Synthetic Metals 245 (2018) 111–115

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet

Achieving ultra-high efficiency by tuning hole transport and carrier balance in fluorescent blue organic light-emitting diode with extremely simple structure

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ARTICLE INFO

Keywords:
Organic light-emitting diode
Fluorescent blue
Hole transport
Carrier balance
Triplet-triplet annihilation

ABSTRACT

Ultra-high efficiency in fluorescent blue organic light-emitting diode (OLED) with extremely simple structure is demonstrated by tuning hole transport and carrier balance. Using 2-methyl-9,10-bis(naphthalen-2-yl)anthracene doped with 3 wt% 1-4-di-[4-(*N,N*-diphenyl)amino]styryl-benzene ([MADN: 3 wt%DSA-Ph]) as hole transport and emissive layer, the OLED gives sky-blue emission with 1931 Commission Internationale d'Eclairage color coordinates of (0.159, 0.281), luminous efficiency of 14.7 cd/A, power efficiency of 13.0 lm/W and external quantum efficiency of 10.0%. The efficiencies have been enhanced by 54.7% (11.4%), 49.4% (11.1%) and 38.9% (5.3%), respectively, in comparison with the counterpart having hole transport layer of NPB (MADN). Current versus voltage characteristics and impedance spectroscopy analysis of hole only cells elucidate that [MADN: 3 wt %DSA-Ph] shows reduced hole mobility as a result of trapping or scattering effect of DSA-Ph. Efficient hole injection and appropriate hole transport favorably tune holes entering into the emissive layer and improve carrier balance. Extra-fluorescent emission generated by triplet-triplet annihilation and broad emission zone by integrating hole transport and emission as a single layer are also responsible for ultra-high device efficiency.

1. Introduction

Blue emission is requisite for realizing organic light-emitting diode (OLED) based full color displays and lightings. Carrier balance and low voltage are key issues of achieving superior device performance and accordingly accelerating application. Interface is ubiquitous in multi-layer structured OLED. Generally, interfacial layer in hetero-junction provides an energetic bridge and facilitates carrier injection. Taking hole injection and transport into consideration, hole injection interfacial layer (HIL) sandwiched between indium tin oxide (ITO) anode and hole transport layer (HTL) can effectively soften energy barrier and promotes power efficiency (PE). Organics (F_4-TCNQ [1], *m*-MTDATA [2], PEDOT:PSS [3]), transition metal oxides (MoO_x [4], WO_3 [5], VO_x [6]) and two-dimensional sheets (GO [7], CN_xH_y [8]) are proven to effectively enhancing hole injection. Graded hole injection structure [9] or composite HILs such as GO + MoO_x [10], PEDOT:PSS + MoO_x [11] and GO + MoS_2 [12] are also proposed for developing robust hole injection particularly for deep-blue and near-ultraviolet emitters with deep highest occupied molecular orbital (HOMO) level [3,11].

It should be noted that abundant holes deteriorate carrier balance, since hole transport materials commonly behave superior hole mobility to electron mobility in electron transport layers (ETLs). Controlling holes entering into the emissive layer (EML) plays a crucial role in regulating carrier balance [13–16]. Chen et al. reports composite HTL for reducing hole transport and achieving carrier balance [14]. Hole block layer also slightly impedes hole entering into the EML and improves device performance [16]. It is well acknowledged that trilayer structure of HTL-EML-ETL shows overwhelming superiority over bi-layer structure of EML (Here, EML also functions as HTL)- ETL or HTL-EML (Here, EML also functions as ETL) in tuning carrier balance and thus regulating OLED efficiency. In this study, we propose constructing highly efficient fluorescent blue OLED with simple bilayer structure of EML-ETL, which decreases interface numbers and facilitates high-throughput production. On the other hand, wide emission zone

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https://doi.org/10.1016/j.synthmet.2018.08.016
Received 23 April 2018; Received in revised form 28 July 2018; Accepted 22 August 2018

considerably promotes device performance in fluorescent blue OLEDs. Mixed host or double EMLs are widely accepted to fulfill such a function [17–19]. However, Mixed host or double EMLs obviously complicates device structure. Here, we incorporate hole transport and emission as a single layer also favors broadening emission zone. Typically, we select 2-methyl-9,10-bis(naphthalen-2-yl)anthracene doped with 3 wt% 1-4-di-[4-(N,*N*-diphenyl)amino]styryl-benzene ([MADN: 3 wt%DSA-Ph]) as hole transport and fluorescent blue emitter, rather than using highly efficient phosphorescent EML [20] and currently used thermally activated delayed blue fluorescence [21] in viewing of their efficiency roll-off and unsatisfactory device durability. Our experiments show maximum luminous efficiency (LE) of 14.7 cd/A, PE of 13.0 lm/W and external quantum efficiency (EQE) of 10.0%, which makes a step forward for fluorescent blue OLED.

2. Experimental

Glass coated with ITO film (sheet resistance of ~15 Ω/□) was used as anode of OLEDs. After routine chemical cleaning and de-ionized water spraying, ITO was further treated with UV-O_3 for 10 min. PEDOT:PSS HIL was spin-coated onto ITO at 4000 r.p.m. for 60 s and annealed at 120 °C for 20 min in atmosphere. Subsequent organic layers and Al cathode were thermally deposited under a base vacuum of ~10^{-7} Torr. Three OLEDs with different hole transport materials of N,N'-bis(naphthalen-1-yl)-*N*,*N*'-bis(phenyl)-benzidine (NPB), MADN and [MADN:3 wt%DSA-Ph] were constructed as follows.

Device N: ITO/PEDOT:PSS/ NPB (35 nm)/ [MADN: 3 wt%DSA-Ph] (45 nm)/ BPhen (30 nm)/LiF (0.7 nm)/Al (100 nm).

Device M: ITO/ PEDOT:PSS/ MADN (35 nm)/ [MADN: 3 wt%DSA-Ph] (45 nm)/ BPhen/.

Device MD: ITO/ PEDOT:PSS/ [MADN: 3 wt%DSA-Ph] (80 nm)/ BPhen/.

[MADN: 3 wt%DSA-Ph] was functioned as hole transport and emission in Device MD. 4,7-diphenyl-1,10-phenanthroline (BPhen) and LiF were used as ETL and electron injection layer, respectively. The deposition rate of organics was 1–2 Å/s, while that of Al was 10–20 Å/s. Schematic structure of devices and molecular structures of some organic materials were shown in Fig. 1.

Current density-voltage-luminance (*J-V-L*) characteristics were measured using Keithley 2636B Source Meter and Konica Minolta LS-150 Luminance Meter. Electroluminescence (EL) spectra and 1931 Commission Internationale d'Eclairage (CIE) color coordinates were measured by Ocean Optics Maya2000pro Spectra Scan. Impedance spectroscopy was measured with Agilent 4294 A Precision Impedance Analyzer. All measurements were carried out at room temperature under ambient conditions.

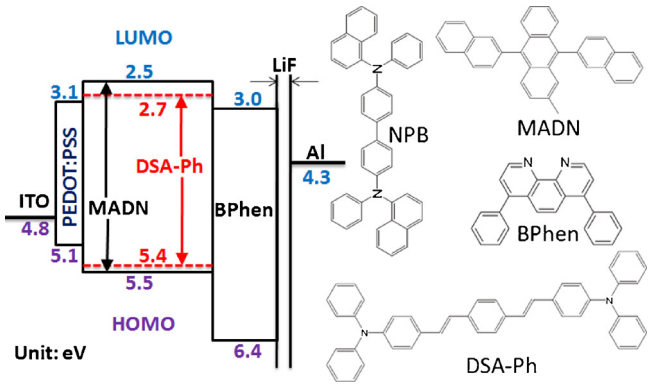

Fig. 1. Schematic device structure and energy alignment of blue OLEDs. The molecular structures of NPB, MADN, DSA-Ph and BPhen are also incorporated in the figure.

3. Results and discussion

Fig. 2(a)–(e) delineate the dependence of *J-V-L* characteristics. Table 1 summarizes some key parameters and comparison with other documented [MADN:DSA-Ph]-based blue OLEDs. It is observed that highly efficient blue OLED is realized by introducing [MADN: 3 wt% DSA-Ph] as HTL. Maximum LE of 14.7 cd/A, PE of 13.0 lm/W and EQE of 10.0% are achieved in Device MD, which has been enhanced by 54.7% (11.4%), 49.4% (11.1%) and 38.9% (5.3%), respectively, in comparison with Device N (Device M) having HTL of NPB (MADN). Device MD also shows high luminance of 33,236 cd/m^2 (at 8 V), satisfactory LE of 14.6 cd/A at L = 10,000 cd/m^2, and low efficiency roll-off at high luminance. The device performance are superior to those with composite HTL [13,14] or mixed-host multi-layer emitter [17], as shown in Table 1. The superior performance is explicitly benefited from favorable hole injection and transport. PEDOT:PSS as an efficient HIL contributes to low driving voltage and high PE. While appropriate hole transport of [MADN:3 wt%DSA-Ph] tunes holes entering into the EML. In such a case, extremely improved carrier balance is obtained, resulting in superior LE and EQE. On the other hand, fluorescent emitters exceed theoretical efficiency limit (internal QE of 25% and EQE of ~5%) is currently observed as a result of triplet-triplet annihilation (TTA) [22–24]. Carrier recombination generates triplet excited molecules (excitons) which resulting in annihilative reaction with other triplet excited molecules and forming singlet excited molecules. The radiative relaxation of the singlet excitons produce extra-fluorescent emission and shed light on the enhancement of quantum efficiency [24,25]. The TTA process may be facilitated particularly under large current density conditions, which also accounts for low efficiency roll-off. In this study, the lowest unoccupied molecular orbital (LUMO) level (2.5 eV) of MADN is shallower than that (2.7 eV) of DSA-Ph, while the HOMO level (5.5 eV) of MADN is deeper than DSA-Ph (5.4 eV), as shown in Fig. 1. DSA-Ph acts as a trap to both electrons and holes. The release and recombination of trapped electrons and holes produce extra-fluorescent emission (or calls delayed EL) [24,26]. In addition, broadened recombination/emission zone, generated by integrating HTL and EML as a single layer, also favors efficiency promotion.

The EL spectra of studied blue OLEDs are depicted in Fig. 2(f). It can be seen that three devices show sky-blue emission with EL peak of ~466 nm and shoulder of ~496 nm ascribed to the dopant emission of DSA-Ph. In-depth investigation shows that an inflexion of ~436 nm (resulted from MADN emission, as marked with arrow) is disappeared and the shoulder emission of ~496 nm is strengthened in Devices M and MD, manifesting a complete energy transfer from the host of MADN to the guest of DSA-Ph. It also suggests that improved carrier balance provides more opportunity for hole-electron recombination in the EML and boosts OLED performance. The CIE color coordinates accordingly shift from (0.154, 0.236) of Device N to (0.156, 0.260) of Device M and (0.159, 0.281) of Device MD.

In order to compare the hole transport capacity, current-voltage (*I-V*) characteristics and impedance spectroscopy analysis are performed by constructing hole-only cells (HOCs) composed of different hole transport materials of NPB, MADN and [MADN:3 wt%DSA-Ph].

Cell H1: ITO/ PEDOT:PSS/NPB (90 nm)/ Al (100 nm)

Cell H2: ITO/ PEDOT:PSS/MADN (60 nm)/ NPB (30 nm)/Al

Cell H3: ITO/ PEDOT:PSS/ [MADN: 3 wt%DSA-Ph] (60 nm) /NPB (30 nm)/Al

Here, 30-nm-thick NPB in Cells H2 and H3 is functioned as electron block layer (EBL). As illustrated in Fig. 3(a), at the same voltage, Cell H1 (NPB as HTL) shows the highest current, followed by Cell H2 (MADN as HTL) and Cell H3 ([MADN:3 wt%DSA-Ph] as HTL), indicating the lowest hole mobility in [MADN: 3 wt%DSA-Ph]. Fig. 3(b) and (c) show impedance (*Z-V*) and phase (*φ-V*) as a function of voltage transition curves. It is observed that all these cells behave insulating state with high impedance of about 10^5 Ω and phase of -90° at low voltage (< 1.3 V). With increasing voltage, the HOCs show semi-