High efficiency non-doped white organic light-emitting diodes based on blue exciplex emission

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ARTICLE INFO

ABSTRACT

High efficiency non-doped white organic light-emitting diodes (WOLEDs) have been realized by inserting an ultrathin yellow fluorescent emitter into a bilayer blue exciplex system. The white emission comes from the incomplete energy transfer from the blue exciplex to the yellow fluorescent emitter. By tuning the location of the ultrathin fluorescent emitter layer in the device, excitons directly formed in the yellow fluorophore can be neglected and the Dexter energy transfer from triplet state of exciplex to yellow fluorophore is also suppressed, contributing to the high efficiency. The WOLED achieves a maximum current efficiency of 27.2 cd/A, with Commission Internationale de l'Eclairage (CIE) coordinates of (0.35 ± 0.02, 0.38 ± 0.02).

1. Introduction

Organic light-emitting diodes (OLEDs) have been considered as the next generation display and lighting technology owing to their attractive properties, such as high luminous efficiency, ultrathin structure, and flexibility [1–3]. Specially, white organic light-emitting diodes (WOLEDs) are attracting much more attention for the application in solid-state lighting sources and full-color displays [4,5]. In general, WOLEDs consist of three primary colors (red, green and blue) or two complementary colors (blue and yellow). Traditional fluorescent emitters can only achieve a maximum internal quantum efficiency (IQE) of 25% because only a quarter of total excitons formed by recombination of injected holes and electrons could be utilized for radiation while the rest triplet excitons decay non-radiatively [6]. Phosphorescent emitters can harvest both singlets and triplets, hence they are often employed in WOLEDs to obtain high efficiency, such as all-phosphorescence and fluorescence-phosphorescence hybrid WOLEDs [7,8]. However, phosphorescent emitters typically contain heavy metal atoms, which have disadvantages of high cost, limited resources, and environment pollution.

Recently, thermally activated delayed fluorescence (TADF) materials have drawn enormous research interests because they can achieve a maximum IQE of 100% without heavy atoms. TADF materials can up-convert triplets to emissive singlets via reverse intersystem-crossing (RISC) because of their small singlet-triplet energy gap [9,10]. Commonly, electron donor and acceptor components are both present in the organic molecules with TADF characteristics [11], which has strict

requirements on the molecular structures. An alternative way to realize TADF is combining individual electron donor and acceptor materials to form exciplex. Hence, the simplicity of acquiring exciplex gives rise to upsurge of researches in this field. Adachi et al. demonstrated exciplex emission with a maximum external quantum efficiency (EQE) and power efficiency (PE) of 10% and 47 lm/W using 4,4′,4″-tris[3-methylphenyl(phenyl)amino]-triphenylamine (*m*-MTADA) as the electron donor material and 2,8-bis(diphenylphosphoryl)dibenzo-[*b*,*d*]thiophene (PPT) as the electron acceptor material [12]. Hung et al. reported an all-exciplex-based tandem WOLED by connecting a blue exciplex emission unit of 1,3-bis(*N*-carbazolyl)benzene (mCP):((1,3,5-triazine-2,4,6-triyl)tris(benzene-3,1-diyl))tris(diphenylphosphine oxide) (PO-T2T) and a yellow exciplex emission unit of 9,9-di[4-(di-*p*-tolyl)ami-nophenyl]fluorine (DTAF):PO-T2T [13]. Zhang at al. obtained exciplex-fluorescence and exciplex-phosphorescence hybrid WOLEDs by doping orange dopant into a blue exciplex host [14]. In these exciplex-based devices, efficient exciplex emission is accomplished by co-depositing electron donor and acceptor materials. However, the co-depositing process is time consuming and not easy to control. Recently, Su et al. demonstrated highly efficient non-doped devices generating green and yellow exciplex emission by simply stacking a p-type hole transport layer and an n-type electron transport layer [15]. However, few works are conducted into efficient non-doped blue exciplex and its utilization in WOLEDs.

Herein, we realized a simple non-doped fluorescent WOLED by introducing an ultrathin yellow fluorescent emission layer into a blue bilayer exciplex system. The blue exciplex is formed by the charge

transfer between an electron donor material 4,4′-bis(9-carbazolyl)-2,2′-dimethylbiphenyl (CDBP) and an electron acceptor material PO-T2T. A fluorescent emitter 2,8-di(*t*-butyl)-5,11-di[4(*t*-butyl) phenyl]-6,12-diphenylnaphthacene (tetra(*t*-butyl)rubrene) (TBRb) is employed as the ultrathin non-doped yellow emission layer. The white emission originates from the incomplete energy transfer from the blue exciplex formed at CDBP/PO-T2T bilayer interface to the yellow fluorescent emitter TBRb layer. The device is simple to fabricate and shows a maximum current efficiency (CE) of 27.2 cd/A. It is suggested that the location of ultrathin TBRb layer plays a key role on the performance of WOLEDs.

2. Experiment

All OLEDs were fabricated on glass substrates with patterned indium tin oxide (ITO) as the anode. The substrates were cleaned by ultrasonification in detergent, deionized water, acetone and isopropyl alcohol for 15 min each and then dried by nitrogen gas flow. All materials were thermally evaporated at a base pressure of 5×10^{-6} Torr, and the thickness of each layer were measured by a quartz crystal. The current density-voltage-luminance characteristics of devices and color coordinates were measured by a computer-controlled system with a Keithley 237 sourcemeter and a Topcon BM-7A Luminance Colorimeter. The electroluminescence (EL) spectra were recorded by Ocean Optics QE65 Pro spectrometer. The photoluminescence (PL) spectra were acquired by Shimadzu RF-5301PC spectrofluorophotometer. All measurements were carried out under ambient atmosphere immediately after fabrication.

3. Result and discussion

Fig. 1 shows the molecular structures and the PL spectra of CDBP, PO-T2T, CDBP:PO-T2T (1:1), and CDBP/PO-T2T bilayer films. The PL of CDBP:PO-T2T mixed film shows a significant red-shifted peak at 480 nm compared to the neat CDBP and PO-T2T films, with a small short wavelength peak at around 360 nm. Considering the very weak PL emission of PO-T2T, the short wavelength emission at 360 nm could be assigned to CDBP, which has an emission peak at 361 nm. The appearance of this short wavelength emission may be due to the fact that not all of the CDBP molecules form exciplex with PO-T2T under excitation. The energy of the emission at 480 nm (2.58 eV) is close to the energy gap (2.61 eV) between the highest occupied molecular orbital (HOMO) of CDBP (5.83 eV) and the lowest unoccupied molecular orbital (LUMO) of PO-T2T (3.22 eV) [16], indicating that the emission at 480 nm originates from the exciplex excited state formed between CDBP and PO-T2T. The PL spectrum of CDBP/PO-T2T excited from CDBP side has the same peak of 480 nm compared to that of the CDBP:PO-T2T mixed film, which suggests that exciplex is also formed at the CDBP/PO-T2T interface. However, the emission peak at 360 nm is

much stronger, proving that the exciplex is only formed at CDBP/PO-T2T interface, while more individual CDBP molecules are excited to emit light.

Based on the PL spectra, a simple non-doped bilayer blue-exciplex device is designed as follows: ITO/MoO$_3$ (1 nm)/1,1-bis[4-[*N*,*N*-di (*p*tolyl)-amino]phenyl]cyclohexane (TAPC) (30 nm)/CDBP (20 nm)/PO-T2T (10 nm)/4,7-diphenyl-1,10-phenanthroline (Bphen) (45 nm)/LiF (1 nm)/Al, defined as device B. In this device, MoO$_3$ is used as hole injection layer. TAPC and Bphen serve as hole transport layer and electron transport layer, respectively. CDBP and PO-T2T can form exciplex and transport charge carriers as well. Under an applied electric field, holes and electrons are injected from the electrodes and transported to CDBP/PO-T2T interface. Due to the large energy barrier at the CDBP/PO-T2T interface, namely 1.15 eV for holes and 0.84 eV for electrons (Inset of Fig. 2(a)), it is difficult for carriers to cross over the interface. Hence, holes and electrons would accumulate and form exciplex at the interface. As shown in Fig. 2(a), the device exhibits a maximum CE and EQE of 18.9 cd/A and 9.6%, respectively, much higher than the theoretical limit of conventional fluorescent devices, demonstrating the TADF characteristic of exciplex [18]. Fig. 2(b) depicts that the EL spectrum of the device shows a blue emission with peak at 490 nm, which is slightly red-shifted compared to its corresponding PL spectrum mentioned above. This could be caused by the different working mechanisms between the EL and PL processes [17].

To obtain white light on the basis of the blue exciplex emission formed by CDBP and PO-T2T, a fluorescent material of TBRb is used for generating the complementary yellow color. Fig. 3(a) shows that the TBRb has absorption at wavelengths between 450 and 550 nm. The overlap between the EL of blue exciplex and absorption of TBRb ensures efficient energy transfer from exciplex to TBRb [19]. To investigate the energy transfer process in the devices, the ultrathin TBRb layer is inserted into CDBP layer at different positions, and the structure of the devices is as follows: ITO/MoO$_3$ (1 nm)/TAPC (30 nm)/CDBP (20-X nm)/TBRb (0.3 nm)/CDBP (X nm)/PO-T2T (10 nm)/Bphen (45 nm)/LiF (1 nm)/Al, where X is 0, 1, 2, 3, 5 and the devices are defined as W11, W12, W13, W14, and W15, respectively.

As seen from the EL spectra depicted in Fig. 3(b), device W11 with TBRb at the CDBP/PO-T2T interface exhibits nearly pure yellow without any blue emission. When the distance between the inserted TBRb layer and CDBP/PO-T2T interface increases, as for device W12, W13 and W14, the blue emission is getting stronger gradually, which is ascribed to the suppressed energy transfer from the exciplex to TBRb.

Since the photoluminescence quantum yield (PLQY) of the TBRb (0.9) is higher than the exciplex formed between CDBP and PO-T2T (0.51) [18,20], EQE will be higher if the energy transfer occurs from the singlets of exciplex to TBRb. However, as depicted in Fig. 4(a), the maximum EQE of all devices from W11 to W15 are lower than that of device B. A possible working mechanism of these exciplex-based WOLEDs is proposed in Fig. 5. Due to the large barrier between CDBP and
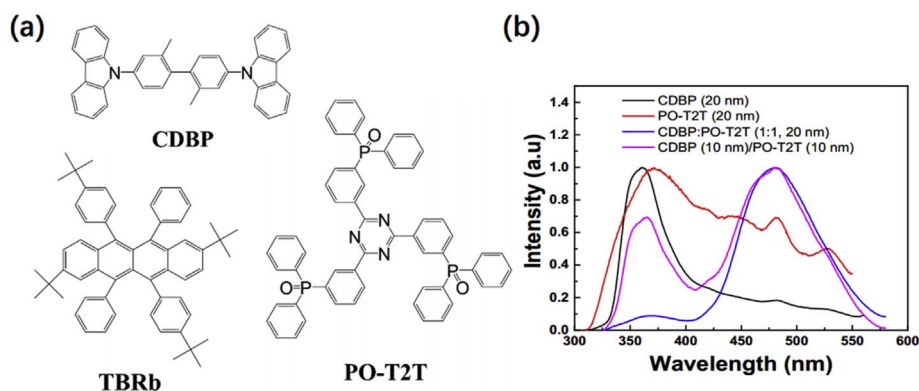

Fig. 1. (a) Molecular structures of CDBP, PO-T2T, TBRb. (b) PL spectra of CDBP, PO-T2T, CDBP:PO-T2T (1:1) mixed film, and CDBP/PO-T2T bilayer film.