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White organic light-emitting diodes based on blue fluorescent bis(2-(2-hydroxyphenyl)benzoxazolate)zinc [Zn(hpb)$_2$] doped with DCM dye

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ABSTRACT

Bright white organic light-emitting diodes (WOLEDs) with single active layer has been demonstrated from blue emitting zinc complex bis(2-(2-hydroxyphenyl)benzoxazolate)zinc [Zn(hpb)$_2$] doped with orange luminescent 4-(dicyanomethylene)-2-methyl-6-(*p*-dimethyl-aminostyryl)-4H-pyran (DCM) dye. White light electroluminescence (EL) spectrum from Zn(hpb)$_2$ has been achieved by adjusting the concentration of DCM dye. WOLED with a structure of ITO/α-NPD/Zn(hpb)$_2$:DCM (*x*%)/BCP/Alq$_3$/LiF/Al has been fabricated. The EL spectra covering the whole visible spectra range of 400–700 nm, with two peaks at 446 and 555 nm has been measured. The device emits white light at 10 V with Commission Internationale de l' Eclairage (CIE) coordinates (0.27, 0.31) and brightness 1083 Cd/m^2. The maximum current efficiency of the device was 1.23 Cd/A at 9.5 V and maximum luminance reaches 2210 Cd/m^2 at 12 V.

1. Introduction

The research on white organic light-emitting diodes (WOLEDs) has steadily increased from 1993 when Kido et al. demonstrated the first white OLED by dispersing blue, red and green fluorescent dye in polyvinylcarbazole (PVK) [1] and is attracting more and more attention for researchers in recent years because of their potential use in full color displays and back lights for LCD displays. Due to various advantages of WOLED, there is a great appreciation for the potential of energy saving, thin and flexible WOLED, to replace traditional incandescent light sources [2]. Several approaches have been proposed to generate white light with various OLED device configurations, such as mixing of three primary colors (red, green and blue) from different emitting molecules, by multilayer structure [3–8], by excimer or exciplex emission [3,9,10], by single emissive layer with several dyes [11], etc. These approaches are usually complicated due to the fact that these devices involve too many layers and dopants. Furthermore bias-dependent color variations create frequent problems in these WOLEDs [12,13]. It is always convenient to have device in which single material emits pure white light but such materials are rare. WOLEDs with a single light-emitting layer doped with different fluorescent dyes show relatively stable color coordinates with respect to the bias voltage. The light emission from the doped active layer is usually governed by the energy transfer from host to the dopant, as well as charge carrier trapping at dopant molecules and subsequent recombination [12–14]. By the controlled doping of a host material with a dye, energy transfer from host to guest molecules can be modulated resulting in desired energy transfer and emission from both the materials [15]. Small organo-metallic complexes of zinc have high stability, high efficiency, and longer life and are ideal for use as emitter materials in OLEDs [16–21]. In 1996, Hamada et al. fabricated a greenish-white OLED using single small fluorescent material based on organo-zinc complex namely Zn(BTZ)$_2$, which was the first WOLED based on single emitting material [22]. In 1994, Nakamura [23] has reported blue electroluminescence from bis(2-(2-hydroxyphenyl)benzoxazolate)zinc [Zn(hpb)$_2$]. However the generation of white light from Zn(hpb)$_2$ by doping has not yet been reported to the best of our knowledge. In this paper we have demonstrated a WOLED from a single layer of Zn(hpb)$_2$ doped with an orange fluorescent dye DCM which emits white light. The device consist of a hole transport layer (HTL) of *N*,*N*-diphenyl-*N*′,*N*′-bis(1-naphthyl)-1,1′-biphenyl-4,4′-diamine (α-NPD) and emitting layer (EML) Zn(hpb)$_2$ doped with various concentrations of DCM dye. BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenonthroline) was used as hole blocking layer (HBL), aluminum tris-8-hydroxy quinoline (Alq$_3$) as electron transport layer (ETL), LiF as electron injection layer (HIL) and aluminum as the cathode metal. We have found that the white emission was dominated by trap assisted recombination of charge carriers at the dye molecules, where as the photoluminescence

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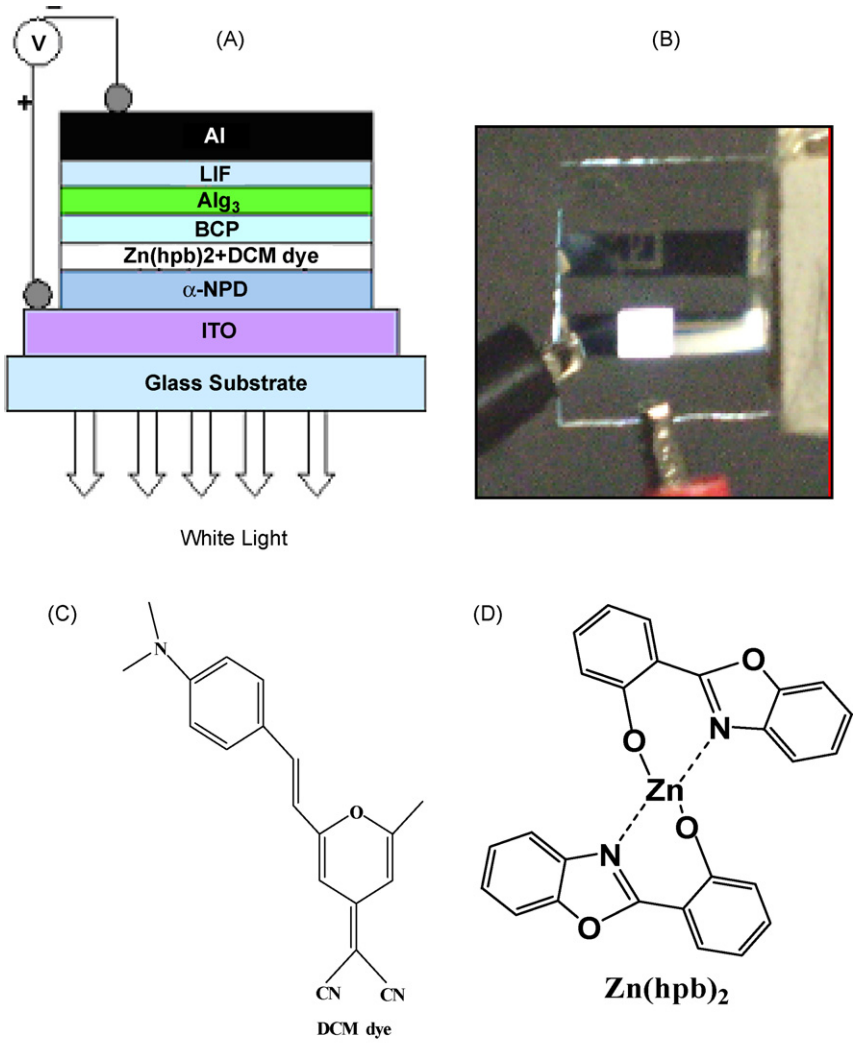

Fig. 1. (A) White organic light-emitting diodes configuration and (B) the photograph of WOLED device and (C and D) Molecular structure of DCM dye and $Zn(hpb)_2$, respectively.

(PL) of DCM dye doped $Zn(hpb)_2$ has been assigned to Förster type energy transfer [24,15]. The white EL spectrum of device with suitable color coordinates was independent of the applied voltage.

2. Experimental

2.1. Material synthesis

2.1.1. Synthesis of bis(2(2-hydroxyphenyl)benzoxazolate)zinc

$Zn(hpb)_2$ was synthesized according to the method reported in the literature [23]. In a 100-ml round-bottomed flask, 2-(2-hydroxyphenyl)benzoxazole (HPB) (0.851 g) (Sigma–Aldrich) was dissolved in 40 ml of anhydrous ethanol at 70 °C under a nitrogen atmosphere. The solution was stirred for 2 h, after which zinc acetate dihydrate (0.438 g) in water (6 ml) was added dropwise to the reaction mixture while stirring continued. After 2 h of stirring a precipitate of the complex was separated, which was filtered and recrystallized from a mixture of acetone and ethanol and dried in a vacuum oven. The synthesized material was further purified by vacuum sublimation. The UV–vis spectrum was recorded using a UV–vis PC spectrophotometer (Shimadzu 2401). Photoluminescence was studied using a spectrofluorometer (Fluorolog Jobin Yvon—Horiba, model-3-11) at room temperature.

2.2. Device fabrication

We have fabricated four devices (A), (B), (C) and (D) with different concentration (x) of DCM dye in $Zn(hpb)_2$ matrix ($x = 0.010$, 0.012, 0.013, and 0.015 wt%, respectively). The WOLED device configuration, the photograph of the device and the molecular structure of emitter materials $Zn(hpb)_2$ and DCM dye are shown in Fig. 1(A–D), respectively. Indium–tin oxide (ITO) coated glass substrate with a sheet resistance 20 Ω/□ was used as anode which were patterned and cleaned using deionized water, acetone, trichloroethylene and isopropyl alcohol sequentially for 20 min using an ultrasonic bath and dried in vacuum oven. Prior to organic film deposition, the ITO surface was treated with oxygen plasma for 5 min to increase the ITO work function. The hole transport layer and the emitting layer were deposited onto the substrate sequentially under high vacuum (1×10^{-5} Torr) at a deposition rate of 0.1 nm/s. Thickness of the deposited layers were measured in situ by a quartz crystal thickness monitor. The typical thickness of the different layers were ITO (120 nm)/α-NPD (35 nm)/$Zn(hpb)_2$:DCM (x%) (30 nm)/BCP (6 nm)/Alq_3 (20 nm)/LiF (1 nm)/Al (150 nm). The size of each pixel was 5 mm × 5 mm. The EL spectrum has been measured with a high resolution spectrometer (Ocean Optics HR-2000CG UV-NIR). The current density–voltage–luminescence