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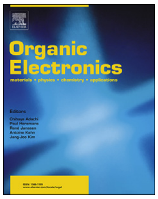

Hole-transporting small molecules as a mixed host for efficient solution processed green phosphorescent organic light emitting diodes

Dan Dong [a], Jingcheng Xia [b], Shuai Yang [a], Xinkai Wu [a], Bingwu Wei [a], Lu Lian [a], Dongxu Feng [a], Youxuan Zheng [b], Gufeng He [a, *]

[a] *National Engineering Lab for TFT-LCD Materials and Technologies, Department of Electronic Engineering, Shanghai Jiao Tong University, Shanghai, 200240, People's Republic of China*
[b] *State Key Laboratory of Coordination Chemistry, Nanjing National Laboratory of Microstructures, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, People's Republic of China*

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ABSTRACT

We have demonstrated highly efficient and reduced efficiency roll-off solution processed green phosphorescent organic light emitting diodes (OLEDs) utilizing two hole-transporting small molecular materials of 1,3-bis(carbazol-9-yl)benzene (mCP) and 4,4′,4″-tris(*N*-carbazolyl)-triphenylamine (TCTA) as a mixed host. Compared with the corresponding two single host devices, the mixed host one shows a superior overall performance. A low driving voltage of 5.5 V at 1000 cd/m^2 with a current efficiency of 39.5 cd/A is achieved in the mCP:TCTA (3:1) mixed host device. Even at the luminance of 10000 cd/m^2, the efficiency still reaches 28.6 cd/A. The enhanced charge carrier balance and broadened exciton recombination zone due to the mixed host contribute to the improvement of efficiency and efficiency roll-off.

1. Introduction

Solution processed organic light emitting diodes (OLEDs) have drawn considerable attention for displays and solid state lighting owing to their simple and low cost fabrication process and large area manufacturability [1,2]. Phosphorescent OLEDs (PHOLEDs) are more attractive because phosphorescent materials can harvest both singlet and triplet excitons to achieve 100% internal quantum efficiency in principle [3]. To date, many groups have reported high performance PHOLEDs fabricated by solution processing [4–6]. However, many issues, such as high driving voltage and short lifetime still remain to be further improved to make PHOLEDs meet the commercialization requirements.

Generally, the emitting layers (EMLs) of PHOLEDs adopt host-guest systems and polymers are commonly used as host materials due to high film density and stable film morphology [7]. Li et al. realized soluble green PHOLEDs based on poly(*N*-vinylcarbazole) (PVK):1,3-bis[(4-*tert*-butylphenyl)-1,3,4-oxadiazolyl] phenylene (OXD-7):*fac*-tris(2-phenylpyridine)iridium [Ir(ppy)$_3$] emitting layer, achieving a current efficiency of 27.7 cd/A [8]. A high current efficiency of 53.8 cd/A with an external quantum efficiency (EQE) of 16.1% is obtained using the PVK:OXD-7 host with solution processed 4,7-diphenyl-1,10-phenanthroline (Bphen) electron transport layer in the green PHOLEDs [9]. However, it is difficult to find wide bandgap and high triplet energy polymers for phosphorescent dopants, especially for green and blue ones. On the other hand, small molecules have a great advantage over polymers in material purity, chemical stability and triplet energy, and have been becoming a popular choice for hosts in solution processed PHOLEDs [10]. Unfortunately, some factors limit the performance of solution processed devices based on small molecular hosts as well. Firstly, a large number of small molecules are unsuitable for solution processing because of insufficient solubility, resulting in poor film quality [11]. Secondly, small molecules may easily crystallize by solution processing due to the lack of molecule entanglement, especially for those with low glass transition temperature [10]. To overcome the drawbacks of solution processed PHOLEDs based on small molecular hosts as mentioned above, and further improve the device

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* Corresponding author.
E-mail address: gufenghe@sjtu.edu.cn (G. He).

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performance, the mixed host system has been proposed as an effective method. Usually, a hole-transporting material is combined with an electron-transporting material to form a mixed host. By changing the composition of the mixed host, charge transport properties can be easily manipulated [12]. More importantly, due to the intermixing of different host materials, the molecular packing of each host material is hindered by the other host material, which effectively suppresses the crystallization of small molecules [13]. Based on the small molecular mixed host system, many solution processed devices have been realized. Doh et al. demonstrated a soluble blue PHOLED with the maximum EQE of 14.6% with a small molecular mixed host system, which consists of hole-transporting 4,4′,4″-tris(*N*-carbazolyl)-triphenylamine (TCTA) and bipolar carrier transporting 2,6-bis(3-(9H-carbazol-9-yl)phenyl)pyridine (26DCzPPy) [13]. A mixed host of hole-transporting 4,4′,4″-tris[*N*-(2-naphthyl)-*N*-phenyl-amino]triphenylamine (2-TNATA) and electron-transporting 1,3,5-tris (*N*-phenylbenzimiazole-2-yl) benzene (TPBi) was employed as the host material for bis(2-phenylquinoline)(acetylacetonate)iridium [Ir(phq)$_2$acac] based red OLEDs [14]. The solution processed device possessed a low driving voltage of 5.2 V at 1000 cd/m^2 and maximum current and power efficiencies of 17.8 cd/A and 11.3 lm/W, respectively. However, in such cases, an additional hole-transporting (electron-blocking) layer is usually required to avoid possible quenching by the hole-injection layer or the anode. Besides, the choice of wide bandgap electron-transporting hosts for solution processing is limited, while many hole-transporting wide bandgap hosts are available. Mixing different hole-transporting small molecular materials as a mixed host by solution processing is seldom reported. Fu et al. achieved highly efficient blue and white phosphorescent OLEDs with hole-transporting mixed host of TCTA:1,1-bis[(di-4-tolylamino)phenyl] cyclohexane (TAPC) [15]. Based on solution processed TCTA:4,4′-bis-(carbazol-9-yl)biphenyl (CBP) mixed host, the maximum current efficiency of the red PHOLED reached 19.9 cd/A, corresponding to an EQE of 11.1% [16].

In this paper, we present solution processed green PHOLEDs with high current efficiency, low driving voltage and reduced efficiency roll-off by utilizing the small molecular mixed host system. The mixed host is composed of two commonly used hole-transporting materials of 1,3-bis(carbazol-9-yl)benzene (mCP) and TCTA, and the recombination zone is tuned a bit away from anode side. Therefore, an additional hole transporting layer can be omitted to simplify the device structure. The driving voltage of the device is effectively reduced from 6.5 V to 5.5 V at 1000 cd/m^2 by replacing the mCP single host with the mixed host (mCP:TCTA (3:1)). Moreover, the mixed host device possesses higher current efficiency and lower efficiency roll-off compared with those of the TCTA single host device. Combining the respective advantages of the two single host devices, the optimized mixed host device shows a maximum current and power efficiency of 39.5 cd/A and 24.5 lm/W, respectively.

2. Experimental

The chemicals were purchased from commercial sources and used as received. The hole injection material of poly(3,4-ethylenedioxythiophene)-poly(4-styrenesulfonate) (PEDOT:PSS) (AI 4083) was purchased from Shanghai Kingtech Chemicals Co. Ltd. Host materials of mCP and TCTA were purchased from Beijing Aglaia Technology Co. Ltd. The electron-transporting material of TPBi was purchased from Taiwan Nichem Fine Technology Co. Ltd. The phosphorescent emitter is a bis-cyclometalated iridium complex of iridium(III)bis(2-(4-trifluoromethylphenyl)pyridine) tetraphenylimidodiphosphinate (Ir(tfmppy)$_2$(tpip)), synthesized by Zheng's group [17], as depicted in Fig. 1a.

The basic device structure with proposed energy level is shown in Fig. 1b. In a general procedure, the glass substrates with patterned indium tin oxide (ITO) were cleaned with detergent, deionized water, acetone and isopropyl alcohol via ultrasonification for 15 min each and then dried by nitrogen flow. The substrates were treated with oxygen plasma before usage. The PEDOT:PSS was spin-coated at 2000 rpm on the pre-cleaned ITO glass substrates with a thickness of about 40 nm, followed by drying at 130 °C for 15 min to remove the residual solvent. mCP, TCTA and Ir(tfmppy)$_2$(tpip) were dissolved in chlorobenzene with the concentration of 20, 10 and 10 mg/ml, respectively. Then different volumes of the respective solutions were blended according to the defined weight ratio of the EML and stirred for 5 min for better mixing. The EML was formed by spin coating the obtained blend solution on top of the PEDOT:PSS film at a speed of 4000 rpm for 60 s and then annealed at 70 °C for 40 min in a glove box with nitrogen atmosphere. Afterward, the samples were transferred into a vacuum thermal evaporation chamber, and a 40 nm thick electron-transporting layer of TPBi, a cathode composed of LiF (1 nm) and Al (100 nm) were sequentially deposited at a base pressure of 5×10^{-6} Torr. The evaporation rates of TPBi, LiF and Al are about 0.5–1 Å/s, 0.1 Å/s and 5–10 Å/s, respectively. The active emissive area of the device is defined by the overlap between ITO and Al electrodes as 9 mm^2.

The current density-voltage-luminance (J-V-L) characteristics were evaluated by a computer-controlled Keithley 2400 source meter and Topcon BM-7A Luminance Colorimeter. The electroluminescence (EL) spectra were recorded by Labsphere CDS-610. KLA-Tencor Profile XP-200 was adopted to determine the film thickness. All the devices were measured immediately after fabrication under the ambient atmosphere without encapsulation.

3. Results and discussion

3.1. Solution processed PHOLEDs based on mCP host with different Ir(tfmppy)$_2$(tpip) doping concentrations

mCP is generally used as the host in PHOLEDs for its relatively high triplet energy and moderate hole-transporting ability [2,10,18], as reported in our group's previous work by vacuum evaporation [19]. Herein, it was chosen as the host material to fabricate the solution processed green PHOLEDs since it is easily dissolved in chlorobenzene. To optimize the doping concentration of Ir(tfmppy)$_2$(tpip) in the EML, devices with the structure of ITO/PEDOT:PSS (40 nm)/mCP:X wt% Ir(tfmppy)$_2$(tpip) (~20 nm)/TPBi (40 nm)/LiF (1 nm)/Al (100 nm) were fabricated. The doping concentration X of Ir(tfmppy)$_2$(tpip) was varied, being 5, 10, 15, respectively.

The current density markedly increases when the Ir(tfmppy)$_2$(tpip) doping concentration is increased in the solution processed devices (Fig. 2a), with the turn-on voltage (defined as the voltage at 1 cd/m^2) decreased consequently. This is related to the intrinsically hole-transporting ability of Ir(tfmppy)$_2$(tpip). With Ir(tfmppy)$_2$(tpip) doping concentration increased from 5 to 15 wt%, holes are easier to transport in the EML by the hopping mechanism, thus strengthening the recombination probability of holes and electrons to increase the exciton density. However, Fig. 2b shows that when the doping concentration of Ir(tfmppy)$_2$(tpip) is increased to 15 wt%, the current efficiency (CE) of the device has already decreased as a consequence of concentration quenching and strong triplet-triplet annihilation of the dopant. The optimized device with 10 wt% Ir(tfmppy)$_2$(tpip) shows a maximum current efficiency of 36.5 cd/A and power efficiency (PE) of 19.1 lm/W at 6 V (~500 cd/m^2).