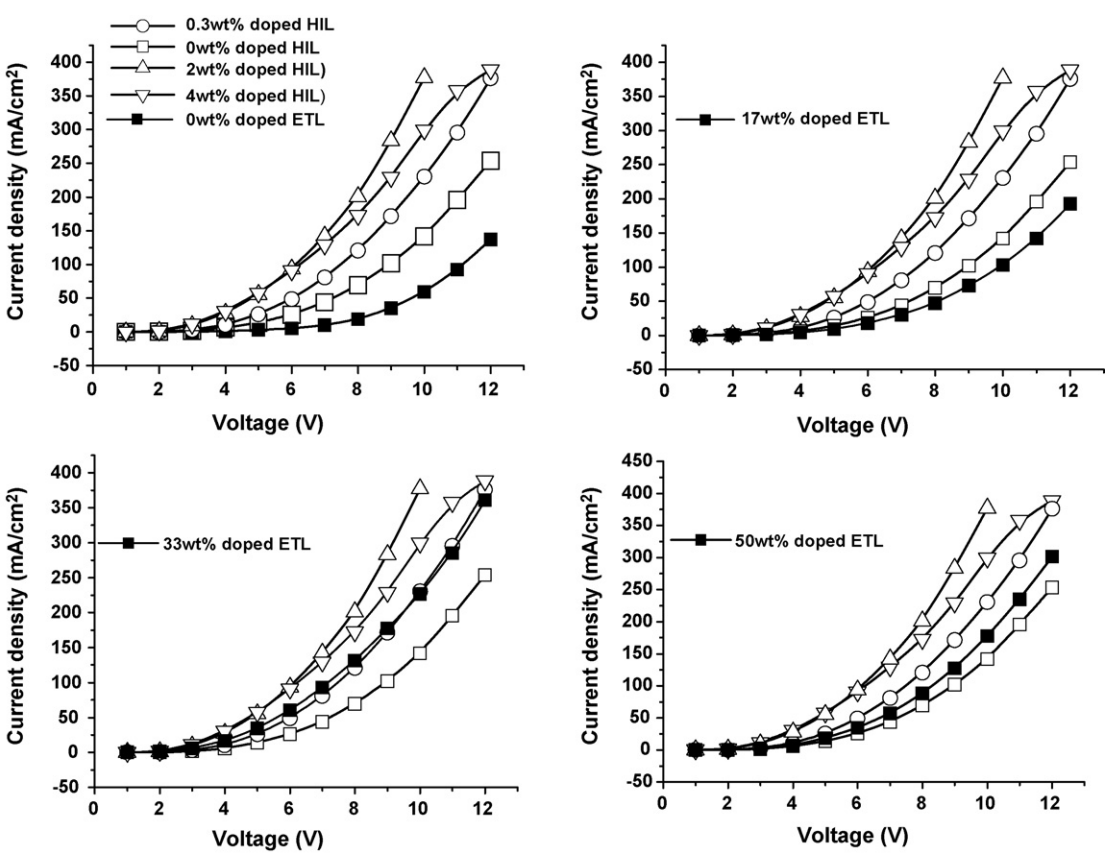



**Fig. 6.** Comparison of current density vs voltage characteristics of *Device E3* (*x* wt.% Liq:BPhen) with all hole-only devices, *x* = 0, 17, 33, 50.

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.

## Acknowledgement

The authors acknowledge the financial support given by The National Natural Science Foundation of China (90201034, 60477014, 60577041), 973 project no. (2002CB613400).

## References

[1] C.W. Tang, S.A. Vanslyke, Appl. Phys. Lett. 51 (12) (1987) 913–915.
[2] J. Huang, M. Pfeiffer, A. Werner, J. Blochwitz, K. Leo, S. Liu, Appl. Phys. Lett. 80 (1) (2002) 139–141.
[3] J.S. Kim, M. Granstrom, R.H. Friend, N. Johansson, W.R. Salaneek, R. Daik, W.J. Feast, F. Cacialli, J. Appl. Phys. 84 (12) (1998) 6859–6870.
[4] M.G. Mason, L.S. Hung, C.W. Tang, S.T. Lee, K.W. Wong, M. Wang, J. Appl. Phys. 86 (3) (1999) 1688–1692.
[5] S.A. VanSlyke, C.H. Chen, C.W. Tang, Appl. Phys. Lett. 69 (15) (1996) 2160–2162.
[6] Y. Yang, A.H. Heeger, Appl. Phys. Lett. 64 (10) (1994) 1245–1247.
[7] T. Grandlund, L.A.A. Pettersson, O. Inganas, J. Appl. Phys. 89 (11) (2001) 5897–5902.
[8] J. Blochwitz, M. Pfeiffer, T. Fritz, K. Leo, Appl. Phys. Lett. 73 (6) (1998) 729–731.
[9] C. Ganzoring, M. Fujihira, Improved drive voltages of organic electroluminescent devices with an efficient p-type aromatic diamine hole-injection layer, Appl. Phys. Lett. 77 (25) 4211–4213.
[10] D.B. Romero, M. Schaer, L. Zuppiroli, B. Cesar, B. Francois, Appl. Phys. Lett. 67 (12) (1995) 1659–1661.
[11] F. Huang, A.G. MacDiamid, B.R. Hsieh, Appl. Phys. Lett. 71 (17) (1997) 2415–2417.
[12] M. Pfeiffer, A. Beyer, T. Fritz, K. Leo, Appl. Phys. Lett. 73 (22) (1998) 3202–3204.
[13] A.R. Brown, D.D.C. Bradley, J.H. Burroughes, R.H. Friend, N.C. Greenham, P.L. Burn, A.B. Holmes, A. Kraft, Appl. Phys. Lett. 61 (23) (1992) 2793–2795.
[14] I.D. Parker, J. Appl. Phys. 75 (3) (1994) 1656–1666.
[15] T. Wakimoto, Y. Fukuda, K. Nagayama, A. Yokoi, H. Nakada, M. Tsuchida, IEEE Trans. Electron Devices 44 (8) (1997) 1245–1248.
[16] L.S. Hung, C.W. Tang, M.G. Mason, Appl. Phys. Lett. 70 (2) (1997) 152–154.
[17] J. Kido, Y. Lizumi, Appl. Phys. Lett. 73 (19) (1998) 2721–2723.
[18] C. Ganzorig, M. Fujihara, Appl. Phys. Lett. 77 (25) (2000) 4211–4213.
[19] P. Piromreun, H. Oh, Y. Shen, G. Malliaras, J.C. Scott, P.J. Brock, Appl. Phys. Lett. 77 (15) (2000) 2403–2405.
[20] Y. Kim, H. Park, J. Kim, Appl. Phys. Lett. 69 (5) (1996) 599–601.
[21] H.H. Fong, W.C.H. Choy, K.N. Hui, Y.J. Liang, Appl. Phys. Lett. 88 (2006) 113510.
[22] J. Kido, T. Matsumoto, Appl. Phys. Lett. 73 (20) (1998) 2866–2868.
[23] G. He, M. Pfeiffer, K. Leo, M. Hofmann, J. Birnstock, R. Pudzich, J. Salbeck, Appl. Phys. Lett. 85 (17) (2004) 3911–3913.
[24] G. He, O. Schneider, D. Qin, X. Zhou, M. Pfeiffer, K. Leo, Appl. Phys. Lett. 95 (10) (2004) 5773–5777.
[25] X. Zheng, Y Wu, R. Sun, W. Zhu, X. Jiang, Z. Zhang, S. Xu, Thin Solid Films 478 (2) (2005) 252–255.
[26] M. Pope, C.E. Swenberg, Electronic Processes in Organic Crystals and Polymers, Oxford University Press, Oxford, 1999, pp. 200.
[27] X. Zhou, J. Blochwitz, M. Pfeiffer, A. Nollau, T. Fritz, K. Leo, Adv. Funct. Mater. 11 (2001) 310.
[28] Jun Ho Kim, Eun Jung Nam, Soo Yeon Hong, Bong Ok Kim, Sung Min Kim, Seung Soo Yoon, Jung Ha Suh, Yunkyung Ha, Young Kwan Kim, Mater. Sci. Eng. C 24 (2004) 167–171.
[29] S. Naka, H. Okada, H. Onnagawa, T. Tsutsui, Appl. Phys. Lett. 76 (2) (2000) 197–199.
[30] H. Aziz, Z.D. Popovic, N.-X. Hu, A.-M. Hor, G. Xu, Science 283 (1999) 1900.