Non-interlayer hybrid white organic light-emitting diodes via a bipolar mixed host for the blue-fluorescent-emitting layer

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ABSTRACT
The reduction of the interlayer in hybrid white organic light-emitting diodes (WOLEDs) provides a potential for improving the device efficiency. Reported herein are non-interlayer hybrid WOLEDs prepared using a mixed host for the blue-fluorescent-emitting layer. The proposed device exhibits high efficiency with the maximum external quantum efficiency up to 17.1%, and stable colors. Moreover, the effect of the interlayer on the device lifetime was demonstrated.

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1. Introduction
White organic light-emitting diodes (WOLEDs) can be used for full-color OLED displays, backlights for liquid crystal displays (LCDs), and solid-state lighting sources. Due to their application potential, WOLEDs have attracted considerable attention [1–3]. Especially, hybrid WOLEDs have been studied by a number of groups due to their advantages of combining the blue fluorophores’ excellent stability and the green and red phosphors’ high efficiency [4–6].

Hybrid WOLEDs have two representative architectures with different color emitters: the multi-emissive-layer (multi-EML) and the single-emissive-layer (single-EML) hybrid WOLEDs. In the single-EML hybrid WOLEDs, the concentrations of the phosphors need to be precisely controlled to achieve the desired spectrum because a small variation in the dopant concentration will result in a significant change in the energy transfer between the emitters. In addition, the spectral variations associated with different driving voltages are among the drawbacks of the single-EML hybrid WOLEDs [7–10].

On the contrary, the multi-EML structure allows the flexible design of the EML system, with better electroluminescence (EL) performance. The multi-EML structure provides a reliable strategy for fabricating hybrid WOLEDs. One common design approach for multi-EML hybrid WOLEDs is introducing an interlayer between the fluorophore and the phosphor to prevent the unwanted mutual exciton energy transfer and quenching processes [5,11–14]. Nevertheless, the use of an interlayer has several disadvantages that limit the device performance. First, the voltage drop across the interlayer cannot be neglected, leading to power efficiency (PE) loss. Moreover, the addition of an interlayer creates additional interfaces, which inevitably increase the possibility of exciplex formation, which diminish the efficiency of hybrid WOLEDs. Thus, if the mutual quenching in a non-interlayer structure can be fully controlled, the efficiency will be further improved [11]. Another way to realize non-interlayer hybrid WOLEDs is by using a blue fluorophore with a high-triplet exciton energy level ($T_1$). Recently, thermally activated delayed fluorescence (TADF) materials were remarkably developed by Adachi et al. [15,16]. The blue TADF materials with high $T_1$ and photoluminescence quantum yield levels can be utilized as hybrid WOLEDs with a non-interlayer structure, and many groups have reported the TADF-based hybrid WOLEDs [17,18]. Even though the reported hybrid WOLEDs based on TADF blue emitters exhibited impressive EL performance, there were still obvious problems, such as severe efficiency roll-off and poor device stability [17,18]. Therefore, the approach of using non-interlayer hybrid WOLEDs based on the...
typical blue fluorophore with a low $T_1$ level to realize high-performance multi-EML hybrid WOLEDs has to be studied.

In this paper, an architecture for achieving high-performance multi-EML hybrid WOLEDs that do not have the conventional interlayer structure is proposed. The main concept is the adoption of mixed hosts for the fluorescent blue EML to manipulate the exciton distribution. The performances of the devices with and without an interlayer were also compared.

2. Experiment

For realizing hybrid WOLEDs, the selection of emitters is important. In this study, 9-(9-phenylcarbazole-3-yl)-10-(naphthalene-1-yl)anthracene (PCAN) was used as a fluorescence blue emitter due to its high-performance deep-blue emission. For the yellow phosphorescence emitter, bis[4-(4-t-butylphenyl)thieno[3,2-c]pyridinato-N,C] acetylacetonate (Ir(tptpy)$_2$(acac)) was used. The hybrid WOLEDs fabricated in this study were composed of 150 nm indium tin oxide (ITO) as an anode, 10-nm-thick MoO$_3$ as a hole injection layer, 50 nm 1,1-bis[(di-4-tolylamino)phenyl]cyclohexane (TAPC) as a hole transport layer, 30 nm 1,3,5-tri(m-pyrid-3-ylphenyl) benzene (TmPyPB) as an electron transport layer, a 0.7-nm-thick layer of lithium fluoride (LiF) as an electron injection layer, and a 100-nm-thick layer of aluminum (Al) as a cathode. The structures of the EMLs that were fabricated in this study are shown in Figure 1. For the blue EML, 4%-PCAN-doped TCTA and co-deposited mixed TCTA and TmPyPB were used, and for the yellow EML, 8%-Ir(tptpy)$_2$(acac)-doped TmPyPB was used. All the layers were deposited in succession, without breaking the vacuum. The devices were encapsulated with a glass lid in a glovebox with an argon (Ar) atmosphere. The current–voltage–luminance characteristics were measured using a Keithley-237 source measurement unit and a Keithley-2000 multimeter. The luminance and efficiencies were calculated from the photocurrent data, which had been obtained with a calibrated Si photodiode (Hamamatsu S5227-1010BQ) and a photomultiplier tube, and the electroluminescence (EL) spectra data were obtained using a spectroradiometer (Minolta CS-2000).

3. Results and discussion

The interlayer suppresses unfavorable exciton transfer between the yellow phosphorescence emitter and the blue fluorescence emitter, and manipulates the exciton distribution, which affects the emission spectra. To reduce the structural heterogeneity, TCTA and TmPyPB are used for the interlayer. To determine the optimal interlayer structure, hybrid WOLEDs with 3 nm interlayers were fabricated with various mixing ratios. Figure S1 shows the efficiencies and emission spectra of the fabricated hybrid WOLEDs with an interlayer. It is obvious that the interlayer composition critically affected the device properties. The 2:1 TCTA:TmPyPB mixture was selected as the optimal interlayer due to its high external quantum efficiency (EQE) and proper white emission spectrum with Commission Internationale de L’Eclairage (CIE) coordinates of (0.40, 0.38).

In the non-interlayer hybrid WOLEDs, the critical problem is the mutual exciton quenching between the phosphorescent yellow emitters and the fluorescent blue emitter when they directly contact each other. The one possible energy transfer path is Dexter energy transfer from the triplet state of Ir(tptpy)$_2$(acac) ($T_1$: 2.2 eV) to the lower-lying non-radiative triplet state of PCAN ($T_1$: 2.0 eV), resulting in energy loss and thus a reduction in the device efficiency [5]. On the other hand, the singlet
excitons in the blue EML can undergo direct radiative decay to blue emission or can be transferred via Förster energy transfer to the yellow EML to enhance the yellow emission. Although this Förster energy transfer is not a loss mechanism, it will lead to insufficient blue emission. The direct contact of the yellow phosphors perturbing the utilization of the singlet excitons for blue emission has a negative effect on the white light. To resolve this issue, a 2:1 TCTA:TmPyPB mixed bipolar host was employed for the PCAN blue fluorescent emitter, which is the key feature of the proposed structure.

Figure 2 shows the device characteristics of the two hybrid WOLEDs: that with the conventional interlayer structure and that with a non-interlayer structure. It is obvious that the additional thick interlayer increases the driving voltage, which limits the PE. The maximum EQE and PE of the non-interlayer device were 17.1% and 36.4 lm/W, respectively, higher than those of the device with an interlayer structure (16.4% and 36.0 lm/W). At the practical luminance of 1000 cd/m², they remained as high as 16.3% and 25.3 lm/W in the non-interlayer device, exhibiting still higher values compared to those of the device with an interlayer (13.5% and 20.1 lm/W). The critical current density $J_c$ of the non-interlayer device, however, where EQE declines by half from its maximum [19], was 74 mA/cm², which is lower than that of the device with an interlayer (187 mA/cm²). The more severe efficiency roll-off in the non-interlayer device is attributed to the inevitable triplet exciton quenching through the blue fluorophore. Figure 2(c, d) shows the current–density-dependent EL spectra of the devices. It is clearly shown that the color shifts of all the devices were small, and that the changes in the CIE coordinates were $< (0.01, 0.01)$, indicating balanced exciton generation. Table S1 summarizes the EL performances of the hybrid WOLEDs in the previous studies. It was found that the EL performance of the proposed non-interlayer device is impressive, without any blue fluorophore with a high-triplet energy level.

To prove the positive effect of the bipolar mixed host in the blue EML for removing the interlayer, two other devices were fabricated for comparison purposes (see Figure S2). Except for the variation of the blue-EML structure, all the other parameters of both devices were kept the same as those of the discussed non-interlayer device. The devices with TCTA and TmPyPB as blue-EML hosts were found to have had a narrow exciton generation zone due to the abrupt interface between the blue EML and the adjacent layer. As shown in Figure S2, the strong yellow emission with negligible blue emission in the device with a TmPyPB host because the recombination zone is located at the interface of the blue and yellow EMLs, and the singlet excitons in the blue EML are largely quenched by the yellow phosphor. Alternatively, the device with a TCTA host exhibited strong blue emission, which suggests that the main recombination zone is located near the blue EML and ETL interface, which is far away from the yellow-phosphor-containing layer. Furthermore, it can be seen that both devices show significant efficiency roll-off, which can be attributed to the quenching effect of space charge accumulation and the high density of the triplet excitons in the narrow exciton
generation zone. On the other hand, in the non-interlayer device with a mixed host, the main exciton generation zone is located across the whole blue EML, where the majority of the injected holes and electrons meet with each other due to the transport properties of the mixed host.

It can be assumed that the triplet excitons generated in the blue EML with a mixed host can diffuse into the adjacent yellow phosphor through Dexter energy transfer. Considering that the triplet energy level of TmPyPB (2.78 eV) is lower than that of TCTA (2.83 eV), the triplet excitons may diffuse through the TmPyPB molecules. To prove this, devices A and B are discussed as shown in Figure 3. Green emission from the (ppy)2Ir(acac) phosphorescent emitter can be seen in device B whereas device A shows negligible green emission. This experimental fact provides evidence for the explanation that the triplet excitons generated in the blue EML can diffuse through the TmPyPB molecules. Meanwhile, to elucidate the efficiency enhancement of the non-interlayer device, it was assumed that a part of triplet excitons on the non-radiative triplet state of PCAN could contribute to yellow emission via the endothermic energy transfer. If the triplet excitons at the triplet state of PCAN can emit via the endothermic energy transfer, a delayed component of yellow emission may exist in the transient EL decay curve [11]. To prove this hypothesis, a device without a PCAN blue emitter but with the same architecture as the non-interlayer device (except for the non-existence of the PCAN blue emitter) was fabricated. As shown in Figure 4, however, there was no delayed component of yellow emission in the two devices, indicating that the endothermic energy transfer does not contribute to efficiency enhancement.

The effect of removing the interlayer on the device lifetime of hybrid WOLEDs was also demonstrated. Figure 5 displays the device lifetime characteristics and the results of the measurement carried out at the initial luminance of 3000 cd/m². As a result, the device lifetime LT50 of the non-interlayer hybrid WOLED was 4.5 h, lower than that of the device with an interlayer (12.7 h). This also corresponds to the trend of the efficiency roll-off properties. In the non-interlayer hybrid WOLED, the inevitable mutual energy transfer between the blue fluorophore and the yellow phosphor could affect the device stability. To clarify this result, the non-interlayer device with a 2% PCAN doping concentration was compared with the device with an interlayer. Due to the low concentration of PCAN, the possibility of energy transfer between the blue and yellow EMLs was reduced. The device with a lower PCAN concentration exhibited an enhanced lifetime of 9.9 h and a higher critical current density $J_c$ of 139 mA/cm², but it still had a lower lifetime than the device with an interlayer, indicating that further study
is necessary for enhancing the stability of non-interlayer hybrid WOLEDs.

4. Conclusion

In this study, the design concept for non-interlayer hybrid WOLEDs was demonstrated. The intrinsic mutual quenching between the fluorescent emitter and the phosphorescent emitter was suppressed by the bipolar mixed host of the blue EML. The discussed non-interlayer device exhibited enhanced efficiency compared to the device with an interlayer, but the lifetime of the non-interlayer device was worse than that of the device with an interlayer due to the inevitable mutual quenching. Although a more precise exciton-confining structure is needed to overcome the lifetime hurdle, it is expected that the result of this study will provide an insight for designing high-performance and stable hybrid WOLEDs.

Disclosure statement

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