

Fluorescent white organic light-emitting diode structures with dye doped hole transporting layer

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Abstract

This work reports on three primary color fluorescent white organic light emitting diode (WOLED) with simple device structure where only a part of the hole transporting layer was doped with dye. The maximum luminance of the device reaches 35000 cd/m² at a drive voltage below 11V and external quantum efficiency of the device is above 1% in the wide range of luminance from 10 to 35000 cd/m² and reaches its highest 1.6% at 500 cd/m². The chromaticity coordinate shift of the device is negligible in this wide range of luminance. The blue shift of emission color with an increase of current density was attributed to the narrowing of recombination zone width with raise of current density.

1. Introduction

Over the last decade, white organic light-emitting diodes (WOLEDs) are of keen interest for general purpose lighting and flat panel display application. Emitting efficiency and spectral characteristics of WOLEDs already surpass that of incandescent bulbs [1, 2]. Although less emitting efficiency comparative to that of phosphorescent or fluorescent-phosphorescent counterparts, fluorescent WOLEDs potentially meets emitting efficiency, color stability and operating life time requirements for the flat panel display application. Therefore it is still vital to find and design fluorescent WOLED device structures suitable for practical use. In this work we offer fluorescent WOLED device structure which is simple for fabrication because only a part of hole transporting layer is needed to be doped for the emissive layer. Single host for all emitters may lead to less color changes during device ageing. In this work, we were mostly focused on energy transfer

mechanism governing the light emission from the device structure and minor attention was devoted to device optimization for achieving efficient white emission. Therefore we will briefly demonstrate our device characteristics and mainly discuss some interesting, in our opinion, details of energy transfer mechanism in host-guest system.

2. Experimental details

The organic light emitting diode (OLED) pixels with active emissive area of 1.4×1.4 mm² were fabricated on glass substrate with pre-patterned indium tin oxide (ITO) anode by sequential deposition of organic layers and LiF/Al cathode in high vacuum of ~ 4×10⁻⁶ Torr without breaking the vacuum. Common materials such as 4,4'-bis[N-1-naphtyl-N-phenyl-amino] biphenyl (α -NPD) and tris-(8-hydroxyquinoline) aluminum (Alq₃) were used as hole- and electron-transport layers (HTL and ETL), respectively, and 5-nm-thick layer of 2,9-dimethyl, 4,7-diphenyl, 1,10-phenanthroline (BCP) was inserted between the HTL and ETL as a hole and exciton blocking layer. ITO substrates were cleaned by five step ultrasonication with isopropyl alcohol (10 min.), de-ionized water (5 min.), acetone (10 min.), de-ionized water (5 min.), and methanol (10 min.). Then substrates were purged with pure nitrogen gas and stored in a drying oven for more than 1 hour of drying at 120°C. Immediately before loading into the vacuum deposition chamber the substrates were UV-ozone treated for 5 min. The current-voltage- luminance (IVL) characteristics of devices were measured with a KEITHLEY 236 source/measure unit and KEITHLEY 2000 multimeter. Electroluminescence intensity was detected through the calibrated silicon photodiode.

The electroluminescent (EL) emission spectra were measured with an ARC SpectraPro-275 monochromator equipped with a photomultiplier tube. IVL characteristic measurements were carried out under ambient atmosphere, but air exposure time before measuring was kept as short as possible, and had not been exceeded 10 minutes for each device.

In order to calculate a Förster radius [3], we also measured photoluminescence (PL) spectra of possible donor molecules α -NPD and 10-(2-benzothiazolyl)-2,3,6,7-tetramethyl-H,5H,11H-(1)-benzopyrroprano (6,7-8-i,j) quinolizin-11-one (C545T) and ultraviolet-visible (UV-Vis) absorption spectra of potential acceptor molecules C545T and 4-Dicyanomethylene-2-methyl-6-(julolidin-4-yl-vinyl) -4H-pyran (DCM2). The organic materials were dissolved in chloroform with concentrations below 5mg/liter. Solution concentrations were low as possible to exclude effects of molecular aggregation on the measuring spectra. Spectra were taken from solution in quartz cuvette with a 1 cm path length. The PL and UV-Vis absorption spectra were measured using a Jasco FP-6500 spectrofluorometer and a Jasco V-530 UV/Vis spectrophotometer, respectively.

3. Results and discussion

Figure 1 shows proposed device structure in terms of HOMO and LUMO energy levels of each layer and dopants. In our simple WOLED device structure of ITO/ α -NPD (50nm)/ α -NPD: C545T: DCM2 (z nm)/ α -NPD (r nm)/ BCP (5nm)/Alq₃ (50nm)/LiF (0.5nm)/Al (100nm), the α -NPD spacer layer inserted between the hole blocking and the dye doped layers served as an exciton formation and blue emitting layer. The thickness of the dye-doped layer was fixed at $z=10$ nm and the doping concentration of DCM2 was fixed at 0.5 wt.%. For the device A, the doping concentration of C545T was 0.8 wt.% and the thickness of spacer layers were varied as $r = 0,1,2,3,4,5$ nm (devices A0, A1, A2, A3, A4, A5). For the device type B, the doping concentration of C545T was 0.5 wt.% and the thickness of the α -NPD spacer layer was fixed at $r = 3$ nm.

Figure 2 shows EL spectra for the set of devices (A0...A5) with different thicknesses (0, 1, 2, 3, 4, 5 nm) of the spacer layer at the same current density of 150 mA/cm². EL spectra contain all three primary

blue, green, red components for white light emission. Well balanced white emission can be achieved in many ways, by changing thicknesses of doped and spacer layers or adjusting thicknesses of the two layers z and r at fixed optimal doping concentrations. For example, the device (A3) with the doping concentrations of 0.5 wt.% (DCM2) and 0.8 wt. % (C545T) and $z = 10$ nm, $r = 3$ nm showed a white emission with the Commission Internationale d'Eclairage chromaticity coordinates (CIE xy) of (0.291, 0.340) at current density of 150 mA/cm². mission color of the device depends on the thickness of blue spacer layer. As can be seen in Fig. 2, the blue emission intensity from the spacer rises nearly proportional with its thickness. At the same current density of 150 mA/cm² the CIE xy coordinates of devices A0...A5 changes linearly from (0.383, 0.463) to (0.261, 0.296). It implies that the majority of excitons are formed in the α -NPD spacer layer, near the α -NPD/BCP interface. The number of excitons recombined inside of the spacer increases with increasing spacer thickness.

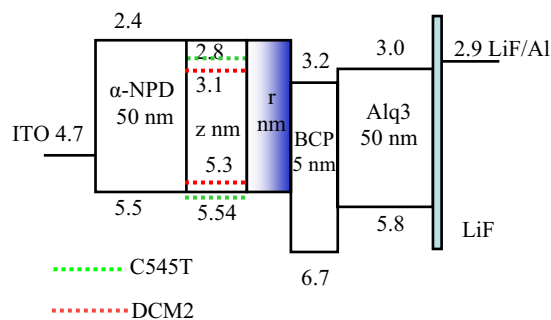


Figure 1. Proposed HOMO and LUMO energy level diagram of the structure. Energies are given in eV. Doped and spacer layer thicknesses are denoted as z and r , respectively.

When the C545T doping concentration was decreased from 0.8 wt.% (device A) to 0.5 wt.% (device B), balanced white emission with the CIE xy coordinates of (0.335, 0.336) can be obtained at the same current density of 150 mA/cm². The external quantum efficiency (QE) of the device B is above 1.0 % in the wide range of luminance from 10 to 35000 cd/m² and reaches its highest value (~1.6 %) at 500 cd/m².

In addition, we found that white emission could be achieved, without a green dopant of C545T, by mixing two complementary colors: blue from α -NPD spacer and yellowish-red from DCM2 dopant. Moreover, the green light emission from Alq3 can be observed when the thickness of the hole blocking BCP layer was decreased below 3 nm, resulting in white light emission with three primary colors without doping C545T. Thinner BCP layer thickness (<4 nm) increases the probability of interlayer sequential energy transfer from α -NPD spacer to the Alq3 ETL across the hole blocking layer [4].

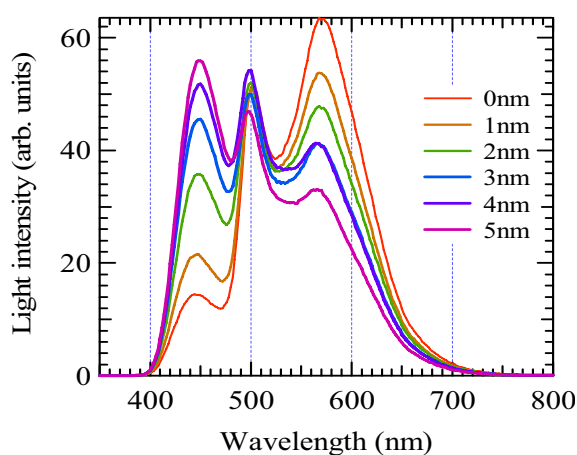


Figure 2. EL spectra for the set of devices A0...A5 with different thicknesses (0,1,2,3,4,5 nm) of the spacer layer at the same current density of 150 mA/cm².

Fig. 2 shows that the emission intensity from the red dopant DCM2 decreases linearly as the α -NPD spacer thickness increases, but the green emission from the C545T dopant changes only slightly. The dependence of EL peak intensities at 448 nm (α -NPD), 500 nm (C545T) and 568 nm (DCM2) on the α -NPD spacer thickness is depicted in the Figure 3. If Förster energy transfer mechanism would be a main excitation process for both dopants, the weak dependence of the green emission from C545T on the spacer thickness is surprising. Förster energy transfer radius from α -NPD host to C545T and DCM2 guests are 3.47 and 3.32 nm (3.35 nm in [5]), respectively, according to our calculations based on the measured PL and UV-vis absorption spectra of these molecules in solution condition (not shown here). Förster energy transfer may also be possible from

green to red dopant. The Förster radius was found as big as 4.8 nm. According to these calculated Förster radii, both dopants may have similar rates of receiving energy from the α -NPD host, and the energy transfer from the green dopant to the red dopant can be efficient. Thus, the green emission would decrease at least as fast as the red one with increasing spacer thickness, in contrary with the observation in Figs. 2 and 3. Although the underlying mechanism of this unusual behavior of the green dopant emission is not clear, we consider that differences in doping concentrations and PL yields (95% for C545T [6] and 52% for DCM2 [5, 7]) of two dopants may play a role.

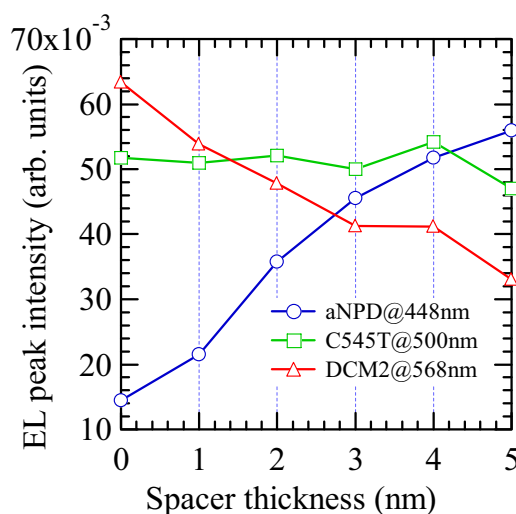


Figure 3. Dependence of EL peak intensities at 448 nm (α -NPD), 500 nm (C545T) and 568 nm (DCM2) on the spacer thickness.

Another well manifested phenomenon observed in this device structure is the blue shift of emission color with an increase of current density (or luminance). For example, the CIE xy coordinates of the device A3 shifts from (0.318, 0.370) to (0.291, 0.340) when the current density rises from 2.5 mA/cm² to 150 mA/cm². Figure 4 shows normalized EL peak intensities of three EL peaks at 448 nm (α -NPD), 500 nm (C545T) and 568 nm (DCM2) as a function of the current density for the devices with the spacer thickness of r=1 nm (device A1) and 5 nm (device A5). The emission from α -NPD increases linearly except at high current density. However, the

emission from two dopants (C545T and DCM2) exhibits a sublinear dependence on the current density way for all spacer layer thicknesses. We can attribute this behavior to the narrowing of recombination zone width with the current density [8]. As the current density rises, the width of electron and hole recombination zone becomes narrow and moves towards the α -NPD/BCP interface so that the exciton energy transfer probability from α -NPD to dopants decreases.

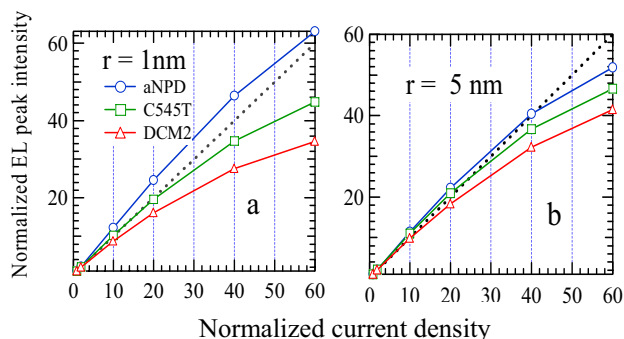


Figure 4. Normalized EL peak intensities of three EL peaks at 448 nm (α -NPD), 500 nm (C545T) and 568 nm (DCM2) as a function of the current density. The spacer thicknesses are 1 nm (a) and 5 nm (b). Dotted line shows hypothetical linear dependence case.

Fig. 4 also shows that the red dopant emission increases slower with increasing current density compared with the green emission. Since DCM2 molecules may act as hole traps in α -NPD, as can be seen from the energy diagram of Fig. 1, the DCM2 molecule sites become increasingly filled by holes with increasing current density. It is known that Förster energy transfer to a positively ionized DCM2 guest molecule is not possible [5]. Therefore, the red emission intensity from DCM2 increases slower compared with the green emission from C545T as the fraction of DCM2 molecules occupied by holes increases with the current density.

3. Summary

In this work, we have demonstrated that white emission with three primary colors can be achieved with a simple device structure. In our device only a part of the hole transporting layer is needed to be doped to build an emissive layer. The external

quantum efficiency of the device is above 1.0 % in the wide range of luminance from 10 to 35000 cd/m^2 and reaches its highest value of 1.6 % at 500 cd/m^2 . The color coordinates shift with an increase of current density was examined and attributed to the narrowing of recombination zone width.

4. Acknowledgements

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5. References

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