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Thick polymer light-emitting diodes with very high power efficiency using Ohmic charge-injection layers

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Abstract

We demonstrate the optimization of single-layer polymer LED structures with active layers with thicknesses of the order of 1 micron. By using a combined approach of the addition of MoO₃, as a bottom hole-injection layer, and the incorporation of such thick active layers, exceptionally high performance metrics are achieved. In particular, brightnesses of 1000 cd m⁻² at driving voltages of only 6.8 V, corresponding to a power efficiency of 7.8 lm W⁻¹, a current efficiency of 17.2 cd A⁻¹, and external quantum efficiency of 5.6%, are reported for devices based on F8BT (Poly[(9,9-di-n-octylfluorenyl-2,7-diyl)-alt-(benzo[2,1,3]thiadiazol-4,8-diyl)]). A side-by-side comparison, between the standard LED structure and hybrid structures, demonstrates that with MoO₃ as bottom hole-injection layer, the electron and hole charge carriers are both giving space-charge limited current for both carriers due to the Ohmic contacts. The devices hence show improved charge carrier balance, and, most importantly, high brightness at low operational voltage. Such thick active-layer devices with high performance metrics, in addition to improved engineering and processing tolerances, are thus especially important for application to high-throughput device fabrication methods.

Keywords: light-emitting diodes, organic semiconductors, charge injection, device processing

(Some figures may appear in colour only in the online journal)

1. Introduction

Conventionally, active layers with thicknesses of 100 nm or less have been used in organic light-emitting diodes (OLEDs) [1, 2]. The polymers used in OLEDs are often rather amorphous, with characteristic low charge mobility and space-charge limited currents (SCLCs), thus requiring active layers to be thin; this is in addition to the high driving fields needed for devices strongly limited by charge injection at electrodes. In recent work, Lu and co-workers [3] have examined the influence of active-layer thickness on the function of OLEDs, and have found that devices

with satisfactory function and performance metrics can be fabricated from F8BT (Poly[(9,9-di-n-octylfluorenyl-2,7-diyl)-alt-(benzo[2,1,3]thiadiazol-4,8-diyl)] layers of up to 1 micron thickness and beyond. These results suggested a possible new paradigm for the processing and manufacture of OLEDs, with much thicker device layers being associated with greatly improved engineering tolerance. In this paper, we study how the performance of thick OLEDs may be enhanced by the use of Ohmic interlayers, pointing towards optimized performance, with balanced charge injection and carrier currents leading to high brightness at lower operating voltages than has been previously attainable.

A fundamental process in OLEDs is charge injection from opposite electrodes into an emissive layer, leading to the

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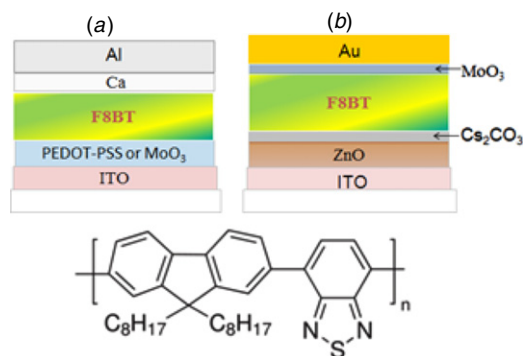


Figure 1. Schematic of device structures studied in this paper; (a) standard polymer light-emitting diodes, (b) hybrid LEDs. The inset below shows the chemical structure of the F8BT active layer.

formation of excitons, which can finally undergo radiative decay. Device performance may be characterized by parameters such as electroluminescence quantum efficiency, power efficiency and brightness [1, 2]. These parameters can be optimized by achieving a balance between the number of electrons and holes injected into devices, where a barrier-free injection is critical. Standard polymer LEDs with a structure of ITO/PEDOT-PSS/polymer/Ca/Al (figure 1(a)) show an unbalanced charge carrier injection due to the mismatch between the workfunction of PEDOT-PSS (Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)) and the HOMO level of fluorene based semiconducting polymers. In the case where F8BT is the emissive layer, the difference between the workfunction of the PEDOT anode (5.2 eV) and the HOMO energy level of F8BT (5.9 eV), gives a significant barrier to hole injection of 0.7 eV. The energy barrier is evidently much larger than $k_B T$ at room temperature, suggesting that Ohmic injection is unlikely, and that injection-limited hole transport is indeed the limiting factor for device performance [4, 5]. In order to improve the hole-injection conditions, transition metal oxides, such as molybdenum oxide, have been used as an interfacial layer on the indium-tin-oxide electrodes in OLEDs [6–10]. You *et al* reported that the use of MoO₃ as a buffer layer on ITO, within a thickness range from 3 nm to 20 nm, significantly improved the device [6]. The use of MoO₃ as top hole-injection layer in hybrid LEDs (HyLEDs) was reported by ourselves and others [3, 11–13]; it has been demonstrated that the device efficiency is greatly improved owing to the enhanced hole injection and reduced optical losses [11, 12]. X-ray photoelectron spectroscopy studies reveal that molybdenum oxide tends to form Mo₃O₉ clusters when deposited by thermal evaporation and provides a high workfunction (6.86 eV) from deep unfilled energy states [13].

Our earlier studies of the thickness dependence and the role of inorganic interlayers show that, using MoO₃ as top hole-injection layer, a single-layer HyLED (with an emissive F8BT layer of around 1 μm thickness) achieves a current efficiency of $\sim 22 \text{ cd A}^{-1}$ (external quantum efficiency (EQE) of 7.3%) using Cs₂CO₃ as inorganic interlayer, and 28 cd A^{-1} (EQE of 9%) while using Ba(OH)₂. This high efficiency is attributed to the unprecedented Ohmic injection for holes provided by MoO₃, whereas the device is electron-injection-limited

[14]. In standard OLEDs, the electron transport in F8BT is bulk-limited due to the Ohmic injection of electrons from the low workfunction metal, i.e. calcium. Calcium has a workfunction matching the LUMO level of F8BT, thus offering perfect electron injection into the high electron-affinity F8BT [5, 8, 14]. Numerous studies have demonstrated that F8BT has an electron mobility in the range of $10^{-3} \text{ cm}^2 \text{ Vs}^{-1}$ to $10^{-7} \text{ cm}^2 \text{ Vs}^{-1}$ [4, 7, 14], whilst our earlier study revealed that F8BT shows a hole mobility of $\sim 10^{-5} \text{ cm}^2 \text{ Vs}^{-1}$ with MoO₃ as the hole-injection layer. These findings have motivated the work presented in this paper, i.e. the study of OLEDs with a structure of ITO/MoO₃/F8BT/Ca/Al, with the goal of barrier-free injection for both holes and electrons, which can neutralize the space-charge in order to greatly reduce the operating voltages for efficient devices with thick ($\sim 1 \mu\text{m}$) active layers.

Here, as a route to the further optimization of thick active-layer OLEDs, a detailed study of the device performance with molybdenum trioxide as a bottom hole-injection layer, instead of PEDOT-PSS, in a conventional structure is reported (see figure 1(b)). The device performance is investigated as a function of MoO₃ thickness and the results show that devices with a 30 nm thick layer of MoO₃ give the highest current efficiency, with a lower operational voltage and high brightness, as compared to devices with a MoO₃ thickness of 10 nm and 20 nm. The results are compared with analogous HyLEDs and standard LEDs with PEDOT-PSS as the hole-injection layer. There is a markedly increased current density and luminance in the devices with MoO₃ as bottom hole-injection layer, which is in good agreement with the presumption of Ohmic injection for both electrons and holes. The current efficiency reaches a maximal value at a lower operating voltage, consequently leading to increased power efficiency. The effect of oxygen and moisture on the function of the MoO₃ layer is also investigated. It is found that the device performance is decreased significantly following exposure of MoO₃ to the ambient atmosphere for 2 h. This is attributed to a lowered workfunction, which leads to an increased injection barrier for holes [15]. This is consistent with the assumption that the improved performance in the device with MoO₃ is due to the Ohmic injection for holes, leading to a balancing of opposite charge carriers in the device.

2. Experimental methods

This section describes the protocols used for the preparation of devices reported in this paper. The ITO substrates were cleaned in acetone and isopropanol in an ultrasonic bath for 10 min each sequentially, then transferred to a thermal evaporation chamber for the deposition of MoO₃ (powder, 99.999% from Testbourne) onto the cleaned ITO surface under high vacuum (1×10^{-6} mbar), followed by spin-coating of F8BT p-xylene solvent (from Sigma-Aldrich) onto the surface of the MoO₃. The substrates are then annealed at 155 $^\circ\text{C}$ for 1 h, followed by the thermal deposition of calcium (30 nm)/aluminium (70 nm), and finally encapsulated for measurement. For devices with PEDOT:PSS (1:16 PEDOT:PSS, approximately 3% solids supplied from Cambridge Display Technology), oxygen plasma treatment was done on the cleaned ITO substrate

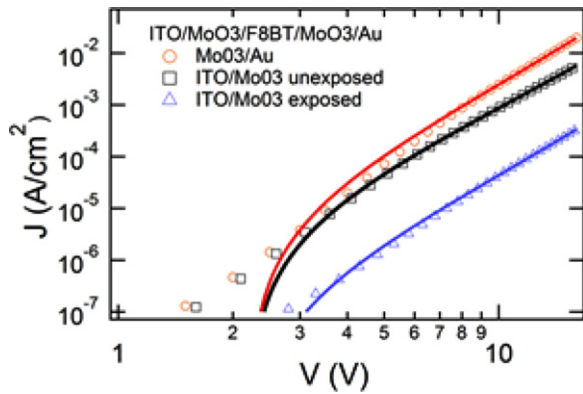


Figure 2. J - V curves of symmetric hole-only devices with architecture ITO/MoO₃/F8BT/MoO₃/Au, for hole injection from the contact electrodes MoO₃/Au (red circles), ITO/MoO₃ (black squares), and ITO/MoO₃ after ambient exposure (blue triangles). The solid-line fits give SCLC zero-field mobility for holes in the range of $4 \times 10^{-6} \text{ cm}^2 \text{ Vs}^{-1}$ for MoO₃/Au, $2 \times 10^{-6} \text{ cm}^2 \text{ Vs}^{-1}$ for unexposed ITO/MoO₃, and a value more than an order of magnitude lower for the exposed ITO/MoO₃ contact with relatively poor fitting.

and then PEDOT:PSS film (50 nm) was immediately spin-coated from a PEDOT:PSS solution, followed by annealing at 230 °C under inert atmosphere for 30 min; the rest of the device fabrication was then the same as for devices with MoO₃. Current density and brightness versus applied voltage (J - V - L) characteristics for the LEDs were measured in air using Keithley 2000/2400 source-meters and a calibrated reference Si photodetector.

3. Results

3.1. MoO₃ as hole-injection layer

Hole-only devices (ITO/MoO₃(30 nm)/F8BT(1200 nm)/MoO₃(10 nm)/Au) were fabricated in order to understand the difference in injection efficiency of MoO₃ film at the MoO₃/F8BT and F8BT/MoO₃ interfaces. The J - V curves of these devices are shown in figure 2. We also studied the J - V characteristics of these devices after ambient exposure to atmosphere of the MoO₃ film on top of the ITO electrode. We noted small changes in current density levels, depending on whether holes were injected from bottom or top MoO₃ layer, and we observed quite symmetric behaviour, in contrast to previous reports [16]. We can explain this discrepancy by exposing our MoO₃ film intentionally to the atmosphere before spin-coating the F8BT film, and in that case we found there is a clear barrier for holes being injected from the bottom MoO₃ layer. Hence, these experimental results suggest that there is not much difference in injection efficiency for F8BT deposited on MoO₃, as compared to MoO₃ deposited on F8BT. However, the MoO₃ film is sensitive to atmospheric exposure, which can cause the evolution of new states [15], resulting in injection barriers or asymmetric J - V characteristics for a symmetric device. As shown in figure 2, Poole-Frenkel

enhanced SCLC fitting of data was performed using the following equation:

$$J = \frac{9}{8d^3} \varepsilon \mu_0 (V - V_0)^2 \exp \left[0.89\beta \left(\frac{V - V_0}{d} \right)^{1/2} \right] \quad (1)$$

where ε (≈ 3.5) is dielectric constant of F8BT, d is the active-layer thickness, μ_0 is mobility, V_0 is the built-in voltage and β the field enhanced term. In our simulation, V_0 was constrained to be of order 2 V and $d \approx 800$ nm, whilst β was allowed to vary for fitting along with μ_0 . The injected hole-current density at the ITO/MoO₃ interface provides mobility values which are different by more than one order of magnitude, when comparing the unexposed and exposed cases; the latter case also gives a relatively poor fit to the data. This qualitatively corresponds to the experimental data, where the current densities differ by around a factor of 20 at biases up to 10 V, thus being in good agreement with previous reports [3]. The reasons for reduced current density in the case of the air-exposed ITO/MoO₃ injecting contact will be further discussed later.

3.2. The optimization of MoO₃-layer thickness

According to earlier work, the HyLED devices achieve optimal performance with a MoO₃ film thickness of 10 nm [3], whilst devices based on the conventional structure with MoO₃ deposited on ITO showed a promising performance within a MoO₃ thickness range from 3 nm to 20 nm [6]. MoO₃ thin films are highly optically transparent under 30 nm, and this has important implications for smoothing the ITO surface roughness, thus preventing shorts and reducing pixel defects [17]. It is hence necessary to study the evolution of device performance, with respect to the MoO₃ thickness up to 30 nm, since the deposition of MoO₃ onto ITO is different from that of an organic film layer.

The results are shown in figure 3; the J - V - L curves in figure 3(a) indicate that the voltage for current turn-on and luminance turn-on are very similar amongst all the devices with different MoO₃ thickness. The current turn-on is in the range of 2.5–2.8 V, which is in good agreement with the workfunction difference between the two opposite electrodes when taking the values 5.7 eV for MoO₃ [9], and 2.9 eV for Ca. It is noted that different values of workfunction for MoO₃ have been previously reported [10, 13, 15]; however, for the present structure of ITO/MoO₃/polymer, 5.7 eV appears to fit closely with the data. It is immediately clear that the device performance improves with the increase of the MoO₃ thickness from 10 nm to 30 nm; the increase in current efficiency is very pronounced when the MoO₃ thickness changes from 10 nm to 20 nm, whilst the increase is more gradual when comparing 20 nm to 30 nm. However, the operating voltage for the device with a MoO₃ thickness of 30 nm is significantly lower at the same current densities, showing both high current density and brightness. In this particular device, a luminance of 1000 cd m⁻² is achieved at only 6.8 V, with a power efficiency of 7.8 lm W⁻¹; remarkable values, given that the emissive layer is 1.2 μm thick (ten times thicker than standard LEDs). The data shows that the device efficiency reaches a plateau with increasing MoO₃ thickness, attaining maximal values for

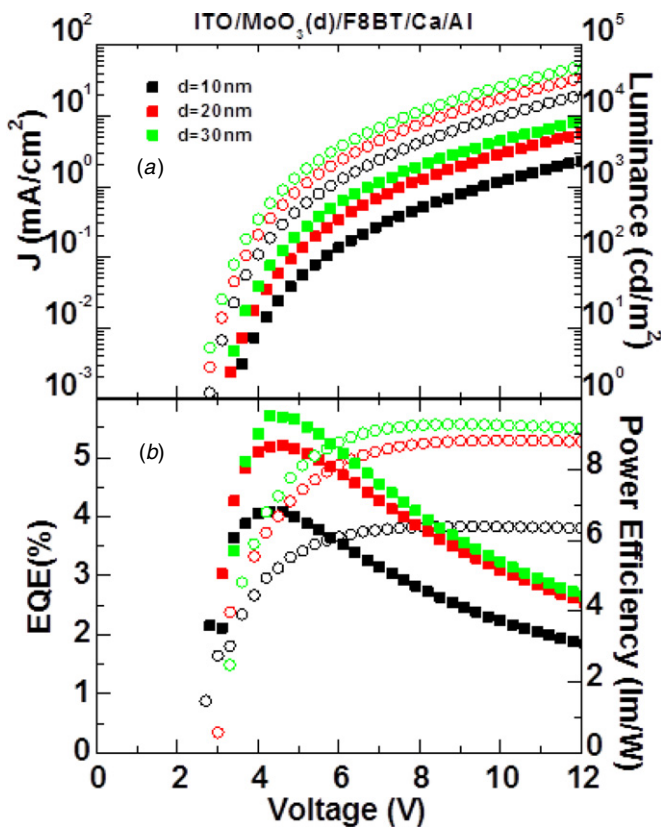


Figure 3. The device characteristics with a structure of ITO/MoO₃/F8BT (1200 nm)/Ca/Al; (a) the J - V - L curves, the empty symbols represent current density and solid luminance, respectively. (b) External quantum efficiency (circles) and power efficiency (squares) versus voltage; black markers represent 10 nm thick MoO₃, red for 20 nm, and green for 30 nm.

Table 1. The device performance parameters of OLEDs (ITO/MoO₃/F8BT/Ca/Al) with different MoO₃ thicknesses. Active-layer thicknesses were ~800 nm.

Structure: ITO/ MoO ₃ /F8BT/ Ca/Al	MoO ₃ (30 nm)	MoO ₃ (20 nm)	MoO ₃ (10 nm)
Bias@ 10 mA cm ⁻²	7.0 V	8.6 V	10.1 V
Bias@ 1000 cd m ⁻²	6.8 V	7.6 V	9.6 V
Peak luminance efficiency (cd A ⁻¹)	17.2@6.8 V	16.4@9.9 V	12.0@12.0 V
Peak EQE (%)	5.6	5.3	3.8
Power efficiency @ 1000 cd m ⁻²	7.8 lm W ⁻¹	6.7 lm W ⁻¹	3.9 lm W ⁻¹

a MoO₃ layer thickness of 30 nm. The parameters for the three device characteristics with MoO₃ thicknesses of 10, 20, and 30 nm are summarized in table 1. We find that there is no pronounced difference between using 30 nm or 40 nm of MoO₃, in terms of the current efficiency; however, other device performance indicators are slightly better with a 30 nm layer.

3.3. HyLEDs and conventional devices with MoO₃ or PEDOT:PSS as bottom hole-injection layer

Figure 4 illustrates the devices characteristics with ITO/PEDOT:PSS or MoO₃(30 nm)/F8BT/Ca/Al and

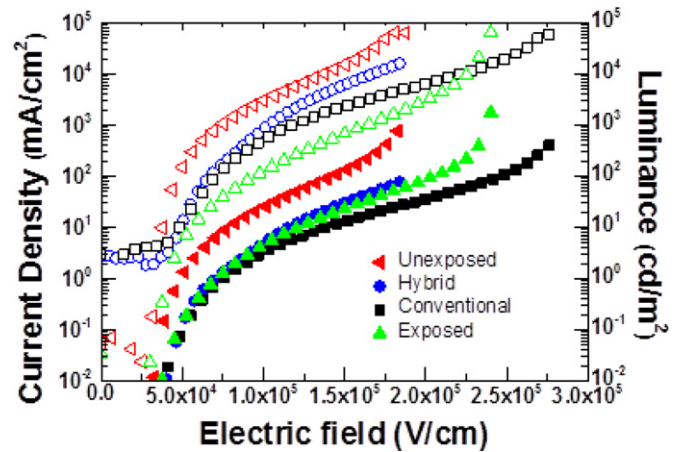


Figure 4. J - E - L device characteristics of structures ITO/MoO₃/F8BT/Ca/Al (red \blacktriangle), ITO/ZnO/Cs₂CO₃/F8BT/MoO₃/Au (blue \bullet), ITO/PEDOT:PSS/F8BT/Ca/Al (black \blacksquare) and ITO/MoO₃ (air-exposed)/F8BT/Ca/Al (green \blacktriangle). The empty symbols represent luminance, and the solid symbols current density. The film thicknesses of all devices were between 800 and 870 nm.

Table 2. The comparison of parameters in OLEDs with various device structures with F8BT film thickness ~800 nm.

Structure	ITO/MoO ₃ / F8BT/Ca/Al	ITO/ZnO/ Cs ₂ CO ₃ /F8BT/ MoO ₃ /Au	ITO/PEDOT- PSS/F8BT/ Ca/Al
Bias@ 10 mA cm ⁻²	6.3 V	10.1 V	12.0 V
Bias@ 1000 cd m ⁻²	5.9 V	9.0 V	10.3 V
Peak luminance efficiency (cd A ⁻¹)	13.0@5.9 V	20.9@14.9 V	19.1@23.3 V
Peak EQE (%)	4.4	6.7	6.2
Power efficiency @ 1000 cm m ⁻²	7.0 lm W ⁻¹	6.1 lm W ⁻¹	5.2 lm W ⁻¹

HyLED (ITO/ZnO/Cs₂CO₃/F8BT/MoO₃/Au architectures). The figure shows the J and L curves as a function of applied field. It is interesting to observe that the diode with MoO₃ as bottom hole-injection layer shows a much higher current density, i.e., one order of magnitude higher than for the hybrid structure. The luminance in this device is also around six times higher than that from the hybrid structure, implying a lower current efficiency. However, the high current and high luminance at a lower operational voltage allows the device to reach a luminance of 1000 cd m⁻² at a much lower operating voltage of 6.8 V, compared to 9.9 V in the hybrid structure. Consequently, the power efficiency is higher, supporting the assumption of barrier-free injection for both electrons and holes. Whilst both the current density and luminance are higher in the device with MoO₃ as the bottom hole-injection layer, the current efficiency starts to decrease after reaching a maximal value at 6.8 V. This observation possibly indicates a quenching of excitons at the MoO₃/polymer interface [3, 12], or inefficient exciton formation at higher current density due to the hole current leakage, since the Ca/Al electrode does not present an extraction barrier for holes [5]. The parameters for the two different architectures of OLEDs are summarized in table 2.

Compared to the conventional device using PEDOT:PSS as hole-injection layer, the current density of the device with MoO₃ is 25 times higher, whilst the luminance is 16 times higher. This observation is in good agreement with the fact that, in the standard device with PEDOT:PSS as hole-injection layer, Ohmic injection is unlikely and hole transport is injection-limited [4]. By contrast, MoO₃ has a workfunction of 5.7 eV [10], which matches the HOMO of F8BT and allows a barrier-free injection for holes. The high current density, accompanied by a high luminance at a lower operational voltage, leads to higher power efficiency. However, the current efficiency is not further increased with the increase of the operating voltage in the device using MoO₃ as hole-injection layer (table 2); behaviour which is very similar to that observed in the hybrid device. Previous studies reveal that PEDOT:PSS undergoes a phase separation and the PSS acts as an extraction barrier for electrons, and blocks the electrons at the interface, thus preventing electron current leakage [4, 18]. By contrast, this is not the case when using MoO₃ as hole-injection layer, as there is space-charge neutralization in the bulk of the film, which results in 15 times higher current as compared to hole-only devices [19].

Surface states of metal oxides play an important role at the interface with organic semiconductors, and these states can be very different in nature in vacuum, as compared to after being exposed to the air. The J - E - L curves for devices ITO/MoO₃/F8BT (800 nm)/Ca/Al with MoO₃, both exposed and unexposed to the air are also compared in figure 4. The device with MoO₃ exposed to the air for 2 h (at 20 °C and a relative humidity of ~50%) shows that the current density is lowered by an order of magnitude compared to its unexposed analogue; however, the luminance is nearly 35 times lower. This results in a large decrease in current efficiency and the device performance in general is significantly reduced compared to the devices where MoO₃ is not exposed to the air, as summarized in table 2. According to previous photoelectron spectroscopic studies [15], after 2 h exposure of the MoO₃ layer to air, the workfunction is lowered from 6.9 eV to ~5.3 eV, due to the chemisorption of oxygen and moisture. This change in workfunction of the MoO₃ interface results in reduced doping of the F8BT, due to the deep HOMO level [15]. The HOMO level of F8BT is 5.9 eV, the offset between the workfunction of exposed MoO₃ and the HOMO of F8BT is therefore 0.6 eV, which is much larger than $k_B T$ at room temperature. It does not, therefore, form an Ohmic contact at the interface of exposed MoO₃/F8BT and this leads to a significant injection barrier for holes. This is also indicative as to why the hole-only device with MoO₃ exposed to the air cannot be fitted with SCLC model (figure 2), as it is injection-limited.

4. Discussion

The standard device with MoO₃ as the bottom hole-injection layer shows a greatly improved current density and luminance which is much higher than both in the hybrid structure and the standard device with PEDOT:PSS as the hole-injection layer. The high bipolar current density and high luminance at a lower operational voltage indicates a good match between electron-

and hole-current density, suggesting an Ohmic injection for both holes and electrons. The Ohmic injection of both carriers builds up space-charge of opposite polarities which cancel-out, resulting in an overall increase in the current density observed for these devices. In all cases the electron mobility is higher than the hole mobility [4, 5, 14]. However, the device architecture of ITO/MoO₃/F8BT/Ca/Al suggests an Ohmic-like injection for both holes and electrons, and the study of MoO₃ thickness dependence shows that the device with 20 nm MoO₃ shows a significant improvement of the luminance and current efficiency compared to the device with 10 nm. These observations suggest a more efficient recombination due to increased hole mobility, as a thick layer of MoO₃ improves the hole injection, whilst negating the effects of roughness of the ITO surface. In circumstances where the ITO may not have been completely covered in the case of a thinner MoO₃ film, this results not only in a reduced hole-injection barrier, but also in a leakage path for electron current. The results also indicate that the ITO/polymer interface might promote excitonic quenching, which is in agreement with the optical study presented recently [3], which shows such a quenching at the ITO/polymer interface. Whilst the device with 30 nm MoO₃ shows optimal performance, results suggests that the thickness dependence is already saturated, as the improvement in the device performance is already small in comparison to the very large change going from 10 nm MoO₃ to 20 nm. This also explains the observed phenomenon that the device (with the 30 nm MoO₃) shows the highest power efficiency. However, the current efficiency is lower as compared to our previous results with hole-blocking layers. In the case where we have Ohmic injections of both carriers, without charge-blocking layers, this is expected to result in a significant increase of the recombination zone width, when considering mobility is also a function of electric field, $\mu = \mu_0 \exp(0.89\beta E^{1/2})$, where μ_0 is zero-field mobility, β is field-effect parameter and E is applied electric field [20]. This will result in the quenching of excitons at contact electrodes which reduces current efficiency, as observed. Importantly, however, the operating voltages of these thick active-layer OLEDs were significantly reduced, whilst maintaining good efficiency, thus addressing essential requirements for high-throughput processing methods.

On a final note, whilst one may speculate as to how improved carrier balance in devices might produce wider recombination zones, in the future it is worth investigating both electron-blocking and hole-blocking layers in this architecture for the purposes of restricting the 'leaking' of charge carriers and thus actively confining the recombination zone width. Also, transient studies on these OLEDs may be able to give a further insight into the role of triplet-triplet annihilation (TTA) in the steady-state EQE values. There might possibly be a reduced contribution of TTA-related singlet exciton generation at higher bipolar current densities in MoO₃ based devices, due to the charge-quenching of triplet states, as compared to PEDOT:PSS based LEDs [21].

5. Conclusions

In summary, polymer light-emitting diodes with active-layer thicknesses of order 1 micron, using MoO₃ as the bottom

hole-injection layer have been studied. The current density and luminance in this device have been greatly improved, and the operational voltage significantly lowered, due to Ohmic injection for both holes and electrons. It is demonstrated that the device with a MoO₃ film thickness of 30 nm shows optimal performance. Some remarkable values for the device performance indicators are achieved; in particular, the current turn-on voltage is as low as 2.5 V and the luminance reaches 1000 cd m⁻² at 6.8 V, corresponding to a power efficiency of 7.8 lm W⁻¹ and a current efficiency of 17.2 cd A⁻¹ (EQE of 5.6%). The study of MoO₃ surface exposure to the air shows that the device efficiency is greatly lowered due to the chemisorption of oxygen and moisture, resulting in an energy barrier for hole injection. This also suggests that the improvement of current and luminance performance is due to the space-charge neutralization by Ohmic injection of both carrier-types. This study hence demonstrates that MoO₃ on ITO is a practical and valuable interfacial modification layer in thick active-layer OLEDs, with their inherent advantages in terms of processing and manufacturing tolerances. The introduction of MoO₃ reduces the driving voltages needed for high brightness, and consequently improves the power efficiency, which offers significant additional benefits for the practical applications of OLEDs.

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