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# Efficient, color-stable flexible white top-emitting organic light-emitting diodes

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ABSTRACT

Flexible white top-emitting organic light-emitting diodes (WTEOLEDs) with red and blue phosphorescent dual-emitting layers were fabricated onto polyethylene terephthalate (PET) substrates. By inserting a 2-nm thin tris(phenypyrazole)iridium between the red and the blue emitters as an electron/exciton blocking layer, significant improvements on luminous efficiency and color stability were observed, reaching 9.9 cd/A (3.74 lm/W) and a small chromaticity change of (0.019, 0.011) in a wide luminance range of 80–5160 cd/m$^2$. The origin on color stability was explored by analyzing the electroluminescent spectra, the time-resolved transient photoluminescence decay lifetimes of phosphors, and the tunneling phenomenon. In addition, mechanical bending lifetimes in WTEOLEDs with spin-coated polymethylmethacrylate (PMMA) and thermally evaporated $MoO_x$ onto the PETs were respectively measured, where PMMA or $MoO_x$ is used as a surface planarization layer. Analysis indicates that the poorer lifetime of PMMA-modified WTEOLED than the $MoO_x$-modified ones is mainly due to the low surface energy of PMMA.



## 1. Introduction

White organic light-emitting diodes (WOLEDs) have been widely investigated due to their potential application in solid state lighting and full-color displays [1–4]. For full-color-display applications, the combination of WOLEDs and color filters is one of the most promising technologies, since it avoids the precise shadow-masking technology that usually used in the separate red–green–blue pixilation and thus is beneficial to realizing of high resolution displays and large-area scale-up. In order to realize organic light-emitting diode (OLED) industrialization, the wonderful device stability is a key factor, which is as important as parameters such as high efficiency, high brightness, and low cost. Here, the device stability includes both a long lifetime and a good chromaticity stability. The stability mechanism of the latter has been intensively explored in recent years by many groups [5–8]. We have recently summarized the color stability mechanism in WOLEDs in our review paper [9], in which we considered that five factors including carrier trapping, recombination zone alteration, exciton quenching rate induced by triplet or electrode mirror, electric field or temperature-induced mobility change, and charge transfer (CT) state induced fluorescence quenching or enhancement with an applied electric field will lead to color shift in white emission. In general, the carrier trapping exists universally in a host–guest doping system if the energy levels of the guest are deeply located within those of the host. While for recombination zone alteration, it usually occurs in white emission structures

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composed of multiple-emitting layers. These emitting layers (EMLs) possess obviously different band gaps in order to realize a white light emission. Injected electrons and holes from the electrodes are preferred to recombine in the EML with the lowest recombination energy, e.g., a red EML, and then in those layers with high recombination energies, e.g., green and blue light layers, as the bias is increased. This resulting change of the recombination zone leads to variation in color in the multiple-EMLs white emission devices. For another factor of the triplet exciton quenching, it includes triplet-polaron quenching (strongly depends on the device charge carrier balance [10]), electric field-induced exciton dissociation (suggested by Kalinowski et al. to be the dominant effect [11], which is not observed for state-of-the-art OLEDs [10]), and triplet–triplet annihilation [11,12]. The field- and electrode–mirror-induced quenching of excitons is a phenomenon that coming with the increased internal electric field, the emission quenching rate increases accompanying with the diffused excitons approaching the electrode, further resulting in the deterioration of the color stability [13]. The electric field-induced mobility change and CT state induced fluorescence quenching/enhancement are phenomena of the mobility/emission affected by an applied electric field, which furthermore influence the chromaticity. However, these characteristics are mainly determined by the intrinsic properties of some materials, so their effects on color shift in WOLEDs are few discussed.

The carrier trapping, as the most serious threat to color stability in WOLEDs, has been intensively investigated and reported in recent years [14–16]. Using energy transfer mechanism between the guest and its host material, instead of carrier trapping, is considered as the most efficient approach to realize a color stable white emission [17]. Another wonderful method to obtain a white emission with a good chromaticity stability is to prohibit both carrier trapping, charge transfer and energy transfer by doping an insulating material into the host:guest matrix [6]. If one has to use the host:guest doping system in their white emission devices, a low dopant concentration of the carrier trapping-type guest is also beneficial to obtain a neglectable chromaticity variation, proved by Jou et al. [14,15], Yang [18], and our previous work [19], respectively.

Compared with single-EML WOLEDs with only one exciton recombination zone, multi-EMLs WOLEDs own two or more exciton recombination zones, meaning the involved influence factors on chromaticity stability are more complicated in this type of WOLEDs. Even if only the energy transfer occurs in the multi-EMLs WOLEDs, it may still exist the variation in color accompanying with the increase of bias or current, totally different from that in single-EML white devices. The exciton recombination zone alteration and this-induced exciton recombination imbalance is considered as a major problem that results in the variation of Commission International de L'Eclairage (CIE) coordinates in multi-EMLs WOLEDs. In 2008, Yu and coworkers [20] published two four-color WOLED structures, namely, BL/TL(2 nm)/RL/YL/GL and BL/RL/TL (2 nm)/YL/GL, where BL, RL, YL, and GL represents blue phosphorescent EML iridium(III)bis[4,6-(di-fluorophenyl)-pyridinato-N,$C^{2\prime}$] picolinate (FIrpic), red phosphorescent one bis(2-benzo[*b*]thiophen-2-ylpyridine)(acetylacetonate) iridium(III), yellow phosphor [$Ir(L)_3$] (HL = 2-(9,9-diethylfluoren-2-yl)pyridine), and green tris(phenylpyridine) iridium (III) ($Ir(ppy)_3$). A thin 1,3,5-tris (N-phenylbenzimidazole-2-yl) benzene (TPBi) namely TL as a hole barrier layer is inserted between BL and RL or RL and YL makes chromaticity change well controlled within a narrow range of (0.01, 0.01) in above devices. Such a small shift is a good manifestation of the proper use and interposition of the hole barrier layer which efficiently confines the excitons in-between the four-EMLs. Due to the insertion of TPBi, the distribution profiles of the holes and electrons are similar but follow opposite directions at both a low and high driving voltages. So, the CIE coordinates could maintain more or less constant during the whole driving process.

Su et al. reported in 2008 a blue–orange complementary-color WOLED showing extremely good electroluminescent (EL) efficiencies and color stability [21]. The impressive results were realized by a wise arrangement of EMLs along with a careful choice of energy-level stepped high-performance functional materials. The combination of the FIrpic-doped 4,4′,4″-tri(9-carbazoyl) triphenylamine host and the bipolar host of 2,6-bis(3-(carbazol-9-yl)phenyl)pyridine as EMLs is also helpful to extend the exciton recombination area, reduce the triplet–triplet annihilation and realize an extremely color stability. The white light emitted from the device shows very encouraging color stability with CIE coordinates slightly shifting from (0.341, 0.396) at 100 cd $m^{-2}$ to (0.335, 0.396) at 1000 cd $m^{-2}$ and very high EL efficiencies with peak external quantum efficiency of 25% and power efficiency of 53 lm $W^{-1}$, which are even higher than those of reported WOLEDs with out-coupling techniques. Recently, Hsiao et al. demonstrated [22] that by putting the charge carrier trapping dopant outside the recombination zone and thus preventing the direct exciton formation on these dopants, it is possible to suppress the obvious color shift generally observed in white OLEDs. In their devices, a carrier trapping-type red fluorescent dye 4-(dicyanomethylene)-2-*tert*-butyl-6-(1,1,7,7-teramethyljulolidyl-9-enyl)-4*H*-pyan (DCJTB) located outside the main exciton recombination zone of $Ir(ppy)_3$ is not only helpful to realize a color stable EL spectra by utilizing the energy transfer of $Ir(ppy)_3$ to the neighboring DCJTB layer but also beneficial to retrieve the originally quenched triplet excitons under triplet–triplet annihilation due to the presence of faster channels for consuming triplet excitons and transfer them to radiative singlet excitons.

In our present work, we fabricated dual-EMLs WOLEDs with a top-emitting structure onto the flexible polyethylene terephthalate (PET) substrates, in which a carrier-trapping guest material is utilized with a high doping concentration. Both the emission efficiency and color stability were improved by inserting a 2 nm-thin tris(phenypyrazole)iridium ($Ir(ppz)_3$) electronic blocking layer between the red and the blue EMLs. The working mechanism on color stability in our devices has been intensively explored. Here, it is noted that compared with bottom-emitting ones, top-emitting OLEDs (TEOLEDs) have many