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Tenfold increase in efficiency from a reference blue OLED

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ABSTRACT

Starting from a reference single-layer light-emitting diode based on the blue phosphorescent bis-cyclometallated iridium complex FIrpic as guest, hosted in a PVK (non-conjugated poly(vynilcarbazole)) matrix, different strategies are followed to improve the efficiency of the devices through the combination of solution processed and evaporated layers. Injection of charges from the electrodes has been varied by using different conductive PEDOT:PSS as hole injection layer and a nanoscale Cs_2CO_3 interlayer as electron injection and hole-blocking film. Furthermore, a separated electron injection/hole blocking evaporated layer, TPBi or 3TPYMB, is introduced in double-layer devices to enhance the minority carriers (electrons) and also to confine holes to the emissive layer. All these modifications lead to an approximate tenfold improvement in efficiency from the initial reference device.

1. Introduction

Since the first report on efficient organic light-emitting diodes (OLEDs) based on phosphorescent emitters published by Baldo et al. in 1998 [1], intense research activities have been stimulated in this field. Thus, the use of organic triplet-state light-emitting materials in OLEDs overcomes the efficiency limit imposed by fluorescent emitters, because they can harvest both electrogenerated singlet and triplet excitons for emission and boost the internal quantum efficiency to 100%. For efficient electrophosphorescence, the triplet energy state of the polymer host must be located at higher energy than that of the guest to avoid reverse energy transfer from the guest to the host. In the case of blue phosphorescent molecules, high-band-gap host materials with very high triplet energy are required to minimize quenching [2]. Arylamino-containing organic compounds are usually the host materials of choice to solve this situation, such as 4,4′-N,N′-dicarbazole-biphenyl (CBP) [3], N,N′-dicarbazolyl-3,5-benzene (mCP) [2] and non-conjugated poly-vynilcarbazole (PVK) [4], among others [5–7]. The external quantum efficiency of a polymer light-emitting diode is affected by the balance and confinement of electrons and holes, and the location of the exciton density within the light-emitting polymer layer [8].

In this work, we report a method to increase the efficiency of a reference blue phosphorescent OLED by controlling the charge injection and hence enhancing the balance between the electron and hole currents. As emitter, iridium (III) bis[(4,6-difluorophenyl)-pyridinato-N, C^2] picolinate (FIrpic) is probably the most used bis-cyclometallated iridium complex, because of its attractive sky-blue emission and high emission efficiency [9]. Due to its photophysical and electrochemical properties, good stability, ease of preparation and processing, FIrpic has been widely used as phosphorescent blue-light-emitting dopant in both monochromatic and white OLEDs [10–14] and LECs [15]. Recently, devices based on FIrpic with η_{ext} above 30% have been reported with current efficiency of 53.6 cd/A. To our knowledge, this is the highest efficiency obtained for blue phosphorescent OLED, but these excellent values were achieved for devices with all layers fabricated by vacuum thermal evaporation [16]. Despite the indubitable improvements in performance obtained by thermal evaporation technology under high vacuum, it does increase fabrication complexity and may be a relatively costly process, besides that the control of reproducibility still hinders the practical applicability of blue phosphorescent OLEDs. In contrast, solution processing techniques, such as spin-coating, are cost-effective and desirable for simple device layouts, which are desirable for large-area devices such as flat panel displays. In this context, Shao and co-workers synthetized a bipolar polymer PczPO as a host for FIrpic and, by the introduction of a hole/exciton blocking layer, they obtained a blue-emitting double-layer PhPLED with a current efficiency of 23.3 cd/A, at a practical brightness of 116 cd/m^2 [5]. More recently, Sun and co-workers synthetized a hybrid polymeric host (PCzSiPh) for FIrpic-

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based devices, which exhibited a maximum current efficiency of 29.3 cd/A [6]. These examples show that, for blue PhPLED, it is possible to achieve considerably high efficiencies using polymeric hosts.

In this work, the light-emitting layer of the reference device is solution-precessed and consists in the commercially available poly-vinylcarbazole (PVK) as the hole transporting matrix, into which the electron transporter 1,3-bis(4-*tert*-butylphenyl) − 1,3,4-oxadiazolyl)) phenylene (OXD-7) and the blue phosphorescent emitter FIrpic are doped. Strategies to achieve highly efficient devices imply the combination of solution processed and evaporated layers. First, hole injection has been modulated by using two grades of poly(3,4-ethylenedioxythiophene): poly(styrenesulfonic acid) (PEDOT-PSS) with different resistivities, between the ITO anode and the emitting composite matrix. Second, a nanoscale cesium carbonate (Cs_2CO_3) interlayer is placed between the cathode and the emissive layer, serving both as electron injection and hole-blocking film [17]. Moreover, a significant increase in the device efficiency is achieved in double-layer devices, by introducing an additional electron injection/hole blocking layer capable to enhance the minority carriers (electrons) that also confines holes to the emitting layer. For this purpose, two different materials, TPBi (2,2′,2″-(1,3,5-benzinetriyl)-tris(1-phenyl-1-*H*-benzimidazole)) and 3TPYMB (tris-[3-(3-pyridyl)mesityl]borane), have been evaporated between the emissive film and the Cs_2CO_3 thin layer. By following these modifications, an approximate tenfold improvement in efficiency has been observed from the initial reference device. In addition, under the premise of the characteristics of a device are conserved, the use of solution processed instead of evaporated layers leads to a cost reduction in multilayer devices [18,19].

Although most of the materials used have been already proposed in literature, they have not been employed together in an electroluminescent device. Hence, this work aims to be a systematic study about the influence of several variables that are not normally mentioned, while being fundamental for non-expert researchers interested on the field.

2. Experimental

2.1. Materials

Solvents, poly-vinylcarbazole (PVK) and the phosphorescent guest iridium (III) bis[(4,6-difluorophenyl)-pyridinato-*N*, C^2] picolinate (FIrpic) were obtained from Aldrich. Aqueous dispersions of poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT: PSS, CLEVIOS P VP AI4083 and CH8000) were supplied by Heraeus Holding GmbH and used as received. Electron transport materials 1,3-bis(4-*tert*-butylphenyl) − 1,3,4-oxadiazolyl)) phenylene (OXD-7), 2,2′,2″-(1,3,5-benzinetriyl)-tris(1-phenyl-1-*H*-benzimidazole) (TPBi) and tris-[3-(3-pyridyl)-mesityl] borane (3TPYMB) were purchased from Sensient GmbH. The chemical structures of these molecules are shown in Scheme 1.

2.2. Device preparation

Indium-tin-oxide (ITO) coated glass substrates were cleaned ultrasonically in water-soap and organic solvents (isopropyl alcohol, acetone, and ethanol), and rinsed in deionized water. After drying, the substrates were placed in a UV-ozone cleaner (Jelight 42–220) for 20 min, prior to the deposition of the layers. An 80 nm layer of PEDOT: PSS was spin-coated on the ITO glass substrate, followed by annealing at 120 °C for 15 min. In this work, two aqueous dispersions of PEDOT: PSS with different resistivities have been used: PEDOT: PSS(1) with $\rho = 500 - 5000\ \Omega\,\mathrm{cm}$ (CLEVIOS P VP AI4083) and PEDOT: PSS(2) with $\rho = 1 \times 10^4 - 3 \times 10^5\ \Omega\,\mathrm{cm}$ (CLEVIOS P VP CH8000). The emitting layer of FIrpic in a composite matrix, comprising 13.5 mg of PVK, 5.6 mg of OXD-7, and 1/2.1/3.3 mg of FIrpic in 1 mL chlorobenzene solution was spin-coated on top of the PEDOT: PSS layer, and dryed at 90 °C for 30 min on a hot plate. All the solutions were filtered over a 0.20 µm PTFE filter. Following, TPBi or 3TPYMB were thermally evaporated using temperature controlled sources and an evacuation chamber integrated in an inert atmosphere glovebox (< 0.1 ppm O_2 and H_2O). The device was completed by a Ba/Ag (5 nm/70 nm) or Cs_2CO_3/Al (0.5 or 1 nm/80 nm) bilayer cathode, which was thermally evaporated through a shadow mask, under a base pressure of 2×10^{-6} mbar. Cs_2CO_3 was evaporated from a low temperature evaporation source. Each substrate contains 4 devices. For each configuration, 3 or 4 substrates have been prepared and measured, i.e. 12–16 devices. The emissive area of the fabricated devices ranged from 0.09 to 0.95 cm^2. Scheme 2 shows the energy-level diagram of the different materials used in this work. Energy levels are taken from the literature [4,20–22] and suppliers.

2.3. Device characterization

The thicknesses of the spin-coated films were determined using an Ambios XP1 profilometer, while those of the evaporated layers were monitored by calibrated quartz-crystal sensors. Current density and luminance versus voltage were measured using a Keithley 2400 source meter and a silicon photodiode coupled to a Keithley 6485 pico-amperometer, using a Minolta LS100 luminance meter to calibrate the photocurrent. An Avantes fiber optics photospectrometer was used to measure the electroluminescent spectra. Devices were characterized in inert atmosphere.

3. Results and discussion

The blue LED device used in this study as the reference consists of a patterned ITO anode, a 80 nm thick PEDOT: PSS(1) hole injection layer, a composite matrix comprising PVK, OXD-7 and FIrpic as the hole transport, electron transport and emission materials, respectively, and a 5 nm Ba and 70 nm silver double layer as the cathode: ITO/PEDOT: PSS (1)/PVK: OXD-7: FIrpic/Ba/Ag.

PEDOT: PSS is commonly used as a buffer layer on the ITO anode to increase the anode work function from 4.7 (bare ITO) to ~5.2 eV. It also reduces the surface roughness of the anode, which allows obtaining stable and pinhole-free electrical conduction across the OLED [23]. As there are commercially available aqueous PEDOT: PSS dispersions with different electrical conductivity, they can be used to modulate the hole injection into the composite emitting layer. PEDOT: PSS(1) refers to the more conductive polymer.

Mathai et al. investigated a similar device [4], in which the FIrpic content was kept constant at 10 wt%, and they found the optimal performance with PVK: OXD-7 in a 7–3 ratio (by wt). In this study, therefore, we have fixed the concentration of the electron-transporting OXD-7 at 30 wt% of PVK host in the light-emitting polymer layer. Regarding to the FIrpic content, different devices with 5, 10, and 15 wt% of FIrpic dispersed in the LEP layer have been prepared, obtaining slightly better results for 15 wt% of FIrpic content (data not shown). From now, EML (emitting layer) means PVK: OXD-7: FIrpic (15 wt%).

Fig. 1 compares the effect of the EML thickness on the characteristics of the reference OLED. Lower mobility materials show larger operating voltage dependence on thickness [24]. However, the device comprising the thinner EML only diminishes the light-onset voltage by 0.2 V (from ~ 3.5 V for 70 nm to ~ 3.2 V for 40 nm), but increasing the thickness causes a significant decrease of the current together with an increase in the luminance (from ~ 1600 $\mathrm{cd/m^2}$ to ~ 1940 $\mathrm{cd/m^2}$ at 8 V). Thus, luminous efficiency is improved from 1.5 cd/A for 40 nm to 2.5 cd/A for 70 nm, measured at a luminance of 1000 $\mathrm{cd/m^2}$. Considering that both PVK and OXD-7 are materials with moderate transport mobilities, the near independence of the operating voltage in this limited thickness range may be related to efficient charge injection from the electrodes into the blend layer [24]. Then, the constant EML thickness at 65–70 nm in all following devices is decided based on