Highly-efficient tandem organic light-emitting device employing bis-4,6-(3, 5-di-3-pyridylphenyl)-2-methylpyrimi-dine doped with cesium azide in charge generation unit

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ABSTRACT

In this research, we have investigated the charge generation and electron injection processes in charge generation unit (CGU) consisting of CsN_3-doped Bis-4, 6-(3, 5-di-3-pyridylphenyl)-2-methylpyrimi-dine (CsN_3:B_3PYMPM)/1, 4, 5, 8, 9, 11-Hexaazatriphenylene-hexacarbonitrile (HAT-CN). By employing this CGU, a high-efficiency phosphorescent tandem device achieving best efficiencies of 164.3 cd/A, 46.51% and 109.8 lm/W has been realized. Particularly, in addition to the improvement in current efficiency by more than two times, the tandem device has better power efficiency compared to the corresponding single-unit device at the same current density. Simultaneously, an efficient tandem white OLED showing high color stability and warm white emission over a wide range of luminance has been also fabricated.

1. Introduction

Tandem organic light-emitting devices generally comprising two emitting units connected in series via charge generation unit (CGU) have attracted considerable attention because of their unique property of achieving high luminance and current efficiency at low current density [1]. Under an applied electric field, electrons and holes generated within CGU inject into the adjacent electron-transporting layer (ETL) and hole-transporting layer (HTL), respectively, and subsequently recombine with holes from anode side and electrons from cathode side to generate photons in each emitting unit. Naturally, the CGU plays an essential role in realizing high-performance tandem OLEDs.

In recent years, researchers have put extensive efforts on the exploration of high-performance CGU based on the structure of electron injection layer (EIL)/electron acceptor which presents excellent characteristics of superior charge generation capability as well as electron injection property and extremely high optical transparency. The electron acceptor typically includes transition metal oxides (MoO_3, WO_3 and V_2O_5) and 1, 4, 5, 8, 9, 11-Hexaazatriphenylene-hexacarbonitrile (HAT-CN) [2–5]. The EIL in common used comprises ultrathin bilayers of metal compounds and aluminum (LiF/Al and Liq/Al) [5,6] as well as n-doped electron-transporting layer (ETL) in which active metals or alkali metal compounds (Mg, Cs, Li, Yb, Cs_2CO_3, Li_2CO_3, Rb_2CO_3 and CsN_3) [2,7–10] are adopted as n-dopants. Within such type of CGU, charges are generated at the interface between electron acceptor and the adjacent HTL, and the EIL assists the electron injection from electron acceptor into the adjacent ETL. Obviously, EIL is critically important to the effectiveness of CGU although it is not directly involved in the charge generation process.

CsN_3 had been utilized as n-dopant in 4,4,4-tris(N-carbazolyl)triphenylamine (BPhen) for realizing efficient EIL in tandem OLEDs. For example, Jun Yeob Lee had mainly studied the effect of CsN_3 dopant on improving the performance of single-unit phosphorescent green OLED and realized an efficient tandem device utilizing CsN_3-doped BPhen/MoO_3 as CGU simultaneously [9]; Jin-Peng Yang had revealed that the benefit of the CsN_3-doped BPhen to the electron injection in CGU

possessing the structure of CsN_3-doped BPhen/MoO_3 [10]. However, in comparison with BPhen, B_3PYMPM is fit for electron-transporting layer in both green phosphorescent and blue phosphorescent OLEDs resulting from its higher triplet energy level [11]. The lowest unoccupied molecular orbital (LUMO) level of B_3PYMPM is as low as $-3.2eV$, as facilitates the electron injection from cathode [12]. However, the electron conductivity of B_3PYMPM is a few orders of magnitude lower than that of BPhen [13]. The low electron conductivity results in electron accumulation at the B_3PYMPM/cathode contact and finally inhibits the electron injection and transportation. By using CsN_3 as n-dopant in B_3PYMPM, the inherent drawback of low electron conductivity can be overcome successfully. Therefore, in this study, we proposed a novel and highly-efficient CGU comprising CsN_3: B_3PYMPM (15%, 10 nm)/Al (1 nm)/HAT-CN (15 nm), in which CsN_3: B_3PYMPM (15%, 10 nm)/Al (1 nm) and HAT-CN (15 nm) functioned effectively as EIL and electron acceptor, respectively. Holes are generated at the Highest Occupied Molecular Orbital (HOMO) of N, N′-diphenyl-N, N′-bis(1-napthyl)-1,1′-biphenyl-4,4′–diamine (NPB) which is adjacent to HAT-CN, while electrons are generated at the Lowest Unoccupied Molecular Orbital (LUMO) of HAT-CN. Applying this CGU to tandem phosphorescent OLED, the electron injection barrier at HAT-CN/B_3PYMPM contact is nearly eliminated and more than twofold improvement in current efficiency is realized. Particularly, the power efficiency is also improved over a wide range of current density even though the luminance of tandem device is more than two times that of the single unit device at the same current density, as is superior to the performance of most reported tandem devices [14–18]. Simultaneously, we also realized an efficient tandem white OLED possessing high color stability and warm white emission over a wide range of luminance by utilizing this CGU. To our best knowledge, it is the first report on employing CsN_3-doped B_3PYMPM in CGU for highly efficient tandem phosphorescent and white OLEDs.

2. Experimental details

All organic materials used in this paper were commercially purchased from Luminescence Technology Corporation. HAT-CN was adopted as hole-injection layer (HIL) and electron acceptor in CGU; B_3PYMPM and BPhen severed as ETL, NPB and bathocuproine (BCP) were employed as HTL and hole-blocking layer (HBL); 4, 4, 4-tris(*N*-carbazolyl)triphenylamine (TCTA), Tris (8-hydroxy-quinolinato) aluminium (Alq) and N, N ′-dicarbazolyl-3,5-benzene (mCP) were used as host materials, while tris(2-phenylpyridine) iridium (Ir(ppy)₃), (3, -difluoro-2-(2-pyridyl) phenyl-(2-carboxypyridyl) iridium (FIrpic), 5,6,11,12-tetraphenylnaphthacene (Rubrene) and iridium(III)bis(2-methyldibenzo-[f,h]quinoxaline)(acetylacetonate) $[Ir(MDQ)]_2(acac)$ functioned as green, blue, yellow and red dopants in host materials.

OLEDs were fabricated on patterned indium-tin-oxide (ITO)-coated glass substrates by thermal evaporation under the vacuum about $3 \times 10^{-5}Pa$ without breaking the vacuum. Before sent to the vacuum chamber, the ITO substrates were treated with oxygen plasma for 15 min after being subjected to a routine cleaning process [19]. The thickness of different layers and deposition rates of individual materials were monitored *in situ* with calibrated oscillating quartz-crystal sensors. Doping processes were realized by thermal co-evaporation from independent sources in which the evaporation rates of host materials and dopants were controlled independently via two quartz-crystal sensors. The active area defined by the overlap of ITO anode and Al cathode was 3×3 mm².

3. Results and discussion

The molecular structures of all organic materials used in this paper are depicted in Fig. 1a. With the aim of demonstrating how charge generation and electron injection occur in CGU, Devices A-D possessing the basic structure of ITO/green phosphorescent electroluminescent

unit (EL-G)/X/yellow fluorescent electroluminescent unit (EL-Y) have been constructed. EL-G stands for HAT-CN (5 nm)/NPB (65 nm)/Ir (ppy)₃:TCTA (15%, 15 nm)/B_3PYMPM (65 nm), while EL-Y comprises NPB (60 nm)/Rubrene:Alq (5%, 20 nm)/BPhen (60 nm)/LiF (1 nm)/Al. X refers to B_3PYMPM (10 nm), B_3PYMPM (10 nm)/HAT-CN (15 nm), CsN_3:B_3PYMPM (15%, 10 nm)/HAT-CN (15 nm) and CsN_3:B_3PYMPM (15%, 10 nm)/Al (1 nm)/HAT-CN (15 nm) for devices A-D, respectively. Fig. 2a displays the electroluminescent (EL) spectra of stacked devices A-D at a given current density of 5 mA/cm². The spectrum of device A exhibits only one emission peak originating from Ir(ppy)₃, indicating electrons can transport to the emitting layer in EL-G while hole transportation to the emitting layer of EL-Y is inhibited because of the excellent hole-blocking ability of B_3PYMPM [20]. Two primary peaks corresponding to Ir(ppy)₃ and Rubrene are observed in device B, which implies charges are generated after the insertion of HAT-CN between B_3PYMPM and NPB. Since the LUMO of HAT-CN ($-6.0eV$) [21] is quite deeper than the HOMO of NPB ($-5.4eV$) [22], electrons at the filled HOMO states of NPB transfer into the unoccupied LUMO states of HAT-CN readily, leading to the generation of holes and electrons at HOMO of NPB and at LUMO of HAT-CN, respectively. The generated holes transport to the emitting layer of EL-Y, resulting in the emission from Rubrene in device B. However, as shown in Fig. 2b which depicts the current density-luminance (J-L) characteristics of devices A-D, the luminance of device B is almost identical with that of device A, which indicates the generated electrons can hardly transport to the emitting layer of EL-G owing to the huge injection barrier for electron existing at the B_3PYMPM/HAT-CN contact. Similar to device B, device C also has two main peaks from Ir(ppy)₃ and Rubrene. However, device C has higher driving voltage as well as weaker emission intensity from Ir(ppy)₃ and lower luminance at 5 mA/cm² relative to device B, implying the CsN_3:B_3PYMPM layer does not decrease the electron injection barrier at the B_3PYMPM/HAT-CN interface and the number of electrons diffusing to the emitting layer of EL-G unit becomes less due to the introduction of CsN_3 dopant. For device D, the emission intensity from Ir(ppy)₃ as well as luminance and operating voltage at 5 mA/cm² are improved dramatically compared with those of device B and device C, which means the insertion of ultrathin 1 nm Al located between CsN_3:B_3PYMPM and HAT-CN facilitates the electron injection from HAT-CN to B_3PYMPM and the generated electrons can transport to the emitting layer in EL-G much more readily. Schematic of charge generation, injection and transportation processes in CGU is demonstrated in Fig. 1b.

To further investigate the role of ultrathin 1 nm Al on electron injection property in CGU, hole-excluding devices (HEDs) having the structures of ITO/bathocuproine (BCP, 30 nm)/Y/LiF (1 nm)/Al have been fabricated. Y stands for B_3PYMPM (70 nm), B_3PYMPM (55 nm)/HAT-CN (15 nm)/B_3PYMPM (15 nm), B_3PYMPM (45 nm)/CsN_3:B_3PYMPM (15%, 10 nm)/HAT-CN (15 nm)/B3PYMPM (15 nm) and B_3PYMPM (45 nm)/CsN_3:B_3PYMPM (15%, 10 nm)/Al (1 nm)/HAT-CN (15 nm)/B3PYMPM (15 nm) for HEDs. 1–4, respectively. Under forward bias, holes from ITO can be hardly injected into these devices because of a large energy barrier at ITO/BCP interface [23]. Fig. 2c presents the current density-voltage characteristics of HEDs 1–4. HED. 1 using 1 nm of LiF layer as EIL shows obvious current response under forward bias since the electron injection from cathode. When 15 nm HAT-CN is inserted between two B_3PYMPM layers for HED. 2, the current density is negligible because of a huge energy barrier existing at the B_3PYMPM/HAT-CN interface. The current density of HED. 3 is nearly the same as that of HED.2, indicating the electron injection property at the interface is not improved in spite of the introduction of CsN_3 dopant in B_3PYMPM. However, the current density of HED. 4 increases sharply and is even higher than that of HED.1, which illustrates the large injection barrier for electron at the interface is eliminated as a result of inserting 1 nm Al between CsN_3-doped B_3PYMPM and HAT-CN. By using the X-ray photoemission spectroscopy (XPS) measurement, Yi had revealed that CsN_3 would be decomposed into N_2