High-efficiency organic light-emitting diodes based on the gradient doping and nonlinear cross-fading doping in transporting layers

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***Abstract* —** We have demonstrated that carrier injection and transporting can be fine-tuned via gradient *p*-doping and *n*-doping in organic light-emitting diodes. The doping profile of gradient doping in transporting layer is ultrahigh at the electrode side, declining gradually with the depth into the device until the emission layer. This not only ensures perfect charge injection from electrode to organic transporting layer but also proves an efficient charge transport for light emission. It is proposed that low doping ratio close to the emission layer may avoid possible quenching of excitons by the diffusion of dopant as well. A device based on gradient doping has been proved to obtain better carrier injection and achieve higher external quantum efficiency. To get smoother charge injection and transporting, and simplify the fabrication process, we have developed a nonlinear cross-fading doping in transporting layer, which has been demonstrated to further enhance the current density characteristics.

Keywords — *organic light emitting, injection, transporting, gradient doping, cross-fading doping.*
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1 Introduction

Organic light-emitting diodes (OLEDs) have attracted extensive research interests over the last two decades and have embraced the mass production. Despite numerous advantages, OLEDs still have some issues to be overcome to obtain lower voltage, higher luminance and efficiency, and better stability. Charge carrier injection and transporting are two important processes for light emission. However, because of large energy barrier between electrode and transporting layer, charge carriers are difficult to be injected into the organic layers, which results in high operating voltage and low efficiency. To solve this problem, an injection layer between electrode and transporting layer and doped transporting layer have been introduced.[1–3]

The injection layer reduces the energy barrier greatly due to the generation of a thin dipole layer.[4] But the mobility of undoped transporting layer is relatively low; therefore, the voltage drop over thick transporting layer is still large, resulting in high operating voltage. On the other hand, doping appropriate dopant material into transporting layer will generate additional charge carriers, and these carriers can almost move freely, resulting increased conductivity. Such conductivity increase can be up to several orders, and the voltage drop over such doped layer is negligible. Furthermore, for the doped transporting layer, a much stronger band bending occurs, and the space charge layer is very thin, which makes the charge carrier injection much easier via tunneling.[5] However, the doping ratio is usually quite low; there is not enough energy barrier reduce caused by the dipole layer at the interface of electrode and transporting layer.[4]

To further reduce the operating voltage, we proposed a gradient doping profile in the transporting layer, where the doping concentration adjacent to the electrode is very high to ensure perfect charge injection, and the concentration decrease gradually with the depth into the device until the emission layer. The medium doping concentration in the middle of the transporting layer still keeps its conductivity at a high level. The low concentration close to the emission layer may avoid the possible quenching of the excitons by the diffusion of dopants. Our results prove that the gradient doping leads to the best power efficiency and external quantum efficiency (EQE). To simplify the process of the gradient doping and diminish the interfacial effects, a nonlinear cross-fading doping is proposed as well. The profile of the cross-fading doping is nonlinear with continuous decrease from ultrahigh at the electrode side to ultralow at the emission layer side. It has been demonstrated that nonlinear cross-fading doping in transporting layer can further enhance the current density characteristics.

2 Experimental

Patterned indium–tin–oxide (ITO) substrates are prepared and precleaned by a multistep solvent process before

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transporting to vacuum thermal evaporator. In this study, [*N*-(1-naphthyl)-*N*-phenyl-amino] biphenyl (NPB) is used as a hole transporting material and 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) is the corresponding *p*-type dopant. High electron mobility (~10^{-3} cm^2/V·s) transporting material VOM1973 is used as electron transporting layer (ETL), and its corresponding *n*-type dopant is 8-hydroxyquinolinolato-lithium (Liq). All devices are fabricated under a base pressure of 5×10^{-6} Torr without breaking the vacuum. The organic materials, except for the dopants, are evaporated at a rate of 0.5 ~ 1 Å/s. At the end, 100-nm-thick aluminum is deposited as the cathode. The active area defined by the overlap of the ITO anode and the Al cathode is 3 mm × 3 mm. The current density–voltage–luminance characteristics of the devices are measured using a computer-controlled Keithley 2400 and Topcon BM-7A measurement system. All the measurements are carried out at room temperature under ambient atmosphere.[6]

3 Gradient doping in electron transporting layer

First of all, different doping concentrations of Liq in VOM1973 are compared as shown in Fig. 1. The device structures are ITO/F4-TCNQ (2 nm)/NPB (50 nm)/8-hydroxyquinoline aluminum (Alq_3) (20 nm)/VOM1973:Liq (40 nm, x wt.%, where x = 0, 20, 30, 40, respectively)/Al (100 nm). The operating voltage at 20 mA/cm^2 of device without Liq doping (around 8 V) is greatly higher than that of doped devices, which is due to a large energy barrier between Al and VOM1973. When the doping ratio in ETL increases up to 30 wt.%, the current density grows to the highest level, indicating that better electron injection has been realized with reduced energy barrier.[7] However, the upward trend tends to be saturated when the doping ratio is further increased to 40 wt.%.

To further improve the electron injection and transport, a gradient doping in transporting layer is introduced with device structure of ITO/F4-TCNQ (2 nm)/NPB (50 nm)/4,4 -bis (carbazol-9-yl)biphenyl (CBP):tris(2-phenylpyridine)iridium ($Ir(ppy)_3$) (20 nm, 8 wt.%)/VOM1973 (10 nm)/VOM1973:Liq (40-y nm, 30 wt.%)/VOM1973:Liq (y nm, 50 wt.%)/Liq (1 nm). Here, y is the thickness of *n*-doped ETL with a high doping ratio of 50 wt.%. Figure 2 illustrates the I–V characteristics of devices with y changing from 0 to 35. Inset figure shows the I–V characteristics relative to a reference device without the 50 wt.% doped layer. When y increases from 5 to 25, all corresponding devices show better current densities at a low driving voltage range. Especially when y is set to 5, the maximum relative current density doubles that of the reference device. In an *n*-type doped ETL system, the Fermi level of ETL shifts towards its lowest unoccupied molecular orbital (LUMO) level.[8] With the higher doping concentration of 50 wt.%, Fermi level moves further towards the LUMO level, and the electron injection barrier between metal and organic material decreases, as shown in Fig. 3(a) and (b), resulting in improved injection currents. In addition, the doped ETLs with various doping concentrations provide intermediate steps for easier electron transporting. If the doping concentration is continuously changed as in a cross-fading profile, a smooth electron transporting path will be created as illustrated in Fig. 3(c).[9] With improved electron injection, the current efficiency of the device increases as depicted in Fig. 4. It is mainly attributed to better charge carrier balance, and the best current efficiency is obtained when the highly doped ETL is 5 nm thick.

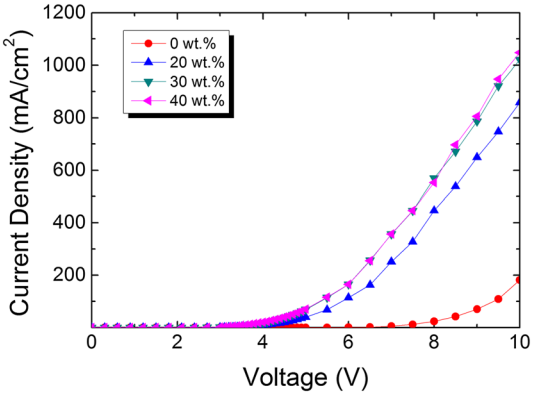

FIGURE 1 — Current density–voltage characteristics of the devices with various doping ratio.

4 Comparison with gradient doping

In order to compare the gradient doping with the conventional uniform doping, a set of devices are fabricated with Ir $(ppy)_3$ doped in 1,4,7-tris(acetato)-1,4,7-triazacyclononane (TCTA) as the light-emitting layer.[10,11] The basic device structure is ITO/F4-TCNQ (2 nm)/NPB (50 nm)/TCTA:$Ir(ppy)_3$ (20 nm, 8 wt.%)/Bphen (10 nm)/ETL/Al (100 nm), where ETL for different devices are depicted as follows:

ETL1: Bphen:Liq (40 nm, 30 wt.%)
ETL2: VOM1973:Liq (40 nm, 30 wt.%)

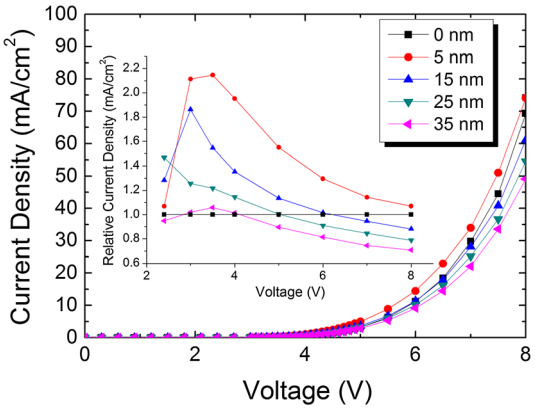

FIGURE 2 — Current density characteristics of devices with various thickness of 50 wt.% doped electron transporting layer at different voltages. Inset is the current density characteristics relative to that without the highly doped electron transporting layer.

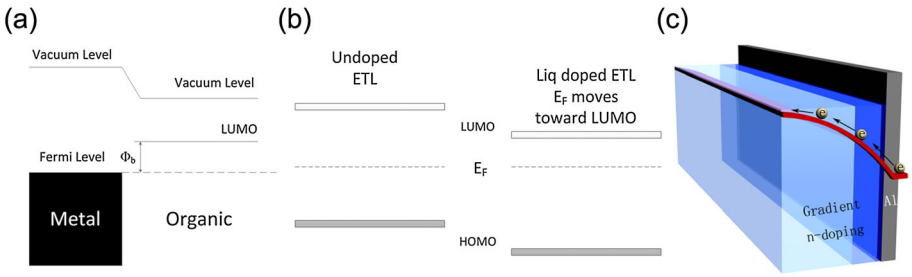

FIGURE 3 — (a) Energy level diagram for Al/organic interface. (b) Fermi level moves with the increase of doping ratio. (c) The deeper the blue, the higher the doping concentration. So electrons will be transported by a smooth energy step with gradient *n*-doping.

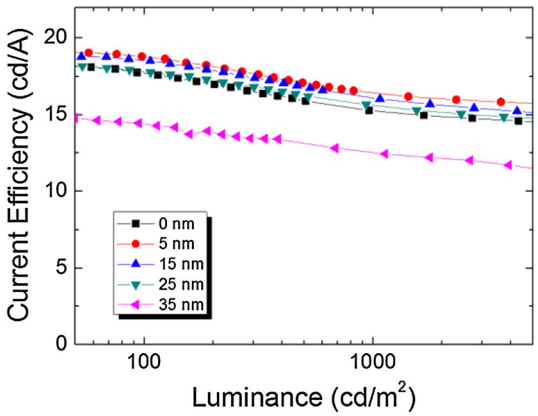

FIGURE 4 — Current efficiency of devices with various thickness of 50 wt.% doped electron transporting layer.

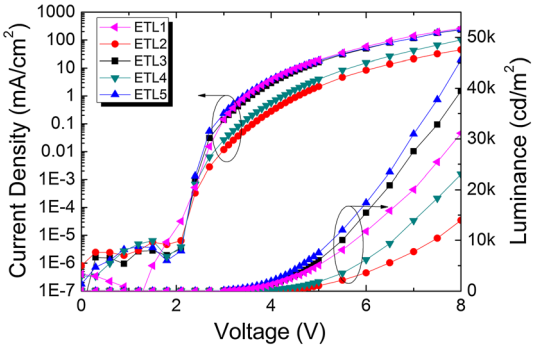

FIGURE 5 — Current density–voltage–luminance characteristics of devices with different electron injection and transporting methods. ETL1: Bphen:Liq (40 nm, 30 wt.%), ETL2: VOM1973:Liq (40 nm, 30 wt.%), ETL3: VOM1973 (40 nm)/Liq (1 nm), ETL4: VOM1973:Liq (35 nm, 30 wt.%)/VOM1973:Liq (5 nm, 50 wt.%), ETL5: VOM1973:Liq (35 nm, 30 wt.%)/VOM1973:Liq (5 nm, 50 wt.%)/Liq (1 nm).

ETL3: VOM1973 (40 nm)/Liq (1 nm)
ETL4: VOM1973:Liq (35 nm, 30 wt.%)/VOM1973:Liq (5 nm, 50 wt.%)
ETL5: VOM1973:Liq (35 nm, 30 wt.%)/VOM1973:Liq (5 nm, 50 wt.%)/Liq (1 nm)

All the devices have a hole blocking layer with 10 nm Bphen, which is deposited to confine holes in light-emitting layer and prevent possible energy transfer from $Ir(ppy)_3$ to ETL.

Figure 5 illustrates the current density–voltage–luminance characteristics of five different structures using aforementioned ETLs. Although there is a better electron mobility of VOM1973 (~10^{-3} $cm^2/V{\cdot}s$) than that of Bphen (~10^{-4} $cm^2/V{\cdot}s$), the current density of ETL2 is still lower than ETL1. This may be because that the LUMO of VOM1973 (2.9 eV) is slightly higher than that of Bphen (3.0 eV), which hinders the electron injection from VOM1973 to Bphen somehow. The carrier injection, rather than the transporting, is the main limitation of the current density in this study. The speculation is confirmed when a thin Liq layer is inserted between Al cathode and VOM1973 as in ETL3, where the current density increases significantly even without doping of ETL. It is clearly indicated that high concentration Liq near the cathode benefits for the improvement of current density characteristics, which is due to the generation of an ultrathin dipole layer at the interface of cathode and ETL. When VOM1973 is doped with Liq as in ETL5, a further slight increase of current density, especially at a low voltage as ~3.0 V, is observed, which is consistent with the results in Fig. 2 and might be attributed to enhanced electron injection with highly Liq doped VOM1973. In addition, the operating voltage of device ETL5 at 10 cd/m^2 is only 2.6 V, which is better than the others at the same luminance (2.7, 3.2, 2.7, and 3.0 V for ETL1, ETL2, ETL3, and ETL4, respectively).

Because the hole mobility is much larger than the electron mobility for most organic materials, the electrons are usually the minority carriers in most OLEDs. Enhancing the electron injection and transporting can improve the charge carrier balance and increase the efficiency significantly. As can be seen from Fig. 6, although ETL1 owns a better electron injection, the EQE is still the lowest of all because Bphen has a poorer electron transporting ability than VOM1973. With the best electron injection and transporting, the device using ETL5 obtains the highest efficiency. The EQE at 1000 cd/m^2 is 16.3%, and the power efficiency is 43.3 lm/W, which is 48% higher than that of the uniformly doped device with ETL2.

5 Nonlinear cross-fading doping

Although the gradient doping obtains the best performance than the others, the complexity is still an issue for mass production. This is because tuning doping ratio in different layers

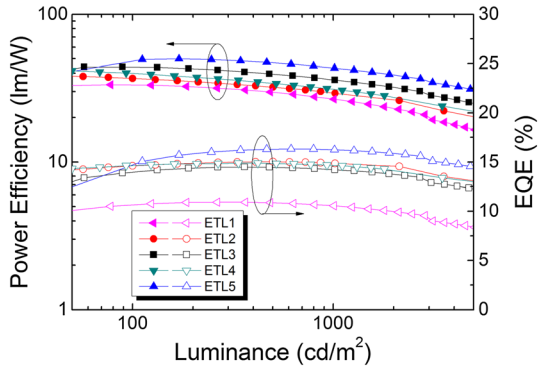

FIGURE 6 — Power efficiency–luminance characteristics (closed) and external quantum efficiency (EQE) (open) of devices with different electron injection and transporting methods.

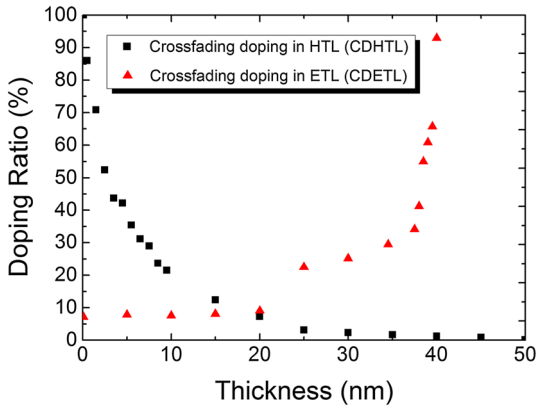

FIGURE 7 — Cross-fading doping profiles in hole transporting layer (CDHTL) and electron transporting layer (CDETL). The doping ratio is tuned with the deposition thickness increase of HTL (square) and ETL (triangle), respectively.

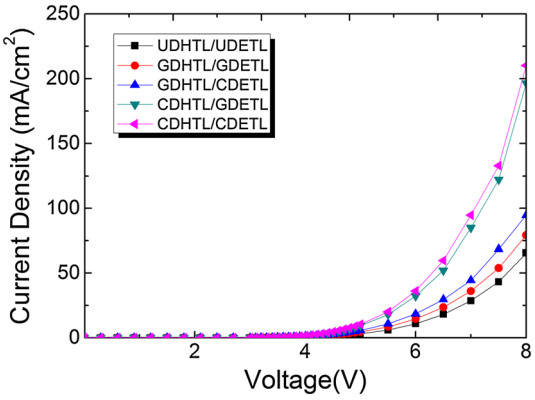

FIGURE 8 — Current density–voltage characteristics of devices with different doping ratio in both hole transporting layer (HTL) and electron transporting layer (ETL).

will cause a waste of time and materials. Therefore, a nonlinear cross-fading doping is introduced in transporting layers in this study. The linear cross-fading doping has been used in emission layer before to extend recombination zone and expand lifetime in OLEDs.[12] The doping concentration is linearly changed over the layer thickness. However, the linear cross-fading is not suitable for the transporting layers. At the interface to the electrode, an ultrahigh doping concentration up to 100% is usually needed to improve the injection, while much lower doping concentration is adopted close to the emission layer to avoid possible quenching of excitons by the dopant. Therefore, a nonlinear cross-fading doping, which fits the gradient doping profile as discussed previously, is developed.

Kido has utilized an inline evaporation technique to facilitate the cross-fading doping process[13] and C. W. Tang also creates a novel thermal deposition boat to control the deposition rate indirectly with fast rate response.[14] But in this study, we just control the doping rate by tuning the temperature of the evaporation source.

For comparison among these doping methods, another five devices with double emission layer have been fabricated. The structures are ITO/hole transporting layer (HTL)/TCTA:Ir(ppy)$_3$ (5 nm, 8 wt.%)/TPBi:Ir(ppy)$_3$ (15 nm, 8 wt.%)/TPBi (10 nm)/ETL/Al (100 nm), in which TPBi is 1,3,5-tris (2-*N*-phenylbenzimidazolyl)benzene. The doping types and their doping profiles in HTL and ETL are shown in Table 1 and Fig. 7.

As depicted in Fig. 8, the cross-fading doping in transporting layers especially in HTL can further reduce the operating voltage significantly because smoother path for charge carriers even than the gradient doping has been established. The most charge-balanced device is the gradient doping in both HTL and ETL whose maximum power efficiency and EQE are 62.9 lm/W and 19.6%, respectively, as shown in Fig. 9. With more efficient hole injection and transporting of cross-fading

TABLE 1 — Various doping types and their profiles.

Doping type	Doping profile
Uniform doping HTL (UDHTL)	NPB:F4-TCNQ (40 nm, 2 wt.%)/ NPB (10 nm)
Uniform doping ETL (UDETL)	VOM1973:Liq (40 nm, 30 wt.%)
Gradient doping HTL (GDHTL)	F4-TCNQ (2 nm)/NPB:F4-TCNQ (10 nm, 20 wt.%)/NPB:F4-TCNQ (30 nm, 2 wt.%)
Gradient doping ETL (GDETL)	VOM1973:Liq (35 nm, 30 wt.%)/ VOM1973:Liq (5 nm, 50 wt.%)/Liq (1 nm)

HTL, hole transporting layer; ETL, electron transporting layer; NPB.

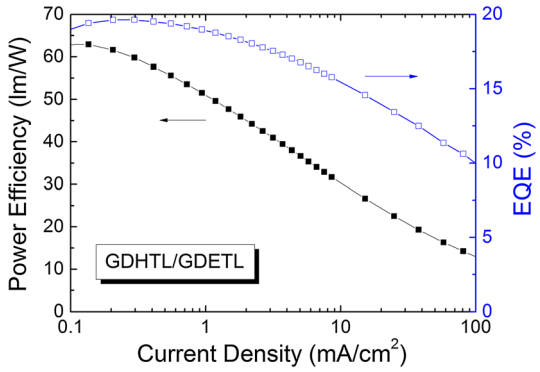

FIGURE 9 — Power efficiency and external quantum efficiency (EQE) of device with gradient doping both in hole transporting layer (HTL) and electron transporting layer (ETL).

doping in HTL, the efficiency is reduced because of a bit poorer charge balance. However, this method provides a new way to improve the carrier injection and transporting and to tune the charge carrier balance. Moreover, by diminishing the interfacial effects, the cross-fading doping may have better stability. In addition, it can also be easily achieved for mass production with novel evaporation processes.

6 Summary

We show that by using the gradient doping, 16.3% EQE is achieved for single emission layer at 1000 cd/m^2 where the power efficiency is also increased by 47.8% compared with the uniform doping device. A maximum EQE of 19.6% and a power efficiency of 62.9 lm/W are also obtained with double emission layer using the gradient doping in HTL and ETL. Finally, an efficient and commercial potential nonlinear cross-fading doping in transporting layer is also proved to further increase the carrier injection and transporting.

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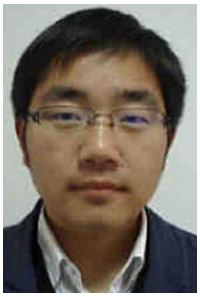

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