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White organic electroluminescent device with photovoltaic performances

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Abstract

Organic device with structure of indium tin oxide (ITO)/1,3,5-tris-(3-methylphenylphenylamino)triphenylamine (*m*-MTDATA)/2-*tert*-butyl-9,10-di-beta-naphthylanthracene (TBADN)/2,9-dimethyl-4,7-diphenyl-1,10-phenan-throline (BCP)/LiF/Al, was fabricated, which show high efficient white electroluminescence (EL) or photovoltaic (PV) properties when it was driven by direct current (DC) bias or illuminated by ultraviolet (UV) light. Under a DC bias, the device shows efficient white EL emission. A maximum luminous efficiency of 1.1 lm/W was obtained at 8 V, which corresponds the Commission International de L'Eclairage coordinates (CIE) of ($x = 0.298$, $y = 0.365$). When the bias was increased to 12 V, the device shows bright white emission with the maximum brightness of 4300 cd/m^2, corresponding CIE coordinates of ($x = 0.262$, $y = 0.280$). When the diode was irradiated by a 365 nm UV-light (4 mW/cm^2), the open-circuit voltage (V_{oc}) of 1.2 V, short-circuit (I_{sc}) of 0.065 mA/cm^2, fill factor (FF) of 0.24 and power conversion efficiency of 0.47% have been determined, respectively. The generation mechanisms of white light and PV of the bi-functional diode were discussed as well.

Keywords: White organic light emitting diode; Photovoltage; Bi-functional diode

1. Introduction

Since Tang group in Kodak has reported efficient organic light-emitting diodes (OLEDs) in 1987 [1] and organic photovoltaic (OPV) device with small molecules in 1986 [2], as its unique potential applications in the future, more and more researchers have devoted to the investigations on the two aspects and more exciting progresses have been made. Because OLEDs and OPV devices posses the similar device structure, it is possible to make same device exhibiting bi-function with both PV properties and EL

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characteristics. Among OLEDs, white light-emitting devices [3,4] have spurred peculiar interest for meeting the require for full-colour displays and backlights. Many efforts have been made to achieve efficient white OLEDs. There are three primary concepts to fabricate white OLEDs based on thermally vacuum deposited organic low molecular materials: (i) White light produced by stacking of red, green and blue emitting layer [5]; (ii) white light generated from doping fluorescent or phosphorescent dyes to a host [6]; (iii) white light produced by emitting from white emission materials [7]. However, the white emission materials are not easy to synthesize and the fabrication processes of (π) or (θ) are more inconvenient. In this work, a white EL combined from a blue component and a yellow emission from a exciplex in the device was observed and the device also shows PV properties which is based on an exciplex formation, as just reported by our group first [8]. Using exciplex emission as yellow component the white EL diodes were fabricated [9,10], but the devices show generally lower luminous efficiency although higher efficient no-white EL devices with exciplex emission were also fabricated [11–13]. PV properties have, however, not yet been found for the diodes based on the exciplex-emitting EL diodes beside reported result in our group [8]. Thus, we have selected and used suitable organic materials to fabricate high efficient white EL device with PV effect. The white EL emission was achieved by making use of the co-emission of blue emission of 2-*tert*-butyl-9,10-di-beta-naphthylanthracene (TBADN) and an yellow exciplex emission in the interface between two organic layers.

2. Experimental

The configuration of the device and the chemical structure of the materials used in this study are shown in Fig. 1. We can see that 1,3,5-tris-(3-methylphenylphenylamino)triphenylamine (*m*-MTDATA) and TBADN were used hole transporting layer and as blue emission-electron transporting layer, BCP was used as hole-blocking layer when the device was used as an EL diode, respectively. When the device was used as PV diode *m*-MTDATA, TBADN and BCP

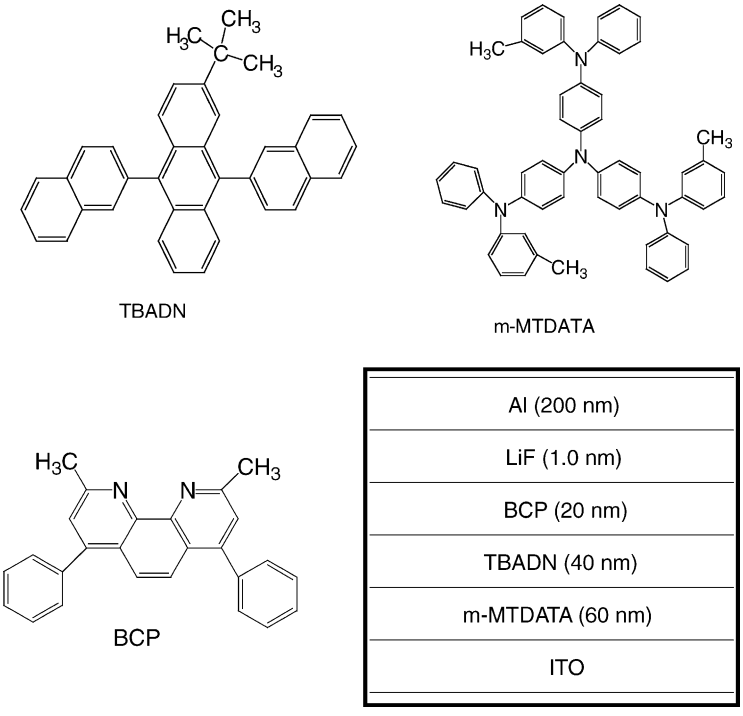

Fig. 1. The chemical structures of materials used and the device configuration.

were used as electron donor, acceptor and exciting blocking layer. The detain role of every organic layer will be discussed in the next session. The organic materials were obtained commercially. The ITO-coated glass has a sheet resistance of 15 Ω^{-2}. The substrates are pre-cleaned by ultrasonic in an alcohol and an acetone, respectively, and then treated by UV-ozone in a chamber. All organic functional layers were deposited by vacuum evaporation in a chamber pressure of about 10^{-7} Torr at a rate of 2 Å/s. The vaporizing rate of LiF and Al were controlled to be 0.5 Å/s and 10 Å/s, respectively. The film thickness was monitored in vacuo with a quartz crystal monitor. The active area of device is 15 mm^2.

The absorption spectra were measured with a Shimadzu UV-3010 PC spectrophotometer. The films for absorption measurements were deposited on quartz substrates. The EL spectra, the Commission Internationale de L'Eclairage coordinates (CIE) were measured with a Hitachi MPF-4 Fluorescence spectrophotometer. The luminance–current–voltage characteristics were measured simultaneously by the EL test system made in Beijing Normal University, PR China. The spectral response curves of the devices were determined by illumination with different wavelengths at a constant power density of 40 $\mu W/cm^2$ (Xe lamp). The incident light for PV measurement was admitted through the glass/ITO side. All the performance measurements were carried out under ambient atmosphere without encapsulation.

3. Results and discussion

Fig. 2 shows the efficiency–voltage characteristics of the device used as EL diode, we can see that the maximum luminous efficiency of the device is 1.1 lm/W under direct current (DC) bias of 8 V, and the EL spectra of the device is also displayed in the insert, indicating obviously that the spectrum is composed of a blue band and a yellow band, their origins will be discussed below.

Fig. 3 displays CIE coordinates of the EL at different DC bias. It is noticed that the emission colour lies at white emission region from 8 to 12 V, and the bright white EL emission corresponds CIE coordinates of ($x = 0.298$, $y = 0.365$). However, when the bias was increased to 12 V, luminous efficiency was

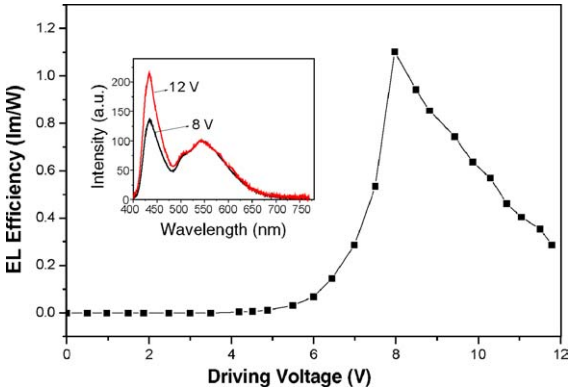

Fig. 2. Luminous efficiency–voltage characteristics of ITO/*m*-MTDATA/TBADN/BCP/LiF/Al (inset: the EL spectrum of the device).

decreased to 0.4 lm/W, the CIE coordinates was changed to be ($x = 0.262$ and $y = 0.280$), the maximum luminance was decreased to 4300 cd/m^2, and EL colour was shifted from yellow to white emission region, respectively. We have also confirmed that white emission was obtained based on the complementary of blue colour of TBADN and yellow emission of exciplex in the interface between two organic layers. The EL white colour was shifted with increasing the bias, showing that the recombination zone is an electric field dependent. That is, at higher bias the carrier recombination site was more approximated to the interface emitting yellow colour, but at lower bias (8 and 12 V) the blue emission of TBADN layer and the yellow emission form the

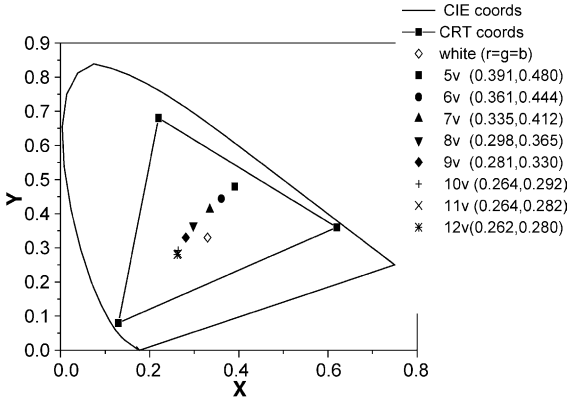

Fig. 3. Electroluminescence CIE coordinates at different applied bias.

interface would simultaneity contribute to the white EL colour. Here it would be confirmed that the exciplex emission is to the death resulted from which interface? Which interface was the active zone of yellow emission for EL diode or excition dissociation resulting in PV effect for PV diode? Because there are two interfaces of organic layers that is *m*-MDATA/TBADN-interface and TBADN/BCP-interface in the device (see Fig. 1).

In order to understand the mechanism, we also fabricated device with the structure of ITO/*m*-MTDATA (60 nm)/TBADN (60 nm)/LiF (1.0 nm)/Al (200 nm) in which there is no longer BCP layer between TBADN and LiF layers. The spectral response curves of the two devices have been determined for comparing their curve shape and the area, as shown in Fig. 4. From Fig. 4, it is confirmed that interface between *m*-MTDATA and TBADN should play the active site for the exciton dissociation. This is explained as following. The first, *m*-MTDATA is a well known hole-transporting and injecting material [14] and it was easily formed exciplex with electron transporting material, such as tri(8-quinolinolato) aluminium (AlQ), which is due to its lower ionization potential (IP) (5.1 eV), and it has been used as an electron-acceptor material in PV diode [15]. The second, TBADN should be also a capable electron-transporting material because it is a derivative of DNA (l-9,10-di-beta-naphthylanthracene), which is a blue host material with electron transporting ability [16]. Thus, *m*-MTDATA also should play an electron-donor role [13] and TBADN should play an electron-acceptor role in our designing PV diode. On the other hand, the interface of TBADN/BCP was not an active site because the two materials posses electron-transporting properties.

As we all know that exciplex must be formed in the interface between those two materials, the one is electron donor (lower electron affinity) and the other is an electron accepter (higher electron affinity) [9,14]. So the exciplex could not be formed in this interface [9]. Since there are the same spectral response region in the two devices although the relative values are different. Fig. 4 shows the absorption spectra of *m*-MTDATA, TBADN, (*m*-MTDATA/TBADN) and BCP films and the photovoltaic spectral response of ITO/*m*-MTDATA/TBADN/BCP/LiF/Al. It is observed that the absorption spectra are corresponding to the PV response region of the device are in the range of λ = 300–435 nm. Thus, it can be concluded that both *m*-MTDATA film and TBADN film have contributed to the PV properties of the device. In other words, the dissociations of the excitons must be took place in interface between *m*-MTDATA layer and TBADN layers. Although there are stronger absorptions for both *m*-MTDATA film and TBADN film from 300 to 330 nm, the PV response of the device is poor, which is attribute to the strong absorption of the ITO glass (Fig. 5). A 365 nm UV-light (4 mW/cm^2) was introduced to determine the PV properties of the device, the device exhibits the PV parameters of the open-circuit voltage (V_{oc}) of 1.2 V, short-circuit current (I_{sc}) of 0.065 mA/cm^{2}and fill factor (FF) of 0.24, and power conversion efficiency (η) of 0.47%, respectively.

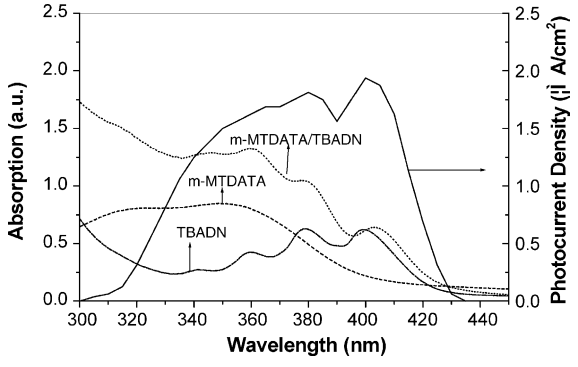

Fig. 4. The absorption spectra of the *m*-MTDATA-film, TBADN-film and BCP-film, as well as the photocurrent response of ITO/*m*-MTDATA/TBADN/BCP/LiF/Al PV diode.

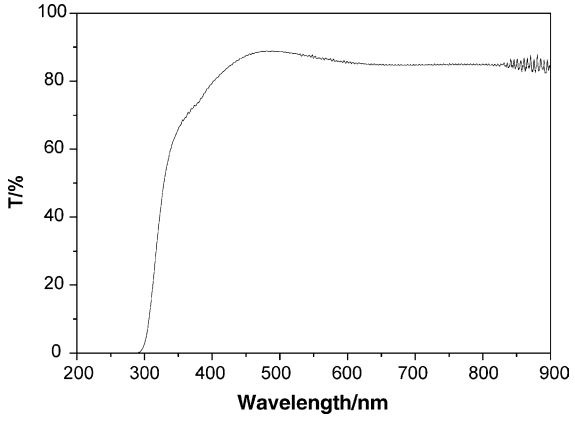

Fig. 5. The UV–Vis absorption spectrum of the ITO-coated glass.

4. Conclusions

In conclusion, we have demonstrated efficient white organic light-emitting device based on exciplex with higher luminance and luminous efficiency. The device also has photovoltaic performance when it was illuminated by 365 nm UV light. The bi-functional device with EL and PV performances is promising to use as white displays or backlight source in the future because it can be charged by solar energy through additional apparatus free of work. In addition, it is also used as an optical sensor to UV light.

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