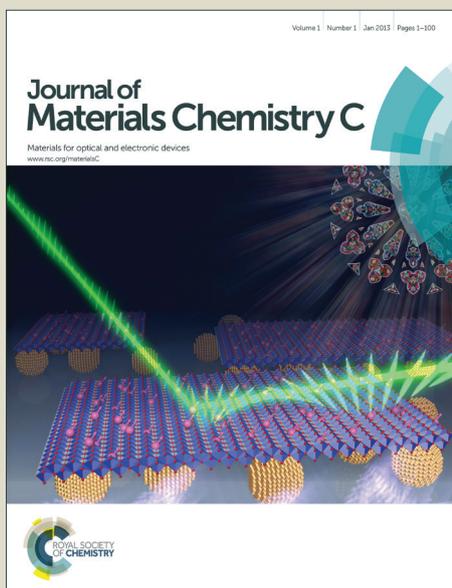


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ARTICLE TYPE

High-efficiency fluorescent organic light-emitting diodes with MoO₃ and PEDOT:PSS composition film as hole injection layer

Hongmei Zhang^{*a,b}, Qiang Fu^c, Wenjin Zeng^{a,b}, and Dongge Ma^{*c}

It has been demonstrated that high efficiency and low efficiency roll-off can be achieved in C545T-based green organic light-emitting diodes (OLEDs) by using molybdenum oxide (MoO₃)/poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) as the interfacial modification layer on Indium Tin Oxide (ITO). The maximum current efficiency (CE), power efficiency (PE), and external quantum efficiency (EQE) reach 23.4 cd/A, 19.5 lm/W, and 6.3% at 1000 cd/m², respectively, and slightly reduce to 22.3 cd/A, 8.3 lm/W and 6.0% at 10000 cd/m². In addition, the dependence of device performance on the thickness of hole-transport layer (HTL) on the top of MoO₃ and PEDOT:PSS was also investigated. The results indicate that MoO₃ as HIL requires a thicker HTL in order to obtain high efficiency compared with PEDOT:PSS as HIL.

1 Introduction

Phosphorescent organic light-emitting diodes (PHOLEDs) have attracted extensive interest due to the demonstrated potential for achieving 100% internal quantum efficiency compared to conventional fluorescent OLEDs because of utilization of both singlet and triplet excitons for light emission.¹⁻³ However, using fluorescence-emitting compounds to fabricate OLEDs yet remains significant due to the advantage of ultra-long lifetime, while it is more challenging for PHOLEDs,⁴ especially for blue-emitting PHOLEDs. Therefore, further enhancing the efficiency of fluorescent OLEDs is necessary. The external quantum efficiency (EQE) of fluorescent OLEDs is considered to be the product of the following four factors: i) the charge balance of holes and electrons, ii) the singlet exciton ratio, iii) the photoluminescence quantum efficiency (PLQE), and iv) the light out-coupling efficiency.⁵⁻⁶ Generally, both charge balance and PLQE can be maximized to 100%. If the out-coupling efficiency is 20%, the upper limit of the EQE is 5%. However, recent reports have shown EQEs of higher than 5%, over the classic upper limit.⁷⁻⁹ A good charge balance is primary for achieving a high EQE.¹⁰ Amongst the factors affecting the charge balance, the interfaces between electrodes and organic semiconductors play important roles in determining the charge balance.¹¹ Therefore, it is important to understand the determining factors of the charge balance. As we know, the control of the electrode/organic interfaces could be beneficial to the optimization of device performance by changing charge carrier injection and transport to obtain charge carrier balance. In order to improve carrier injection, many approaches in terms of the surface modification of indium-tin-oxide (ITO) anode have been reported, such as oxygen plasma,¹² ultraviolet-ozone,¹³ and self-assembling strategies,¹⁴ as well as insertion of an ultra-thin buffer layer such as CuPc, AgO, WO₃ and p-dopant 15-18 etc. It is clear that the modification of electrode/organic interface will directly influence the charge carrier injection, then improve the device performance.¹⁹⁻²⁰ It has also been proven that the utilization of MoO₃ and PEDOT:PSS as anode

modification layers significantly improves the efficiency and lifetime of OLEDs.²¹⁻²⁷ So far, there is limited study on systematic and detailed comparison between the effect of MoO₃ and PEDOT:PSS as hole injection layer (HIL) on the charge balance. In addition, there is no report on the effect of MoO₃/PEDOT:PSS composite as the interfacial modification layer on the charge balance, leading to the efficiency enhancement of OLEDs.

In this paper, we compare the role of MoO₃, PEDOT:PSS and MoO₃/PEDOT:PSS as HIL in enhancing the efficiency of OLEDs with green 10-(2-benzothiazolyl)-2,3,6,7-tetrahydro-1,1,7,7-tetramethyl-1H,5H,11H-(1-benzopyrroprano(6,7-8-I_j))quinolizin-11-one (C545T) as emitter in details. We note that the utilization of MoO₃ and PEDOT:PSS as the HIL requires different thickness of NPB as hole transport layer (HTL). It was demonstrated that the efficiency of the fluorescent OLEDs can be further improved by using MoO₃/PEDOT:PSS composition film as HIL. The peak current efficiency of 23.4 cd/A and external quantum efficiency of 6.3% have been achieved. We clearly proof the charge balance of the hole and electron injection and transport by the spatial electric field theory.

2 Experimental

2.1 Device fabrication

C545T-based green fluorescent OLEDs consist of tris-(8-hydroxyquinoline) aluminum (Alq₃) as the electron-transport layer (ETL) and host, *N,N'*-di(naphthalene-1-yl)-*N,N'*-diphenylbenzidine (NPB) as the HTL layer. Here, C545T is a green fluorescent dye, Alq₃ is a good electron transport molecule and NPB has a high hole mobility. They are widely used in OLEDs. The HILs of MoO₃, PEDOT:PSS, and MoO₃/PEDOT:PSS, as well as the HTL thickness have been optimized to control the charge balance. Fig. 1a) and b) show the energy level diagrams of the devices and the molecular structures of C545T, Alq₃, and NPB used in these devices.

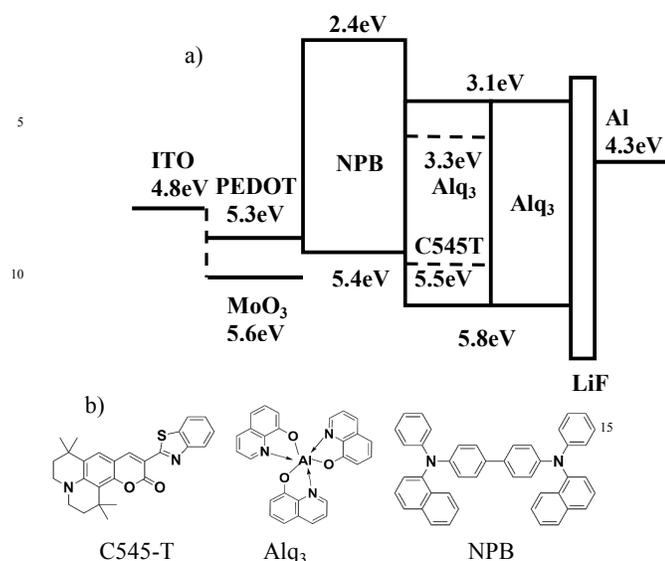


Figure 1 a) Energy level diagrams of the fabricated OLEDs and b) molecular structures of C545T, Alq₃, and NPB used in this study.

The device structures in this study are ITO/MoO₃(10 nm) or PEDOT:PSS (30 nm)/NPB (x nm)/Alq₃:C545T (35 nm)/Alq₃ (35 nm)/LiF (1 nm)/Al (120 nm) and ITO/MoO₃ (10 nm)/PEDOT:PSS (30 nm)/NPB(x nm)/Alq₃:C545T (35 nm)/Alq₃ (35 nm)/LiF (1 nm)/Al (120 nm). The commercial ITO-coated glass with a sheet resistance of around 10 Ω/□ was used as the anode. ITO glass substrates were successively rinsed with detergent, de-ionized water, acetone, and isopropyl alcohol. Each rinsing step was carried out in an ultrasonic bath for 10 min. The cleaned and dried substrates were treated with oxygen plasma for 3 min. PEDOT:PSS was spin coated at 3000 rpm for 60 s. The PEDOT:PSS films were slowly dried in covered petri dishes at 120 °C on hot plate for 30 min. The OLEDs were prepared by thermal evaporation in a high-vacuum system with pressure of less than 5 × 10⁻⁴ Pa. MoO₃, NPB, Alq₃:C545T, and Alq₃, LiF (1 nm) and Al (120 nm) were evaporated onto ITO in turn. The concentration of C545 in Alq₃ was controlled at 1 wt%. The evaporation rates were monitored by frequency counter, and the thickness of each layer was calibrated by Dektak 6M Profiler (Veeco). The overlap between ITO and Al electrodes was 16 mm² as the emission area of devices. The variation of each layer thickness in all devices is listed in Table I, and all devices have the same thickness of Alq₃ (35 nm), LiF (1 nm), and Al (120 nm).

2.2 Device characterization

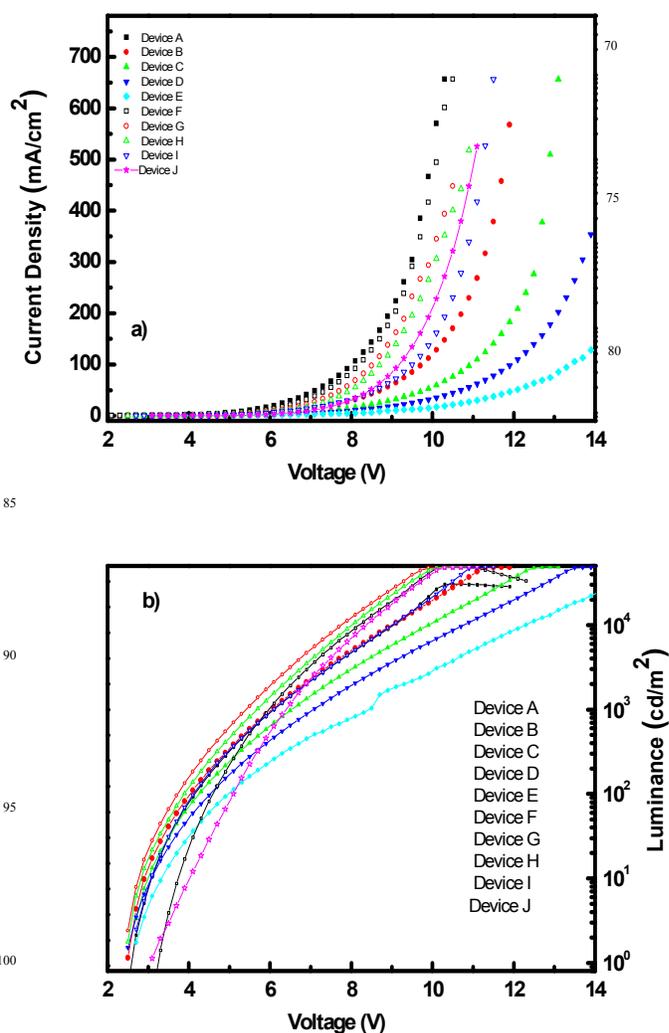
The current-voltage-brightness characteristics were measured by using a Keithley source measurement unit (Keithley 2400 and Keithley 2000) with a calibrated silicon photodiode. Electroluminescent (EL) spectra were measured by using PR655. All devices were measured without encapsulation at room temperature.

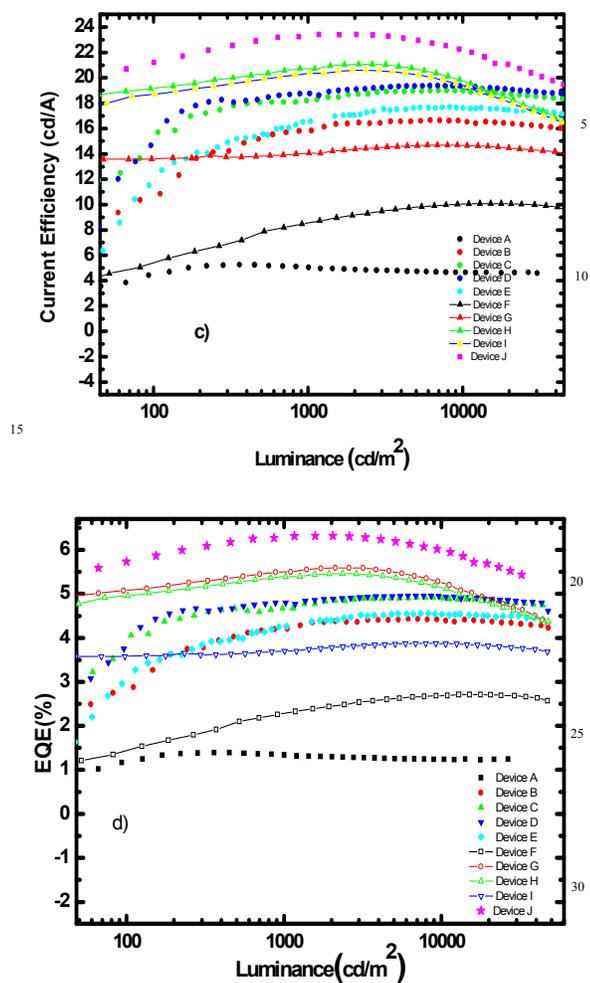
Table I Detailed device structures of Device A-J with the same thickness of emitting layer Alq₃:C545T (35 nm), ETL Alq₃ (35 nm), and cathode of LiF (1 nm)/Al (120 nm)

Devices	Thickness (nm)			Devices	Thickness (nm)		
	MoO ₃	PEDOT:PSS	NPB		MoO ₃	PEDOT:PSS	NPB
A	10	0	0	F	0	30	0
B	10	0	70	G	0	30	25
C	10	0	100	H	0	30	35
D	10	0	120	I	0	30	45
E	10	0	150	J	10	30	25

3 Results and discussion

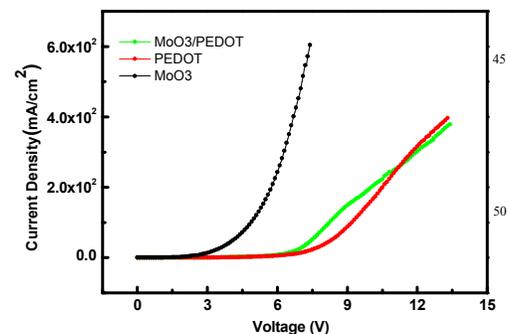
The EL performances of OLEDs with different materials as anode modification layer and different NPB thickness were investigated. Fig. 2 shows the current density-voltage (J-V), luminance-voltage (L-V), current efficiency-luminance (CE-L), and external quantum efficiency-luminance (EQE-L) characteristics. Their corresponding main parameters are tabulated in Table II. It can be seen that the device with MoO₃- as HIL shows slightly high current density. However, Device A shows lower luminance and efficiency compared with the devices with PEDOT:PSS as HIL for the case without NPB.





35 **Figure 2 EL performance:** (a) Current density versus voltage, (b) Luminance versus voltage, (c) Current efficiency versus luminance, (d) EQE versus luminance (color on line).

In order to well understand the phenomenon, we also made hole-only devices with the structure of ITO/MoO₃ or PEDOT:PSS/NPB/Au. The J-V characteristics of two devices are shown in Fig. 3.



55 **Figure 3 J-V characteristics** of hole-only devices for hole injection from MoO₃ (black solid circle), from PEDOT:PSS (red solid circles), and from MoO₃/PEDOT:PSS (green solid circle).

It can be seen that the hole-current density of the hole-only device

with MoO₃ is greater than that with PEDOT:PSS. This provides
60 clear and remarkable evidence for facile hole injection from MoO₃, meaning that the device with MoO₃ (Device A) has more holes injection than the device with PEDOT:PSS (Device F). Due to the high barrier for hole injection, as shown in Fig. 1(a), and the lower hole injection from PEDOT:PSS to NPB, the hole current is greatly limited in Device F. Then we evaluated the free charge distribution inside the device by using simulation software (SimOLED). As shown in Fig. 4, the holes from MoO₃ as HIL cannot be limited in recombination zone, which will be discussed later, and meanwhile the device with MoO₃ as HIL has higher
70 hole carrier density than that with PEDOT:PSS as HIL. This indicates that more balanced injection and transport for electrons and holes are realized in Device F and the unbalanced electron and hole recombines in Device A. Obviously, HIL is crucial for the balance of electrons and holes in emissive layer of
75 OLEDs.

Based on the fact that the different HILs have the different effect on the performance of the device, the performance of the OLEDs with the different HIL (MoO₃ and PEDOT:PSS) as the function of the thickness of the HTL thicknesses was investigated. From Fig. 2
80 and Table II, the devices with MoO₃ and PEDOT:PSS as HILs

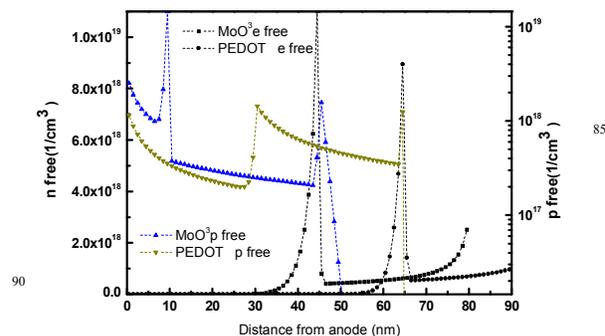


Figure 4 Free charge density distribution in the devices.

95 have gradual reduction in the current density when the NPB thickness is increased and the turn-on voltage of 2.5 V (defined as the voltage required for the luminance of 1 cd/m²) almost does not change. The lower current density shows the dependence of electric field on the device thickness. Therefore, the current densities of the devices with PEDOT:PSS as HIL and NPB as HTL are higher than those of the devices with MoO₃ as HIL and thicker NPB. In addition, all devices with NPB have higher efficiency than those without NPB. However, the higher luminance, current efficiency, and EQE were achieved as NPB thickness increases for the device with MoO₃ as HIL. The device with 120 nm NPB (Device D) exhibits the highest current efficiency of 19.4 cd/A and EQE of 5.0 %. For the device with PEDOT:PSS as HIL, the luminance and EL efficiency are also dependent on the thickness of NPB, i.e. the efficiency reduces
100 with the thickness increasing. Clearly, Device G with 25 nm NPB achieves the highest current efficiency of 21.1 cd/A at the current density of 10.1 mA/cm² and EQE of 5.6%. However, the NPB thickness in device with PEDOT:PSS as HIL is relatively thinner than that in device with MoO₃ as HIL. This is consistent
115 with the case that PEDOT:PSS has lower hole injection and transport capacity than MoO₃. The best EL efficiency in device

with PEDOT:PSS as HIL can be obtained by using 25 nm NPB, but the devices with MoO₃ as HIL need thicker HTL over 100 nm. This implies that the devices with different HIL materials and identical HTL materials need different optimal thicknesses of HTL. PEDOT:PSS has lower mobility and work function which leads to unbalanced injection and transport as the NPB thickness increases. Therefore, the hole-electron recombination probability is reduced. As a result, the device with PEDOT:PSS as HIL requires a thin NPB as HTL. Similarly, MoO₃ has higher mobility and work function, resulting in unbalanced hole-electron recombination without NPB as HTL, thus the luminance and EL efficiency increase as the NPB thickness increases due to the improvement

Table II

The maximum current and quantum efficiency of the Devices A-J, and the current and quantum efficiency @ 100 cd/m² and 10000 cd/m²

Devices	Turn on (V)	CE _{max} (cd/A) @ mA/cm ²	EQE _{max} (%) @ mA/cm ²	100 cd/m ²		10000 cd/m ²	
				CE	EQE	CE	EQE
A	2.6	5.25@6.85	1.4@6.85	4.48	1.2	4.65	1.24
B	2.7	16.7@37.0	4.4@37	10.7	2.8	16.6	4.4
C	2.6	19.0@41.5	4.92@41	15.1	4.0	19	4.9
D	2.5	19.4@35.5	4.96@35	15.0	3.92	19.3	4.94
E	2.6	17.6@74.6	4.6@46.8	11.9	3.1	17.6	4.55
F	3.1	10.1@150.2	2.71@150	5.37	1.44	10	2.7
G	2.4	14.7@46.7	3.88@46.7	13.6	3.6	14.65	3.86
H	2.4	21.1@10.1	5.6@10	19.2	5.1	19.8	5.3
I	2.5	20.6@11.5	5.46@9.39	18.7	4.96	19.45	5.1
J	3.0	23.4@4.98	6.31@4.98	21.2	5.73	22.2	6.0

as HIL in Device A. However, the EL spectra of Device C, D, and E (with thicker NPB) are slightly red-shifted with the increase of NPB thickness. This could not be explained only by the recombine zone at the interface of Alq₃:C545/Alq₃. The spectral change in Device C, D, and E should be ascribed to the interference effect between the direct emission out of active layer and the reflection by metal electrode. The EL spectra of Device F, G, H, and I at 5 V are shown in the inset of Fig. 5. Their EL spectra are similar, where the pure green emissions of C545 (located at 521 nm) from these devices is observed, likely attributed to the exciton recombination zone away from the interface of Alq₃:C545/Alq₃.

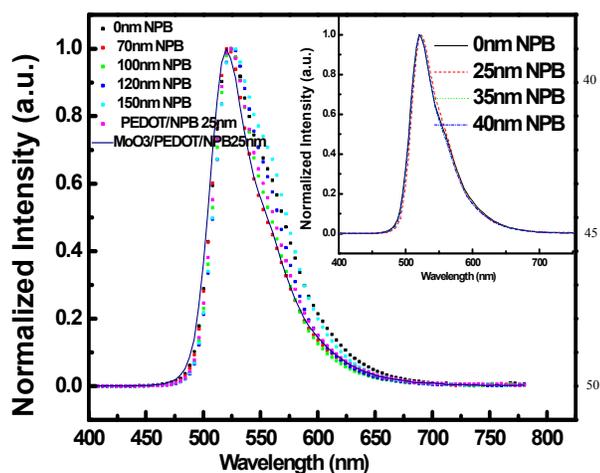


Figure 5 EL spectra of Device A, B, C, D, E, F, and J. The inset shows the EL spectra of Device F, G, H, and I. Although the PEDOT:PSS as HIL leads to a higher efficiency at

of balanced injection and transport of holes and electrons.

The exciton recombination zone has been explored from the point of view of spectrum. Fig. 5 shows the EL spectra of Devices A, B, C, D, and E at 5 V, exhibiting the green emission from C545 located at 521 nm for all devices. The broad EL spectrum of Device A should be attributed to the exciton recombination zone at the interface of Alq₃:C545/Alq₃, where the EL spectrum of Alq₃ exists. This is consistent with the case that the unbalanced carrier injection takes place and the recombination zone cannot be limited only in the Alq₃:C545 emission layer due to the rapid hole injection by MoO₃.

low luminance than MoO₃ as HIL, the efficiency roll-off at high luminance in device with PEDOT:PSS as HIL is larger, indicating that PEDOT:PSS as HIL on ITO is prone to degrade OLEDs, which is attributed to the interfacial degradation at ITO/PEDOT:PSS.¹⁹ Comparatively, MoO₃ as HIL on ITO stabilizes the devices, which is in agreement with the demonstration that insertion of MoO₃ enhances the interfacial stability of MoO₃/NPB and the morphology stability of NPB on MoO₃.¹¹ In addition, by comparison between MoO₃ and PEDOT:PSS used individually as the HIL, it is found that MoO₃ as HIL in OLEDs with thicker NPB can obtain a reduced efficiency roll-off and enhanced device stability, and meanwhile PEDOT:PSS as HIL in OLEDs with thinner NPB HTL can achieve a higher efficiency. However, the issue of PEDOT:PSS as HIL is that it causes the device degradation at high luminance. In order to further improve the performance of the OLEDs, the combination of bilayer MoO₃/PEDOT:PSS film is used as HIL. As shown in Fig. 2, the EL efficiency is greatly enhanced and the efficiency roll-off is also remarkably improved in the devices with thinner NPB. The maximum current efficiency of 23.4 cd/A and EQE of 6.31% at 4.98 mA/cm² and 22.2 cd/A and 6.0% at 10000 cd/m² are achieved, respectively, for Device J with 25 nm NPB. These values are significantly higher than those of other devices with MoO₃ or PEDOT:PSS individually used as HIL. As expected, the insertion of MoO₃ between ITO and PEDOT:PSS avoids the interfacial degradation on ITO due to the acid property of PEDOT:PSS. The utilization of MoO₃/PEDOT:PSS composition film as HIL also tunes the hole injection well, as shown in Fig. 3. As a result, the efficiency is greatly improved and the efficiency roll-off is largely reduced, leading to the enhancement in the device stability. Therefore, the conclusion can be drawn that MoO₃/PEDOT:PSS composition film is a

promising HIL in OLEDs in order to achieve high device performance.

4. Conclusions

It is clearly seen that the effects of MoO₃ and PEDOT:PSS as HIL in OLEDs are completely different, which requires different thickness of HTL to obtain the best EL performance. In addition, we have achieved a remarkable improvement in the performance of C545T-based green OLEDs by introducing MoO₃/PEDOT:PSS bilayer as the HIL. The utilization of MoO₃/PEDOT:PSS composition film not only significantly enhances the EL efficiency by effectively tuning the electron and hole balance in emissive region, but also greatly reduces the efficiency roll-off at high luminance by avoiding the interfacial degradation caused by PEDOT:PSS. The maximum current efficiency, power efficiency, and EQE reach 23.4 cd/A, 19.5 lm/W and 6.3%, respectively. Our results indicate that the proper combination of different interfacial layer materials for anode modification could be an effective approach to construct high-performance HIL in OLEDs.

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