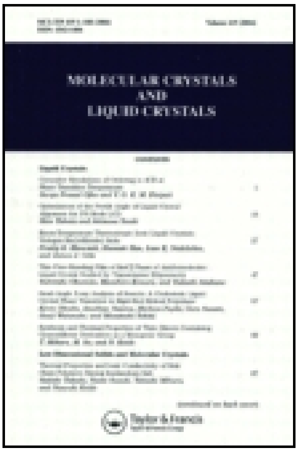


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# Enhancing the Hole Injection and Transporting of Organic Light-Emitting Diodes by Utilizing Gradient Doping

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# Enhancing the Hole Injection and Transporting of Organic Light-Emitting Diodes by Utilizing Gradient Doping

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*We demonstrate significant improvement of hole injection and transporting in organic light-emitting diodes (OLEDs) by utilizing gradient doping in hole transporting layer (HTL). An ultrahigh doping concentration at the anode side to enhance the hole injection, whereas low doping concentration close to emission layer to avoid possible quenching of excitons. A plural HTL with concentration step are introduced in between to smooth the hole transporting. Compared to conventional hole injection technologies, the gradient doping significantly enhances the current density and luminance of the OLED.*

**Keywords** Gradient doping; hole transporting layer; organic light-emitting diodes

## Introduction

Since the first efficient organic light-emitting diode (OLED) was reported by Tang [1], this new technology has attracted extensive researches for its bright prospects in display and lighting. However, to achieve widespread application, OLEDs must have low operating voltage, high efficiency, and low process cost. For multilayer OLEDs, the energy barrier between electrodes and transporting layers will cause ohmic losses and block the carrier injection. An excellent solution is to introduce electrical doping technology into transporting layers. The key effect of doping is the generation of ohmic contacts through a thin barrier formed by space charge layers [2]. Blochwitz et al. [3] doped 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane ($F_4$-TCNQ) in hole transporting layer (HTL) and demonstrated that the doped charge transporting layers based on molecular dopants lead to low operating voltage and high efficiency. $F_4$-TCNQ is a widely used p-type dopant material, which has been proved to be well doped in 4,4′,4′′-tris(N-3-methylphenyl-N-phenylamino)triphenylamine (m-MTDATA) [4], zinc phthalocyanine (ZnPc) [5], and N,N,N′,N′-tetrakis(4-methoxyphenyl)benzidine (MeO-TPD) [6], and improves the performance of devices. In these researches [3–6], $F_4$-TCNQ is usually uniformly doped through the entire HTL, and doping concentration is as low as around 2 wt%. An interlayer is often

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added between p-doped HTL and light-emitting layer (EML) to prevent $F_4$-TCNQ diffusing into EML and quenching the excitons. Recently, inserting a thin buffer layer of $F_4$-TCNQ between indium tin oxide (ITO) and HTL, which is called heterostructure, has been proved to improve the hole injection dramatically. It is proposed that a large number of interfacial dipoles are generated between ITO and HTL by introducing a $F_4$-TCNQ buffer layer [7,8].

To lower the operating voltages and increase the efficiencies, it is necessary to improve the carrier injection and transporting. In this paper, we introduce a gradient doping [9–12] in HTL to facilitate hole injection and transporting, which is expected to work at electron side as well. With gradient doping, concentration of $F_4$-TCNQ is transited from 100 wt% near the anode to 0 wt% near the emission layer in 4,4′-bis [N-(1-naphthyl)-N-phenyl-amino] biphenyl (NPB). These transition layers provide a smooth path for holes to transport. We further optimize the thickness of transition layer to obtain a better performance in terms of hole injection and transporting.

## Experiment and Device Structures

Patterned ITO substrates are prepared and precleaned by a multistep solvent process before transporting to vacuum thermal evaporator. All devices are fabricated under a base pressure of $5 \times 10^{-6}$ Torr without breaking the vacuum. Organic materials are evaporated at a rate of 0.5 Å/s to 1 Å/s, followed by a metal cathode. In our study, three types of HTL are compared, which are listed as following:

(1) Uniform doping: NPB:F4-TCNQ (40 nm, 2 wt%)/NPB (10 nm)
(2) Heterostructure: F4-TCNQ (2 nm)/NPB (50 nm)
(3) Gradient doping: NPB:F4-TCNQ (2 nm, 100 wt%/8 nm, 40 wt%/10 nm, 20 wt%/10 nm, 10 wt%/10 nm, 5 wt%/10 nm, 2 wt%/10 nm, 0 wt%)

Green phosphorescent material tris(2-phenylpyridine)iridium [$Ir(ppy)_3$] doped in 4,4′-bis(carbazol-9-yl)biphenyl (CBP) is working as a EML [13,14]. Afterward 50-nm-thick 4,7-diphenyl-1,10-phenanthroline (Bphen) layer is deposited to transport electrons and block holes. Finally, a 1-nm 8-hydroxyquinolinolato-lithium (Liq) to improve electron injection and 120-nm Al as cathode are evaporated one after the other. So the basic device structure is ITO/HTL (50 nm)/CBP:$Ir(ppy)_3$ (20 nm, 8 wt%)/Bphen (50 nm)/Liq (1 nm)/Al (120 nm). Figure 1 illustrates the detail doping profile of the three types of HTL compared in this experiment.

The current density–voltage–luminance (*I–V–L*) characteristics of the devices are measured using Keithley 2400 and Topcon BM-7A. All the measurements are carried out at room temperature under ambient atmosphere.

## Results and Discussion

Figure 2 compares the *I–V–L* characteristics of gradient doping with uniform doping and heterostucture. It is shown that the current density and luminance are significantly increased by utilizing gradient doping. The turn-on voltage of gradient doping and heterostructure device is 3.4 V, around 0.5 V lower than that of the uniform doping device. As a strong electron acceptor, $F_4$-TCNQ can trap electrons of NPB, leading to a layer of interfacial dipoles between ITO and NPB HTL [15,16]. Therefore, a 2-nm $F_4$-TCNQ layer in gradient doping or heterostructure devices generates interfacial dipoles to enhance the hole injection efficiently and decrease the voltage [8].

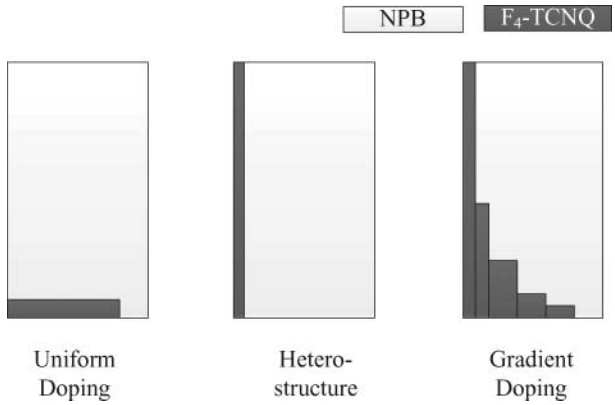


**Figure 1.** The column bar is respect for concentration of $F_4$-TCNQ. Uniform doping concentration is only 2 wt%. Heterostructure has a 2-nm $F_4$TCNQ between ITO and NPB. Gradient doping owns a smooth variation of concentration.

However, it is observed in Fig. 3 that heterostructure has lower power efficiency than uniform doping and gradient doping devices. When $F_4$-TCNQ is doped in NPB, as a strong electron acceptor, $F_4$-TCNQ removes the electrons from the highest occupied orbital (HOMO) states of NPB and generates holes. These holes are mobile and improve the hole transporting significantly. As in heterostructure device, although large amount of holes are injected into the device via $F_4$-TCNQ interlayer, they are hindered by the undoped NPB layer. It might lead to unbalanced hole and electron carriers and result in slightly lower efficiency. In the gradient doping device, the $F_4$-TCNQ concentration in NPB varies from 100 wt% near the anode to 0 wt% near the emission layer. Therefore, both hole injection

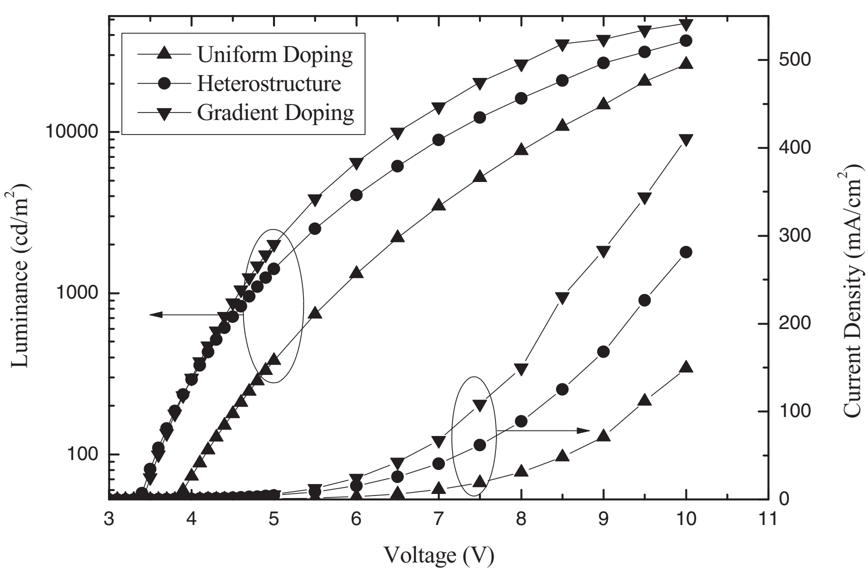


**Figure 2.** *I–V--L* characteristics of OLEDs with uniform doping, heterostructure, and gradient doping.

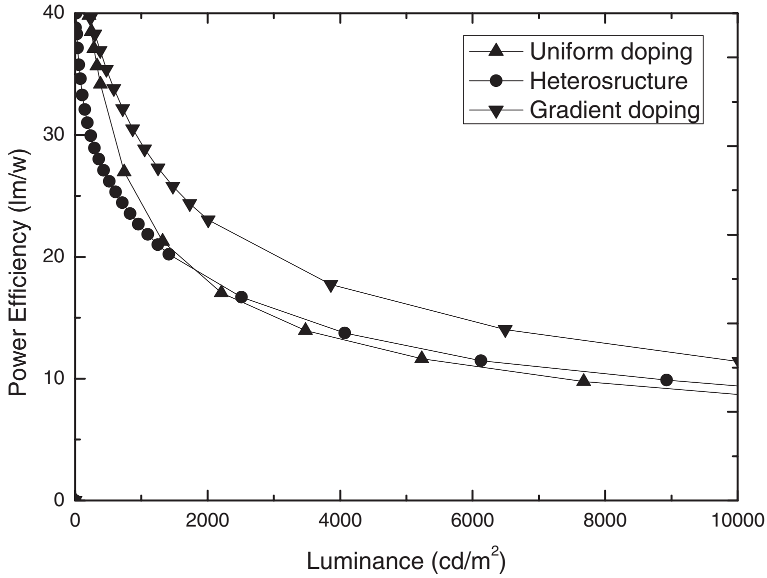


**Figure 3.** Power efficiency–luminance curves of OLEDs with uniform doping, heterostructure, and gradient doping.

and transporting are enhanced by heavy doping near the anode and wide range of light doping through the NPB, respectively. In consequence, the power efficiency of gradient doping reaches 31.8 lm/w when the luminance is 2000 cd/cm$^2$, whereas that of uniform doping and heterostructure are both around 25 lm/w at the same luminance as shown in Fig. 3. Moreover, with increasing doping, the Fermi level moves toward the transport states [2], so the gradient doping concentration provides a smooth path for holes to transport and will not emerge a distinct energy barrier.

To further optimize the doping profile, the thicknesses of transition layer are varied. The full HTL consists of four NPB:$F_4$-TCNQ layers with different concentrations. The layer thickness of 40% doping is increased from 5 nm to 35 nm with 10 nm step. To keep the total HTL thickness same, the thickness of undoped NPB layer is reduced accordingly. The layer structure is as following: NPB:$F_4$-TCNQ (2 nm, 100 wt%)/NPB:$F_4$-TCNQ ($x$ nm, 40 wt%)/NPB:$F_4$-TCNQ (5 nm, 10 wt%)/NPB($45 - x$ nm), $x$ is set to 5, 15, 25, and 35 nm, respectively.

It is obviously observed that in Fig. 4 current density increases after inserting a heavy p-doped layer. This is also a very powerful evidence to prove that gradient doping has efficient hole injection and transporting ability. As the transition layer becomes thicker, the voltage is continuously reducing. However, when the thickness is more than 25 nm, the voltage will not reduce any more. It indicates that when the thickness is 25 nm, $F_4$-TCNQ captures the largest amount of electrons from NPB. However, no more electrons can be captured with less NPB molecules existing in HTL when the thickness is larger than 25 nm.

## Summary

We have demonstrated that gradient doping in HTL can obtain better performance of hole injection and transporting than uniform doping and heterostructure. Heterostructure

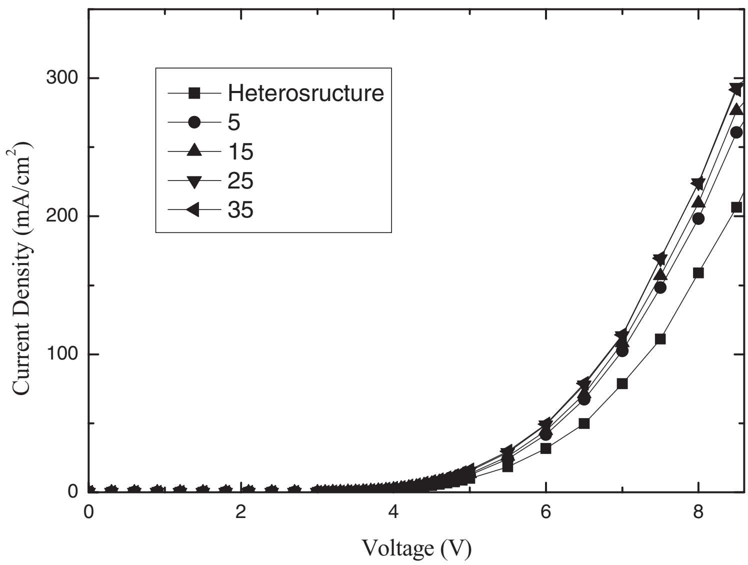


**Figure 4.** *I–V* characteristics of gradient doping with different transition thickness.

acquires better hole injection ability, and uniform doping acquires better hole transporting ability. By inserting a transition layer of heavily doped HTL, the current density, luminance, and current efficiency are all improved. The transition layer in gradient doping has many variable quantities, such as the thickness of different doping concentration, the doping concentration of each layer, and so on. In this paper, we just optimized the thickness of 40 wt% doping layer, which is the most important role in transition. A thickness of 25-nm transition layer has been proved to obtain the best *I–V* performance. Actually, to tune the variable quantities of transition layer in gradient doping also provides an adjustment of charge balance for different device structure.

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