

Color-stable all-fluorescent WOLEDs with single bipolar host based on a red TADF emitter

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Abstract. High color rendering index and color-stable all-fluorescent white organic light-emitting devices (WOLEDs) with a red thermally activated delayed fluorescence (TADF) emitter using 2,3,5,6-tetrakis(3,6-diphenylcarbazol-9-yl)-1,4-dicyanobenzene (4CzTPN-Ph) and a blue fluorescent emitter (DSA-Ph) doped in a bipolar host emitter were fabricated. Extended exciton recombination zone by a bipolar host emitter contributes to balance the distribution of carriers in the emitting layer. The device exhibits high color stable white emission with a slight Commission International de l'Eclairage (CIE) coordinates variation of (0.002, 0.001) at a luminance ranging from 500 cd m⁻² to 5000 cd m⁻², the CIE coordinate of (0.40, 0.38) and the CRI up to 74. These results indicate that the application of a single bipolar host, a spacer-free layer structure, and a TADF emitter has a significant effect on achieving spectrally stable emission, improving the color rendering index, and reducing the efficiency roll-off of the fluorescent WOLEDs.

1. Introduction

White organic light emitting diodes (WOLEDs) are attracting much more attention in the past decades due to their potential application as the solid-state light source, backlights for flat-panel displays, and full color OLEDs, which has been considered as the most promising technology for the next generation display and solid-state lighting applications.[1-2] Currently, the best WOLEDs are all-phosphorescent WOLEDs, during which the singlet and triplet excitons generated in the luminescent layer can be effectively utilized via reasonable structure design.[3] However, the development of phosphorescent WOLEDs has been limited due to the lack of long lifetime, stable blue phosphorescent guest materials.[4]

To overcome the blue phosphorescence instability in WOLEDs, fluorescence/Phosphorescence mixed WOLEDs has been developed, combined with the stable blue fluorescence and phosphorescence, so as to extend the lifetime.[5] In 2010, Wang [6] developed a simple hybrid WOLEDs with stable complementary color emissions, in which doping DSA-Ph as blue fluorescence layer in MADN, NPB as spacer to separate blue fluorescent emitting layer and Ir(Cz-CF₃):CBP orange phosphorescent layer. The maximum current efficiency (CE) and power efficiency (PE) of the optimized device reach 42.5 cd A⁻¹ and 24.9 lm W⁻¹, respectively. However, in these complementary WOLEDs, the CRI is low (no more than 60). In 2012, Ma [7] developed a new fluorescence/Phosphorescence mixed WOLEDs with improved efficiency and color stability, in which TCTA: Beqq2 Hybrid as Phosphor Material, the PE and EQE are 27.1 lm W⁻¹ and 13.7% respectively at 1000 cd m⁻², CRI as high as 89, CIE coordinate of



(0.43, 0.43). Full phosphorescent device and Fluorescence/phosphorus white devices increased the production cost of the device because of heavy metal doped complex luminescent material.

In recent years, Adachi [8] committed to TADF material looking for a new way to develop a delayed fluorescence based OLED device. TADF could reach up to IQE 100% due to no heavy metals included, high fluorescence quantum, converting of triplet excitons to singlet through RISC. It is reported that the EQE for green and red materials are 20%, 10% respectively, which could be comparable to highly efficient phosphorescent materials. In 2015, Adachi combined full-fluorescent WOLEDs used blue delayed fluorescent Material DMAC-DPS, green and red fluorescent material, the EQE was 12%, CIE coordinate of (0.25, 0.31), CRI 74. TADF material has great potential in implement efficient full-fluorescent WOLEDs. But only few full-fluorescent WOLEDs are reported because structural complexity, different color (blue, green, red) dopants have different effects on the formation of excitons.

In this paper, a new complementary color fluorescence WOLEDs are developed using red TADF emitter (4CzTPN-Ph) and blue fluorescence emitter (DSA-Ph) with spectral stability and high CRI. A bipolar host CBP was used to form the light-emitting layer, which was the single host of all guest materials. The application of bipolar host contributes to expand excimer complex and balance distribution of carriers in the luminescent layer effectively, so that the emission spectrum of the fluorescent WOLEDs can be more stable. The device also shows a high CRI at high brightness.

2. Experimental

The device structure and energy level diagram of the full-fluorescent WOLED are shown in Figure 1. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) values for organic material were obtained from references. TAPC was used as hole transport layer (HTL) in this device. TAPC is suitable for HTL due to high hole mobility ($\sim 10^{-2} \text{ cm}^2 / \text{Vs}$) and wide band gap with high triplet energy (2.98 eV). TmPyPB is suitable for Electronic Transport Layer (ETL) due to high electron mobility and wide band gap with high triplet energy (2.78 eV). As the host of transmitter, CBP showed bipolar transport characteristics. 4CzTPN-Ph was used as orange TADF material, DSA-Ph as blue fluorescent dopant, MoO₃ and LiF were used as hole injection and electron injection materials respectively.

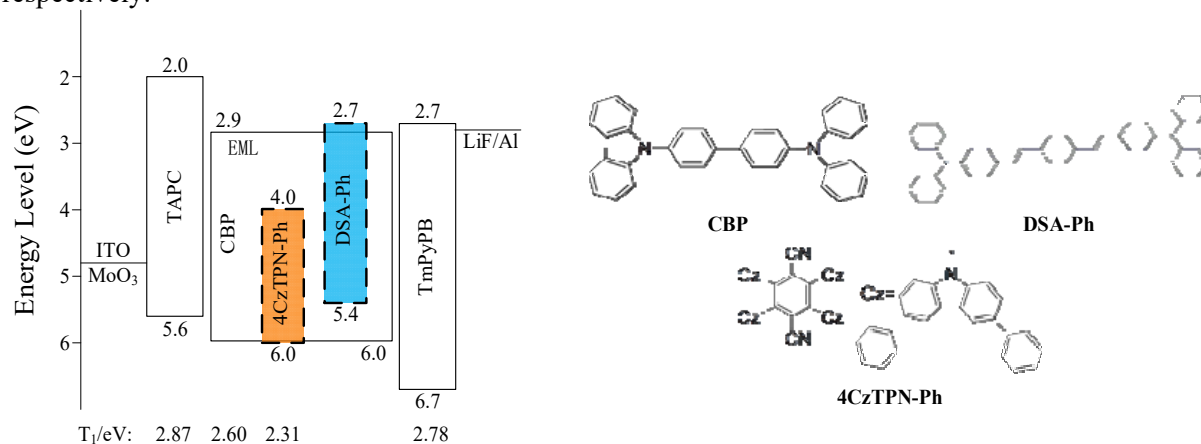


Figure. 1 Chemical structures and Schematic energy level diagram of the WOLEDs organic materials

All devices were fabricated through thermal deposition onto a patterned indium-tin-oxide (ITO)-coated glass substrates as anode with a sheet resistance of 15 Ω/sq . Prior to the deposition of the organic layers, the pre-cleaned ITO substrates were routinely cleaned through a continuous ultrasonic treatment with acetone, ethanol, and deionized water for 20 min in sequence, then it was dried at 120 $^{\circ}\text{C}$ in drying oven before it was loaded into the deposition system. It should be exposed to ultraviolet (UV) ozone for 10 minutes before putting into vacuum evaporation system. Under the pressure of $2 \times 10^{-4} \text{ Pa}$, the organic layer was deposited on the glass at the speed of 1 $\text{\AA}/\text{s}$ by thermal evaporation. For MoO₃ and LiF, the

speed should be 0.1 \AA/s , and the speed for co-deposited layer was 1 \AA/s totally. The current density-voltage-lightness characteristics (J-V-L), electroluminescence spectra and CIE for WOLEDs are measured by Keithley Digital Sources List 2400 and Spectroradiometer PR655. All devices were unpackaged and measured in air directly. EQE were calibrated by angle dependent PL carefully.

3. Results and discussion

A fluorescent device was designed with single host structure and double light emitting layer. The structure of device A was: ITO/MoO₃(5 nm)/ TAPC(35 nm)/CBP:6% 4CzTPN-Ph(14 nm)/ CBP:5% DSA-PH(4 nm)/TmPyPB(50 nm)/LiF(1 nm)/Al(120 nm), the structure shown in figure 1. The red TADF 4CzTPN-Ph transmitter and blue fluorescent DSA-Ph transmitter as different luminescent material. Figure 2 showed the current density-voltage-lightness characteristics (a) of device A, current efficiency-lightness-power (b) and normalized electroluminescence spectra (c) under different current density. It is clear that the emission peak of blue fluorescent dye DSA-Ph is at the point of 472nm, and there is another followed peak at the point of 500nm. The emission peak of 588nm comes from red TADF 4CzTPN-Ph. Under the condition of low current density, the blue emission peak is stronger than red emission peak. If under high current density, the red peak is a little stronger than before. This device showed an excellent spectrum, there is nearly no drift at the range of 500 to 5000 cd m^{-2} , CIE changed little, from (0.407, 0.387) to (0.409, 0.387), $\Delta \text{CIE}(x,y) < (0.002, 0.001)$, the CRI as high as 74. This device showed a excellent warm white light emission.

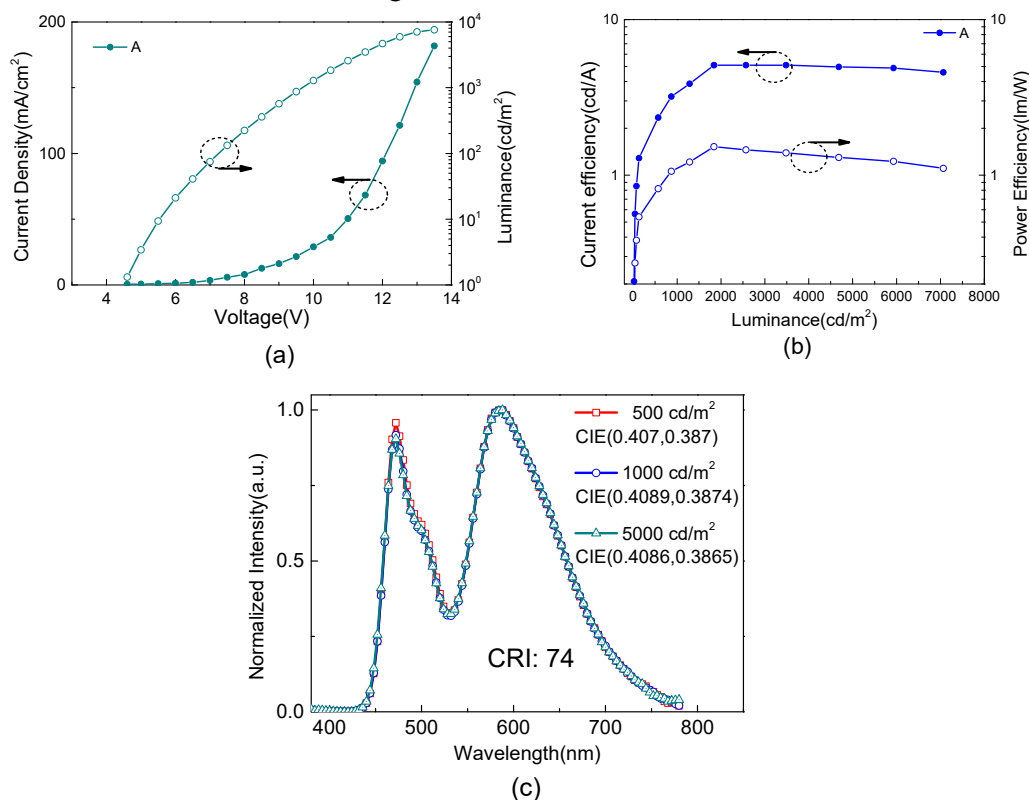


Figure. 2 (a) Current density-Voltage-Luminance; (b) Current efficiency-Luminance-Power efficiency; (c) EL Spectra at different current density

The luminescence spectrum stability reasons for device A were analyzed through material level shown in figure 1. It is probably because, in device A the hole injection material MoO₃ was used, which could make the hole transfer easily from hole transport layer TAPC to TAPC/EML interface. The bipolar host material CBP and red guest material 4CzTPN-Ph do have the same HOMO energy level -6.0 eV, so that the hole could be transferred to guest 4CzTPN-Ph and host CBP respectively. Additionally, the

LUMO level difference of 4CzTPN-Ph and host material CBP was up to 1.1 eV. Most of the electrons are captured by 4CzTPN-Ph molecules. While the hole were transferred to blue and red guest interface, a part of hole and electrons captured by 4CzTPN-Ph composited and emit red light. The other part of hole transferred to blue layer. As the HOMO energy level of blue guest DSA-Ph and host CBP are -5.4 eV and -6.0 eV respectively, the 0.6eV energy level difference make DSA-Ph become hole trap. Holes are mainly transmitted on DSA-Ph molecules. Electrons injected from the cathode transferred through TmPhPB to blue interface, the LUMO energy level is -2.7 eV the same as blue guest level, the LUMO level of blue host CBP is -2.9 eV. So, electrons can be transmitted on the object DSA-Ph and the bipolar body CBP, respectively, which was combined to hole at the interface of CBP/TmPyPB could emits blue light. In red layer, under low current density condition, the emission of 4CzTPN-Ph is mainly based on carrier capture; under high current density condition, mainly based on energy transfer from CBP subject to object; in blue layer, the luminescence of DSA-Ph originates from the self-composition radiation of DSA-Ph molecules and the energy transfer from CBP to DSA-Ph, respectively. Since electrons are mainly transported by the bipolar bulk CBP, CBP has a higher hole transport capability than electron transport at low current densities, so at low current densities blue light is slightly stronger than red light.

Device A balances carrier injection due to the use of a single bipolar body CBP. As can be seen from Figure 2b, the device shows a lower efficiency roll-off at high brightness, maximum current efficiency and power efficiency are 5.09 cd A⁻¹ and 1.52 lm W⁻¹ respectively, corresponding current density and brightness are 36 mA cm⁻² and 1842 cd m⁻² respectively.

4. Conclusion

Complementary color full-fluorescence WOLEDs were designed using red TADF material and blue fluorescent material. Complementary color full-fluorescence WOLEDs show excellent color stability, there is nearly no drift at the range of 500 to 5000 cd m⁻², CIE changed little, from (0.407, 0.387) to (0.409, 0.387), $\Delta\text{CIE}(x, y) < \pm(0.002, 0.001)$, the CRI as high as 74. The results show that, single host and all-fluorescent device structure would make the WOLEDs better performance, such as high efficiency, high CRI and color stability, which could be widely used in next-generation lighting.

Acknowledgments

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References

- [1] B. W. D'Andrade, S. R. Forrest. White Organic Light-Emitting Devices for Solid-State Lighting[J]. *Advanced Materials*, 2004, 16(18):1193-1203.
- [2] Reineke S, Lindner F, Schwartz G, et al. White organic light-emitting diodes with fluorescent tube efficiency[J]. *Nature*, 2009, 459(7244):234-8.
- [3] Sun Y, Forrest S R. High-efficiency white organic light emitting devices with three separate phosphorescent emission layers[J]. *Applied Physics Letters*, 2007, 91(26):197.
- [4] Mulder C L, Celebi K, Milaninia K M, et al. Saturated and efficient blue phosphorescent organic light emitting devices with Lambertian angular emission[J]. *Applied Physics Letters*, 2007, 90(21):2082.
- [5] Schwartz G, Reineke S, Rosenow T C, et al. Triplet Harvesting in Hybrid White Organic Light - Emitting Diodes[J]. *Advanced Functional Materials*, 2009, 19(9):1319-1333.
- [6] Wang Q, Ho C L, Zhao Y, et al. Reduced efficiency roll-off in highly efficient and color-stable hybrid WOLEDs: The influence of triplet transfer and charge-transport behavior on enhancing device performance[J]. *Organic Electronics*, 2010, 11(2):238-246.
- [7] Zhao F, Sun N, Zhang H, et al. Hybrid white organic light-emitting diodes with a double light-emitting layer structure for high color-rendering index[J]. *Journal of Applied Physics*, 2012, 112(8):663-912.
- [8] Uoyama H, Goushi K, Shizu K, et al. Highly efficient organic light-emitting diodes from delayed

fluorescence.[J]. Nature, 2012, 492(7428):234-238.