Ionically Assisted Charge Injection in Hybrid Organic−Inorganic Light-Emitting Diodes

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ABSTRACT We have developed hybrid organic−inorganic light-emitting diodes (HyLEDs) featuring a buffer layer of a conjugated polyelectrolyte (CPE) sandwiched between a light emitting polymer (LEP) film and a ZnO electron injection layer. Efficacies exceeding 5 cd/A and the possibility of employing various LEPs are demonstrated. These improvements, compared to HyLEDs without any interlayer, are attributed to the redistribution of ions in the CPE film, causing hole accumulation at the CPE/LEP interfaces and enhanced electron injection from the ZnO into the electroluminescent polymer. The intrinsic air-stability of the electrodes used in HyLEDs, together with the solution processability of the ZnO/CPE/LEP system, make them interesting as potentially encapsulation-free, low-cost, light-emitting devices.

KEYWORDS: OLED • ZnO • conjugated polyelectrolyte

INTRODUCTION

Organic light-emitting diodes (OLEDs) represent the most advanced technology in the emerging field of organic electronics. Because of their intrinsic properties, such as color tunability, high brightness, and high efficiency, they have already entered the market of flat panel display, emerging as real competitors to the established liquid crystal display (LCD) technology. Moreover the reports of efficient broadband white emitting devices have widened the potential applications of OLEDs to the lighting market (1, 2). However, high efficiency in OLEDs is achieved using multilayer architecture prepared by subsequent thermal vacuum evaporation of small molecular weight semiconducting and light-emitting materials. Furthermore, low work-function cathodes, such as calcium, barium, or magnesium, or other air-sensitive materials are commonly used in order to enhance the charge injection into the device (3). Thus efficient OLEDs rely on expensive manufacturing techniques and need to be encapsulated to prevent rapid degradation. A strong reduction in the production costs is required in order to make OLEDs a competitive alternative to the present light sources. Different strategies have been explored to overcome these limitations. From one side, solution-processed small molecule OLEDs and polymer light emitting diodes (PLEDs) allow in principle to reduce the fabrication costs by employing low-cost deposition techniques (4). On the other side, the use of air stable cathodes would permit the preparation of devices that do not need a rigorous encapsulation, also aiding to reduced costs of the final products. Recently, hybrid organic inorganic light-emitting diodes (HyLEDs) have been reported to meet both these requirements. They rely on solution processed polymer emitting layers and semiconducting metal oxides as air

stable charge injection layers (5−7). The use of metal oxides in OLEDs is intriguing because it takes advantage of the peculiar properties of this class of inorganic materials, such as their high transparency, charge mobility, good stability, solution processability and tunable morphology. The first examples of HyLEDs used poly(9,9-dioctylfluorene-alt-benzothiadiazole) (F8BT) as the light-emitting polymer (LEP), which was sandwiched between a thin film of titanium dioxide (TiO_2) or zinc oxide (ZnO) as the electron injection layer and a molybdenum oxide (MoO_3) hole injecting layer. This architecture should render HyLEDs less sensitive to air, because no reactive materials are employed and the organic layer is protected from atmospheric agents by the two metal oxides. However, because of the significant energy barrier for electron injection the device performances are limited (8). Because of this, high brightness values (1×10^3 to 1×10^4 cd/m^2) can be obtained only when F8BT is used as the LEP, because of its unique low energetic lowest unoccupied molecular orbital (LUMO) level (−3.5 eV from vacuum level, VL) that is close to the conduction band of TiO_2 and ZnO ($\sim$ −4 eV), limiting the barrier for electron injection. Even in these cases, the reported efficiencies were low (<2 cd/A), caused by the high current density, probably due by charge recombination close to the metal oxide surface and inefficient hole blocking at that interface. One successful strategy to enhance the electron injection from the metal oxide cathode into the device and, at the same time, efficiently confine the holes into the LEP, is the insertion of a thin layer of Cs_2CO_3 in between the metal oxide and the polymer (9). This method yields devices with high brightness (>20000 cd/m^2) and efficiency ($\sim$ 8 cd/A) and creates the possibility of using more efficient LEPs like poly(phenylene vinylene) (PPV). Additionally, it allowed for the use of triplet emitters and the achievement of white light emission (10−12). Another elegant approach has been recently reported, where wide band gap semiconductors such as zirconium oxide (ZrO_2), hafnium oxide (HfO_2) or magnesium oxide (MgO) are
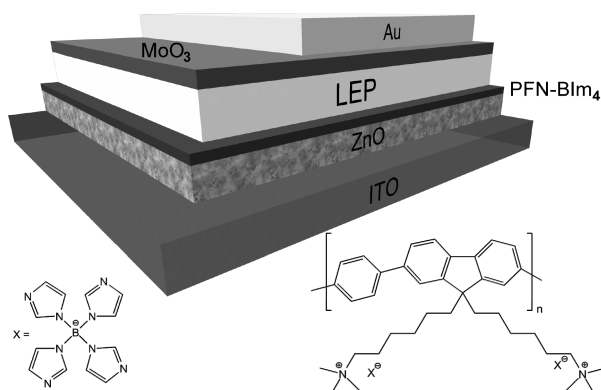
FIGURE 1. Device scheme of the HyLED and molecular structure of the PFN-BIm$_4$.

used as electron injection layers instead of ZnO or TiO$_2$ (13, 14). The low-energy valence band characteristic of those materials efficiently blocks the holes, whereas the electron injection into a variety of LEPs is assured by the high-lying conduction band. Another way to decrease the electron injection barrier is obtained by the functionalization of the metal oxide cathode with a self-assembled monolayer of charged amphiphilic molecules (15). The redistribution of ions under the applied bias creaes a strong interfacial field that assists and promotes the injection of electrons, a principle that has been already exploited in light-emitting electrochemical cells (LECs) (16).

A similar approach in which conjugated polyelectrolytes (CPEs) are used as electron injection materials has recently been demonstrated in OLEDs (17−19). In those cases, the polymer electrolyte acts as an n-type buffer layer in between the cathode and the light-emitting layer, enhancing the electron injection thanks to ions displacement and efficient hole blocking properties. In this communication, we extend the use of CPEs as efficient electron injecting layers (EILs), employing the tetrakis(imidazolyl)borate of poly(9,9′-bis(6″-(N,N,N-trimethylammonium)hexyl) fluorene-*alt-co*-phenylene) (PFN-BIm$_4$) in HyLEDs, thus opening the door to fully solution-processed air-stable devices. We demonstrate how the electron injection can be efficiently enhanced by the insertion of a very thin layer of PFN-BIm$_4$ in between a ZnO cathode and the LEP. Both the EIL and the LEP are deposited by spin-coating and no significant dissolving of the bottom PFN-BIm$_4$ layer is observed because of the orthogonality of the two solvents used. With this method, high efficiency and luminance values are obtained using a variety of LEPs that result in devices emitting over a wide region of the visible spectra.

EXPERIMENTAL SECTION

The molecular structure of the polymer electrolyte used in this work and a simple device scheme are shown in Figure 1. The light-emitting polymers, F8BT, RedF, and GreenK, were supplied by Sumitomo Chemical Company, Ltd. PFN-BIm$_4$ was prepared according to a previously reported procedure (20, 21). Solvents and inorganic reagents were obtained from Aldrich and used without any further purification. The ZnO layers were prepared by spray pyrolysis using

a method described previously (22−24). Briefly, zinc acetate dihydrate was dissolved in a mixture of ethanol and water (3:1). Acetic acid was added in order to avoid the formation of zinc hydroxide, Zn(OH)$_2$, and to enhance the film deposition. This solution was sprayed onto prepatterned ITO glass plates (prior to deposition, the ITO-coated glass substrates were extensively cleaned, using chemical and UV-Ozone methods) at 400 °C on a hot plate and the layers were subsequently annealed in a furnace at 450 °C for 12 h. PFN-BIm$_4$ was dissolved in water (5 g L^{-1}) and spin-coated on top of the metal oxides obtaining about 15 nm thick layers. After an annealing step at 150 °C for 15 min, LEPs were spin-coated from chlorobenzene solutions (∼10 g L^{-1}) at appropriate speed in order to achieve about 80 nm layer thickness. Before spin coating all solutions were filtered over a 0.20 μm PTFE filter. After spin coating the thin films were dried and transferred into a high-vacuum chamber integrated in an inert atmosphere glovebox (<0.1 ppm O$_2$ and H$_2$O). Gold and MoO$_3$ were thermally evaporated under a base pressure of 1×10^{-6} mbar serving as the anode contact and as an optical mirror to enhance the unidirectional illumination of the device. Although the workfunction of gold is close to the highest occupied molecular orbital (HOMO) energy of common LEPs, no efficient hole injection was observed without the presence of a thin (5−20 nm) MoO$_3$ layer (25). Thicknesses of the inorganic layers and spin coated thin films were determined using an Ambios XP1 profilometer. Current density and luminance versus voltage were measured using a Keithley 2400 source meter and a photodiode coupled to a Keithley 6485 pico-amperometer using a Minolta LS100 to calibrate the photocurrent. The current drop through the wiring is compensated by employing the Keithley 2400 in the "four wire" mode. The photodiode is calibrated at high luminance values, the error in these measurements is below 10 %. An Avantes luminance spectrometer was used to measure the EL spectrum.

RESULTS AND DISCUSSION

A HyLED based on F8BT and without any interlayer in between the LEP and the ZnO was prepared using a ZnO coated ITO as the transparent cathode and MoO$_3$ and Au as the anode (Figure 1). The $J-V-L$ characteristics of this device are depicted in Figure 2a. The turn-on voltage for the luminance is very low, approximately 1.8 V, in accordance with the small difference in energy between the conduction band of ZnO, at −4 eV, and the workfunction of Au, at −5.4 eV. However, as commonly measured in HyLEDs, the current onset occurs at a slightly lower voltage, indicating the preferential injection of holes through the MoO$_3$ into the F8BT. Once injected, the holes are transported through the F8BT layer toward the negatively biased ZnO film, and an internal field is built up across the ZnO/F8BT interface facilitating the injection of electrons (8). A high luminance level exceeding 5000 cd/m^2 at 10 V, accompanied by an efficacy (Figure 2b) of about 2 cd/A, is obtained.

The insertion of a thin PFN-IBm$_4$ film in between the ZnO and the LEP layers results in a drastic change in the current density and luminance curves (Figure 2a). First, the current
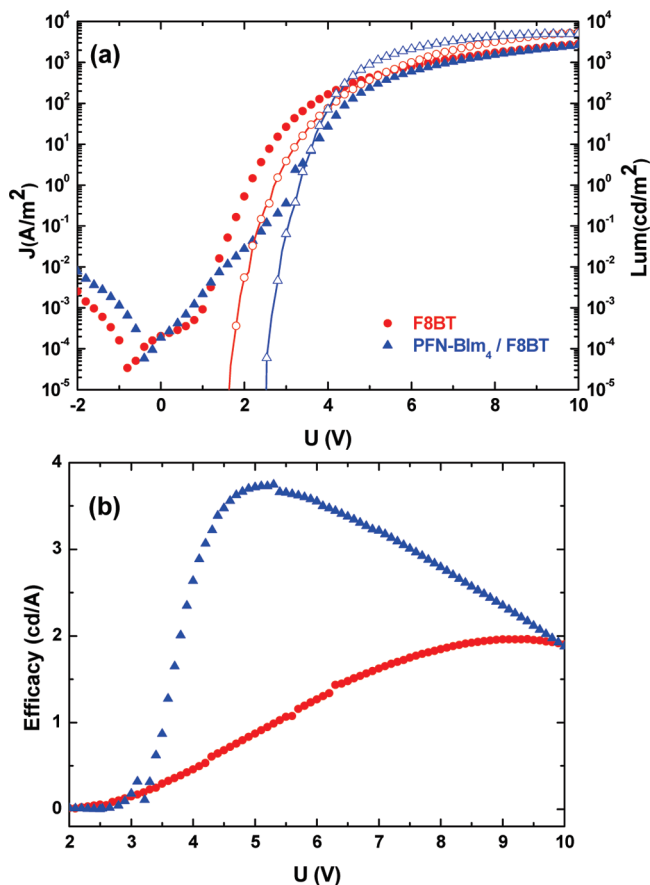
FIGURE 2. (a) Current density (full symbols) and luminance (lines) versus applied voltage for an ITO/ZnO/F8BT/MoO₃/Au (red circles) and for an ITO/ZnO/PFN-IBm₄/F8BT/MoO₃/Au (blue triangles) device, where ITO-ZnO is biased negatively. (b) Efficacy versus applied bias for these two devices.

density turn-on is not as steep as observed in the device without the EIL. The current density then raises rapidly, reaching values similar to the device without the interlayer at about 6 V.

The turn-on of the electroluminescence occurs at about 2.6 V, after which it increases rapidly reaching 1000 cd/m² at 5 V and about 5000 cd/m² at 10 V. The electron injecting/transporting properties of the polyelectrolyte are reflected in a lower current density and higher luminance at lower voltage, causing an enhanced efficacy with a maximum value of 3.8 cd/A at 5 V. At higher voltages the efficacy decreases matching the reference device maximum of 2 cd/A at 10 V. The efficacy of 3.8 cd/A is slightly higher compared to what has been achieved in an OLED using the same light emitting layer (material and thickness) (26). It is lower than values reported recently for OLEDs employing thicker (200−1450 nm) layers of F8BT (27).

The origin of the increased turn-on voltage for light emission is in principle expected due to a significant barrier for the electron injection from the ZnO into the LUMO of the CPE (∼ 2 V, Figure 3). The operating mechanism of this HyLED is related to the presence of mobile ions in the device, as already observed for these systems and in LECs. Holes are efficiently injected from the anode into the F8BT HOMO and migrate toward the PFN-BIm₄/F8BT interface where they
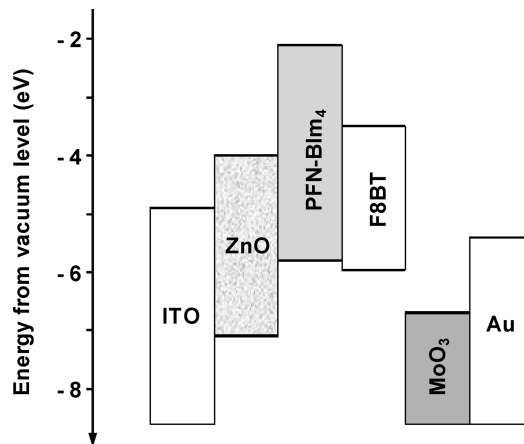

FIGURE 3. Energy levels scheme for a HyLED with F8BT as the active polymer.

accumulate, screening the electric field in the light-emitting polymer. Thus, the electric field drops entirely in the poly-electrolyte layer where the anions are free to move, inducing a strong interfacial field at both the LEP/EIL and EIL/ZnO interfaces, lowering the electron injection barrier (16, 28). Subsequently, electrons are injected into the F8BT layer through the thin PFN-Bim₄ layer, and electroluminescence is observed. Both our experimental data and previous reports on conjugated polyelectrolytes in blue PLEDs confirm this effect (29). In the CPE containing HyLEDs, the electron barrier is decreased by the effects of the ions close to the electrode interface. The particular CPE employed in this work has a LUMO level that is rather close to the vacuum level implying that no longer only light emitting materials with low LUMO levels, like F8BT, are suitable for use in HyLEDs.

To verify if by using the CPE interlayer other light-emitting materials with higher-lying LUMO levels can be used, we
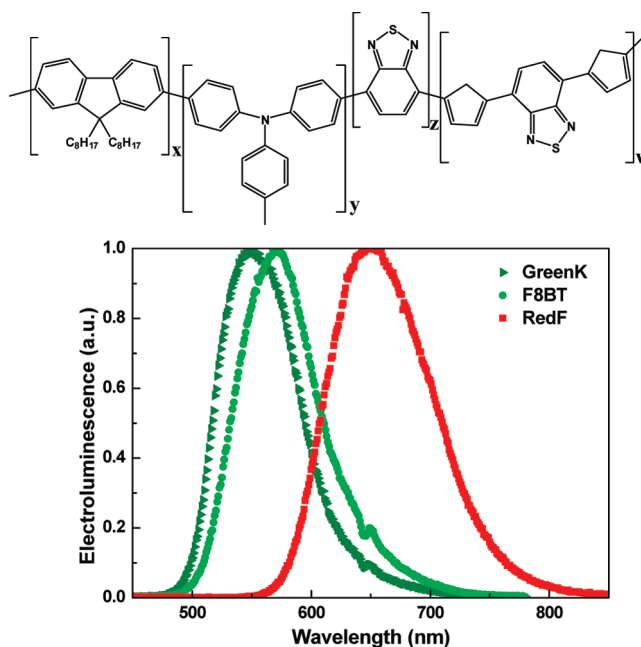

FIGURE 4. Chemical structure of RedF (with composition as follows: $x = 50$, $y = 5$, $z = 40$, $w = 5$) and normalized electroluminescence spectra for HyLEDs employing different LEPs.
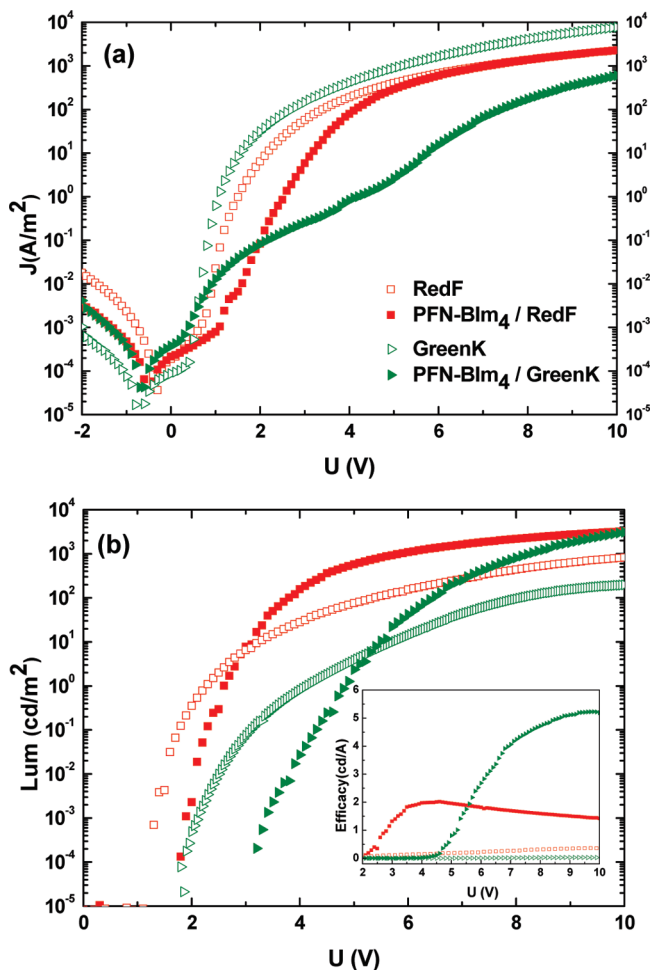
FIGURE 5. (a) Current density and (b) luminance versus applied voltage for ITO/ZnO/LEP/MoO₃/Au (empty symbols) and ITO/ZnO/PFN-IBm₄/LEP/MoO₃/Au (full symbols) devices using GreenK and RedF as the LEPs (green triangles and red squares, respectively), where ITO-ZnO is biased negatively. The inset in b shows the efficacy versus applied bias for this series of devices.

evaluated two other light-emitting materials, referred to as RedF and GreenK. The chemical structure of RedF is displayed in the inset of Figure 4. GreenK is a green-light-emitting polyfluorene for which the chemical structure was not disclosed. The emission spectra of these devices are shown in Figure 4, demonstrating that a wide range of emission colors can be obtained using the HyLED approach. The current density versus voltage profile of these HyLEDs is depicted in Figure 5a: both devices without the PFN interlayer show high current densities similar in magnitude, as is observed for the devices employing F8BT as the light emitting layer. As observed when using F8BT, the presence of the PFN-BIm₄ buffer layer reduces considerably the current density flowing through the device at low bias (Figure 5a).

After a threshold voltage, the current densities for both devices increases, and in the case of the HyLED employing RedF is approaching the values of the device without the PFN interlayer. The current density of the HyLED using GreenK remains lower than that observed for the device without the PFN interlayer throughout the evaluated voltage range. The luminance for the HyLEDs based on RedF and GreenK when

Table 1. Summary of the Performances of HyLEDs Employing Different LEPs

LEP	Lum$_{max}$ (cd/m²)	Eff$_{max}$ (cd/A)	λ_{max}	EQE$_{max}$
F8BT	5375	2.0	570	0.59
PFN-BIm₄/F8BT	4970	3.8		1.13
GreenK	196	0.02	548	5×10^{-3}
PFN-BIm₄/GreenK	3075	5.2		1.36
RedF	820	0.4	648	0.56
PFN-BIm₄/RedF	3250	2.0		3.17

employing the PFN interlayer reaches levels around 3000 cd/m², significantly higher than observed for the devices without the PFN layer. This is the reason for the increased efficacy values obtained for the RedF-based HyLED. The GreenK-based HyLED shows a much higher efficacy, 5.2 cd/A, as here the high luminance value is obtained with a significantly lower current density. As the chemical structure of GreenK was not fully disclosed to us, one can only speculate as to what is the origin of this decreased current density. It is known that a small amount of tris-arylamine units are present in the polymer structure of GreenK, which have a lower ionization potential than the fluorene subunits. These tris-arylamine units are known for their good hole-transporting properties; however, at concentrations below 20% in a polyfluorene they are in fact hole traps. The presence of hole traps, as we showed previously, can lead to a strong reduction of the current density in HyLEDs (8). Hence, it is possible that also in this case the presence of hole traps is the reason for the reduced current density and as a result the higher efficacy.

CONCLUSIONS

In conclusion, we demonstrate how the efficiency of Hyleds can be improved through the use of CPEs layers in between the metal oxides and the LEP. The high-lying LUMO and the presence of mobile ions make CPEs a good candidate as electron injection layer in HyLEDs. Moreover, their unique solubility in polar mediums allows for the preparation of efficient devices by simple solution processing.

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