Color-stable, reduced efficiency roll-off hybrid white organic light emitting diodes with ultra high brightness*

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High-brightness and color-stable two-wavelength hybrid white organic light emitting diodes (HWOLEDs) with the configuration of indium tin oxide (ITO)/ N, N, N′, N′-tetrakis(4-methoxyphenyl)-benzidine (MeO-TPD): tetrafluoro-tetracyanoqino dimethane (F4-TCNQ)/N,N′-di(naphthalene-1-yl)-N,N′-diphenyl-benzidine (NPB)/ 4,4-N,N-dicarbazolebiphenyl (CBP): iridium (III) diazine complexes $(MPPZ)_2Ir(acac)$/NPB/2-methyl-9,10-di(2-naphthyl)anthracene (MADN): p-bis(p-N,N-di-phenyl-aminostyryl)benzene (DSA-ph)/ bis(10-hydroxybenzo[h] quinolinato)beryllium complex ($Bebq_2$)/LiF/Al have been fabricated and characterized. The optimal brightness of the device is 69932 cd/m^2 at a voltage of 13 V, and the Commission Internationale de l'Eclairage (CIE) chromaticity coordinates are almost constant during a large voltage change of 6–12 V. Furthermore, a current efficiency of 15.3 cd/A at an illumination-relevant brightness of 1000 cd/m^2 is obtained, which rolls off slightly to 13.0 cd/A at an ultra high brightness of 50000 cd/m^2 . We attribute this great performance to wisely selecting an appropriate spacer together with effectively utilizing the combinations of exciton-harvested orange-phosphorescence/ blue-fluorescence in the device. Undoubtedly, this is one of the most exciting results in two-wavelength HWOLEDs up to now.

Keywords: white light, color stability, efficiency roll-off, high brightness

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1. Introduction

White organic light emitting diodes (WOLEDs) have attracted considerable attention due to their potential applications as liquid crystal display (LCD) backlights and light sources for indoor lighting.[1–5] Three kinds of WOLEDs have been reported, including all-phosphorescent WOLEDs,[6] all-flourescent WOLEDs,[7] and WOLEDs based on hybrid emissive materials which are called hybrid WOLEDs (HWOLEDs).[8] Among these types, phosphorescent (P) WOLEDs are widely considered to be outstanding because they have been demonstrated to harvest 100% of the excitons generated by the electrical injection, corresponding to a fourfold increase in efficiency compared to that achieved in singlet-harvesting fluorescent (F) WOLEDs.[9] To date, unfortunately, there is no proper blue P material in terms of operational lifetime and color stability, limiting the development of all-phosphor-doped WOLEDs.[10] Luckily, in recent years, more and more researchers have paid attention to HWOLEDs that combine stable F blue emitters with P green-red (or orange) emitters because of their advantages, such as high efficiency and long lifetime. In fact, a great number of remarkable HWOLEDs have been achieved, such as managing singlet and triplet excitons within an ambipolar host,[11] the utilization of a P sensitizer,[12] and the p–i–n junction structure.[13] On the other hand, since the efficiency of WOLEDs has experienced step-by-step increase over the past years, the research focus is now shifting towards the problems such as enhancing the device color stability and reducing the efficiency roll-off at high brightness in order to satisfy the future lighting requirements.[14] However, there are few such reports for HWOLEDs.

In this paper, we report the realization of reduced efficiency roll-off HWOLEDs with good color stability based on a simple architecture combining a blue F material with an orange P material to furnish the white emission. The optimized device shows a peak brigthness of 69932 cd/m^2 at a voltage of 13 V, which is, to the best of our knowledge, the highest brightness in two-wavelength HWOLEDs reported in the literature so far. When the driving voltage increases from 6 V to 12 V, the color rendering index (CRI) changes from 67 to 69, the Commission Internationale de l'Eclairage (CIE) chromaticity coordinates slightly change from (0.37, 0.36) to (0.36, 0.35), which is a negligible change. Moreover, a cur-

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rent efficiency (CE) of 15.3 cd/A at an illumination-relevant brightness of 1000 cd/m^2 is obtained, which suffers no roll-off at a rather high brightness of 10000 cd/m^2, and even at an ultra high brightness of 50000 cd/m^2, the CE only rolls off slightly to 13.0 cd/A. It is beyond doubt that the optimized device represents one of the best-performance two-wavelength HWOLEDs.

2. Experimental details

Figure 1 depicts the HWOLEDs studied. The fabricated WOLEDs were formed on precleaned indium tin oxide (ITO) glass substrates. Then 100 nm MeO-TPD: F4-TCNQ (as a hole injection layer), 20 nm NPB (as a hole transporting layer), 20 nm CBP: $(MPPZ)_2Ir(acac)$ (as an orange-light-emission layer), X nm NPB (as spacers, $X = 0$, 1, 4, 6), 30 nm MADN: DSA-ph (as a blue-light-emission layer), 25 nm $Bebq_2$ (as an electron transporting layer), and finally 1 nm LiF and 200 nm Al cathode were evaporated in turn, where MeO-TPD is N, N, N′, N′-tetrakis (4-methoxyphenyl)-benzidine, F4-TCNQ is tetrafluoro-tetracyanoqino dimethane, NPB is N,N′-di(naphthalene-1-yl)-N,N′-diphenyl-benzidine, CBP is 4,4-N,N-dicarbazolebiphenyl, $(MPPZ)_2Ir(acac)$ is iridium (III) diazine complexes, MADN is 2-methyl-9,10-di(2-naphthyl)anthracene, DSA-ph is p-bis(p-N,N-di-phenyl-aminostyryl)benzene, and $Bebq_2$ is bis(10-hydroxybenzo[h] quinolinato)beryllium complex. The devices with the NPB spacers of thicknesses 0 nm, 1 nm, 4 nm, 6 nm are referred to as devices A, B, C, and D, respectively. All organic materials were purchased commercially, and all layers were deposited without breaking the vacuum by thermal deposition at a base pressure of 5×10^{-8} Torr. All the organics were evaporated at a rate of 0.1 nm/s, and the metallic cathode was evaporated at a rate of 0.1–0.5 nm/s. The devices were encapsulated immediately after preparation under a nitrogen atmosphere using epoxy glue and glass lids. The electroluminescent (EL) spectra, CRI, and CIE color coordinates of the packaged devices were obtained by using a Photo Research PR705 spectrascan system. The emission area of the devices was 0.09 cm^2 as defined by the overlapping area of the anode and the cathode.

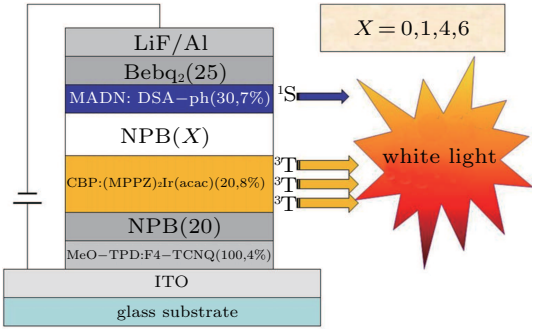


Fig. 1. (color online) Schematic layer structure of processed HWOLEDs. Layer thicknesses are given in nm.

The brightness–current density–voltage characteristics were recorded simultaneously using a computer-controlled source meter (Keithley 2400) and a multimeter (Keithley 2000) with a calibrated silicon photodiode. All the measurements were carried out at room temperature under ambient conditions.

3. Results and discussion

In order to achieve high-performance HWOLEDs, several approaches have been employed. First of all, to maximize exciton formation and emission in WOLEDs, it is necessary to optimize the concentration in the host–guest doped system.[15] By running a serial of experiments, for blue guest and orange dopant, it is found that the optimized concentrations are 7% and 8%, respectively. Secondly, similar to other multilayer WOLED systems, the thickness of each organic layer significantly affects the EL efficiency and the spectrum.[16] As determined in our lab, the thicknesses of the electron transporting layer and the p-doped hole injection layer/hole transporting layer should be 25 nm and 100 nm/20 nm, respectively, which can greatly enchance the balance of carriers. Last but not least, since the Dexter energy transfer requires a spatial overlap of the involved molecular orbitals and is significant only within the range of 1–2 nm,[17] the mutual quenching can therefore be omitted by introducing an appropriate spacer with high triplet energy between the two emitters. In addition, the Förster radius is about 3 nm.[11] Therefore, a thin NPB (4 nm or 6 nm) spacer is introduced between the orange P layer and the blue F layer. In fact, the thin spacer will facilitate the hole injection into the blue F layer and block electrons at the MADN side, ensuring the blue emission. As a contrast, HWOLEDs with no spacer and with 1 nm spacer are also fabricated. With the above considerations, we come up with the structure of HWOLEDs in Fig. 1.

As clearly shown in Fig. 2, when the thickness of the NPB spacer increases from 0 nm to 6 nm, the EL spectra of devices are significantly affected. On one hand, as mentioned above, without the spacer or a too thin spacer can not effectively eliminate the influence of the Dexter and the Förster energy transport. On the other hand, since the NPB is a hole-transporting material, it can facilitate the hole diffusion into the blue region to ensure the blue emission. Decreasing or omitting this layer will dramatically decrease the intensity of the blue emission, and hence we could not get a reasonable white light. At a current density of 20 mA/cm^2, the CIE coordinates of devices A, B, C, and D are (0.50, 0.45), (0.51, 0.45), (0.36, 0.36), (0.35, 0.35), respectively. In fact, we can not classify devices A and B into WOLEDs because they are far away from the white equivalent-energy point (0.33, 0.33). Therefore, we will not discuss devices A and B further.

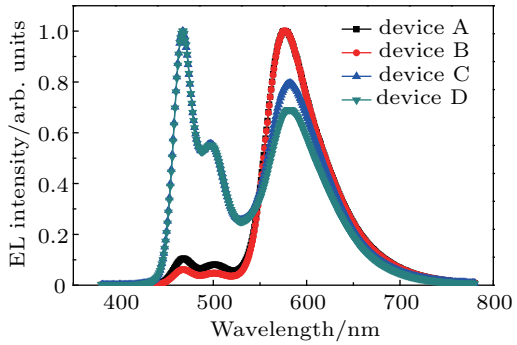


Fig. 2. (color online) EL spectra of HWOLEDs at a current density of 20 mA/cm^2.

Figure 3 shows the typical current density–brightness–voltage characteristics of devices C and D. At the same driving voltage, device C exhibits higher current density and brightness than device D, indicating that only a spacer of an appropriate thickness is suitable for the high-performance device. For device C, the turn-on voltage (defined as the voltage at which the luminance of 1 cd/m^2 is reached) is as low as 3.9 V. At the luminance of 1000 cd/m^2, the applied voltage is 6.9 V, and at the luminance of 10000 cd/m^2, the applied voltage is 9.3 V. The maximum luminance of 69332 cd/m^2 is obtained at a driving voltage of 13 V. The operational voltage for these devices is considerably lower than that described previously.[4,18] Furthermore, the lower operational voltage can also mitigate the degradation of OLEDs.[19]

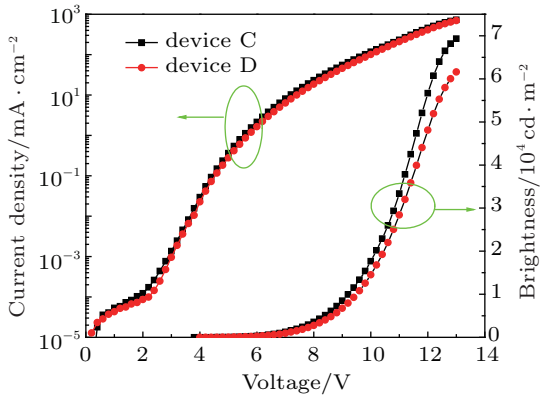


Fig. 3. (color online) Current density–brightness–voltage characteristics of devices C and D.

The CE and the power efficiency (PE) of HWOLEDs (as a function of brightness) are shown in Fig. 4. At the same current density, device C exhibits a higher efficiency. For device C, the maximum PE of 13.8 lm/W is achieved at about 1 cd/m^2. At the typical brightness of 1000 cd/m^2, the PE is 7.0 lm/W. Remarkably, a CE of 15.3 cd/A at a display-relevant brightness of 1000 cd/m^2 is obtained, which remains unchanged at a rather high brightness of 10000 cd/m^2, and even at an ultra high brightness of 50000 cd/m^2, the CE only rolls off slightly to 13.0 cd/A. This little decrease in the CE at such a high brightness is very impressive. Compared with the conventional all-phosphor-doped WOLEDs,[10] which always exhibit a tremendous efficiency roll-off at high brightness, our device can effectively solve this notorious roll-off problem. Moreover, we note that the device outperforms the reported HWOLEDs in the literature in efficiency.[4,17,20–23] Besides, it is important to note that a much higher efficiency can be expected if we utilized out-coupling techniques.[24]

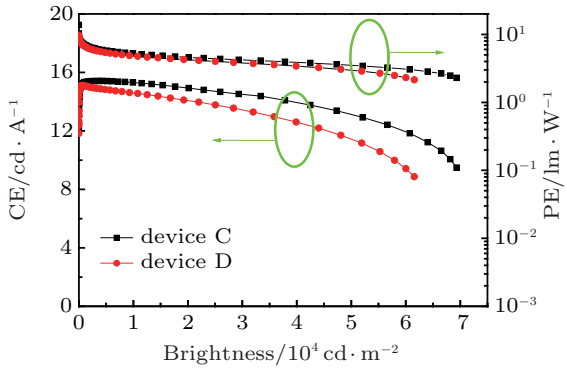


Fig. 4. (color online) The CE and PE of the HWOLEDs as a function of brightness.

The spectral stability upon the change of the applied voltage is also studied. It is noted that no significant EL spectrum change can be observed in device C as the driving voltage increases from 6 V to 12 V, as illustrated in Fig. 5, which is important for illumination. The corresponding CIE coordinates in device C are (0.37, 0.36) at 6 V and (0.36, 0.35) at 12 V, which are very close to the white equivalent-energy point (0.33, 0.33). The variation of (0.01, 0.01) is much less than that observed by the human eye, implying that device C demonstrates excellent color stability. On the other hand, the CRI changes from 67 to 69 as the driving voltage increases from 6 V to 12 V.

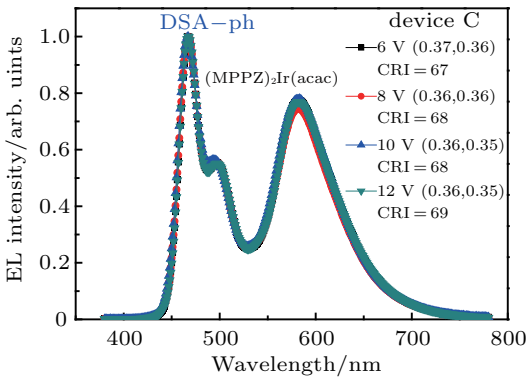


Fig. 5. (color online) EL spectra and CRI of device C at different applied voltage.

Finally, it is interesting to study the mechanism of the efficient white emission from this system. Three reasons may explain the relatively high performance of the HWOLEDs.

Firstly, it is universally acknowledged that the NPB has the property of hole transporting/electron blocking, which plays a crucial role in improving the color performance. By placing a thin NPB spacer between the orange and the blue emitters, it well balances the injection and transport of electrons and holes in orange and blue emissive regions, thus achieving reduced efficiency roll-off and stable white emission. Besides, the NPB spacer, with a high triplet energy ($T_1 \sim 2.29$ eV),[16] can effectively suppress the triplet quenching between P and F regions. In addition, since the Dexter energy transfer can only occur within 1–2 nm and the Förster radius is around 3 nm, by introducing the 4 nm NPB spacer between P and F regions, both singlet and triplet excitons are confined efficiently, whereas the charge carriers still flexibly transport across this thin spacer bridge. In such a device, the blue F dopants harvest the majority of the singlet energy, with the remainder of triplets diffusing into the $(MPPZ)_2Ir(acac)$ doped CBP layer to excite the orange phosphor, which together result in pure white light. Overall, by virtue of wisely selecting an appropriate spacer together with effectively utilizing the combinations of exciton-harnessed orange-phosphorescence/blue-fluorescence in the device, rather high color stability and reduced efficiency roll-off can be simultaneously achieved in this ultra high brightness HWOLED.

4. Conclusion

We have successfully realized high-performance HWOLEDs with an uncomplicated architecture, combining blue F and orange P emissions via two individual emission layers. Impressively, the optimized device not only achieved an ultra high brightness of 69932 cd/m^2, but also obtained a reduced efficiency roll-off, from 15.3 cd/A at 1000 cd/m^2 to 13.0 cd/A at 50000 cd/m^2. Furthermore, the color stability of the device was also excellent. The stable white emission can be obtained in a wide range of driven voltages. Comprehensive experimental and theoretical evidences demonstrated that the wise management of the singlet and triplet excitons as well as the superior charge injection and diffusion balance is the key to realize the reduced efficiency roll-off and excellent color rendition. Undoubtedly, the results will be very beneficial to the design of both material and device structure for high-performance WOLEDs and the next-generation solid-state lighting sources.

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