Color tunability in multilayer OLED based on DCM doped in a PVK matrix

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Abstract. In this work, we present our achievements in color tunability in novel multilayer organic light-emitting diodes (OLEDs) based on DCM (4-(Dicyanomethylene)-2-methyl-6-[p-(dimethylamino)styryl]-4H-pyran) as red emitter doped in a composite PVK:TPD hole-transporting layer, DPVBi (4,4′-Bis(2,2-diphenylvinyl)-1,1′-biphenyl) as a separate blue emitting layer, BAlq (aluminum bis(2-methyl-8-quinolinate)-4-phenylphenolate) as hole-blocking layer and blue emitter at the same time, and Zn(BTz)₂ (zinc bis(2-(2-hydroxyphenyl)benzothiazole)) as yellow emitter and electron transporting layer. By modification of the OLED structure and changing the DCM doped concentration in the matrix (in the range of 0 up to 5 %) the color tunability of OLED structures has been obtained. The efficiencies, luminance and chromaticity coordinates of the fabricated OLED structures have been specified.

1. Introduction
Organic light-emitting devices (OLEDs) have received considerable attention as a promising technology for flat-panel displays [1] and solid-state lighting [2]. The successful developments of OLEDs imply the capability to obtain emission over the full visible spectrum and the generation of white emission. During the past two decades, researchers have invested a great deal of effort in developing WOLEDs. However, lifetime, performances and costs still have to be optimized to make WOLEDs commercially competitive as alternative lighting sources. Much research has been spent on finding the suitable materials to realize improvements in device architectures, to enhance OLED efficiency, and to development of new systems with low cost and low energy consumption. Various methods for generating white light have been reported [3]. Generation of white electroluminescence in WOLEDs involves simultaneous emission of light of the three primary colors (red, green and blue) or of two complementary colors (e.g. orange and blue). Combination of emitters of different colors requires proper control of energy transfer processes [4], adjustment of their relative amounts and control of their interactions on both the molecular and the device scale [5, 6]. The management of such energy transfer to ensure simultaneous light production from all the different emitting centers is a critical issue in all the methods for obtaining white light.

In this work, we report an investigation on color tunability in a novel multilayer OLED based on DCM (4-(Dicyanomethylene)-2-methyl-6-[p-(dimethylamino)styryl]-4H-pyran) as red emitter doped in a composite PVK:TPD hole-transporting layer, DPVBi [4,4′-Bis(2,2-diphenylvinyl)-1,1′-biphenyl] as a separate blue emitting layer, BAlq (aluminum bis(2-methyl-8-quinolinate)-4-phenylphenolate) as hole-blocking layer and blue emitter at the same time, and Zn(BTz)₂ (zinc bis(2-(2-hydroxyphenyl)benzothiazole)) as yellow emitter and electron transporting layer to achieve white emission. Different
types of OLEDs with differing multilayer structure and doping concentrations of DCM were studied and their electroluminescent characteristics were established.

2. Experimental

We investigated the electroluminescent devices with the conventional structure: ITO/HTL/EL/M, where ITO was 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 10 wt% N,N’-bis(3-methylphenyl)-N,N’-diphenyl-benzidine (TPD) incorporated in poly(N-vinylcarbazole) (PVK) matrix. Devices with area of 1 cm$^2$ were prepared on commercial polyethylene terephthalate (PET) substrates coated with ITO (60 Ω/sq). The undoped and doped with DCM (from 0.15 up to 5 %) HTL (31 nm) of PVK : TPD composite films were obtained by spin-coating from 0.75 % solution in dichloroethane at 2000 rpm. The ELs of DPVBi, BAlq and Zn(BTz)$_2$ (with total thickness of 75 nm) and metal cathode (120 nm) were deposited by thermal evaporation in vacuum better than $10^{-4}$ Pa at rates of 2-5 Å/s. The thickness of every sublayer included in the El layer is denoted as a superscript index $x$, whereas the weight percentage of DCM component in the PVK matrix is denoted as $y\%$. Quartz crystal microbalance was used for an in situ monitoring of the vacuum depositions.

The PVK, TPD, DCM and BAlq were purchased from Sigma-Aldrich, ITO covered PET substrate and DPVBi from Kintec Company, Zn(BTz)$_2$ from Yurui (Shanghai) Chemical Co. Ltd.

All measurements were performed with unpackaged devices, at room temperature and under ambient atmosphere. Electroluminescence spectra (El) and chromaticity coordinates (CIE - Commission Internationale de L’Eclairage) were recorded with 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 Labview 7.1 written software. The luminescence (L) was measured in DC (direct current) mode and the light output was detected using a calibrated Hamamatsu silicon photodiode S2281-01. The efficiency ($\eta_L$) was calculated by equation (1) and used for quantifying the properties of the OLEDs.

$$\eta_L = L/I,$$

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

3. Results and discussion

DPVBi is widely known to be a blue emission material in OLEDs, and normally interposed between a hole-transporting layer of NPB and an electron-transporting layer of Alq$_3$. DCM derivatives have been used as red doping molecules to produce OLEDs with improved efficiency and color purity. Red emission is commonly obtained by doping a red fluorescent dye into a host material that has a wider band gap than that of the dopant. Generally, Alq$_3$ and DPVBi, or other blue emitters are used as a host

![Figure 1. Schematic energy band diagrams for the investigated three types of OLED structures: a) ITO/ PVK:TPD/ DPVBi$/^5$/ Zn(BTz)$_2$/ $^{5-x}$/ Al, b) ITO/ PVK:TPD/ Zn(BTz)$_2$/ $^{5}$/DPVBi$^5$/Zn(BTz)$_2$/ $^{6x}$/ Al and c) ITO/ PVK:TPD/ DPVBi$^5$/ Zn(BTz)$_2$/ $^{5}$/BAIq$^5$/ Zn(BTz)$_2$/ $^{6x}$/ Al.](image-url)
PVK:TPD, which allowed DCM to be incorporated in the PVK matrix.

To obtain white emission we combined the light emitted by separate layers irradiating in blue (DPVBi), yellow (Zn(BTz)$_2$) and red (DCM). The first layer in the investigated OLED structures is made from the composite PVK:TPD hole transporting layer which doped with DCM acts as a red light emitting layer. The red emission can be obtained either through direct excitation of the DCM fluorophores or through Förster energy transfer from the excited host matrix [7]. The second layer is of blue light-emitting material DPVBi. BAlq is added to some of structures as hole blocking and blue emitting layer at the same time. The last Zn(BTz)$_2$ layer is used as electron transporting and yellow emitting layer simultaneously.

We fabricated three types of multi-layer devices, which schematic energy band diagrams are shown in figure 1. The HOMO and LUMO values are taken from the literature [8-11].

3.1. Comparison of the different undoped structures
The first were investigated and compared three types of OLED structures with different positions and thicknesses of the color layers, as follows:

HTL/DPVBi$^{75-x}$/Zn(BTz)$_2$ (5nm/60nm)
HTL/Zn(BTz)$_2$/DPVBi$^{65}$/Zn(BTz)$_2$ (5nm/60nm)
HTL/DPVBi$^{5}$/Zn(BTz)$_2$ (5nm)/BAlq$^{5}$/Zn(BTz)$_2$ (60nm)

The luminance–voltage curves ($L$–$V$), current efficiency ($\eta$) and EL spectra of these devices are shown in figures 2 and 3, and summarized in table 1. It was found that the structure of type HTL/DPVBi$^{75}$/Zn(BTz)$_2$, where x = 15 nm shows higher with 0.74 cd/A efficiency and lower with 320 cd/m$^2$ electroluminescent intensity in comparison with the device with 5 nm thick DPVBi layer. The current efficiencies and Luminance of structures HTL/DPVBi$^{75}$/Zn(BTz)$_2$, (shown in Fig. 2a and 2b) are better than these of the device HTL/DPVBi$^{75}$/Zn(BTz)$_2$/BAlq$^{5}$/Zn(BTz)$_2$, but BAlq layer stabilize OLED performance and optimize characteristics of the structure.

![Figure 2](image_url)

**Figure 2.** a) Electroluminescent intensity (L) and b) Current efficiency ($\eta$) of OLEDs with different architecture: ITO/HTL/DPVBi$^{75}$/Zn(BTz)$_2$/DPVBi$^{65}$/Zn(BTz)$_2$/Al and ITO/HTL/DPVBi$^{75}$/Zn(BTz)$_2$/BAlq$^{5}$/Zn(BTz)$_2$/Al.

The device with EL structure DPVBi$^{75}$/Zn(BTz)$_2$, shows a broad emission band centered at wavelength of 513 nm in the green range (0.2698, 0.4435), while the DPVBi$^{65}$/Zn(BTz)$_2$ device demonstrates a narrow blue emission band at 497 nm with CIE (x,y) coordinates 0.2389, 0.3922. At the thinner DPVBi layer the EL intensity of the yellow emission is stronger. It can be assumed that as the recombination zone within the DPVBi layer is thinner, because of its reduced thickness, the blue color intensity is reduced. When added a BAlq layer to the basic structure DPVBi$^{75}$/Zn(BTz)$_2$, a broad emission band appears at 504 nm - CIE (x,y) coordinates 0.2532, 0.4225. Consequently, BAlq enhances the blue emission without reducing the yellow emission.
In the structure HTL/Zn(BTz)$_2$$_5$/DPVBi$_5$/Zn(BTz)$_2$$_6$$_5$ where 5 nm Zn(BTz)$_2$ layer is placed between HTL and 5 nm DPVBi an expansion of the El spectrum is observed (broad band at 522 nm and shoulder at 560 nm) and the emitted light has CIE (x,y) coordinates - 0.2863, 0.4551, but the electroluminescent efficiency and luminance intensity vastly reduce, see figure 2. Unfortunately this device shows the lowest current efficiency and luminance intensity, among discussed in this section structures.

Table 1. Characteristics of OLEDs with a structure: ITO/ PVK:TPD/ emitting layers/ Al. The sequences of the emitting layers are given in the first column.

| Sequences of the emitting layers in OLEDs. | L$_{max}$ (cd/m$^2$) | $\eta_L$ (cd/A) | $\lambda_{max}$ at 16V (nm) | Shoulder (nm) | CIE at 16V (x,y) |
|------------------------------------------|---------------------|----------------|----------------------------|--------------|-----------------|
| DPVBi$_5$/Zn(BTz)$_2$$_6$$_5$            | 929                 | 3.21           | 497                        | 524 weak     | 0.2389, 0.3922  |
| DPVBi$_5$/Zn(BTz)$_2$$_6$$_5$/BAlq$_5$/Zn(BTz)$_2$$_6$$_5$ | 1247               | 2.47           | 513 broad                  | 560          | 0.2698, 0.4435  |
| Zn(BTz)$_2$$_5$/DPVBi$_5$/Zn(BTz)$_2$$_6$$_5$ | 695                | 1.85           | 522 broad                  | 560          | 0.2863, 0.4551  |
| DPVBi$_5$/Zn(BTz)$_2$$_5$/BAlq$_5$/Zn(BTz)$_2$$_6$$_5$ | 770                | 2.64           | 504 broad                  | 560          | 0.2532, 0.4225  |

3.2. Influence of DCM dye doping concentrations on the OLED performance

The second experiment was aimed to obtain a white emission via doping of the HTL with DCM in the structure HTL:DCM$_y$/DPVBi$_5$/Zn(BTz)$_2$$_5$/BAlq$_5$/Zn(BTz)$_2$$_6$$_5$. Fine tuning of the color by changing the DCM concentration in HTL at constant thickness of the layers building the basic structure was carried out. Devices with different DCM doping concentrations from 5 to 0.15 wt % were fabricated.

The characteristics of these devices are presented in figures 4 and 5, and summarized in table 2. As seen (figure 4b), the doping to 2.5% with DCM significantly increases the efficiency in comparison with the undoped structure and this doped with 5% DCM. It is interesting to note that the structures

Table 2. Characteristics of the OLEDs with structure: HTL:DCM$_y$/DPVBi$_5$/Zn(BTz)$_2$5$/BAlq25$/Zn(BTz)$_2$60$ by different DCM doping concentrations.

| Wt% DCM doping concentrations | L$_{max}$ (cd/m$^2$) | $\eta_L$ (cd/A) | $\lambda$ (nm) | $\lambda_{max}$ at 16V (nm) | Shoulder (nm) | CIE at 16V (x,y) |
|------------------------------|----------------------|----------------|----------------|----------------------------|--------------|-----------------|
| 5% DCM                       | 753                  | 3.07           | 613            | 575                        | 491, 530     | 0.4263, 0.4501  |
| 2.5% DCM                     | 1065                 | 5.22           | 571            | 493, 529, 613              | 0.4092, 0.4587 |
| 1.25% DCM                    | 1090                 | 4.62           | 566 broad      | 496, 525                   | 0.3851, 0.4697 |
| 0.6% DCM                     | 841                  | 4.6            | 570            | 528, 495                   | 0.3875, 0.4664 |
| 0.3% DCM                     | 1340                 | 4.70           | 531            | 494 weak                   | 0.3525, 0.4678 |
| 0.15% DCM                    | 1266                 | 4.74           | 496            | 524                        | 0.2984, 0.4477 |
with 0.15, 0.3, 0.6 and 1.25 wt% DCM show similar current efficiencies. The luminance intensity of devices with 0.15 and 3% is strongest.

For all devices, it was observed that increasing of the DCM concentration, the intensity of the red emission increased, with respect to the intensity of the blue emission (figure 5). It can be seen that increasing DCM concentration the El spectrum of devices shifts to the red. The wavelengths of peak positions, which were in the orange-red region, are depicted in table 2.

The CIE coordinates at different DCM concentrations, given in table 2, show displacement from (0.4263, 0.4501) to (0.2984, 0.4477) with decreasing of the dopant concentration. As is apparent, the red emission predominates in the emitted light from OLEDs at all DCM concentrations, except of OLED with 0.15 wt% DCM which emission is the closest to the white light.

From the results obtained, it can be concluded that the optimal dopant DCM concentration is very low 0.15 - 0.3 wt%. In practice, the effective doping range requested to keep the OLED efficiency unchanged is very narrow, and limited to a few tenths of percent of the optimal concentration [12-15].

3.3. Comparing the two types of structures by equal DCM doped concentration

A comparison of the characteristics of the two types of studied structures: ITO/HTL:DCM$^y$/DPVBi$^5$/Zn(BTz)$_2$/$\mathrm{Zn(BTz)}_2$, where $y = 5\%$, 2.5\%, 1.25\%, 0.6\%, 0.3\% and 0.15\%.

From the results obtained, it can be concluded that the optimal dopant DCM concentration is very low 0.15 - 0.3 wt%. In practice, the effective doping range requested to keep the OLED efficiency unchanged is very narrow, and limited to a few tenths of percent of the optimal concentration [12-15].
determined optimal (0.15 and 0.3 wt%) DCM doped concentration was done. The characteristics of these devices are presented in table 3 and figures 6 and 7. As seen in the figure 6b, the efficiencies of the devices HTL:DCM\(^{0.35}/\)DPVBi\(^5/Zn(BTz)\(_2\)/BAIq\(_5/Zn(BTz)\(_2\)/Al are identical while these of the devices HTL:DCM\(^{0.35}/\)DPVBi\(_{15}/Zn(BTz)\(_2\)/Al are different each other. The efficiency of doped with 0.15 wt% DCM is 1.4-fold higher than that of this with 0.3 wt% doped DCM. The figure 6a shows clearly, that BAlq presence stabilize the recombination zone in the investigation structures and only one maximum is observed at Electroluminescence/Voltage curves of HTL:DCM\(^{0.35}/\)DPVBi\(_5/Zn(BTz)\(_2\)/BAIq\(_5/Zn(BTz)\(_2\)/Al devices. At Electroluminescence/Voltage curves of HTL:DCM\(^{0.15}/\)DPVBi\(_{15}/Zn(BTz)\(_2\) devices, where BAlq is missing, second maximum by increase the voltages is observed, which indicates that the recombination zone is shifted with an increase of the voltage.

Table 3. Characteristics of the OLEDs with structure: HTL:DCM\(^{0.35}/\)DPVBi\(_{15}/Zn(BTz)\(_2\)/Al by 0.3 and 0.15 wt% DCM doping concentrations.

| Wt% DCM doping concentrations | \(L_{\text{max}}\) (cd/m\(^2\)) | \(\eta_c\) (cd/A) | \(\lambda\) (nm) | \(\lambda_{\text{max}}\) at 16V (nm) | Shoulder (nm) | CIE at 16V (x, y) |
|-------------------------------|-------------------------------|----------------|----------------|----------------------------------|---------------|-------------------|
| DCM\(^{0.35}/\)DPVBi\(_{15}/Zn(BTz)\(_2\)/Al | 923 at 20V | 3.05 | 496 | 529 | 561 | 0.3391 | 0.4601 |
| DCM\(^{0.15}/\)DPVBi\(_{15}/Zn(BTz)\(_2\)/Al | 792 at 17V | 4.16 | 496 | 525 | 560 | 0.2976 | 0.4364 |

![Figure 6](image_url)

Figure 6. a) Electroluminescent intensity (L) and b) current efficiency (\(\eta_c\)) of the OLEDs: ITO/HTL:DCM\(^{0.35}/\)DPVBi\(_5/Zn(BTz)\(_2\)/BAIq\(_5/Zn(BTz)\(_2\)/Al and ITO/HTL:DCM\(^{0.35}/\)DPVBi\(_{15}/Zn(BTz)\(_2\)/Al.

From presented in figure 7 spectra of the compared structures can be seen that the electroluminescent spectra of both devices with 0.15% DCM is very similar each other regardless of different device structures. This is also observed in the devices with 0.3% DCM. It is seen from the summarized data in table 2 and 3 that the CIE coordinates of the emitted light from OLEDs: PVK:TPD+DCM\(^{0.15}/\)DPVBi\(_{15}/Zn(BTz)\(_2\)/Al and PVK:TPD+DCM\(^{0.15}/\)DPVBi\(_5/Zn(BTz)\(_2\)/BAIq\(_5/Zn(BTz)\(_2\)/Al are almost the same. This is also observed and at OLEDs PVK:TPD+DCM\(^{0.35}/\)DPVBi\(_{15}/Zn(BTz)\(_2\)/BAIq\(_5/Zn(BTz)\(_2\)/Al.

It could be noted that, although BAlq was reported as a very good hole-blocking and blue-light-emission material, the results of these investigations suggested that by inserting a certain thickness of DPVBi layer (in our study 5 and 15 nm) plays an important role to modify device characteristics,
which also can act as recombination-controlling layer in the multilayer devices. It offers simple way to fabricate color-tunable OLEDs by just changing the thickness of this layer.

4. Conclusion
We investigated multilayer OLEDs based on DCM as red emitter doped in a composite PVK:TPD hole-transporting layer, DPVBi as a separate blue emitting layer, BAuq as hole-blocking layer and blue emitter at the same time, and Zn(BTz)2 as yellow emitter and electron transporting layer. It was shown that, via changing the OLED structure architectures and the DCM doped concentration in the matrix (in the range of 0 up to 5 %) a fine color tuning of the emitted light can be obtained. It was established that, in all of the OLED structures with doped DCM, independently of presence of the blue emitting layer, the red emission color is predominated according to the DCM concentration in the matrix. The doped OLEDs by DCM concentrations of 0.15 and 0.3 wt% show the maximum current efficiency - two times higher in comparison with undoped structure PVK:TPD/DPVBi5/Zn(BTz)25/BAlq5/Zn(BTz)260.

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