



Opposing influence of hole blocking layer and a doped transport layer on the performance of heterostructure OLEDs

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Abstract

This paper reports on heterostructure small molecule organic light emitting devices (OLEDs), the design of which includes doped hole and electron transport layer (HTL and ETL) and a hole blocking layer (HBL) which can be either doped or not. Doped transport layers are expected to lower the operating voltage of devices. Insertion of a hole blocking layer increases the carrier and exciton confinement which consequently improves the recombination rate and the device efficiency. Nevertheless, an HBL tends to increase the threshold voltage. The opposing influence of doped transport layers and HBL is evidenced in this study and compromise structures are presented. The doped HTL material is *N,N'*-bis(3-methylphenyl)-*N,N'*-diphenylbenzidine (TPD) doped with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-quinodimethane (F4-TCNQ). A comparison with undoped TPD and poly(*N*-vinylcarbazole) (PVK) HTL is given. Devices with doped HTL show a lowering of the operating voltage from 6.5 (PVK) down to 4 V (these voltages refer to those necessary to achieve a luminance $L = 10 \text{ Cd/m}^2$). A constant current efficiency higher than 2 Cd/A is obtained in the voltage range 5–9 V with doped HTL. Insertion of a 5–20 nm thick HBL made of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (Bathocuproine BCP) between an 8-(hydroquinoline) aluminum (Alq_3) electron transport layer (ETL) and a DCM doped Alq_3 emitting layer (EML) induces both a detrimental effect (increase of the operating voltage to 6 V attributed to a low electron mobility in BCP) and beneficial effect (strong increase of the luminance and doubling of the current efficiency which reach to about 4.5 Cd/A thanks to improved carrier and exciton confinement). An optimization of the thickness of the doped EML and of BCP is also reported. The doping of the HBL and of the ETL with 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) leads to devices with luminance as high as 1000 Cd/m² at 5.3 V and a maximum efficiency of 1 Cd/A at 4 V.

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1. Introduction

Since the first reports on two-layer and three-layer organic light emitting diodes [1–3], much

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work was devoted to electroluminescent devices based on heterojunctions of small organic molecule thin films deposited by vacuum evaporation. An organic heterostructure consists of a stack of at least two layers, a hole transport layer (HTL) and an electron transport layer (ETL) which is often the emitting layer (EML) as well. Several papers did show that this structure design strongly improves the carrier balance and consequently the diode efficiency when compared to the single layer devices. Operating voltage was also observed to be lowered with these devices. Continuous improvements in the design of the structure and in the nature of materials were sought after, all of them aiming at increasing the luminance and the efficiency and at decreasing the operating voltage. Breakthroughs came from the use of dye doped emitter layer, the insertion of a hole injection layer (HIL) between the ITO anode and the HTL, the confinement of the carriers at selected interfaces with hole or electron blocking layers (HBL and EBL respectively), the use of more conductive HTL and ETL by electrical doping. Among these, the first one was to use ETL or EML doped with emitting molecules [3]. Whether efficient energy transfer (Förster type) from the host material (e.g. Alq₃) towards the guest molecule can be achieved, strong enhancement of the luminescence yield was observed as well as an efficient color tuning [4,5]. Because of the high energy barrier between ITO and most of HTL, the deposition of HIL onto ITO anode for barrier lowering or smoothing was proposed. Poly-3,4-ethylenedioxythiophene doped with polystyrenesulphonate—commonly named PEDOT—was the most striking HIL polymer for that purpose [6] but self-assembled mono-layers were also proposed [7] as well as evaporated small molecules (e.g. copper phthalocyanine CuPc) [8]. On the cathode side, the control of injection barrier was overcome by the use of low Li [9] or LiF [10] thin layer between the ETL and the cathode metal. HBL and EBL were proved to be very useful for carrier and exciton confinement. For example, the efficiency of polyfluorene based polymer LEDs were shown to be improved with a poly(*p*-phenylene vinylene) (PPV) electron blocking layer [11]. However, usual HTL (e.g. TPD) have a sufficiently high LUMO level for pretty

good electron blocking in the EML and generally act also as EBL. So the effort was mainly put on HBL which must offer a high barrier to holes and a good electron conduction as well. The use of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (Bathocuproine BCP) was recently reported as HBL in red dye doped Alq₃ base devices [12] and as EIL [13,14]. Because of its wide gap and largely negative HOMO position relative to the vacuum level, BCP is well suited for hole and exciton blocking layer (XBL). These characteristics also proved to be beneficial for the design of photovoltaic cells where BCP was deposited between the cathode and the active material to avoid exciton quenching at the electrode surface [15]. Recently, a new class of benzene derivated hole blocking materials was disclosed [16]. In order to lower the operating voltage, the resistance of HTL and ETL could be decreased by appropriate doping with acceptor (p-doping) or donor (n-doping), respectively. Karl Leo's IAPP group (TU Dresden, Germany) strongly contributed to OLEDs with doped transport layers. Devices based on PII or PIN structures present a p-doped HTL, an intrinsic EML, a HBL and either a non-doped (resulting in a PII structure) or an Li-doped ETL (resulting in a PIN structure). Record operating voltages were obtained with only 3.2 V to achieve a luminance $L = 100 \text{ Cd/m}^2$ [17–19]. 2-(4-Biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (*t*Bu-PBD) was used as an EIL as well as a hole and exciton blocking layer electron injection in view to fabricate white OLEDs [20]. At last, let us mention a possible alternative which would replace standard abrupt heterojunctions (HJ) by graded mixed HTL–ETL layers. These devices were shown to provide improved efficiency [21] and lifetime [22].

This paper presents the results of an exhaustive investigation on the respective influences of the nature of the HTL, of its p-doping, and of insertion of a HBL and of its doping with organic electron donor molecules on the threshold voltage, luminance and current efficiency of devices. We first determine the optimized thicknesses of the DCM doped Alq₃ EML and of the 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (Bathocuproine BCP) HBL in undoped devices. Then, typical *N,N'*-bis(3-methylphenyl)-*N,N'*-diphenylbenzidine

(TPD)/8-(hydroquinoline) aluminum (Alq₃) based heterojunction diodes were fabricated with the following modifications: TPD was p-doped with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-quinodimethane (F4-TCNQ) acceptor molecule and BCP either undoped or mixed with various amounts of *t*Bu-PBD was inserted between the DCM doped Alq₃ EML and the Alq₃ ETL. The combination of optimized device design with doped TPD and doped BCP allowed us to obtain high performance devices with a luminance threshold at 2.8 V and 1000 Cd/m² at 5.3 V.

2. Experimental procedure

The devices were prepared by sequential vacuum evaporation of commercial molecules in the same pump down onto poly-3,4-ethylenedioxythiophene/polystyrenesulphonate (PEDOT/PSS) covered ITO substrates (Merck, Germany, sheet resistance: 17 Ω/□). The materials were used as received (from Aldrich and from Exciton) without further purification. They were kept in nitrogen flux before loading in the evaporation cells. Before PEDOT spinning, the ITO substrates were carefully cleaned in successive bathes of solvents and treated by a low power oxygen plasma in a reactive ion etcher (RIE). This treatment makes the surface very hydrophilic (contact angle: ~10°). Right after this treatment, a 30 nm thick PEDOT layer was spun on and annealed under nitrogen for 1 h at 125 °C. Although most devices were using TPD as HTL, some have been done with poly(*N*-vinylcarbazole) (PVK) for comparison (molecular weight 1,100,000, purchased from Aldrich). A solution of PVK in monochlorobenzene (C₆H₅Cl) was spun on annealed PEDOT to a thickness of 40 nm and dried under nitrogen flow at a moderate temperature. A previous paper reported in detail the hole injection and transport properties of ITO/PEDOT/PVK/Al devices [23]. TPD, F4-TCNQ doped TPD, Alq₃, 4-dicyanomethylene-2-methyl-6-(*p*-dimethylaminostyryl)-4*H*-pyran (DCM) doped Alq₃ (denoted as Alq-DCM in the following) and BCP mixed with *t*Bu-PBD (denoted as BCP-PBD in the following) were evaporated under vacuum better than 2 × 10⁻⁶ mBar at a rate of 0.2 nm/s.

Fig. 1 gives the chemical structure of the molecules used. The device is completed by the evaporation of a 150 nm thick Mg–Ag cathode. The active area is 5 mm². The diodes were then rapidly transported in air to a cryostat where they were characterized under vacuum (~10⁻³ mbar). A Keithley 2400 source-meter and a calibrated Si photodiode (Hamamatsu) were used to simultaneously record current–voltage and light–current characteristics. Electroluminescence (EL) spectra were recorded with a Horiba Jobin-Yvon CCD camera.

3. Results and discussion

3.1. Undoped devices

In this section, we examine the influence of the thickness of the BCP HBL and of the Alq-DCM EML on the electrical and emission characteristics of the devices. The diodes have the following structure (from substrate to top): ITO/PEDOT (35 nm)/PVK (40 nm)/DCM-doped Alq₃ (5–50 nm)/BCP (0–15 nm)/Alq₃ (30 nm)/Mg–Ag. Fig. 2 reports the current density versus voltage (*J*–*V*) and luminance versus current density (*L*–*J*) characteristics as well as the electroluminescence spectra for devices with a 10 nm thick BCP HBL and a Alq-DCM emitting layer of variable thickness in the range 5–50 nm. We observe that increasing the EML thickness continuously shifts the diode threshold toward a higher voltage (Fig. 2(a)). This is to be attributed to the increased thickness of the Alq-DCM layer and to the correlative modification of the internal field distribution. In a previous report [24] we showed, that in PVK/Alq₃ devices, the total diode current was mainly limited by electron current in Alq₃. Similar conclusions were drawn for TPD/Alq₃ structures where the electric field was shown to be essentially located in Alq₃ [25]. Hence as the thickness of Alq-DCM layer increases, the electric field and the electron mobility decrease, leading to a lowering of the current. As the EML is doped with DCM, electron trapping on DCM sites is likely to contribute to current lowering. The luminance plotted in Fig. 2(b) and EL spectra (Fig. 2(c)) clearly show that an optimum thickness around 10 nm corresponds to

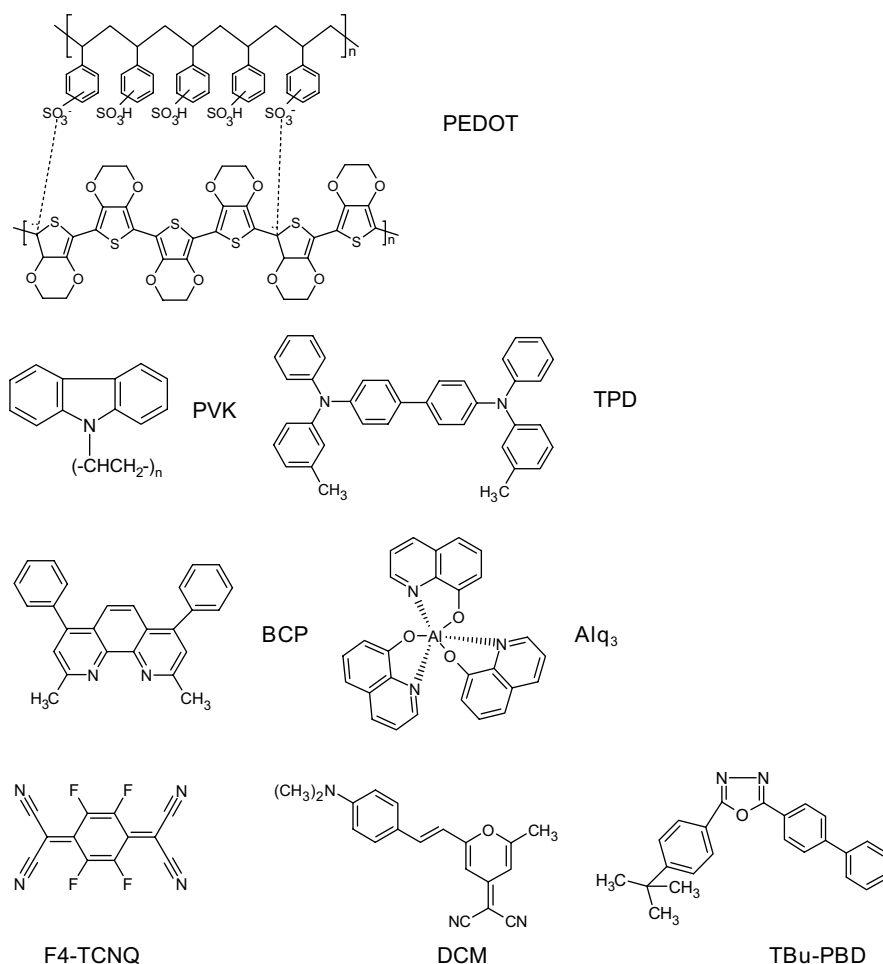


Fig. 1. Chemical structures of the organic materials used in this study.

the achievement of a maximum luminance. When Alq–DCM is too thin, recombination is insufficient and emitted power is rather low. At thickness above 20 nm, the luminance decreases again. All spectra were recorded exactly the same way to be comparable in intensity. It is seen (Fig. 2(c)) that emitted light originates almost only from Alq₃ when the doped Alq–DCM layer is very thin (5 nm) because of a very limited energy transfer. When thicker Alq–DCM layers were deposited, the spectra are red shifted and their shapes are similar whatever this thickness is. The spectra are essentially due to DCM with a contribution from Alq₃ (10 and 20 nm). For 50 nm thick Alq–DCM,

only DCM emission is observed. It is clearly seen in Fig. 2(c) and quantified in Fig. 2(b) that 10 nm Alq–DCM gives the highest luminance. In that case, exciton recombination is expected close to the Alq–DCM/BCP interface. At thicker Alq–DCM thickness, the electric field decreases and the electron current as well. Furthermore holes injected at the PVK/Alq–DCM interface can no longer diffuse throughout the Alq–DCM layer and accumulate at the Alq–DCM/BCP interface according to the fact that their diffusion length in Alq is estimated to be 37–40 nm [26]. The recombination then occurs closer from the PVK/Alq–DCM. In that scheme, the lowering of electron

current and probable hole trapping on DCM sites, lead to a decreased carrier balance, a loss of confinement and, consequently, to a decrease of luminance.

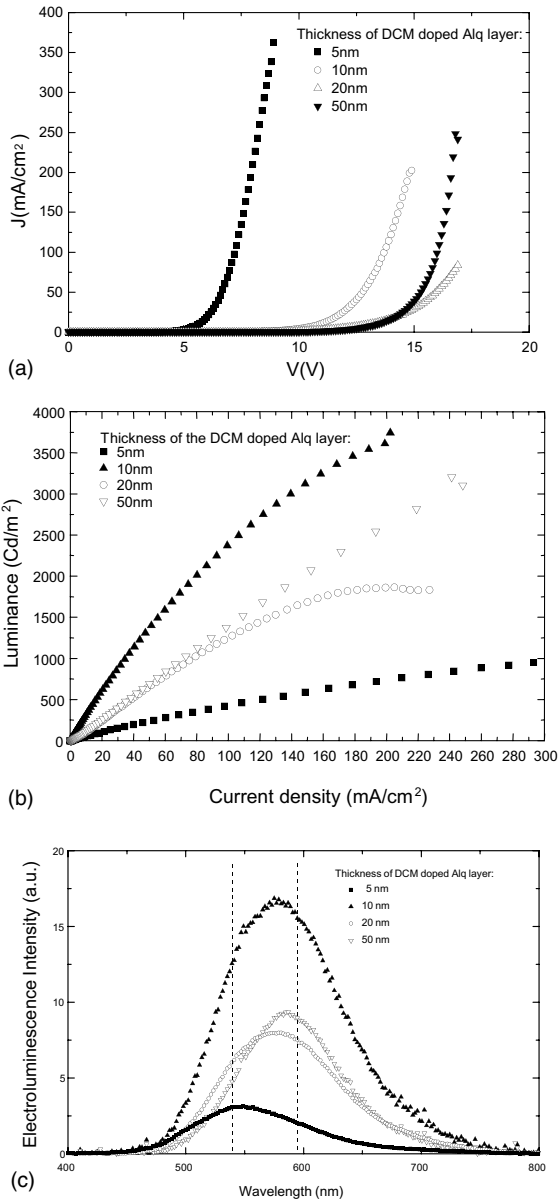


Fig. 2. Current–voltage (a) and luminance (b) characteristics and electroluminescence spectra (c) for ITO/PEDOT/PVK/Alq–DCM/BCP/Alq₃/Mg–Ag diodes with variable thicknesses of DCM doped Alq₃ emitting layer.

Fig. 3 reports the same plots as those in Fig. 2 for similar devices except two differences: the Alq–DCM thickness is kept constant at 10 nm and the BCP thickness is varied from 0 to 15 nm. The J – V

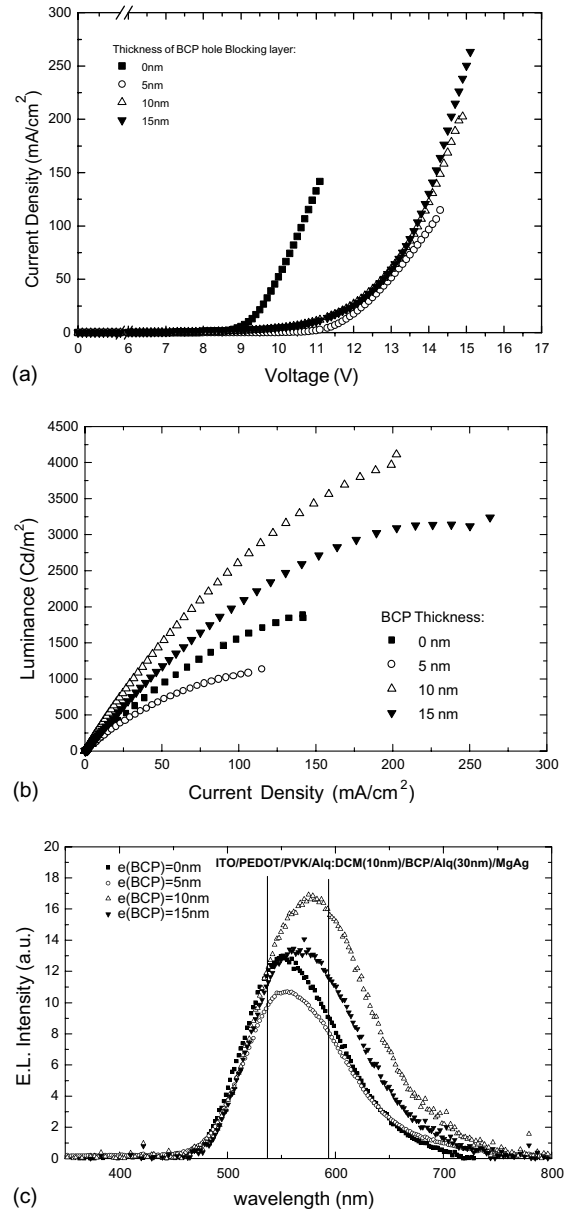


Fig. 3. Current–voltage (a) and luminance (b) characteristics and electroluminescence spectra (c) for ITO/PEDOT/PVK/Alq–DCM(10nm)/BCP/Alq(30nm)/Mg–Ag diodes with variable thicknesses of BCP hole blocking layer.

characteristics (Fig. 2(a)) shows that the insertion of the BCP layer shifts the threshold voltage from 9 V for devices without BCP to ~ 11 V for devices with a 5–15 nm thick BCP layer almost independently of the BCP thickness in this range. This bears out the strong hole blocking effect of BCP attributed to the high hole barrier at the EML–HBL interface as depicted by the band diagram shown in Fig. 4. A BCP layer as thin as 5 nm is sufficient to efficiently block the holes and reduce the total current to an electron current and a recombination current. Other results (not reported in this paper) showed that for ITO/PVK/BCP/Alq₃/Mg–Ag diodes with 0, 20 and 50 nm thick BCP, the threshold voltage continuously shifts to a higher value as BCP thickness increases but no light emission is observed for BCP thicker than 20 nm. From these latter results and considering that light emission from Alq₃ is observed for 15 nm BCP (Fig. 3(b)), we can state that the diffusion length of holes in BCP probably lies in the 15–20 nm range and that the electric field distribution in BCP does not affect too much the electron mobility as long as the BCP thickness is below 20 nm. For thicknesses larger than 20 nm, the limited electron mobility in BCP [12] leads to a decrease of the current. Figs. 3(b) and (c) report L – J and spectra for various BCP thickness. Spectra in Fig. 3(c) show that, either without or with a thin (5 nm) BCP layer, emission essentially comes from Alq₃ due to poor confinement. Optimized confinement

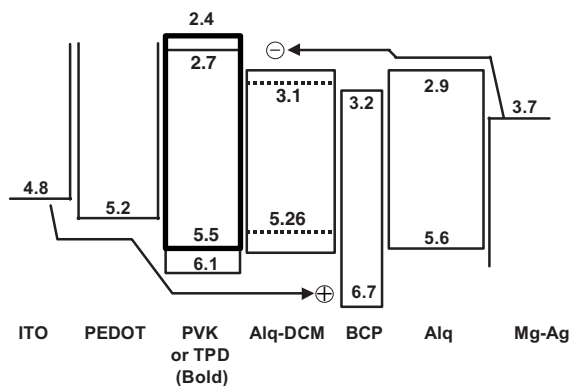


Fig. 4. Schematic band diagram of the investigated devices. The two HTL used (PVK and TPD) are shown.

is achieved with 10 nm BCP which corresponds to the highest luminance (b) and a better transfer to DCM (c). Thicker BCP leads to a decrease of luminance which could be attributed to a decrease of the electron density arriving at the Alq–DCM/BCP interface and thus to a degradation of the carrier balance (b). The spectrum is also a little bit green shifted probably because the recombination at the BCP/Alq interface between injected electrons and hole diffusing through the BCP layer became relatively more important. It is noteworthy that although a 5 nm thick BCP is sufficient to block the holes at the Alq–DCM/BCP interface and thus induce a carrier and exciton confinement, luminance and efficiency are somewhat degraded compared to devices without BCP. This point is not fully understood but could be accounted for by the determining influence of ill defined interfaces on the exciton quenching.

The current efficiency (Cd/A) and the external quantum efficiency are reported in Fig. 5 as a function of the luminance with BCP thickness as a parameter. All devices have a 10 nm Alq–DCM emitting layer. Again, there is a clear evidence that 10 nm BCP is the optimized thickness to achieve the highest current efficiency (3.5 Cd/A) and external quantum efficiency (2.3%). Furthermore, these values are obtained at a low current density since we observe from Fig. 3 that 100 and 1000 Cd/m² are respectively obtained at 3.5 and 35

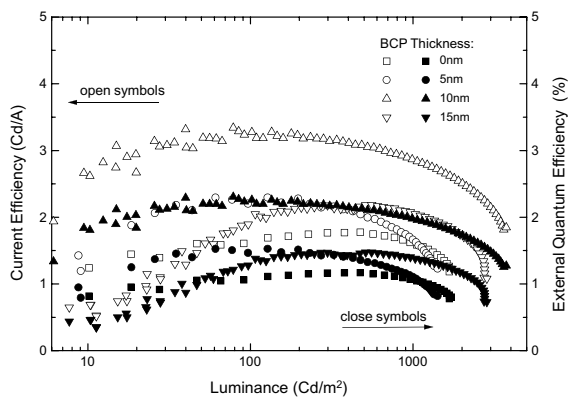


Fig. 5. Current efficiency (Cd/A) as a function of the luminance for different thicknesses of BCP as a parameter for ITO/PEDOT/PVK/Alq–DCM/BCP/Alq₃/Mg–Ag devices. Thickness of Alq–DCM layer: 10 nm.

mA/cm^2 . The beneficial influence of BCP is then not only related to the magnitude of the efficiency but also to the luminance range which this improvement is observed on. Fig. 5 indeed shows that when BCP is used, the improved confinement shifts the maximum efficiency towards a lower luminance (down triangle) as compared to what is obtained on devices without BCP (up triangles). For instance, the efficiency at $50 \text{ Cd}/\text{m}^2$ is more than double whereas the increase is about 50% at $1000 \text{ Cd}/\text{m}^2$.

3.2. Devices with a doped hole transport layer and without hole blocking layer

In the preceding section, undoped PVK was used as HTL. In this section, we report results where TPD was employed in place of PVK. TPD is expected to allow for a lower operating voltage thanks to a higher hole mobility (about $2 \times 10^{-3} \text{ cm}^2/\text{Vs}$ against $\sim 10^{-6} \text{ cm}^2/\text{Vs}$ for PVK [27,28]) and an improved injection due to a lower barrier at the interface with ITO (Fig. 4). Furthermore, a highest LUMO level than PVK favors the electron confinement in the EML by opposing a higher barrier to electrons crossing the Alq-DCM emitting layer (Fig. 4). In order to further increase the conductivity of the HTL, TPD was “electrically doped” with 2 wt.% of 2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-quinodimethane (F4-TCNQ). F4-TCNQ is known as a strong electron acceptor which would form shallow acceptor levels [18]. Three devices were compared to assess the influence of the nature of the undoped HTL (PVK and TPD) and the influence of TPD doping. The thicknesses of each layer are kept constant. The device structures are the following:

Device 1: ITO/PEDOT/PVK (40 nm)/Alq₃ (50 nm)/Mg–Ag

Device 2: ITO/PEDOT/TPD (40 nm)/Alq₃ (50 nm)/Mg–Ag

Device 3: ITO/PEDOT/F4-TCNQ doped TPD (40 nm)/Alq₃ (50 nm)/Mg–Ag

Fig. 6 gives the current density versus voltage (a), luminance versus voltage (b) and current efficiency versus voltage (c) characteristics of these

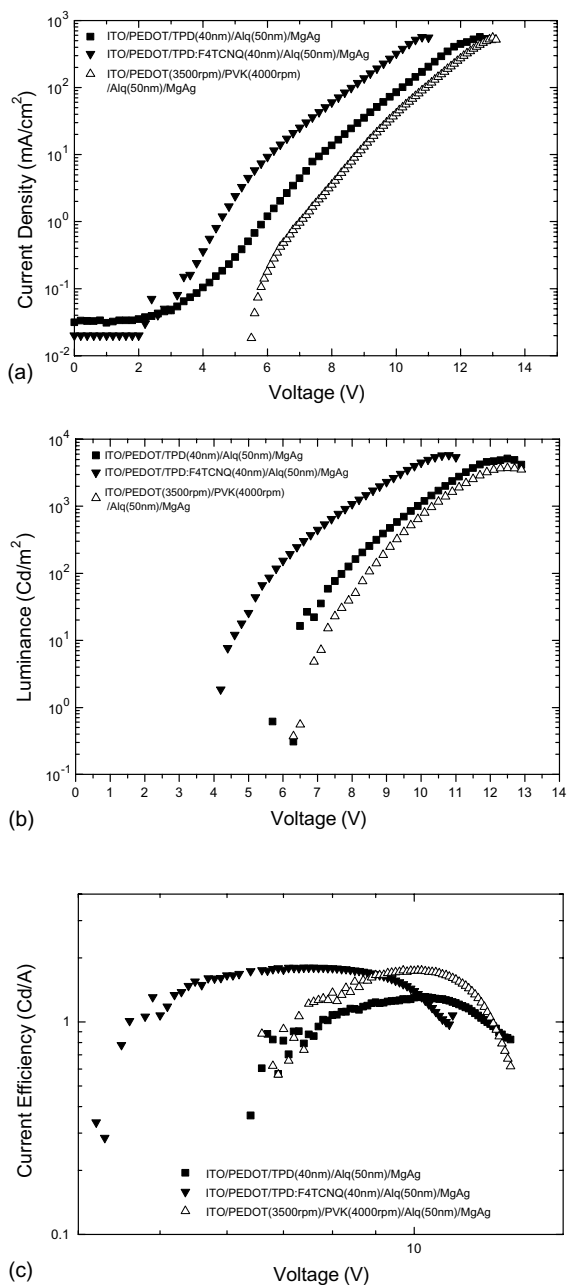


Fig. 6. Current–voltage (a), luminance–voltage (b) and efficiency–luminance (c) characteristics for ITO/PEDOT/HTL/Alq₃/Mg–Ag diodes with PVK, TPD and F4-TCNQ doped TPD as HTL.

three devices. A large decrease of the threshold voltage for high injection from 5.5 V (device 1) to

4 V (device 2) and 3 V (device 3) is clearly observed in Fig. 6(a), bearing out our expectations. Similarly, Fig. 6(b) shows that the luminance threshold voltage $V_{T,L}$ is also strongly lowered when either undoped TPD ($V_{T,L} = 5.5$ V) or doped TPD ($V_{T,L} = 4$ V) are used in place of PVK ($V_{T,L} = 6.5$ V). Luminance characteristics of devices with undoped TPD are only slightly improved as compared to those with PVK whereas doped TPD leads to luminance between one and two orders of magnitude as high as these latter. A higher hole density may explain this result. As the hole mobility in TPD is high, enhanced conductivity of F4-TCNQ doped TPD is expected to mainly result from a large increase of the carrier density. A higher hole density in doped TPD also comes from easier injection from ITO into the shallow acceptor level located above TPD LUMO level. Hole injection in Alq-DCM thus increases leading to an enhanced luminance. Current efficiency reported in Fig. 6(c) as a function of the voltage shows that devices with undoped TPD or with PVK exhibit similar characteristics. A slightly higher efficiency is nevertheless observed with PVK. Devices with doped TPD HTL show an improved maximum efficiency as compared to undoped TPD with a maximum efficiency similar to that reached with PVK. The key point however is that the current efficiency is now constant and maximum over a wide voltage range between 5 and 10 V corresponding to a luminance range 50–6000 Cd/m² whereas the efficiency with undoped TPD is dramatically reduced below 6.5 V.

In conclusion, undoped TPD improves the threshold voltage compared to PVK but leads to slightly less efficient devices. TPD doping with F4-TCNQ significantly lowers the operating voltage (e.g. 100 Cd/m² at 5.2 V) and also improves the current efficiency. Devices with 2 Cd/A maximum efficiency on a wide luminance range (corresponding to a small applied voltage) were achieved.

3.3. Devices with a doped hole transport layer and an undoped hole blocking layer

The results presented in the two preceding sections show that the operating voltage is decreased when a doped HTL is used. However, the current

efficiency is significantly lower than that obtained in Section 3.1 where a BCP HBL was used. In the next two sections, we report on the optimization of devices incorporating both doped HTL and HBL, either undoped (Section 3.3) or doped with organic electron donor molecules (Section 3.4).

Devices investigated in this section have the following structures (from substrate to top): ITO/PEDOT/F4-TCNQ doped TPD (10–20 nm)/Alq-DCM (10 nm)/BCP (10 nm)/Alq₃ (30 nm)/Mg-Ag. Three different TPD thicknesses were compared: 10, 15 and 20 nm. Results are reported in Fig. 7.

Figs. 7(a) and (b) respectively show the $J-V$ and the $L-J$ characteristics. Compared to what is observed in Fig. 6(a), it is clearly evidenced that inserting an HBL shifts the threshold voltage to a higher value, from 3 to 5.5 V in our case. The thickness of the doped HTL does not seem to have a significant influence on the characteristics. As mentioned in the preceding section, this is probably to be related to the high conductivity of F4-TCNQ doped TPD wherein no important potential drop occurs. Furthermore, the range of thickness investigated, 10–20 nm, is not so wide. Nevertheless, the thickness of doped TPD strongly influences the luminance as seen in Fig. 7(b). This figure actually shows that increasing the thickness from 10 to 20 nm enhanced the luminance by about 50%. It is also observed that carrier and exciton confinement by the BCP layer enhances the luminance as expected. The reason why the thicker the doped TPD layer the higher the luminance is not fully understood. A likely reason would be that the interface between doped TPD and the Alq-DCM layer is of higher structural quality when the thickness of the HTL is sufficient. Too thin TPD could induce rather a rough interface because of incomplete grain growth and consequently to some intermixing between the HTL and EML. Low efficient exciplex emission could result from this.

Fig. 7(c) reports the current efficiency (Cd/A) as a function of the voltage for the four devices. The use of BCP HBL increases the device efficiency to about 4 Cd/A. The thickness of the doped HTL is also shown to influence the efficiency, and the optimum thickness was 20 nm. Thinner HTL leads to lower efficiency (3 Cd/A). Maximum efficiency

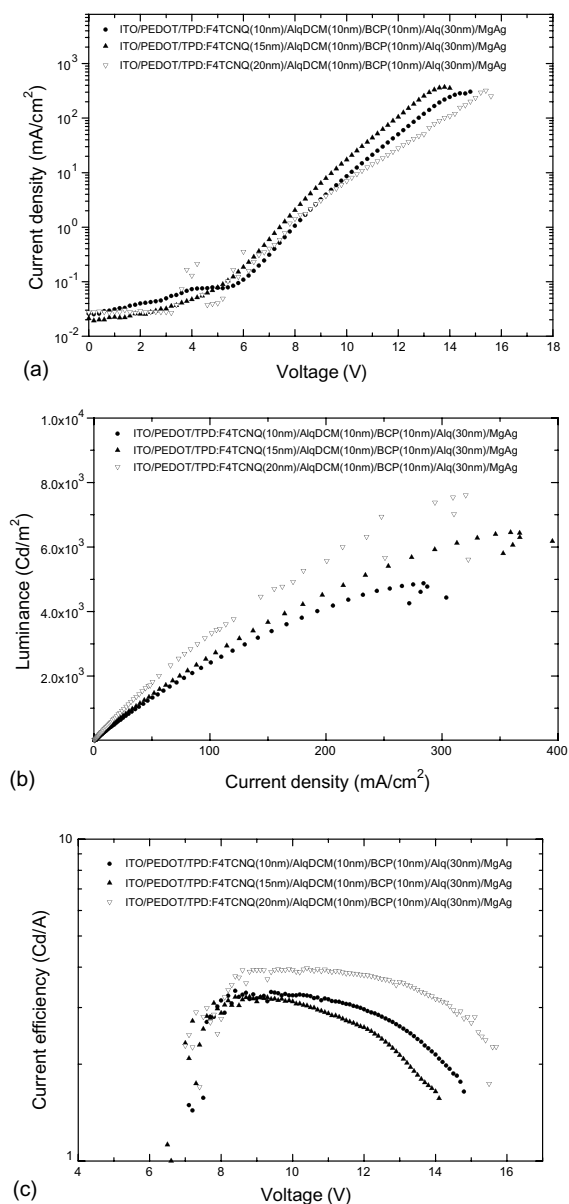


Fig. 7. Current–voltage (a), luminance–voltage (b) and efficiency for devices ITO/PEDOT/F4-TCNQ doped TPD/Alq–DCM (10 nm)/BCP (10 nm)/Alq₃ (30 nm)/Mg–Ag for different thicknesses of the doped TPD layer.

was obtained over a wide span of current density almost between 2 and 100 mA/cm².

The comparison with the results reported in Fig. 6 on devices without BCP points out two opposing influences of a hole blocking layer: on

one hand, a detrimental effect namely the increase of the operating voltage, and on the other hand, a beneficial effect on the luminance and the current efficiency which are significantly improved. Since one of the main challenges with OLEDs remains to achieve the highest luminance and efficiency at the lowest voltage, improved confinement and carrier transport must be concomitantly reached.

3.4. Devices with a doped hole blocking layer

In the preceding section, we saw how the insertion of an undoped BCP hole blocking layer shifts the luminance thresholds towards higher voltages. This drawback originates from the rather poor electron conductivity of BCP. In order to improve this conductivity, BCP was mixed with a strong electron donor, say *t*Bu-PBD. Four different concentrations in BCP were investigated: 2, 5, 28 and 50 wt.% denoted in the following BCP:*x*% PBD where *x* is the wt.% concentration of PBD. The structure of the four different devices is the following (from substrate to top): ITO/PEDOT/TPD:2% F4-TCNQ (20 nm)/Alq–DCM (10 nm)/BCP:*x*% PBD (10 nm)/Alq (30 nm)/Mg–Ag. The actual influence of the Alq₃ EIL was evidenced by comparing with two other devices: one without Alq₃ EIL (ITO/PEDOT/TPD:2% F4-TCNQ (20 nm)/Alq–DCM (10 nm)/*t*Bu-PBD (28%)–BCP (10 nm)/Mg–Ag) and another one with a *t*Bu-PBD doped Alq₃ EIL (ITO/PEDOT/F4-TCNQ doped TPD (20 nm)/Alq–DCM (10 nm)/*t*Bu-PBD (28%)–BCP (10 nm)/Alq:5% PBD/Mg–Ag).

Fig. 8(a) shows the *J*–*V* characteristics of the five devices. We observe that, for a given voltage, the current increases upon increasing the concentration of *t*Bu-PBD in BCP. However, the threshold voltage shows almost no change. The device with 50% *t*Bu-PBD exhibits a very high current below strong injection onset probably due to leakage. The doping of Alq strongly increases the current density and the characteristics also exhibit leakage below the threshold (~4 V). At last, device without an Alq₃ layer on top of BCP exhibits an extremely low voltage threshold (2.6 V). These observations evidence the resistive nature of Alq₃ EIL. In Fig. 8(b) is reported the luminance as a function of the voltage. It is

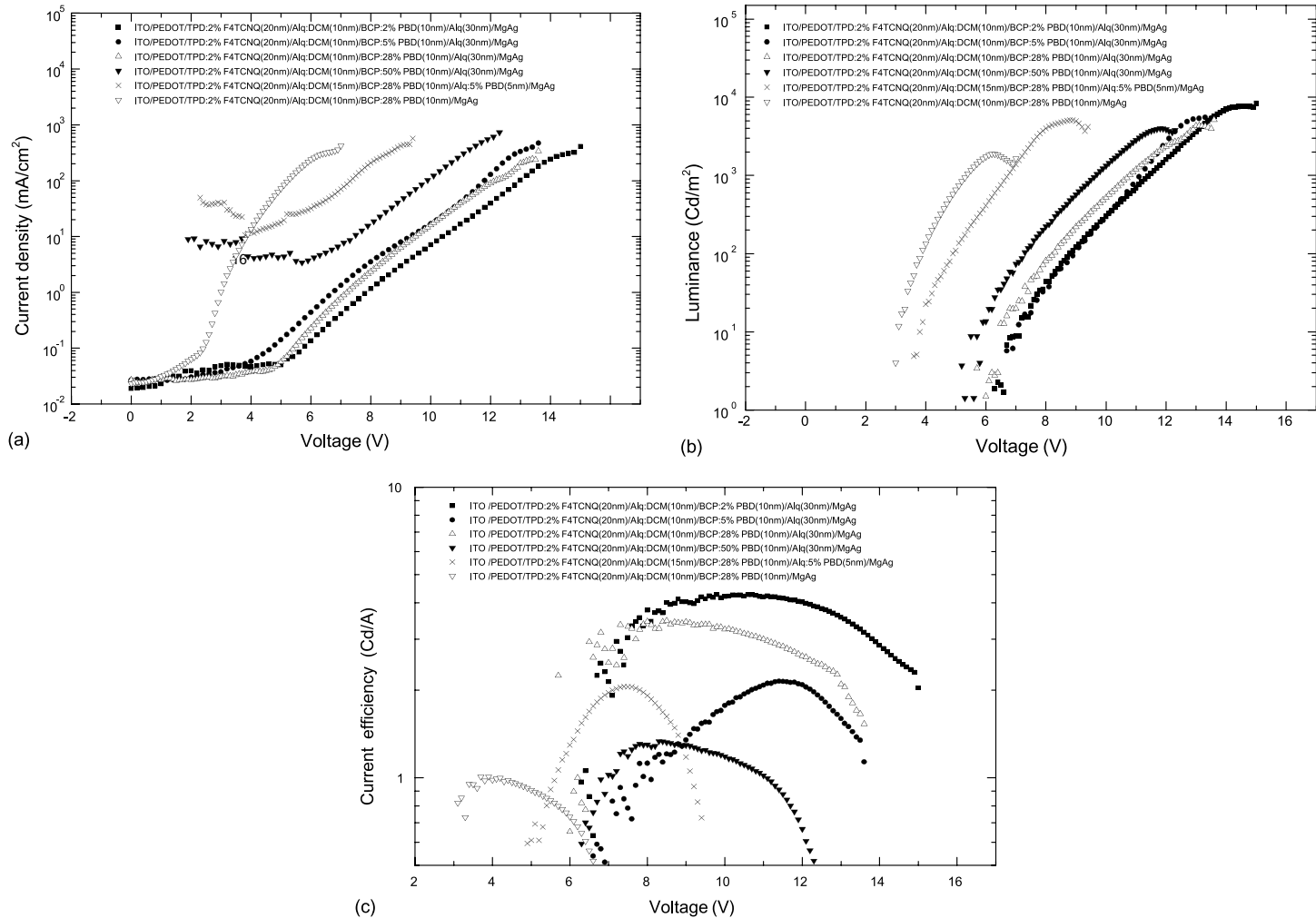


Fig. 8. Current–voltage (a), luminance–voltage (b) and efficiency for devices ITO/PEDOT/F4-TCNQ doped TPD/Alq₃-DCM (10 nm)/PBD doped BCP (10 nm)/Alq₃ (30 nm)/Mg–Ag for different doping levels of BCP from 2% to 50%. Devices without Alq₃ top layer and with PBD doped Alq₃ top layer are also shown for comparison.

Table 1

Summary of relevant optoelectronic data of OLED shown in Figs. 7 and 8 (details of the device structures are given in the text and in the inserts of Figs. 7 and 8)

Concentration of <i>t</i> Bu-PBD in BCP (wt.%)	Nature of Alq EIL	Voltage (V) for a luminance of 10 Cd/m ²	Voltage (V) for a luminance of 1000 Cd/m ²	Maximum current efficiency (Cd/A)	Voltage range (V) around this maximum
0	Undoped	7.2	12	4	8–12
2	Undoped	7	11.5	4.5	8–12
5	Undoped	7	11.2	2.2	11–13
28	Undoped	6.5	10.7	3	7–10
50	Undoped	5.6	9.6	1.3	7–10
28	<i>t</i> Bu-PBD doped (5 wt.%)	3.8	6.7	2	6.5–8
28	No Alq	3	5.3	1	3.5–5

observed that at low doping level (2 and 5 wt.%) the luminance plots are similar and the luminance is slightly higher than that with undoped BCP. The higher the *t*Bu-PBD concentration, the lower the luminance voltage. Doping Alq EIL or suppressing it further reduces the voltage threshold to 3.8 and 3 V respectively.

Fig. 8(c) reports the current efficiency versus voltage. The efficiency decreases from 4 to 1.5 Cd/A when the concentration level of *t*Bu-PBD in BCP increases from 2% to 50%. However, the maximum efficiency only slightly shifts to a lower voltage. The characteristics for device without Alq₃ EIL shows a rather low efficiency (1 Cd/A) but with a maximum at voltage as low as 4 V. The device with a doped Alq₃ EIL exhibits an intermediate behavior with a 2 Cd/A maximum efficiency at 7 V. Table 1 summarizes the optoelectronic data of OLEDs shown in Figs. 7 and 8. The table reports the voltages needed to achieve 10 and 1000 Cd/m², the maximum current efficiency, the voltage range at this maximum for devices with either undoped or doped Alq EIL and for the device without Alq EIL. It clearly evidences the decrease of the operating voltage upon doping of the EIL or/and of the HBL but also, and in a correlated way, the decrease of the efficiency.

4. Conclusions

In this work we presented results on the influence of inserting hole blocking layers (HBL) and

of electrical doping of hole transport layers (HTL), electron injection and transport layers (EIL, ETL) and hole blocking layers on the electrical and emission performance of OLEDs. The influence of the HBL in confining the carriers and the excitons was clearly evidenced by a strong increase of the luminance and of the device efficiency. However, insertion of HBL causes the increase of the threshold voltage. Electrical doping of carrier injection and transport layers was thus investigated with the aim of lowering this operating voltage. Effective decrease of the operating voltage was observed since devices exhibiting 100 Cd/m² at 3.5 V were obtained. In order to achieve both low threshold voltage and high efficiency devices, we demonstrate that conveniently doped HTL, ETL and HBL are necessary to build an optimized heterostructure device.

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