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Highly efficient red phosphorescent organic light-emitting devices based on solution-processed small molecular mixed-host

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ABSTRACT

Highly efficient solution-processed red phosphorescent organic light-emitting devices were developed using 4,4′,4″-tris (N-carbazolyl)-triphenylamine (TCTA) blended with 4,4′-bis-(carbazol-9-yl)biphenyl (CBP) as a mixed-host for the emitting layer. The performances of the fabricated devices made with different mixing ratios of host materials were investigated, and were found to depend on the mixing ratios. Under the optimal TCTA:CBP ratio (3:7), the maximum luminous efficiency of the device reached 19.9 cd/A, corresponding to external quantum efficiency of 11.1%. Moreover, this device with the mixed-host structure shows over 50% enhanced efficiency compared with the device using CBP as the single host. These improvements were attributed to the mixed-host structure, which effectively enhanced the hole injection/transport properties and gave a good charge carrier balance.

1. Introduction

Organic light-emitting devices (OLEDs) have well-recognized advantages in simple structure, low-driving voltage, flexibility and large area. They show tremendous commercial applications in the flat panel displays and solid state lighting, and have been one of the most attractive projects in the optoelectronic information field over the past decades [1–4]. In particular, phosphorescent OLEDs are attractive due to their potential for achieving unity internal quantum efficiency through harvesting both singlet and triplet excitons [1]. Generally, highly efficient phosphorescent OLEDs could be fabricated by vacuum-evaporation deposition with multilayer device structure, which benefits the fine tuning of charge carrier balance in the emissive layer. However, one of the main challenges facing the industrialization of OLEDs is the manufacturing cost. As an alternative approach, the solution-process is a more desirable technique for low-cost manufacture and compatible with low-cost, large area manufacture technology such as spin-coating [5], ink-jet printing [6], screen-printing [7] and roll-to-roll coating [8].

In the past few decades, phosphorescent dyes doped polymeric host materials have been mainly studied as emitting layer (EML) [9–11]. However, the efficiencies and lifetimes of the solution-processed polymer devices are inferior to those of the small molecule devices due to several issues such as phase separation, localization of excitons, intrinsic difficulties in purifying the polymeric materials, and so on [12–14]. Recently, solution processed small molecular OLEDs have drawn much attention because it was found that highly efficient small molecular materials, which were usually used in vacuum-deposition, can be utilized in this process [15–21]. More importantly, the solution-process avoids the complexities of the co-evaporation of dopants and host materials in the vacuum deposition. Thus, it is a good strategy to develop OLEDs based on solution processible small molecules, which would open up exciting possibilities for commercialization of printed OLEDs for displays and lighting.

On the other hand, to ensure high performance, efficient charge injection and transport balance are also very important for the solution-processed OLEDs. This can be achieved in the vacuum-deposited devices by stacking different functional layers. However, it is difficult to form multilayer structure by the solution process because of the dissolution of the former layer by the later solution. Many methods were proposed to improve the performance of solution-processed phosphorescent OLEDs, such as synthesizing new bipolar host materials [22–25], modifying the electrode

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interfaces [26,27] and developing multilayered devices with cross-linkable molecules [21,28,29]. Recently, an effective method of mixed-host (MH) structure was proposed to improve the performance of solution-processed phosphorescent OLEDs [14,17]. The improvement was attributed to the more balanced charge injection and extended recombination zone in the EMLs [12,18]. An appropriate combination of a hole-transport-type host and an electron-transport-type host was effective in reducing driving voltage and increasing device efficiency.

In this work, highly efficient red phosphorescent OLEDs employing dye doped small molecular MH were developed via solution-process. A soluble small molecule MH system consisting of hole-transport-type host material 4,4′,4″tris (N-carbazolyl)-triphenylamine (TCTA) and bipolar host material (4,4′-N,N′-dicarbazole) biphenyl (CBP), possesses a good solubility and film forming properties. Using this MH, we fabricated red phosphorescent OLEDs by doping red dye iridium(III) bis(2-phenylquinoline)(acetylaceton) ($Ir(pq)_2(acac)$) into the MH. We found that the MH can significantly improve the luminance and luminous efficiency of the devices than those made of single host. We further investigated the optimal TCTA:CBP ratio by fabricating devices with different MH ratios. At a weight ratio of 3:7 (TCTA:CBP), the device exhibited a maximum current efficiency of 19.9 cd/A, which is 1.5 times and 2.0 times compared with the devices using CBP and TCTA as the single host, respectively. The significant improvement was attributable to the mixed-host structure, which effectively improved the charge carrier balance of device.

2. Experimental

The hole-injection material of poly(3,4-ethylenedioxythiophene):poly (styrenesulfonic acid) (PEDOT:PSS, AI4083) was purchased from H. C. Starck Inc. The hole-transporting material of TCTA, the phosphorescent host material of CBP, the electron-transporting material of 1,3,5-tris[N-(phenyl)benzimidazole]-benzene (TPBi), and the phosphorescent dopant of $Ir(pq)_2(acac)$ were purchased from Nichem Fine Technology Co. Ltd. All the above-mentioned materials were used as-received without further purification. The chemical structures of the host materials and dopant used in this study are shown in Fig. 1(a).

In the experiment, the patterned indium tin oxide (ITO) glass substrates were ultrasonically cleaned with detergent, alcohol and acetone, deionized water and then dried at 120 °C in a vacuum oven for more than one hour. After ultraviolet (UV)–ozone treating for 4 min, a 20 nm PEDOT:PSS was spin coated on the ITO substrate and dried at 120 °C in a vacuum oven for 15 min to remove residue solvent. Afterward, the samples were moved into a glove box under a nitrogen-protected environment, and the EMLs were spin-coated on top of PEDOT:PSS from chlorobenzene and then annealed using a hot plate at 80 °C for 20 min to extract residual solvent. The thickness of the EMLs is about 40 nm. Following that, the samples were transferred to a thermal evaporator chamber connected to the glove box without exposure to the atmosphere. The TPBi (60 nm), LiF (1 nm), and Al (100 nm) were deposited by thermal evaporation under a pressure of 5×10^{-4} Pa. For the single-carrier devices, the NPB (20 nm) and TPBi (20 nm) were thermally deposited under high vacuum. An alcohol soluble electron-injection layer of TrOH was spin-coated on ITO substrate from 0.5 mg/ml methanol solution [30], and prevented the hole injection from the ITO anode. The EML was spin-coated upon the TrOH layer. The active area of the device is 12 mm^2. The structure and schematic energy-level diagram of the device are shown in Fig. 1(b) and (c).

The luminance-current–voltage characteristics of the devices were recorded using a combination of a Keithley source-meter (model 2602) and a calibrated luminance meter. Electroluminescence (EL) spectra and Commission International de l'Eclairage (CIE) coordinates were obtained using a spectra-scan PR655 spectrophotometer. The thickness of the organic films was measured with a spectroscopic ellipsometry (α-SE, J.A. Wollam Co. Inc.). All the measurements were carried out at room temperature under ambient conditions.

3. Results and discussion

CBP is a widely used commercial host material for phosphorescent OLEDs due to its bipolar charge-transport property (hole-mobility $\sim10^{-3}$ $cm^2/V\,s$ and electron mobility $\sim10^{-4}$ $cm^2/V\,s$) and high triplet energy level ($T_1=2.56$ eV) [31–33]. Besides, it has demonstrated that high quality film of CBP could be afforded by solution-process [34–36]. Thus, we chose CBP as one of the host materials to fabricate solution-processed red phosphorescent OLEDs. In order to optimize the doping concentration of $Ir(pq)_2(acac)$, the devices with different doping concentrations were fabricated based on the host of CBP. Fig. 2 shows the luminous efficiency–current density and EL spectra of the devices with doping concentrations of 5 wt%, 6 wt%, 7 wt% and 8 wt%. It is found that all of the devices only exhibit a red emission with a peak at 600–604 nm, which is the characteristic of the emission of $Ir(pq)_2(acac)$. The best device performance is obtained when the doping concentration of $Ir(pq)_2(acac)$ is 6 wt%. However, compared with the same state-of-the-art red phosphorescent OLEDs [37], these devices have high turn-on voltages and low efficiencies, for example, the turn-on voltage (1 cd/m^2) and maximum luminous efficiency of the device with 6 wt% $Ir(pq)_2(acac)$ are 6.4 V and 12.9 cd/A respectively. These could be attributed to the large hole-injection barrier and/or unbalanced charge injection/transport.

According to the energy level diagrams in Fig. 1(c), the energy barrier is −0.1 eV for electrons to inject from TPBi to the host of CBP, meaning that the electrons can freely enter the CBP host with no barrier. However, the hole injection in the device would be much harder than electron because of the large hole-injection barrier (0.8 eV) from PEDOT:PSS to CBP. In addition, the highest occupied molecular orbital (HOMO) values of CBP and $Ir(pq)_2(acac)$ are 6.0 eV and 5.2 eV, respectively. Presumably, the $Ir(pq)_2(acac)$ molecules can act as deep traps for holes in the EML, causing an increase in the drive voltage of the device and a decrease in the hole mobility of the EML. In previous work, it has been reported that the hole mobility of CBP strongly decreases when doping with the phosphorescent material of $Ir(ppy)_3$ due to the effect of the hole traps formed by the dopant molecules [31]. Recently, Yun et al. reported that the dominating type of charge carriers in the $Ir(ppy)_3$ doped CBP EML was electrons, and the emission zone was located close to the interface between the EML and the hole transport layer [38]. Here we found that the doping of $Ir(pq)_2(acac)$ into CBP also influenced the hole transport in the solution-processed films. Fig. 3 shows the characteristics of current density in the hole-dominated devices of ITO/PEDOT:PSS(20 nm)/CBP or 6 wt% $Ir(pq)_2(acac)$-doped CBP (70 nm)/NPB(20 nm)/Al (100 nm). It is obvious that the hole current density decreases dramatically when $Ir(pq)_2(acac)$ is introduced in the CBP matrix. The decrease in the hole current density should be attributed to the deep trapping of holes on the $Ir(pq)_2(acac)$ molecules. The characteristic of current density in the electron-dominated device of ITO/TrOH/6 wt% $Ir(pq)_2(acac)$-doped CBP (70 nm)/TPBi (20 nm)/LiF(1 nm)/Al is also shown in Fig. 3. It can be found that the electron current density of the electron-dominated device is much higher than the hole current density of the hole-dominated device for the 6 wt% $Ir(pq)_2(acac)$ doped CBP film. This implies that electrons are the major carriers and holes are the minor carriers in the 6 wt% $Ir(pq)_2(acac)$ doped CBP film. The imbalance of holes and electrons in the device should lead to the triplet quenching, which will reduce the light emission [39].