Synthetic Metals 220 (2016) 573–577

Contents lists available at ScienceDirect

Synthetic Metals

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

Triplet emitter doped exciton harvesting layer for improved efficiency and long lifetime in blue phosphorescent organic light-emitting diodes

Jeong Min Choi, Jun Yeob Lee*

School of Chemical Engineering, Sungkyunkwan University, 2066, Seobu-ro, Jangan-gu, Suwon, Gyeonggi, 440-746, Korea

ARTICLE INFO

Article history:
Received 16 June 2016
Received in revised form 18 July 2016
Accepted 28 July 2016
Available online 4 August 2016

Keywords:
Efficiency
Lifetime
Exciton harvesting
Exciton blocking layer
Blue device

ABSTRACT

Efficiency and lifetime improvement of blue phosphorescent organic light-emitting diodes (PHOLEDs) was achieved by introducing a triplet emitter doped exciton harvesting layer. A green triplet emitter doped electron transport layer was the exciton harvesting layer of the blue PHOLEDs, which doubled the lifetime and enhanced the efficiency of the blue PHOLEDs compared with a common electron transport layer. Blocking of triplet exciton quenching of the blue triplet emitter by the exciton harvesting layer was proposed as the main mechanism of improved efficiency and lifetime.

1. Introduction

Lifetime is the most serious problem of organic light-emitting diodes (OLEDs) due to intrinsic instability of organic materials. In particular, the lifetime of blue OLEDs is shorter than that of red and green OLEDs, and is the first priority to improve in the development of long living OLEDs.

Although the lifetime of both fluorescent and phosphorescent blue OLEDs is an issue, the relatively short lifetime of the blue phosphorescent OLEDs (PhOLEDs) is even more serious than that of the blue fluorescent OLEDs [1–9] . Several factors can be listed as the lifetime shortening parameters of the blue PhOLEDs, but one of the most critical factors is triplet exciton quenching of the blue triplet emitters by charge transport materials [7,9–16]. Exciton diffusion length of blue triplet emitters can be as long as 100 nm, which requires high triplet energy charge transport layers with a triplet energy higher than 2.7 eV as the triplet energy of the blue triplet emitters is above 2.6 eV. However, only a few hole or electron transport materials were successful as the high triplet energy and stable charge transport materials [9,12,15]. In the case of the hole transport materials, 9,9-dimethyl-10-(9-phenyl-9H-carbazol-3-yl)-9,10-dihydroacridine (PCZAC) and 1,3-bis(9,9-dimethylacridin-10(9H)-yl)benzene (mAP), could perform as the stable high triplet energy charge transport materials [9,16]. In the case of the electron transport materials, only 3,3-di(9H-carbazol-9-yl)biphenyl (mCBP) was known as the high triplet energy electron transport material for the blue PHOLEDs because no stable electron transport material for blue PHOLEDs was developed [7,8]. One difficulty of developing the stable electron transport materials for blue PhOLEDs is the lack of stable electron deficient moieties with high triplet energy. Only limited number of electron transport units are available to block triplet exciton quenching. Therefore, it would be better to find a way of harvesting the triplet emission during driving rather than developing the high triplet energy electron transport materials.

In this work, lifetime and efficiency improvement of blue PhOLEDs using a green triplet emitter doped emitting layer as the triplet harvesting layer was investigated. In comparison with a common electron transport layer, the green emitter doped emitting layer doubled the lifetime of the blue PhOLEDs. An investigation of the device operation process proposed that exciton harvesting green emitting layer is a main contributor of the long lifetime and improved quantum efficiency (QE).

2. Experimental

Lifetime of the blue PhOLEDs was tested using the blue devices with a basic device stacking sequence of *N,N′*-diphenyl-*N,N′*-bis-[4-(phenyl-m-tolyl-amino)-phenyl]-biphenyl-4,4′-diamine (DNTPD), *N,N,N′N′*-tetra[(1,1′-biphenyl)-4-yl]-(1,1′-biphenyl)-4,4′-diamine (BPBPA), tris[1-(2,4-diisopropyldibenzo[b,d]furan-3-yl)-2-phenylimidazole] iridium(III) ($Ir(dbi)_3$) doped mCBP, 2-[4-(9,10-Di-naphthalen-2-yl-anthracene-2-yl)-phenyl]-1-phenyl-1H-

* Corresponding author.
E-mail address: leej17@skku.edu (J.Y. Lee).

http://dx.doi.org/10.1016/j.synthmet.2016.07.033
0379-6779/

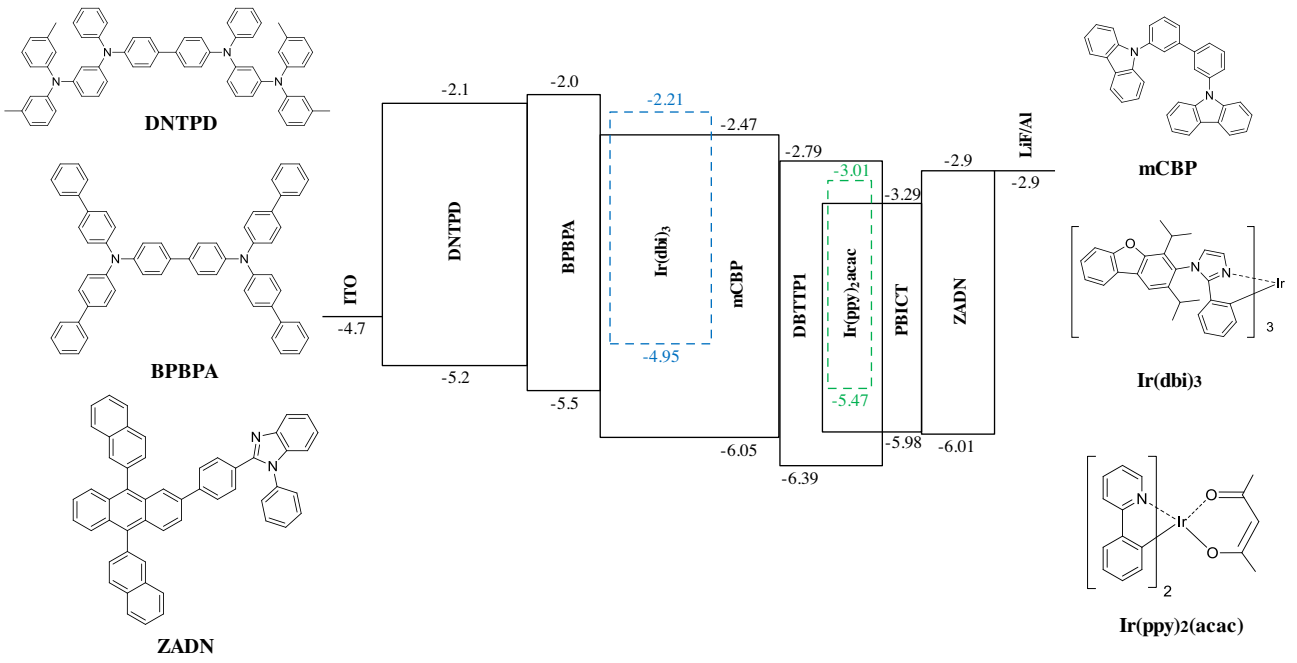

Fig. 1. Chemical structure of materials and device structure.

benzimidazole (ZADN), LiF, and Al on 120 nm thick indium tin oxide substrates. Thickness of each layer was as follows.

ITO/DNTPD (60 nm)/BPBPA (30 nm)/mCBP:Ir(dbi)$_3$ (30 nm)/ZADN (35 nm)/LiF (1 nm)/Al (200 nm). Ir(dbi)$_3$ as dopant was doped in the mCBP at a doping concentration of 10%.

A control device had no triplet harvesting layer between mCBP:Ir(dbi)$_3$ (30 nm) and ZADN, but the triplet harvesting device had an extra triplet exciton harvesting electron transport layer made up of 5 nm thick iridium (III) bis(2-phenylpyridinato-N,C2′)acetylacetonate (Ir(ppy)$_2$(acac)) doped 4-(3-(triphenylen-2-yl)phenyl) dibenzo[*b,d*]thiophene (DBTTP1) [17]: 2-phenyl-4,6-bis(12-phenylindolo[2,3-*a*]carbazole-11-yl)-1,3,5-triazine (PBICT) [18] green emitting layer. Ir(ppy)$_2$acac was doped in PBICT:DBTTP1 exciton harvesting layer at a doping concentration of 10%. The DNTPD is hole injection layer(HIL), BPBPA is hole transport layer(HTL), and mCBP is host, Ir(dbi)$_3$ is dopant, DBTTP1 and PBICT are triplet harvesting hosts, Ir(ppy)$_2$(acac) is triplet emitter, ZADN is electron transport layer. Schematic diagram showing the device structure and molecular structure of organic materials is in Fig. 1.

Lifetime evaluation method of the blue PhOLEDs was fixed current driving at the same initial luminance of 1000 cd/m^2. Electroluminescence (EL) spectra were also traced before and after lifetime evaluation using CS 1000 spectroradiometer.

3. Results and discussion

Stability of the blue PhOLEDs evaluated by luminance decay according to device operation time at a fixed current density is correlated with efficiency reduction events which occur in the device. The efficiency degradation processes include triplet exciton quenching of triplet emitters by charge transport materials. Therefore, a device structure reducing the triplet exciton quenching by electron transport layers can elongate the lifetime of the blue PhOLEDs.

A traditional way of avoiding the triplet exciton quenching was to insert a high triplet energy electron transport layer between the blue emitting layer and an electron transport layer. However, the instability of the high triplet energy electron transport material motivated us to come up with a new way of harvesting triplet excitons of blue triplet emitters. As the efficiency drop of the blue device is caused by triplet exciton quenching by the electron transport layer due to emission zone shift to the electron transport layer side during driving, the lifetime might be increased by making an energy transfer channel in the electron transport layer. The energy transfer process may retard efficiency drop and stabilize the blue PhOLEDs during long-term driving of the devices. The energy transfer channel can be generated using a green triplet emitter doped emitting layer as a triplet exciton harvesting layer between the blue emitting layer and an electron transport layer. The green triplet emitter in the triplet exciton harvesting layer can suppress exciton quenching by electron transport layer through triplet exciton harvesting in the green triplet emitter by energy transfer process. Without the green emitter doped layer, the blue excitons would be quenched by the electron transport layer, decreasing the efficiency of the blue devices. Basic concept of the triplet exciton harvesting electron transport layer for extended lifetime is depicted in Fig. 2.

The effect of the Ir(ppy)$_2$(acac) doped exciton harvesting layer on the current density and luminance characteristics of the blue PhOLEDs is shown in Fig. 3. The Ir(ppy)$_2$(acac) doped exciton harvesting layer reduced current density of the blue PhOLEDs because of relatively poor electron transport character of the Ir(ppy)$_2$(acac) doped DBTTP1:PBICT layer. However, the luminance was rather increased because of efficient exciton formation in the emitting layer as presented in the QE data.

The QE plot according to luminance of the blue PhOLEDs in Fig. 4 described more than 20% improvement of the QE by the introduction of the Ir(ppy)$_2$(acac) doped electron transport layer. Maximum QE and QE at 1000 cd/m^2 were 11.2/8.8% and 9.2/6.9% in the blue PhOLEDs with and without the Ir(ppy)$_2$(acac) doped exciton harvesting layer. The consistent increase of the QE of the blue PhOLEDs suggests that excitons are efficiently generated or converted into photons. In our previous work, the emission zone of the mCBP:Ir(dbi)$_3$ emitting layer is localized on the hole transport layer side by shallow highest occupied molecular orbital (HOMO) induced hole trapping by Ir(dbi)$_3$ [19]. However, triplet exciton