Color tunability in multilayer OLEDs based on DCM and DPVBi as emitting materials

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Abstract. We report studies on the color tunability of a novel type of multilayer organic light-emitting diodes (OLEDs) based on three emitting materials: DCM (4-(Dicyanomethylene)-2-methyl-6-[p-(dimethylamino)styryl]-4H-pyran) as a red emitter, DPVBi [4,4′-Bis(2,2-diphenylvinyl)-1,1′-biphenyl] as a blue emitter and zinc bis(2-(2-hydroxyphenyl)benzothiazole) (Zn(BTz)2) as a yellow emitter, and an electron transporting layer. We established that the positions and thicknesses of the different emitting layers determine the efficiencies, luminance and color of the light emitted by the OLEDs.

1. Introduction

During the last two decades, OLEDs have attracted a wide scientific and commercial interest because of their high potential for applications as paper-like light sources, backlight for liquid crystal displays, and full-color OLEDs [1-4]. With the ability to be self-emissive, and being extremely thin and light, OLEDs are particularly suitable to be the future commonly-used light sources. The successful development of OLEDs relies on the capability to obtain emission over the full visible spectrum. OLEDs emit various colors depending on the emitting fluorescent dyes used, which are also the key materials affecting the luminance, efficiency, turn-on voltage and lifetime. White OLEDs (WOLEDs) are of foremost interest for lighting and display applications [5]. Several routes are usually employed to obtain white light, such as, e.g., mixing of three (red, blue, green) or two (complementary) colors in a single host matrix [6,7,8], using several physically separate layers [9] emitting simultaneously different colors [10,11,12], using bimolecular excited species (excimer/exciplex emission [13,14]), etc. However, fine tuning of the color emission and achieving bright white emission are still problematic.

In this work, we report an investigation on the color tunability of a multilayer OLED based on three emitting materials: DCM (4-(Dicyanomethylene)-2-methyl-6-[p-(dimethylamino)styryl]-4H-pyran) as a red emitter, DPVBi [4,4′-Bis(2,2-diphenylvinyl)-1,1′-biphenyl] as a blue emitter and zinc bis(2-(2-hydroxyphenyl)benzothiazole) (Zn(BTz)2) as a yellow emitter and an electron transporting layer to achieve white emission. Three types of OLED structures with different sequences and thicknesses of the undoped emitting layers were studied and their electroluminescent characteristics were established.

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2. Experimental

We investigated electroluminescent devices with a conventional structure: ITO/HTL/EL/M, where ITO is a transparent anode of In$_2$O$_3$:SnO$_2$; HTL, a hole-transporting layer; EL, emitting layers; and M, a metal Al cathode. As HTL we used an in-house developed composite film of TPD incorporated in a poly(N-vinylcarbazole) (PVK) matrix. Devices with area of 1 cm$^2$ were prepared on commercial polyethylene terephthalate (PET) substrates coated with ITO (60 $\Omega$/sq). The HTL (31 nm) of PVK:TPD$_x$ ($x = 10$ w$\%$ with respect to PVK) composite films were obtained by spin-coating at 2000 rpm from a 0.75 $\%$ solution in dichloroethane. The ELs of DPVBi, DCM and Zn(BTz)$_2$ (with total thickness of 75 nm) and the metal cathode (120 nm) were deposited by thermal evaporation in vacuum better than 10$^{-4}$ Pa at rates $2\times10^{-5}$ Å/s. An in-situ quartz crystal was used to monitor the thickness of the vacuum depositions. The PVK, TPD and DCM were purchased from Sigma-Aldrich, the ITO-covered PET substrate and the DPVBi, from Kintec Company, and the Zn(BTz)$_2$, from Yurui (Shanghai) Chemical Co. Ltd.

All measurements were performed with unpackaged devices, at room temperature and under ambient atmosphere. The electroluminescence spectra (El) and the chromaticity coordinates (CIE – Commission Internationale de L’Eclairage) were recorded by an Ocean Optics HR2000+ spectrophotometer. The current-voltage ($I$-$V$) and luminance–voltage ($L$-$V$) characteristics were measured by National Instruments Data Acquisition boards controlled by the Labview 7.1 software. The luminance ($L$) was measured in a DC mode, while the light output was detected using a calibrated S2281-01 Hamamatsu silicon photodiode. The electroluminescent efficiency ($\eta_L$) was calculated by equation (1) and used for quantifying the properties of the OLEDs:

$$\eta_L = \frac{L}{I},$$

where $L$ is the luminance (in cd/m$^2$) and $I$ is the current density (in A/m$^2$).

3. Results and discussion

The DCM molecule is a highly fluorescent orange-red laser dye widely used in OLEDs. The red emission can be obtained either through direct excitation of the DCM fluorophores or through Förster energy transfer from the excited host matrix. DPVBi is known as a blue emitting material in OLEDs, usually used as an emissive layer interposed between HTL and EL.

To generate white emission, we mixed the light emitted by separate layers emitting in red (DCM), yellow Zn(BTz)$_2$ and blue (DPVBi). We investigated two types of structures: based on two emitters – blue (DPVBi) and yellow (Zn(BTz)$_2$), and on three emitters (DPVBi, Zn(BTz)$_2$ and DCM). The total thickness of the electroluminescent layers in all the structures was kept constant at 75 nm. Figure 1 shows the schematic energy-band diagrams of these devices. The HOMO and LUMO values are taken from the literature [15-17].

3.1. Structures based on two emitters - DPVBi and Zn(BTz)$_2$

OLEDs with three different thicknesses of the DPVBi layer (5 nm, 15 nm and 60 nm) in the structure HTL/DPVBi$^x$/Zn(BTz)$_2^{75-x}$/Al were investigated. The luminance–voltage curves ($L$-$V$), the
electroluminescent efficiency ($\eta_L$) and the El spectra of these devices are shown in figure 2 and summarized in table 1. It was found that decreasing the thickness of the DPVBi layer from 60 nm to 5 nm raises the electroluminescent intensity and efficiency of the devices (from 384 cd/m$^2$ to 1240 cd/m$^2$ and from 1.61 to 2.47 cd/A, figures 2a and 2b), passing through a maximum at a thickness of the DPVBi layer of 15 nm.

The structure based entirely on DPVBi (60 nm) emits at 496 nm (figure 2c). The device with DPVBi$^{15}$/Zn(BTz)$_2$ showed a narrow blue emission band at 497 nm; that with DPVBi$^5$/Zn(BTz)$_2^{70}$, a broad emission band centered at 513 nm with a full width at half maximum (FWHM) of 27 nm. It was established that the decrease in the DPVBi layer thickness ($x$) shifts the CIE ($x,y$) coordinates of the

**Figure 2.** a) Electroluminescent intensity (L), b) Electroluminescent efficiency ($\eta_L$) and c) El spectra (at 16 V DC) of devices based on two emitters ITO/PVK:TPD/DPVBi$^5$/Zn(BTz)$_2^{75-x}$/Al.

**Figure 3.** a) Electroluminescent intensity (L), b) Electroluminescent efficiency ($\eta_L$) and c) El spectra (at 16V DC) of the devices based on three emitters PVK:TPD/DCM$^1$/DPVBi$^5$/Zn(BTz)$_2^{74-x}$/Al.
emitted light from the greenish-blue region (0.2074, 0.3232) at \(x = 60\) nm to the yellowish-green one (0.2698, 0.4435) at \(x = 5\) nm. This shift is due to the displacement of the recombination zone from the HTL/DPVBi interface (for the thick DPVBi layer) to the DPVBi/Zn(BTz)\(_2\) interface (for the thinner DPVBi layer).

The insertion of a 5-nm Zn(BTz)\(_2\) layer between HTL and a 5-nm DPVBi in the multilayer structure HTL/Zn(BTz)\(_2\)/DPVBi/DCM/Na/Zn(BTz)\(_2\) strongly reduces the electroluminescent efficiency but widens the EL spectrum (a broad band at 522 nm and a shoulder at 560 nm). The CIE \((x, y)\) coordinates of the emitted light are 0.2863, 0.4551, which are referred to in the literature as coordinates of “warm white” light.

### 3.2. Structures based on three emitters – DPBi, Zn(BTz)\(_2\) and DCM – emitting in the blue, yellow and red

#### 3.2.1. Structure with DCM evaporated on the HTL

The idea was to achieve a white emission via mixing red light emitted by a 1-nm thick DCM layer, with blue light emitted by a DPVBi layer with different thicknesses \(x\), and yellow emission from Zn(BTz)\(_2\), where the DCM layer lies on the HTL. Devices with structure PVK:TPD/DCM\(_1\)/Zn(BTz)\(_2\)/Al with \(x = 5\) nm, 15 nm and 20 nm (figure 1 b) were fabricated. Their \(L–V\) curves, \(\eta_L\) and El spectra are presented in figure 3 a), b) and c), and the results obtained are summarized in table 1.

From the \(L–V\) curves and the data in table 1 one can conclude that the device with a 15-nm DPVBi showed the best electroluminescent intensity (821 cd/m\(^2\)) and efficiency (2.69 cd/A). As seen in figure 3c, the emission band of the DCB-based OLED is at 650 nm. The addition of DCM to the double emitting DPVBi/Zn(BTz)\(_2\) structure leads to a red shift and a widening of the El spectrum of the OLED. For devices in which the DCM lies on the HTL, a broad emission band centered at 575 nm to  DPVBi, were observed. Increasing the DPVBi layer thickness from 5 nm to 15 nm shifts the CIE \((x, y)\) coordinates of the emitted light from the orange (0.4223, 0.4311) to the orange-red region (0.4851, 0.4288). A further increase of the DPVBi thickness from 15 nm to 20 nm causes a slight reversion to the orange region (0.4493, 0.4507).

#### 3.2.2. Structure with DCM evaporated on a HTL/DPVBi layers stack

Devices with structure HTL/DPVBi\(_1\)/DCM\(_1\)/Zn(BTz)\(_2\)\(_7\)/DPVBi\(_1\)/Zn(BTz)\(_2\)\(_7\) with \(x = 5\) nm, 15 nm and 20 nm were fabricated; their \(L–V\) characteristics, \(\eta_L\) and El spectra are presented in figure 4 a), b) and c), respectively. It is seen that the device with 15-nm DPVBi shows again the best performance: an electroluminescent intensity of 777 cd/m\(^2\) and an efficiency of 2.22 cd/A.
As seen in figure 4 c), a red and a weak blue emission band (from DPVBi) at about 491 nm predominate in the EL spectra of the devices with this structure. As can be seen, the increase in the DPVBi layer thickness leads again to a shift of the EL spectra of the devices to the longer wavelengths and a displacement of the CIE \((x, y)\) coordinates from the orange-red (0.5156, 0.3874) for the 5-nm DPVBi layer to the red (0.5597, 0.3732) region for the 20-nm DPVBi layer.

Figure 4 presents the performance of another device, for which the thin DCM layer of the structures discussed above is inserted between a 5-nm and a 10-nm DPVBi layers.

The device HTL/DPVBi5/DCM1/DPVBi10/Zn(BTz)2 demonstrates still higher values of the electroluminescent intensity \((923 \text{ cd/m}^2)\) and efficiency \((2.33 \text{ cd/A})\). In the spectrum of this structure, a broad band emission is observed centered at 572 nm with a FWHM of 15 nm. Weaker emissions of DPVBi and DCM are seen as shoulders at 493 and 613 nm, respectively. However, the broad emission range notwithstanding, the device emits most intensely in orange-red.

The variation of the dominating emission color from the OLEDs can be explained by the different position of the recombination zone in the structures ensued from the different mobility of the charges in the emitting layers [18]. Thus, by changing the thickness of the DPVBi, one can adjust the recombination zone and the resulting color of the emitted light.

In the device HTL/DCM/DPVBi/Zn(BTz)2, where the DCM is inserted between the HTL and DPVBi, there is one barrier for electrons on the HTL/DCM interface \((\Delta E_e = 9 \text{ eV})\) and one for holes on the DCM/DPVBi interface \((\Delta E_p = 0.5 \text{ eV})\). When the DCM is placed between the DPVBi and the Zn(BTz)2 in the device HTL/DPVBi/DCM/Zn(BTz)2, there are two barriers for electrons: \(\Delta E_e = 0.4 \text{ eV}\) on the DCM/DPVBi interface and \(\Delta E_e = 0.5 \text{ eV}\) on the DPVBi/HTL interface; and one for holes \((\Delta E_p = 0.5 \text{ eV})\) on the HTL/DPVBi boundary. As the mobility of electrons in organic compounds is twice as low as that of holes, increasing the thickness of the DPVBi layer impedes the motion of electrons to a larger degree than that of holes, the number of electrons accumulated on the DCM/DPVBi boundary starts decreasing and, as a result, a red shift of the recombination zone toward the DCM is observed for both structures. In this way, by changing the thickness of the DPVBi, fine tuning of the emission spectrum from orange to red can be achieved.
The results from the measurements reported suggest that the thickness of the DPVBi – which can act as a recombination-controlling layer in the multilayer devices – plays an important role in modifying the device’s characteristics. It also provides a simple way of fabricating color-tunable OLEDs by simply changing the thickness of this “recombination-controlling” layer.

4. Conclusions
We investigated multilayer OLED structures based on two and three emitters DCM, Zn(BTz)\textsubscript{2} and DPVBi, emitting in red, yellow and blue, for different sequence of the emitters and variation of their thicknesses, with the aim to achieve fine tuning of the device’s color. We showed that the spectral emission depends on both the location of the emitters and the layers’ thicknesses, and also established that an accurate control of the emitted color can be obtained by finely adjusting both of these parameters. We obtained an efficient warm white-light emission (CIE 0.2698, 0.4435) from the device PVK:TPD/ DPVBi (5 nm)/ Zn(BTz)\textsubscript{2} (70 nm) with a luminance of 1247 cd/m\textsuperscript{2} and a luminous efficiency of 2.47 cd/A.

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