Organic Light-Emitting Diodes by Doping Liq into an Electron Transport Layer*

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Abstract： Organic light emitting diodes (OLEDs) incorporating an n-doping transport layer comprised of 8-hydroxy-quinolinato lithium (Liq) doped into 4'7- diphyenyl-1,10-phenanthroline (BPhen) as ETL and a p-doping transport layer that includes tetrafluro-tetracyano-quinodimethane (F_4- TCNQ) doped into 4,4´,4″-tris (3-methylphenylphenylamono) triphenylamine (m-MTDATA) are demonstrated. In order to examine the improvement in the conductivity of transport layers，hole-only and electron-only devices are fabricated. The current and power efficiency of organic light-emitting diodes are improved significantly after introducing an n-doping (BPhen：33wt% Liq) layer as an electron transport layer (ETL) and a p-doping layer composed of m-MTDATA and F_4- TCNQ as a hole transport layer (HTL). Compared with the control device (without doping)，the current efficiency and power efficiency of the most efficient device (device C) are enhanced by approximately 51% and 89%，respectively，while driving voltage is reduced by 29%. This improvement is attributed to the improved conductivity of the transport layers that leads to efficient charge balance in the emission zone.

Key words： p-i-n；n-doping；current efficiency；electron transport；conductivity
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1　Introduction

Since the discovery of organic light-emitting devices (OLEDs)，there has been considerable interest in developing OLEDs with high efficiency for display applications[1]. In order to enhance power efficiency and lower driving voltage，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 the ITO surface[4]. It can also be enhanced by introducing a 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/HTL interface.

Recently，the p-doping of a hole transport layer (HTL) for enhancing hole injection and lowering drive voltages in OLEDs has attracted much attention. 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 minimize the voltage drop across the ITO/HTL interface and the judicial control of doping levels can also lead to efficient carrier injection by tunneling[12].

However，organic molecules are known to be poor in electron injection and transport compared with their efficiency with respect to hole injection and transport. Many attempts have been made to improve the electron injection and transport，including using low work function metals[1,13~15] as cathodes，or inserting a thin interlayer between the cathode and electron transporting layer[16~20] to enhance electron injection.

Great efforts have been made to enhance the electron transport conductivity[21~24]. Kido[22] reported improved electron transport by doping Li into Alq_3. Fong[21] also demonstrated that the device performance was enhanced significantly by doping 4'7- diphyenyl-1,10-phenanthroline (BPhen) into Alq_3 as a co-host electron transport layer (c-ETL).

However，few studies have reported using a lithi-

um quinolinato complex such as 8-hydroxy-quinolina-to lithium（Liq）as an electron injection layer[25] due to the difficulty of depositing Liq onto substrate，especially when it is doped into other materials and no work has yet been reported using Liq-doped BPhen as electron transport layer（ETL）. In addition，the application of Liq to other emissive materials is worthy of study. We use the method of co-vaporation（vaporizing Liq and BPhen at the same time）to deposit Liq and BPhen simultaneously and the result is acceptable.

In this paper，devices with an n-doping（33wt% Liq：BPhen）layer as ETL and p-type（m-MTDATA：$x$wt% F$_4$-TCNQ）layer as HTL are established. 33wt% Liq is chosen because the device with the doping ratio of 33wt% Liq demonstrates the best J-V curve among all the electron only devices. The method of co-vaporation（vaporizing Liq and BPhen at the same time）is used to deposit Liq and BPhen simultaneously.

2　Experiment

Glass coated with indium-tin oxide（ITO）was used as a starting substrate. The sequence of pre-cleaning prior to loading into the evaporation chamber consisted of soaking in ultra-sonic detergent for 30min，spraying with de-ionized（DI）water for 10min，soaking in ultrasonic DI water for 30min，oven bake-dry for 30min，and ITO surface stabilizing ultra-violet ozone illumination for 10min. The devices were prepared by vapor deposition onto an indium tin oxide coated glass substrate with a sheet resistance of 20Ω/□. The organic layer and the cathode layer were deposited by vacuum vapor deposition at 1.0×10^{-5} torr. The device structure is ITO/ 4，4′，4″-tris（3-methylphenylphenylamono）triphenylamine（m-MTDATA）：$x$wt% F$_4$-TCNQ（40nm）/ NPB（10nm）/ Alq$_3$（20nm）/ BPhen：$x$wt% Liq（50nm）/ LiF（10nm）/ Al（130nm）. m-MTDATA：$x$wt% F4-TCNQ and BPhen：x wt % Liq were used as a p-doping hole transport layer（HTL）and an n-doping electron transport layer（ETL），respectively. NPB and Alq$_3$ were used as the interlayer and emission layer（EML），respectively，while LiF and Al were used as the electron injection layer and cathode，respectively.

The active area of the devices was 5mm × 5mm. The thickness of the organic layers was monitored with a quartz-crystal monitor. The current density versus voltage（J-V）and luminance characteristics were measured by a computer controlled programmable Keithley 2400 DC Source Meter and Minolta LS-110 luminance meter.

3　Results and discussion

For the study of hole-injection and transport ability of m-MTDATA：F4-TCNQ films，a series of hole only devices were fabricated. These hole-only devices have the following structures：

Device H1：ITO/ m-MTDATA（40nm）/ NPB（10nm）/ Al（130nm）

Device H2：ITO/ m-MTDATA：0.3wt% F$_4$-TCNQ（40nm）/ NPB（10nm）/ Al（130nm）

Device H3：ITO/ m-MTDATA：2wt% F$_4$-TCNQ（40nm）/ NPB（10nm）/ Al（130nm）

Device H4：ITO/ m-MTDATA：4wt% F$_4$-TCNQ（40nm）/ NPB（10nm）/ Al（130nm）.

A series of electron only devices were also fabricated in order to obtain data on the electron transport ability of BPhen：Liq films.

The structures of the electron-only devices are as follows：

Device E1：ITO/ BCP（5nm）/ BPhen（50nm）/ Al（130nm）

Device E2：ITO/ BCP（5nm）/ BPhen：17wt% Liq（50nm）/ Al（130nm）

Device E3：ITO/ BCP（5nm）/ BPhen：33wt% Liq（50nm）/ Al（130nm）

Device E4：ITO/ BCP（5nm）/ BPhen：50wt% Liq（50nm）/ Al（130nm）.

Figure 1 shows the molecular structures of main materials used in our research. The schematic structures of both hole-only and electron-only devices are depicted as the inset in Figs. 2 and 3，respectively. Figure 2 shows the current density versus voltage characteristics at various doping ratios of F$_4$-TCNQ to m-MTDATA for the hole-only devices. Figure 3 shows the current density versus voltage characteristics at various doping ratios of Liq to BPhen for the electron-only devices.

In the hole-only devices，a dramatic increase of the device current was observed when F$_4$-TCNQ was doped into an m-MTDATA layer. Compared with the device with an undoped m-MTDATA layer，the slight doping strikingly decreased the onset voltage. The J-V characteristics are strongly dependent on the doping ratio of the hole transport layer. At the same voltage，the current density increased as the doping rate increased. The highest current density was observed at the doping rate of 2wt% F$_4$-TCNQ，indicating that the conductivity of the p-doped layer increased due to the doping of F$_4$-TCNQ into m-MTDATA.

In the electron only devices，a thin layer of BCP was used to prevent holes from entering the ETL because of its high highest occupied molecular orbital
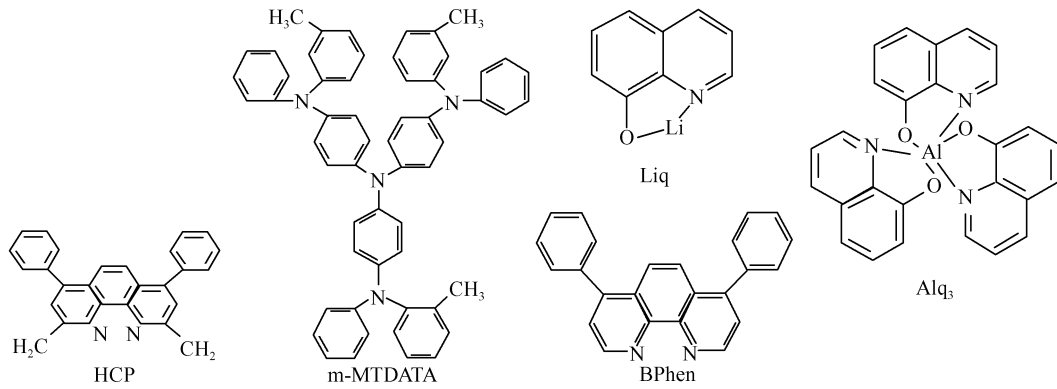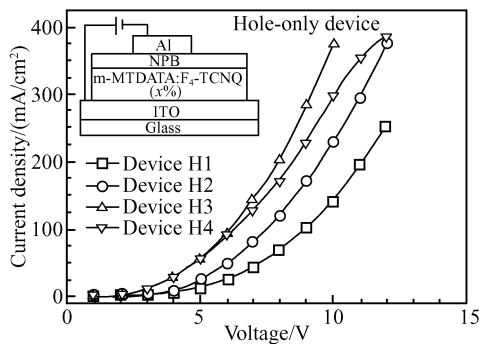
Fig.1   Molecular structures of main materials used

Fig.2   Current density versus voltage characteristics of hole-only devices with 0,0.3,2 and 4wt% F_4-TCNQ doped into M-MT-DATA   Inset：the schematic structure of hole-only device.

(HOMO) level （6.7eV）[26]. A rapid increase of the device current was observed when Liq was doped into a BPhen layer. Compared to the device with an undoped BPhen layer，the slight doping strikingly decreased the onset voltage. The *J-V* characteristics are strongly dependent on the doping ratio of the electron transport layer. In the device with the doping ratio of 33wt%Liq，the best *J-V* curve was obtained. The current density decreased when the doping ratio of Liq reached 50wt%. The current enhancement of both the hole-only devices and the electron-only devices is attributed to the decrease of the resistivity and activation energy，which leads to decreased ohmic losses.
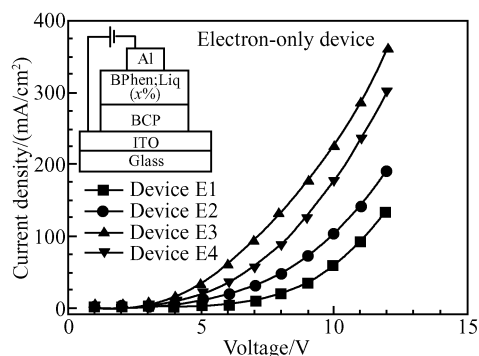

Fig.3   Current density versus voltage characteristics of electron-only devices of 0,17,33 and 50wt% Liq doped into BPhen   Inset：the schematic structure of electron-only device.

The experimental results on the electron-only devices have shown that further experiments should focus on a series of devices with a BPhen：33wt% Liq （n-doping） layer as ETL. The advantage of using BPhen：Liq as ETL can be explained by both its considerable high electron mobility （$\sim 5 \times 10^{-4}$cm^2/（V·s）） among the electron dominant materials[27]，and electron hopping exchange along their lowest unoccupied molecular orbitals （LUMOs）. The LUMO-LUMO difference between BPhen[27]（3.0eV） and Liq[26] （3.1eV） is neglectable，due to their similar LUMOs. Transport manifolds along their LUMOs are expected to exhibit a certain extent of overlap after mixing. Therefore，it is 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[27].

Tables 1 and 2 show the voltages at 20 and 100mA/cm^2 for the hole-only and electron-only devices，respectively. The tables indicate that the voltage decreases as the concentration of F_4-TCNQ into m-MTDATA and Liq into BPhen increases. However，the lowest voltages are obtained in Device H3 （2wt% F_4-TCNQ：m-MTDATA） and Device E3 （33wt% Liq：BPhen）. When the concentrations of F_4-TCNQ and Liq increase，the corresponding voltages increase. The concentration quenching at high doping ratios leads to the decrease of current density and the increase of voltage.

Table 1   Voltages of hole-only devices at various current densities

Devices	Device H1	Device H2	Device H3	Device H4
Voltage at 20mA/cm^2（V）	5.7	4.6	3.6	3.4
Voltage at 100mA/cm^2（V）	9.1	7.5	6.1	6.3

Table 2   Voltages of electron-only devices at various current densities

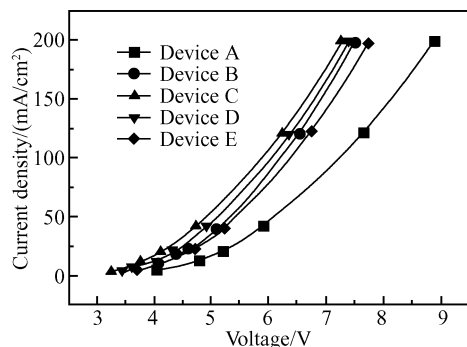| Devices	Device E1	Device E2	Device E3	Device E4
Voltage at 20mA/cm^2（V）	8.0	6.0	4.2	5.1
Voltage at 100mA/cm^2（V）	11.1	9.9	7.1	8.3

Fig. 4 Current density versus voltage characteristics of the complete devices

A series of complete devices were fabricated with a 33wt% Liq：BPhen（n-doping）layer as ETL. Among them, there are Device A（control device, undoped）with the structure of ITO/ m-MTDATA（40nm）/ NPB（10nm）/ Alq$_3$（20nm）/ BPhen（50nm）/ LiF（1nm）/ Al（130nm）fabricated for comparison and several devices with a p-doping m-MTDATA：x% F$_4$-TCNQ layer as HTL fabricated to balance the enhanced electron-injection with the n-doping layer. The F$_4$-TCNQ weight percentages are 0, 0.3, 2 and 4% for Devices B, C, D and E, respectively. The structures of these devices are as follows：

Device A（control device）：ITO/ m-MTDATA（40nm）/ NPB（10nm）/ Alq$_3$（20nm）/ BPhen：0wt% Liq（50nm）/ LiF（1nm）/ Al（130nm）；Device B：0wt% F$_4$-TCNQ（HTL）, 33 wt% Liq（ETL）；Device C：0.3wt% F$_4$-TCNQ（HTL）, 33wt% Liq（ETL）；Device D：2wt% F$_4$-TCNQ（HTL）, 33wt% Liq（ETL）；Device E：4wt% F$_4$-TCNQ（HTL）, 33wt% Liq（ETL）.

We did not attempt to optimize the thicknesses of these devices to the maximal luminous efficiency.

The current density versus the voltage, the current efficiency versus the current density, and the power efficiencies versus the current density characteristics of the complete devices are shown in Figs. 4,
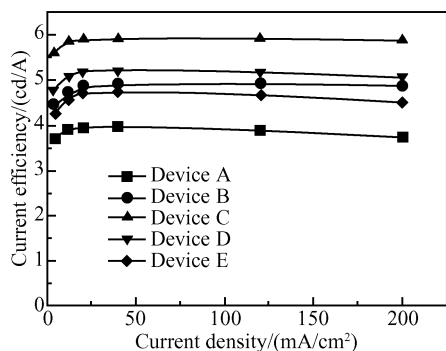

Fig. 5 Current efficiency-current density characteristics of the complete devices
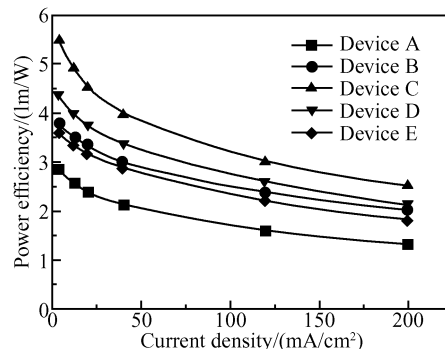

Fig. 6 Power efficiency versus current density characteristics of the complete devices

5 and 6, respectively. Compared with the *J-V* curve of Device A（undoped）, the *J-V* curve of Device B is significantly enhanced, indicating that the conductivity of the device can be improved by using n-doping ETL. Both the current and the power efficiencies of Device B（undoped HTL and n-doped ETL）are considerably increased compared to Device A（control device）with a layer of 33wt% Liq：BPhen being used as ETL. Both the currents and the power efficiencies of Devices C, D and E are also increased compared to Device A when a p-doped HTL is used along with an n-doped ETL. However, the maximum value of current and power efficiencies are obtained only when the doping ratio of F$_4$-TCNQ into m-MTDATA is 0.3wt%（Device C）. Among all the *J-V* curves, the best one is that of Device C, which indicates the improved conductivity of this device. Table 3 summarizes the data of all devices obtained in experiments from Device A to Device E at 20mA/cm^2. Table 3 shows that the current efficiency, power efficiency, and voltage of Device C（the most efficient device）have been improved by approximately 51%, 89%, and 29%, respectively, compared to Device A（control device）. This significant enhancement in the device performance is attributed to the improved transport conductivity of both the p-doped hole transport layer and the n-doped electron transport layer for a particular doping concentration of F$_4$-TCNQ into m-MTDATA and Liq into BPhen, with the result that an efficient carrier balance is reached in the emission zone, leading to enhanced current and power efficiency at low driving voltages.

Table 3 Performance of devices at 20mA/cm^2

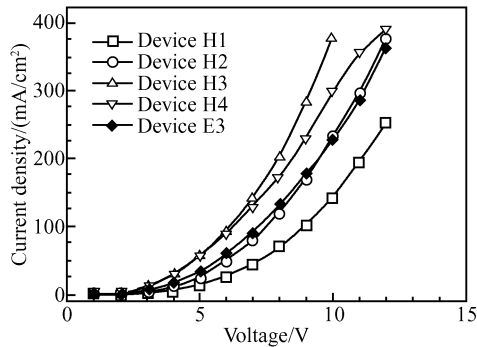| Devices	Driving voltage/V	Current efficiency /（cd/A）	Power efficiency /（lm/W）
Device A	5.31	3.92	2.38
Device B	4.58	4.81	3.30
Device C	4.10	5.90	4.51
Device D	4.35	5.20	3.74
Device E	4.66	4.70	3.17

Fig. 7　Comparison of current density versus voltage characteristics of Device E3（33wt% Liq：BPhen）with all hole-only devices

In order to discovery why Device C performed best, a series of *J-V* characteristics of all hole-only devices were compared with that of each electron-only device, which is shown in Fig. 6. Figure 6 demonstrates that the *J-V* curve of 0.3wt% F_4-TCNQ：m-MTDATA is very close to that of 33wt% Liq：BPhen, indicating that there is a good balance between the hole-only device for 0.3wt% F_4-TCNQ：m-MTDATA and the electron-only device for 33wt% Liq：BPhen, where the doping ratio is exactly the same as that of Device C（Fig. 4）. Thus, the enhancement in the device performances is the result of an efficient charge balance in the emission layer caused by conductivity improvement in the transport layers.

4　Conclusion

A good carrier balance is considered to be one of the most important factors for improving OLEDs. In this paper, we use Liq as a dopant to fabricate p-i-n devices with a novel n-doping（33wt% Liq：BPhen）layer as ETL and a p-doped（0, 0.3, 2 and 4wt% F_4 TCNQ：m-MTDATA）layer as HTL. We have also 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/cm² in Alq_3 based p-i-n OLEDs. The *J-V* comparison between the electron-only devices and hole-only devices has been presented to determine the reason for the significant improvement in performance. We conclude that an effective carrier balance（the number of holes is equal to the number of electrons）between holes and electrons is achieved due to the enhanced conductivity of the transport layers, leading to enhanced efficiency in our devices.

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具有新型电子传输层的有机薄膜电致发光器件[*]

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摘要:将 8-hydroxy-quinolinato lithium (Liq)掺入 4'7- diphyenyl-1,10-phenanthroline(BPhen)作为 n 型电子传输层(ETL),将 tetrafluro-tetracyano-quinodimethane(F$_4$-TCNQ)掺入 4,4′,4″-tris(3-methylphenylphenylamono)triphenylamine(m-MTDATA)作为 p 型空穴传输层(HTL),制作了 p-i-n 结构有机电致发光器件. 为了检验传输层传导率的改善情况,制备了一系列单一空穴器件和单一电子器件. 在引入 BPhen:33wt% Liq 作为 ETL 后,x% F$_4$- TCNQ:m-MTDATA 作为 HTL 后,器件的电流和功率效率明显改善. 与控制器件(未掺杂)相比,性能最佳的掺杂器件的电流及功率效率分别提高了51%和89%,电压下降了29%. 这是由于传输层传导能力的提高使得载流子在发光区域达到有效平衡.

关键词:p-i-n;n 型掺杂;电流效率;电子传输;传导率

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