Thin Solid Films 518 (2010) 7119–7123

Contents lists available at ScienceDirect

Thin Solid Films

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

Study on energy relation between blue and red emissive layer of organic light-emitting diodes by inserting spacer layer

Xiaobo Zhang [a,b,*], Fuxiang Wei [b], Xiang Liu [b], Wenqing Zhu [b], Xueyin Jiang [b], Zhilin Zhang [b]

[a] *School of Physics and Electronic Information, Huaibei Normal University, Dongshan Road 100, Huaibei 235000, Anhui Province, People's Republic of China*
[b] *Materials Science and Engineering School, Shanghai University, Chengzhong Road 39, Jiading District 201800, Shanghai, People's Republic of China*

ARTICLE INFO

Article history:
Received 19 February 2009
Received in revised form 29 June 2010
Accepted 5 July 2010
Available online 29 July 2010

Keywords:
Energy transfer
Emissive layer
Spacer
Organic light-emitting diodes (OLEDs)

ABSTRACT

In this paper, energy relation between blue emissive layer (blue-EML) and red emissive layer (red-EML) in organic light-emitting diodes based on blue-emitting and red-emitting phosphorescent dopants, bis(3,5-difluoro-2-(2-pyridyl)phenyl-(2-carboxypyridyl) iridium III (Firpic) and bis(2-(2′-benzo[4,5-α]thienyl) pyridinato-N,C3′)iridium(acetylacetonate) ($Btp_2Ir(acac)$), was studied. Two phosphorescent dopants, Firpic and $Btp_2Ir(acac)$, were co-doped in the single emissive layer, and the results exhibit complete energy transfer from Firpic to $Btp_2Ir(acac)$. Then, Firpic and $Btp_2Ir(acac)$ were doped into blue-EML and red-EML, separately. By inserting 4,4′-bis(N-carbazolyl)biphenyl (CBP) spacer between blue- and red-EML, energy relation between blue- and red-EML was researched. The results of this work reveal that, CBP spacer may strengthen energy transfer between blue- and red-EML. The reason is that CBP triplets at blue-/red-EML interface can transfer their energies to both CBP molecules of red-EML and Firpic molecules of blue-EML in spacer-without devices, while CBP triplets in the spacer can transfer their energies only to CBP molecules of red-EML. Therefore, energy flow from blue- to red-EML is strengthened because of the avoidance of energy transfer from CBP triplets in the spacer to Firpic molecules of blue-EML, leading to the relative enhancement of red emission in CBP-spacer devices.

1. Introduction

White organic light-emitting devices (WOLEDs) are currently attracting considerable attention for potential applications in making full-color display as well as in next-generation light source [1–5]. Highly bright and efficient white emission is often obtained by hybrid two or three complementary color light [6–10], e.g., blue combined with red emission, blue combined with green emission, or blue combined with red and green emission. To realize these different color-light emissions, the emissive layer (EML) of WOLEDs usually comprises blue-emissive layer (blue-EML), green-emissive layer (green-EML) or/and red-emissive layer (red-EML). The blue emission often origins from the fluorescent or phosphorescent dye doped in blue-EML, and the green and red emissions usually come from the phosphorescent emitters doped in green-EML and red-EML for the purpose of utilizing the 100% internal quantum efficiency of phosphors. However, this complementary color system introduces possibly energy transfer from blue-EML to green- and red-EML, because high energy excitons of either dopant or host in blue-EML can transfer energy to low energy green and red phosphors via Förster or Dexter process, which leads directly to the relative enhancement of green and red emission and the instability of color purity in WOLEDs. In order to solve this problem, a spacer layer is inserted in the midst of the emissive layer to separate blue-EML from green- and red-EML in space. The spacer layer, with the thickness of 1 nm up to ~10 nm, has been proved to prevent availably energy transfer between blue-EML and green- and red-EML. Sun et al. [11] demonstrated that, placing an undoped host spacer between the blue fluorophore and the phosphors prevents direct energy transfer from the blue dopant to the green and red phosphors. Chen et al. [12] also showed that by introducing a 2 nm bipolar transport 4,4′-bis(N-carbazolyl)biphenyl (CBP) layer between the fluorescent and phosphorescent emission layers, the Dexter energy transfer between the two emitters is eliminated.

In this paper, two phosphorescent dyes, blue-emitting bis(3,5-difluoro-2-(2-pyridyl)phenyl-(2-carboxypyridyl) iridium III (Firpic) and red-emitting bis(2-(2′-benzo[4,5-α]thienyl)pyridinato-N,C3′)iridium(acetylacetonate) ($Btp_2Ir(acac)$), were respectively doped in blue- and red-EML and white electrophosphorescent organic light-emitting devices were made. A thin spacer film was inserted between blue-EML and red-EML and the red-shift in color coordinates of spectra was observed. And the energy relation between blue- and red-EML is discussed.

2. Experimental details

Organic light-emitting devices used in this work were constructed with the structure of: indium tin oxides (ITO)/NPB(30 nm)/

---

* Corresponding author: Fax: +86 5613803394.
E-mail address: zhangxiaobo@chnu.edu.cn (X. Zhang).

0040-6090/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2010.07.012

EML(60 nm)/BAlq(5 nm)/Alq(10 nm)/LiF(1 nm)/Al. Here, N,N′-bis (1-naphthyl)-N,N′-diphenyl-1.1′-bipheny1-4-4′-diamine (NPB) is the hole transporting layer; (1,1′-biphenyl-4′-oxy)bis(8-hydroxy-2-methylquinolinato)-aluminum (BAlq) is the hole and exciton block layer; tris(8-quinolinolato)aluminum complex (Alq) is the electron transporting layer; and LiF/Al is lithium fluoride/aluminum composite cathode. The EML layer of devices used in this work includes two structures: single-EML and double-EML (blue-EML/ with or without spacer/red-EML). The total thickness of EML in all devices is kept at 60 nm, and the blue and red phosphorescent dopants, Firpic and $Btp_2Ir(acac)$, are doped into host at a fixed concentration of 6% and 8% relative to the mass of the host, respectively. The molecular structure and device configuration used in this study are shown in Fig. 1.

The devices were fabricated as follows [13–15]: ITO glasses (sheet resistance: 20 Ω/square) were cleaned in a detergent solution and deionized water by sonication, successively, followed by drying up and UV-ozone treatment. Then, the organic layers and the composite cathode LiF/Al were sequentially deposited by conventional vacuum vapor deposition in the same chamber without breaking the vacuum. The deposition rate of NPB, BAlq, Alq and CBP spacer was controlled at 0.2 nm/s and that of LiF and Al 0.1 nm/s and 1 nm/s, respectively. For the deposition of the EML layer, a certain amount of host and dopant materials was weighed according to their mass ratio and ultrasonic dispersed in the chloroform or acetonitrile solution. After drying up the solvent with an infrared lamp, the uniform mixture of host and dopant remained. The obtained uniform mixture of host and dopant was then delivered into a molybdenum boat and evaporated with the deposition rate of 0.6–0.8 nm/s. The deposition thicknesses of the layers were controlled by a quartz crystal monitor. The pressure of the chamber was kept at 8×10^{-4} Pa. The active area of the electroluminescence device, defined by the overlap of ITO anode and Al cathode, was 5×5 mm^2.

The electroluminescent (EL) spectrum and the Commission Internationale de I'Eclairage (CIE) coordinates were measured by Pr650 Spectroscanner, the luminance–current–voltage characteristics were measured by Keithley 2400 Source Meter. All measurements are conducted at room temperature.

3. Results and discussion

3.1. Single-EML devices

The structure of single-EML devices is ITO/NPB(30 nm)/single-EML(60 nm)/BAlq(5 nm)/Alq(10 nm)/LiF(1 nm)/Al. Here, single-EML

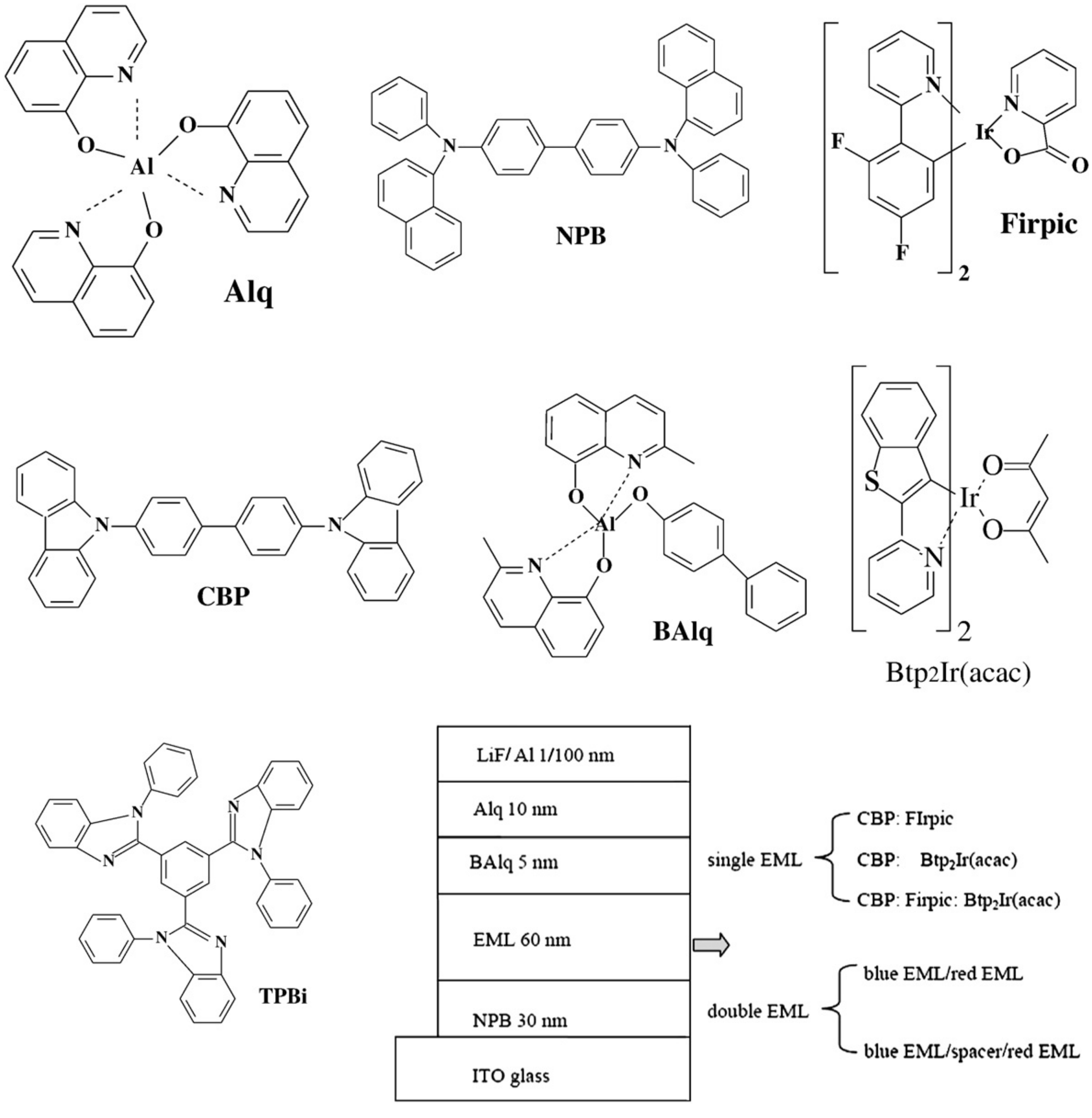

Fig. 1. Molecular structures of the organic materials and device configuration.