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White Hybrid Organic−Inorganic Light-Emitting Diode Using ZnO as the Air-Stable Cathode

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In the past decade, organic light-emitting diodes (OLEDs) have attracted considerable attention as a potential next-generation technology for flat panel displays, and first prototypes are now entering the market. However, in order to raise efficiency, brightness and lifetime, these OLEDs rely on multilayer architecture, obtained by sequentially evaporating the active materials under high vacuum conditions. Additionally, air-sensitive low work function metals or charge injecting materials are employed, requiring rigorous device encapsulation to ensure high lifetime values. More recently, reports of efficient white OLEDs have generated significant interest for solid-state lighting applications, due to the potential savings in both costs and energy use.[1,2] Besides the device optimization, a strong reduction in production costs is needed in order to make organic lighting competitive with current technologies. In this context, polymer light emitting diodes (PLEDs) are of particular interest because they can be fabricated using a range of printing techniques on a wide variety of substrates at low temperatures. Many strategies have been use to prepare white PLEDs,[3] however, the conventional PLED structure also employs reactive metals as electron injecting contact and therefore needs hermetical encapsulation to ensure stability. Recently transition metal oxides (TMO) have been employed as charge transport and particularly as electron injection layers in hybrid organic−inorganic light emitting diodes (HyLEDs), demonstrating the possibility to prepare air-stable electroluminescent devices.[4−7] The preparation of such devices is simple, and consists of the deposition of a thin TMO film on top of an indium tin oxide (ITO) covered glass substrate, followed by the solution processing of the light-emitting polymer (LEP) and the deposition of a high workfunction gold anode. TMO cathodes like titanium oxide (TiO_2) and zinc oxide (ZnO) provide favorable properties like good mechanical and compositional stability, transparency, good electrical conductivity, and easy deposition with great control on the film morphology.[8,9] HyLEDs have originally suffered low efficiency because of the unique hole-dominated operating mechanism: initially holes are efficiently injected into the LEP through a molybdenum oxide (MoO_3) layer placed in between the polymer and the anode.[6,10] Thus, positive charge carriers accumulate at the metal oxide-polymer interface creating a strong interfacial field that assists the electron injection. In all previous reported HyLEDs, poly(9,9-dioctylfluorene-*co*-benzothiadiazole) (F8BT) was exclusively used as the electroluminescent material. The use of F8BT, because of its low LUMO energy (3.5 eV to the vacuum level), decreases the energy barrier for electron injection from the metal oxide conduction band, but it has limited the versatility of the HyLEDs approach as better performing electroluminescent materials have higher LUMO energy. This limitation has been overcome evaporating a thin layer of cesium carbonate (Cs_2CO_3) in between the TMO cathode and the LEP, resulting in enhanced efficiency (∼7 cd/A) that made HyLEDs competitive to conventional PLED architectures.[11] Recently, we showed that with this approach it is possible to obtain efficient HyLEDs employing a more representative LEP, like a polyphenylenevinylene derivative (PPV).[12]

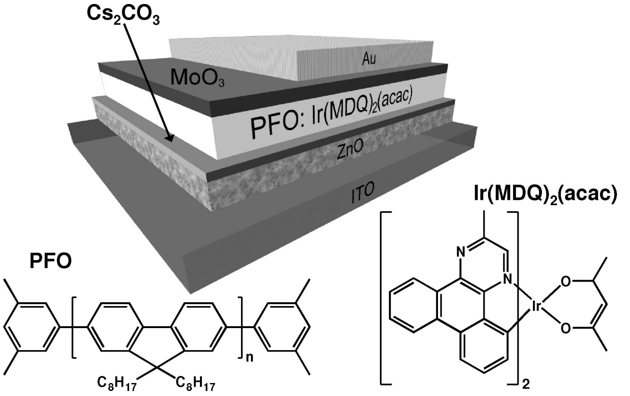

Figure 1. Schematic device layout and chemical structure of the electroluminescent species.

In this paper, we demonstrate the potential of this class of devices by presenting the first white HyLED using air stable ZnO as the cathode. To obtain white electroluminescence, we used a single active layer consisting of a blue polymer matrix doped with a phosphorescent iridium complex. We choose the well studied poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO) as the blue emitting host and the iridium-(III)bis (2-methyldibenzo-[f,h] quinoxaline) (acetylacetonate) (Ir(MDQ)$_2$(acac)) as orange dye (Figure 1), as it is reported to be an efficient emitter in hole-dominated charge transport-

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ing environments and it has already been employed in multilayer white OLEDs.[13,14]

Additionally, our work shows how HyLEDs and phosphorescent emitters are compatible, which is important considering the limited efficiency that can be obtained relying only on fluorescent emitters. Hence, it shows that HyLEDs can be a real competitor to OLED technology.

The architecture of the devices is reported in Figure 1. Eighty-nanometer-thick ZnO layers were deposited on ITO coated glass substrate by spray pyrolysis, following a procedure similar to that reported earlier.[15,16] Ir(MDQ)$_2$(acac) and PFO were purchased from American Dye Source (ADS076RE and ADS129BE, respectively) and used as received. Different concentrations of Ir(MDQ)$_2$(acac) into the PFO host were explored. PFO was dissolved in chlorobenzene and the concentration of the iridium complex was controlled by adding the appropriate amount of a diluted chlorobenzene solution of the orange emitter. The solutions were filtered over a 0.20 μm polytetrafluoroethylene filter and spun on the substrates obtaining a thickness of approximately 70 nm. Cs_2CO_3, MoO_3, and Au (5 nm, 20 and 80 nm layer thickness, respectively) were evaporated in a high vacuum chamber integrated in an inert glovebox atmosphere under a base pressure of 1×10^{-6} mbar. Cs_2CO_3 coated substrates were annealed in air at 120 °C for 15 min before deposition of the organic film. The Cs_2CO_3 layer will change its constitution during thermal evaporation, exposure to air and annealing; however, for simplicity, we will refer to this layer as Cs_2CO_3.[17] Thicknesses of the ZnO and spin coated LEP films were determined using an Ambios XP1 profilometer. The current density vs voltage ($J-V$) and electroluminescence vs voltage ($L-V$) characteristics were collected using a Keithley 2400 source measurements unit and a Si-photodiode coupled to a Keithley 6485 picoamperometer, respectively. The photocurrent was calibrated using a Minolta LS100 luminance meter. Electroluminescence spectra were recorded using an Avantis fiber optics photospectrometer. All device measurements were performed in inert atmosphere.

In Figure 2 the $J-V$ and $L-V$ characteristics of a series of devices with decreasing concentration of metal complex into the PFO host is presented. The turn on voltage for current and light is as low as 1.5 and 2 V, respectively, which is low for a blue light-emitting polymer as PFO that shows a bandgap larger than 3 eV.[18]

It is interesting to note that after the turn on voltage the slope of the $J-V$ characteristic is not monotonic, possibly because of the presence of the thin Cs_2CO_3 layer on the interface between ZnO and the LEP. For all the devices, independently of the amount of Ir(MDQ)$_2$(acac) complex into the active layer, the current density increases rapidly to a value of about 1000 A/m^2, saturating at voltages higher than 8 V. The luminance turns on at about 2 V and reaches levels higher than 2000 cd/m^2 at 8 V, for the device with a concentration of Ir(MDQ)$_2$(acac) of 0.5% w/w into the PFO. The delayed turn on voltage for light with respect to the current is probably due to a shift in the emission zone toward the center of the active layer. As the device is hole dominated, it is possible that at low voltages the emission zone is located very close to the surface of the ZnO$-Cs_2CO_3$ cathode, which can efficiently quench the generated excitons.

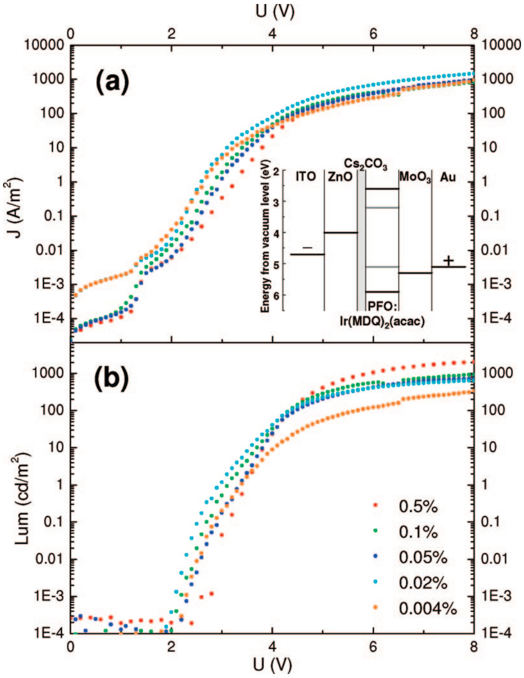

Figure 2. (a) Current density and (b) luminance versus applied voltage for a series of ITO/ZnO/Cs_2CO_3/PFO:Ir(MDQ)$_2$(acac)/MoO_3/Au devices with different concentration of the triplet emitter (expressed as w/w %). Inset of Figure 2a shows a scheme of the energy levels of the materials used in the device. The plus and minus symbols indicate the anode and the cathode, respectively.

Lowering the concentration of the triplet emitter the luminance appears to diminish, till a minimum value of about 300 cd/m^2 at 8 V that corresponds to a concentration of 0.004% w/w of the complex. This effect can be attributed to the limited amount of complex that, at high concentration, is capable of harvesting both triplet and singlet excitons electrically generated on the PFO to its triplet state, leading to high luminance value. As a consequence, the efficacy (current efficiency) of the device decreases strongly when the concentration of the Ir(MDQ)$_2$(acac) is lowered (Figure 3). A value of 2.7 cd/A efficacy is obtained for the high metal complex concentration device; this value is not the highest reported for this class of device; however, it represents the first example of an efficient HyLEDs employing phosphorescent emitters. It should be noted that this efficacy is reached for an orange emitting device. More remarkable are the electroluminescence spectra recorded as a function of the orange dopant (Figure 4). At a concentration of 0.5% w/w, the spectra is typical of the orange emitter Ir(MDQ)$_2$(acac), and almost no contribution from the PFO host is visible.[13]

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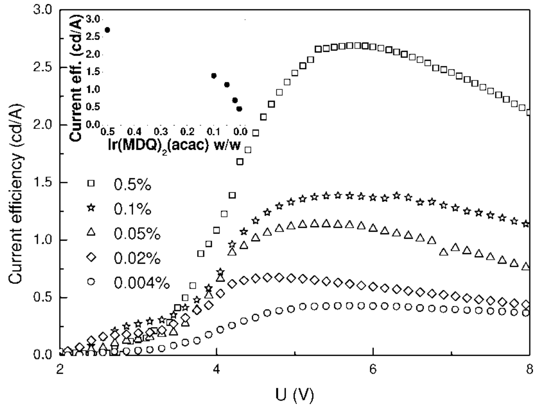

Figure 3. Current efficiency (efficacy) versus driving voltage for a series of ITO/ZnO/Cs_2CO_3/PFO:Ir(MDQ)$_2$(acac)/MoO_3/Au devices with different concentration of the triplet emitter (expressed as w/w %). Inset show the trend of the efficacy versus the concentration of the complex.

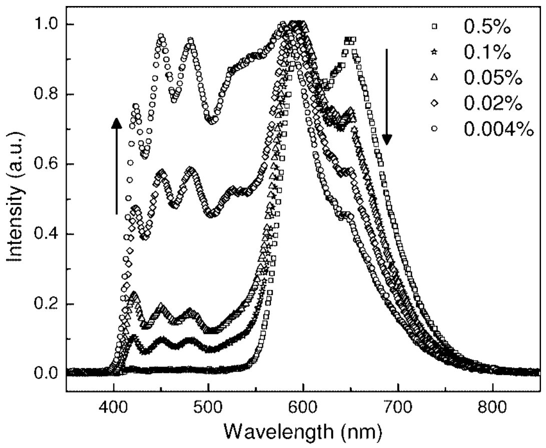

Figure 4. Normalized electroluminescence spectra for a series of ITO/ ZnO/ Cs_2CO_3/PFO:Ir(MDQ)$_2$(acac)/MoO_3/Au devices with different concentration of the triplet emitter (expressed as w/w %). Spectra were registered at 6 V bias.

When the concentration of the Ir complex is decreased, the orange phosphorescence is gradually reduced and the blue fluorescent component with the typical features of PFO emission starts to rise.[19] This behavior can be observed on the CIE chromaticity plot (Figure 5) where the color of the luminescence moves dramatically with only small changes in the amount of Ir(MDQ)$_2$(acac) introduced in the blue host.

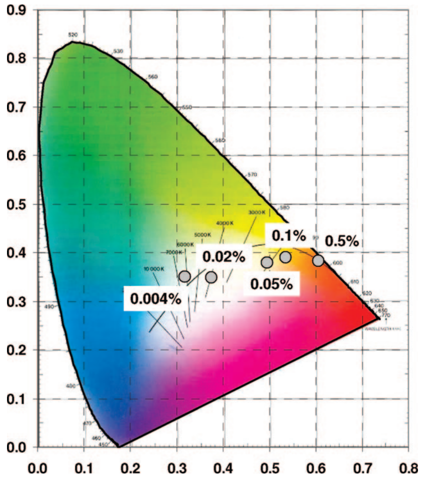

Figure 5. CIE chromaticity diagram for a series of ITO/ ZnO/ Cs_2CO_3/ PFO:Ir(MDQ)$_2$(acac)/MoO_3/Au devices with different concentration of the triplet emitter (expressed as w/w %).

The most important fact is that when the concentration of the complex is changed from 0.5 to 0.02% w/w, the emission color shifts from a pure orange to the white zone in the middle of the CIE diagram, moving subsequently toward the blue part at lower concentration (≤0.004%). At a concentration of 0.02% w/w of Ir(MDQ)$_2$(acac) into the PFO the CIE $x-y$ coordinates are 0.37 and 0.35, respectively, corresponding to pure white emission close to the blackbody curve characteristic in the visible spectrum.

A white solution processed electroluminescence device was obtained using an airstable metal oxide as the cathode. This shows that the barrier for electron injection can be efficiently overcome and additionally, that the design rules generally used for OLEDs are also valid for HyLEDs. Additionally, since HyLEDs offer the promise for less rigorous encapsulation they are especially suited for low-cost lighting applications. Hence, the demonstration of white light emitting HyLEDs clearly shows the potential that these devices have for that type of application.

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