Regulating Carriers and Excitons in Simplified Hybrid WOLEDs by Using a Bipolar Interlayer Switch

Baiquan Liu[1], Jianhua Zou[1], Miao Xu[1], Lei Wang[1], Hong Tao[1], Yueju Su[2], Dongyu Gao[2], Linfeng Lan[1], and Junbiao Peng[1]

[1]Institute of Polymer Optoelectronic Materials and Devices
State Key Laboratory of Luminescent Materials and Devices
South China University of Technology, Guangzhou 510640, China
[2]New Vision Opto-Electronic Technology Co., Ltd, Guangzhou 510530, China

Abstract— As phosphorescent (P) emitters allows for a conversion of up to 100% of injected charges into emitted photons, resulting in a theoretical internal quantum efficiency of unity, P materials are usually imperative to boost the efficiency of white organic light-emitting diodes (WOLEDs). Unfortunately, there is still no proper blue P material in terms of operational lifetime and color-stability until now, limiting the development of all-phosphor devices. To solve the above conflicts, the hybrid WOLEDs, combining blue flourescent (F) emitters with P green-red/orange emitters, are considered to be an effective way due to their merits, such as high efficiency, stable color and long lifetime. A key feature of designing HWOLEDs is utilizing an appropriate interlayer, which locates between the F emitter and the P emitter. Herein, by mixing 4,4-N,N-dicarbazolebiphenyl (CBP) with bis[2-(2-hydroxyphenyl)-pyridine] beryllium ($Bepp_2$) as the interlayer, a simple hybrid with dual-emitting-layer a realized. The device with the bipolar interlayer shows higher performance than the device with CBP, $Bepp_2$interlayer and the device without interlayer. The reasons can be attributed to the bipolar interlayer which not only regulating the carriers in the device, but also eliminate the both the non-radiative Dexter energy Förster energy transfer between the two layers. The resulting device exhibits a total current efficiency of 23.6 cd/A and power efficiency of 16.2 lm/W at the illumination-relevant luminance of 1000 cd/m^2, respectively. Besides, a Commission Internationale de L'Eclairage (CIExy) variation of (0.31, 0.41) and a high color rendering index of 85 at 1000 cd/m^2 can be obtained. Moreover, the lifetime of the device is also discussed.

1. INTRODUCTION

White organic light-emitting diodes (WOLEDs) are now entering mainstream display markets and also being explored for next-generation lighting applications owing to their high efficiency, light weight and low cost [1]. Generally, WOLEDs are classified into three kinds according to the used emissive materials, including all-phosphorescent WOLEDs, all-flourescent WOLEDs and hybrid WOLEDs (HWOLEDs) which are based on hybrid (flourescent (F) and phosphorescent (P)) emissive materials [2–4] Among them, the utilizition of P emitters is desirable because P emitters are able to harvest both singlet and triplet excitons. Therefore, devices with internal quantum efficiencies up to 100% have been demonstrated. However, there is no perfect blue P material in terms of lifetime and color-stability untill now, limiting the development of P devices. In recent years, several publications have been devoted to address the conflict by creating HWOLEDs [2–4], which combine stable F blue emitters with P green-red/orange emitters. Sun et al. took the first step to realize HWOLEDs with high efficiency by using the combination of stacked F-interlayer (IL)-P-P-IL-F emitters, achieving a maximum total power efficiency (PE) of 37.6 lm/W and 23.8 lm/W at 500 cd/m^2 [2]. Since then, a large number of attentions have been paid to HWOLEDs. A key feature of designing HWOLEDa is utilizing an appropriate IL, which locates between the F emitter and the P emitter. Playing the crucial role in HWOLEDs, ILs can not only prevent Förster energy transfer (ET) from the F blue emitters to the red-green/orange P emitters, but also eliminate the non-radiative Dexter ET between the two layers [2]. Furthermore, emission color can also be tuned by changing the IL thickness. Therefore, by using a thin IL, both singlet and triplet excitons can be effectively managed. So far, 4,4-N,N-dicarbazolebiphenyl (CBP) is the most popular and efficient spacer owing to its high triplet energy (2.6 eV) and bipolar conducting properties [5]. However, it is found that its hole mobility of CBP is $10^{-3}\,cm^2/V\,s$, much higher than its electron mobility ($10^{-4}\,cm^2/V\,s$) [5], leading to unbalanced carriers in this spacer. Hence, CBP can not be considered as an ideal spacer. In order to solve the issue, it is wise to mix an appropriate n-type material with CBP as the spacer, however, reports about it are scarce. On the other hand, it is easily noted that the HWOLED created by Sun et al. shows complicated structure and the efficiency roll-off is serious To simplify structures, an alternative way is the utilization of stacked P-IL-F emitters to realize HWOLEDs. In fact, tremendous efforts have been devoted to the pursuit of this simple approach. For example, Ho et al. constructed a two-element HWOLED with the P-IL-F structure by utilizing a heteroleptic orange Ir-complex, obtaining a maximum total PE of 23 lm/W and 13.2 lm/W at 1000 cd/m^2 [3]. Yang et al. fabricated the P-IL-F device by applying a naphthalenebenzofuran compound as the deep-blue F emitter, achieving a maximum efficiency of 25 lm/W and 7.0 lm/W at 500 cd/m^2 [4]. From these facts, it is noted that the P-IL-F structure is simplified and the efficiency of these devices has experienced step-bystep increase in the last few years. However, the efficiency roll-off is still being a big obstacle. Moreover, the color rendering index (CRI) of this kind devices, which is important for the lighting applications [6], is paid negligible attention. As a result, the CRI of these simple devices is usually below 75. Therefore, there is an urgent need to simultaneously realize high efficiency, low efficiency roll-off and high CRI WOLEDs with the simplified P-IL-F structures.

In this paper, the device performance is greatly improved via an effective IL. The optimized device exhibits a maximum total current efficiency (CE) and PE of 24.7 cd/A and 16.2 lm/W during a large range of luminance, respectively. And the device exhibits a total CE of 23.6 cd/A and PE of 16.2 lm/W at 1000 cd/m^2, respectively. Besides, a high CRI of 85 is obtained, which is the highest value in the WOLEDs with P-IL-F structures, to the best of our knowledge. Moreover, the device shows rather low efficiency roll-off. Such presented results demonstrate that high efficiency, low efficiency roll-off and high CRI can be simultaneously realized in simple WOLEDs.

2. EXPERIMENTAL

As depicted in Figure 1, the configuration of the resultant device ($W4$) is ITO/MeO-TPD: F4-TCNQ (100 nm, 4%)/NPB (15 nm)/TCTA (5 nm)/MADN: DSA-ph(9 nm, 1%)/CBP: $Bepp_2$ (8.5:1.5, 5 nm)
/$Bepp_2$: $Ir(ppy)_3$: $Ir(piq)_3$ (1: 0.06: 0.01, 25 nm, 5%)/$Bepp_2$ (25 nm)/LiF (1 nm)/Al (200 nm), where ITO is indium tin oxide, 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, TCTA is 4,4',4"-tri(9-carbazoyl) triphenylamine, $Ir(ppy)_3$ is tris(2-phenylpyridinne)iridium(III), $Ir(piq)_3$ is tris(1-phenylisoquinolinolato-C^2, N) iridium(III), DSA-ph is p-bis(p-N,N-di-phenyl-aminostyryl) benzene, MADN is 2-methyl-9,10-di(2-naphthyl)anthracene, $Bepp_2$ is bis[2-(2-hydroxyphenyl)-pyridine] beryllium. The detailed fabrication and measurement of devices followed well-established processes and as reported elsewhere [7].

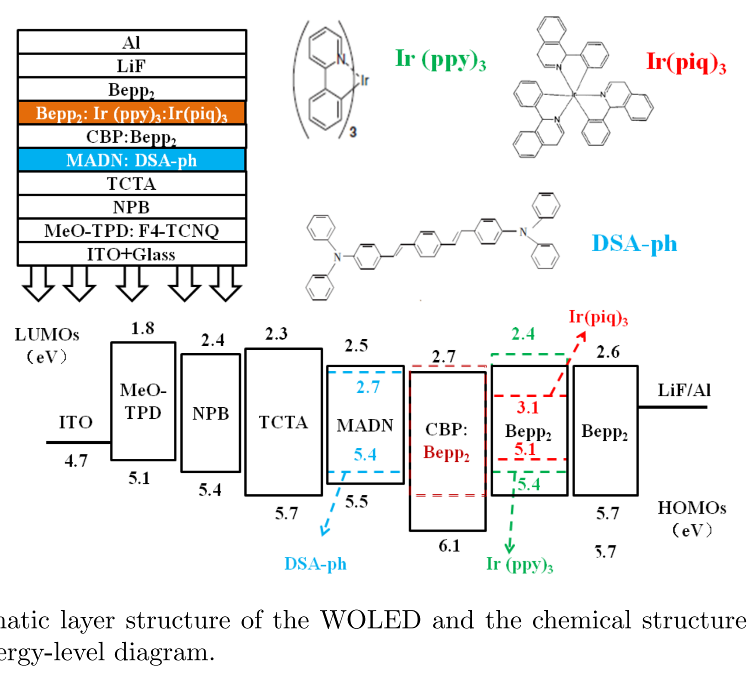

Figure 1: Top: Schematic layer structure of the WOLED and the chemical structure of emissive dopants. Bottom: Proposed energy-level diagram.

3. DISCUSSION AND RESULTS

Since improvement of both efficiency and stability in WOLEDs can be expected by rational design of the structure several strategies are employed to achieve high efficiency, low efficiency roll-off together with high CRI for our HWOLED with P-IL-F structure

First, to lower manufacturing cost, device architectures should be simple. Thus, we utilized double emitting layer to furnish white emission, surprisingly, performances of the simple device are very impressive. Second, to maximize exciton formation and emission in WOLEDs, it is necessary to optimize the concentration in the host-guest doped system. Therefore, monochromatic devices with various concentrations of dopant were tested to determine the best concentrations, as shown in Section 2. Third, emission peaks at 512 nm and 615 nm originating from $Ir(ppy)_3$ and $Ir(piq)_3$ ensure that P-EML exhibits broad emission spectra covering about three fourth of the visible spectrum. The F-EML is formed by doping DSA-ph into MADN (emission peak at 463 nm), greatly overcoming the color-stability limitations found for P WOLEDs. Consequently, high CRI and stable color are expected. Next, the p-doped hole injection layer improves holes injection from ITO anode into NPB hole transporting layer and prevents pinhole defects [7]. Moreover, the $Bepp_2$ electron transport layer exhibits high electron mobility $[10^{-4}\,cm^2/(Vs)]$, giving effective electrons injection and thus an improved carrier balance [8]. Additionally $Bepp_2$ blocks holes and confines excitons in the EML because of its deep HOMO (5.7 eV) and high triplet energy (2.6 eV) [8]. Therefore, a carrier- and exciton-confining structure is formed via the combination of TCTA and $Bepp_2$, boosting efficiencies [7]. Finally, since the Dexter energy transfer can only occur within 1–2 nm and the Förster radius is around 3 nm, by introducing the 5 nm IL 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 [2]. Based on these considerations, we put forward a simple HWOLED, simultaneously achieving high efficiency, low efficiency and high CRI

As shown in Figure 2, by using different ILs, the electroluminescent (EL) spectra of devices are significantly affected. At the illumination-relevant luminance of $1000\,cd/m^2$ the CIE coordinates of device $W1$ (without IL), $W2$ (with $Bepp_2$ IL), $W3$ (with CBP IL), and $W4$ (with CBP: $Bepp_2$ IL) are (0.18, 0.29), (0.19, 0.29), (0.31, 0.45) and (0.31, 0.41), respectively. In fact, we can not classify $W1$ and $W2$ into WOLEDs because they are far away from the white equivalent-energy point of (0.33, 0.33). Although the color of $W3$ is located in the white region, the CRI is only 71, which is not satisfied the demand of lighting applications. By using the more balanced IL, $W4$ shows a high CRI of 85. Moreover, the combination of high CRI, correlated color temperature (CCT), which is better located between 2500 and 6500 K, and the special CRI R9, which quantifies the color reproduction of saturated red and should be positive, is very interesting for commercial applications. $W4$ shows a CCT of 6245 K and a R9 of 63 at $1000\,cd/m^2$.

The reasons for this phenomenon are explained as follows. Since the triplet energy of $Bepp_2$ and $Ir(ppy)_3$ are much higher than that of DSA-ph and MADN, $W1$ without IL can not effectively eliminate the influence of Dexter ET between the F emitter and the P emitter, leading to no green and red intensity and hence we can not obtain a balanced white color For $W2$, holes are difficult to pass through the 5 nm $Bepp_2$ IL since $Bepp_2$ is an n-type material, leading to no white color. In the case of $W3$, although CBP is a bipolar material, its hole mobility is greater than electron mobility. Namely, elecrons will be more difficult than holes passing through the CBP bridge, implying few electrons can reach the blue emissive layer to recombine with the holes injected from the anode, which leads to weak blue intensity and hence we can not get a reasonable white light. On the other hand, by slightly codoped $Bepp_2$ with CBP as the IL, a more balanced carrier is achieved, leading to more balanced color.

The CE and PE of $W4$ in dependence of the luminance are shown in Figure 3. At the typical luminance of $1000\,cd/m^2$, the forward-viewing CE and PE are 13.9 cd/A and 9.5 lm/W, respectively. Since illumination sources are typically characterized by their total emitted power [2], $W4$ exhibits a total CE of 23.6 cd/A and PE of 16.2 lm/W at $1000\,cd/m^2$, respectively. Obviously, it is noted that the efficiency of this simplified device is higher than that of previous HWOLEDs at the practical luminance of $1000\,cd/m^2$ [2–4]. And much higher efficiency can be expected if we replaced the ETL with an n-doped layer to form a pin structure or utilized out-coupling techniques to increase the light extraction

More remarkably, $W4$ shows rather low efficiency roll-off. For example, a maximum forward-viewing CE of 14.5 cd/A is obtained at $2200\,cd/m^2$, which remains unchanged to a rather high brightness of 4700 cd/m^2, and even at an ultra high brightness of $10000\,cd/m^2$, the CE rolls off slightly to 13.6 cd/A. A maximum forward-viewing PE of 9.5 lm/W is obtained at $600\,cd/m^2$,

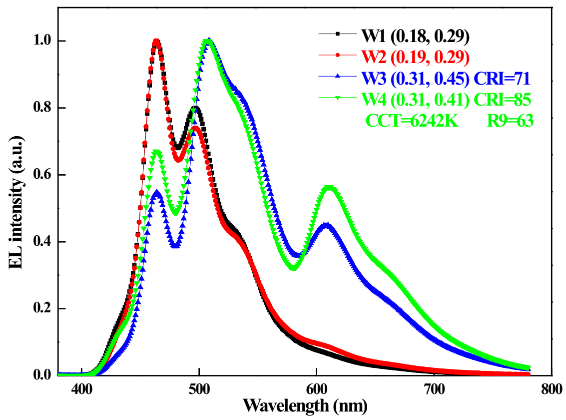

Figure 2: EL spectra of devices at a luminance of $1000\,\mathrm{cd/m^2}$.

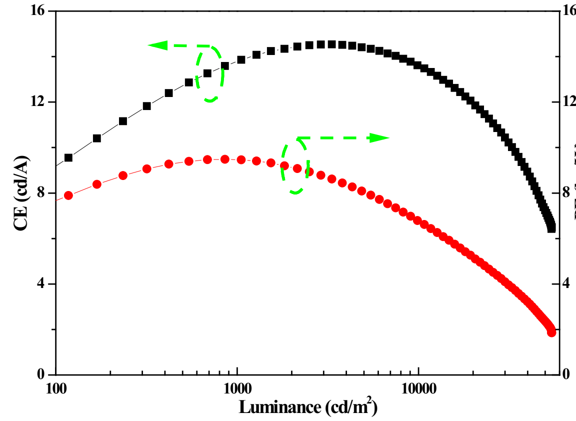

Figure 3: Power and current efficiencies as a function of luminance.

which remains unchanged to a high brightness of $1100\,\mathrm{cd/m^2}$, and even at an high brightness of $5000\,\mathrm{cd/m^2}$, the PE rolls off slightly to 8.1 lm/W. Apparently, the efficiency roll-off is much lower than previous HWOLEDs [2–4]. In fact, this is one of the lowest efficiency roll-off in WOLEDs in the literature so far, to our knowledge.

Finally, it is deserved to discuss the lifetime of $W4$, although there is no report has been documented on the lifetime of HWOLEDs in the revealed literature so far, which may be attributed to the lifetime of HWOLEDs is still poor nowadays. The lifetime of $W4$ at an initial illumination of $1000\,\mathrm{cd/m^2}$ is only ~ 1 hour. The poor lifetime can be attributed to the poor lifetime of CBP and TCTA. More stable charge transport materials and state-of-the-art emitters are expected to prolong lifetime.

4. CONCLUSIONS

In conclusion, we have successfully demonstrated a three-color hybrid WOLED with the P-IL-F structure. By using an effective IL, the device performance is dramatically boosted. The optimized device exhibits a maximum total CE and PE of 24.7 cd/A and 16.2 lm/W during a large range of luminance, respectively. Besides, a high CRI of 85 and rather low efficiency roll-off are achieved. We believe such presented results would provide an instructive guide for the rational design of ultra high-performance HWOLEDs, which will be very advantageous for the realization of next-generation solid-state indoor lighting sources in the future.

REFERENCES

1. Sasabe, H. and J. Kido, "Development of high performance OLEDs for general lighting," *J. Mater. Chem. C*, 1, 1699, 2013.
2. Sun, Y., et al., "Management of singlet and triplet excitons for efficient white organic light-emitting devices" *Nature*, Vol. 440, 908, 2006.
3. Ho, C. L., et al., "A multifunctional Iridium-Carbazolyl orange phosphor for high-performance two-element WOLED exploiting exciton-managed fluorescence/phosphorescence," *Adv. Funct. Mater.*, Vol. 18, 928, 2008.
4. Yang, X. H., et al., "Fluorescent deep-blue and hybrid white emitting devices based on a naphthalene-benzofuran compound," *Org. Electron.* Vol. 14, 2023, 2013.
5. Zhang, D., et al., "Extremely low driving voltage electrophosphorescent green organic light-emitting diodes based on a host material with small singlet–triplet exchange energy without p- or n-doping layer," *Org. Electron.*, Vol. 14, 260, 2013.
6. Jou, J., et al. "Efficient very-high color rendering index organic light-emitting diode," *Org. Electron.*, Vol. 12, 865, 2011.
7. Liu, B., et al., "Investigation and optimization of each organic layer: A simple but effective approach towards achieving high-efficiency hybrid white organic light-emitting diodes," *Org. Electron.*, Vol. 15, 926, 2014.
8. Zhao, F., et al., "A hybrid white organic light-emitting diode with stable color and reduced efficiency roll-off by using a bipolar charge carrier switch," *Org. Electron.*, Vol. 13, 1049, 2012.