Color-Stable White Organic Light-Emitting Diodes Utilizing a Blue-Emitting Electron-Transport Layer

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Supporting Information

ABSTRACT: We have fabricated efficient and color-stable white organic light-emitting diodes (WOLEDs) based on a simple double-layer device structure consisting of a blue-emitting oligoquinoline electron-transport layer and a poly(N-vinyl carbazole) layer doped with phosphorescent green and red iridium emitters. Pure white color with the CIE coordinates from (0.30, 0.31) to (0.34, 0.37) in the whole operating bias voltage range and luminous efficiency higher than 7 cd/A at a brightness up to 12,000 cd/m² was achieved. These results demonstrate a new strategy to realizing easily processable, highly efficient, and color-stable WOLEDs with a simple structure.

INTRODUCTION

White organic light-emitting diodes (WOLEDs) are of great interest in solid-state lighting and other applications. A variety of approaches have been proposed for the realization of white emission. On the basis of the device-processing methods, WOLEDs can be divided into small-molecule1,6−8,11,13−18 and polymer-based devices.2,3,9,19−22 The small-molecule devices are fabricated by thermal evaporation in which multiple layers can be deposited in a one-run, whereas the later polymer-based devices can be processed by spin-casting, screen printing, or inkjet printing techniques. The greatest advantage of the later approach is that it can significantly reduce the cost in mass production especially for large-area displays. The performance of both small-molecule1,6,23 and polymer9,24−26 WOLEDs has been greatly enhanced by the use of phosphorescent compounds as the emitters because both singlet and triplet excited states can be utilized. For small-molecule WOLEDs, the phosphors were doped into the host by coevaporation and the white light was realized by several active layers with each layer emitting a primary color17,23 or from a triple-doped emissive layer.6,27 This method of coevaporation is complicated and expensive because very precise control of the ratios of the red-, green-, and blue-emitting dopants is needed to obtain white emission. In contrast, in polymer WOLEDs, the dopants can be easily and accurately controlled by wet or solution processing.

However, the performance of polymer-based phosphorescent WOLEDs is far behind that of small molecules although singly doped red and green polymer phosphorescent devices using poly(N-vinyl carbazole) (PVK) as the host have shown high efficiency comparable to that of small molecule-based devices. One reason is that the band gap of the polymers is not high enough to confine blue phosphorescent emitters. The blue-emitting component in WOLEDs so far reported was mainly from the polyfluorene-based polymer host or backbone, fabricated either by doping red and green phosphorescent small molecules into the polymer matrix2,19,25 or by attaching the phosphorescent species into the polymer backbone9,20 and/or side chains.9,20 These polymer white light-emitting devices suffer from the following drawbacks: (i) low efficiency because the PL quantum efficiency of the polymer in the solid-state film is low because of polymer interchain interactions;3 (ii) color instability, emission color that is sensitive to applied voltage,19,29 a problem with the different components doped into the same layer, and (iii) efficiency roll-off, whereby the efficiency decreased dramatically at higher current density because of unbalanced charge injection and transport.20 Obviously, blue emission has remained a bottleneck for the performance of polymer-based WOLEDs.

Received: August 19, 2018
Accepted: September 19, 2018
Published: October 3, 2018
In this paper, we report the fabrication of a simple double-layer WOLED in which blue-emitting oligoquinoline is used as an electron transport layer (ETL) and a PVK layer doped with red- and green-emitting phosphorescent dyes. A luminous efficiency of 8.6 cd/A and a brightness of 25,990 cd/m² were achieved from such a simple device architecture. This device also showed a very high color and efficiency stability over the whole operating voltage range. These results demonstrate a new strategy for achieving high performance and color stability while taking advantage of the ease of processing of polymer WOLEDs.

## RESULTS AND DISCUSSION

Figure 1 shows the molecular structures of the materials used in this study. The WOLEDs have the following structure: ITO/PEDOT:PSS/PVK/2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD)/Ir(ppy)₃/Ir(piq)₂(acac)/oligoquinoline 6,6′-bis(2-p-biphenyl)-4-phenylquinoline (B2PPQ)/LiF/Al, where PBD was used to enhance electron transport in the polymer blend layer, and the PVK/PBD ratio was fixed at 30:13 (by weight). Optimal composition of the PVK blend layer and the relative thickness between the PVK blend and B2PPQ layers was essential to achieve stable white electroluminescence (EL) spectra. The best ratio of Ir(ppy)₃/Ir(piq)₂(acac) to achieve balanced red and green emission was found to be about 1:2. The PVK/PBD/Ir(ppy)₃/Ir(piq)₂(acac) ratio was thus fixed at 69.1:30:0.29:0.60 (wt %) in this study. The optimal thicknesses of the PVK blend and B2PPQ layers giving pure white emission were found to be around 60 and 20 nm, respectively.

Figure 2 shows the EL spectra and the current density–luminance and efficiency curves from device A (ITO/PEDOT:PSS(40 nm)/PVK/PBD/Ir(ppy)₃/Ir(piq)₂(acac)(60 nm)/B2PPQ(20 nm)/LiF(1 nm)/Al). This device emits pure white light that spectrally covers the whole visible range from 400 to 750 nm. The observed three peaks at 457, 508, and 620 nm are from B2PPQ, Ir(ppy)₃, and Ir(piq)₂(acac), respectively. The Commission Internationale de l’Eclairage (CIE) coordinates of device A are nearly identical to pure white through the whole bias voltage range, ranging from (0.30, 0.31) to (0.34, 0.37) (Table 1). A maximum forward view luminous efficiency of 8.6 cd/A was achieved at 11.7 V and 15.3 mA/cm², at which the luminance was 1316 cd/m². This corresponds to an external quantum efficiency of 4.5%. Brightness as high as 25,990 cd/m² was observed at 15.2 V bias voltage and a current density of 500 mA/cm². The performance of device A at various voltages is summarized in Table 1. It is clear that the efficiency is very stable over a wide operating range as also can be seen from Figure 2b. The
luminous efficiency remains >7 cd/A at a luminance up to 12 000 cd/m².

From the electroluminescence spectra shown in Figure 2a, it is obvious that the relative emission intensity of the red and green components is independent of the applied voltage over the whole voltage range, and the blue emission intensity of B2PPQ only slightly varied as the applied voltage changed. As a result of the stable relative emission intensities of the blue, green, and red EL bands, very stable white LEDs were obtained. The color stability of the WOLEDs arises from the electron transport properties of B2PPQ and the well-aligned energy levels of the two layers. As shown in Figure 1b, the highest occupied molecular orbital energy levels of PVK and B2PPQ are 5.8 and 5.5 eV, respectively, and the lowest unoccupied molecular orbital energy levels of PBD and B2PPQ are 2.4 and 2.7 eV, respectively. There is a 0.3 eV electron injection barrier from the PVK blend layer to the B2PPQ layer. Thus, at low bias voltage, a little more charges recombine in the B2PPQ layer than in the PVK blend layer. Increased bias voltage overcomes the electron injection barrier, leading to a more balanced charge injection and distribution between the two layers and consequently exhibiting uniform and stable emission of red, green, and blue from both layers.

To further understand the efficiency and color stability of the WOLEDs, device A: ITO/PEDOT:PSS(40 nm)/PVK/PBD/Ir(ppy),Ir(piq),acac(69:1:30:0.29:0.60)(55 nm)/B2PPQ(20 nm)/LiF(1 nm)/Al, device B: ITO/PEDOT:PSS(40 nm)/PVK/PBD/Ir(ppy),Ir(piq),acac(69:1:30:0.29:0.60)(75 nm)/LiF(1 nm)/Al, and device C: ITO/PEDOT:PSS(40 nm)/PVK(55 nm)/B2PPQ(20 nm)/LiF(1 nm)/Al showed an efficiency and highest brightness obtained from the WOLED is 8.6 cd/A at a brightness of 1316 cd/m², and the efficiency was maintained higher than 7 cd/A up to a brightness of 12 000 cd/m². The CIE coordinates remained in the pure white region, ranging from (0.30, 0.31) to (0.34, 0.37) throughout the whole operating bias voltage range. The high efficiency and color stability of the WOLEDs are because of the utilization of the oligoquinoline ETL, which facilitates well-balanced charge injection and distribution between the polymer layer and ETL with well-aligned energy levels. The present strategy thus combines simple device architecture and easy processing with achievement of but also allows high color stability and less rolling off in efficiency. We note that the performance of this dual-layer WOLED still has large room for further improve-

CONCLUSIONS

In summary, we have demonstrated that highly efficient WOLEDs can be realized from a simple double-layer structure consisting of a blue-emitting electron-transport layer and a polymer layer doped with red and green phosphorescent dyes. The peak efficiency obtained from the WOLED is 8.6 cd/A at a brightness of 1316 cd/m², and the efficiency was maintained higher than 7 cd/A up to a brightness of 12 000 cd/m². The CIE coordinates remained in the pure white region, ranging from (0.30, 0.31) to (0.34, 0.37) throughout the whole operating bias voltage range. The high efficiency and color stability of the WOLEDs are because of the utilization of the oligoquinoline ETL, which facilitates well-balanced charge injection and distribution between the polymer layer and ETL with well-aligned energy levels. The present strategy thus combines simple device architecture and easy processing with achievement of but also allows high color stability and less rolling off in efficiency. We note that the performance of this dual-layer WOLED still has large room for further improve-

Figure 3. Comparison of (a) EL spectra and (b) luminous efficiency—current density curves of device A: ITO/PEDOT:PSS(40 nm)/PVK/PBD/Ir(ppy),Ir(piq),acac(69:1:30:0.29:0.60)(55 nm)/B2PPQ(20 nm)/LiF(1 nm)/Al, device B: ITO/PEDOT:PSS(40 nm)/PVK/PBD/Ir(ppy),Ir(piq),acac(69:1:30:0.29:0.60)(75 nm)/LiF(1 nm)/Al, and device C: ITO/PEDOT:PSS(40 nm)/PVK(55 nm)/B2PPQ(20 nm)/LiF(1 nm)/Al.
ment, for example, by performing fabrication in an inert atmosphere and by employing more efficient phosphorescent dyes.

**EXPERIMENTAL SECTION**

B2PPQ, was synthesized in our lab as previously reported. The green and red phosphorescent dyes fac-tris(2-phenylpyridine) iridium (Ir(ppy) 3) and iridium bis(2-phenylquinoil-N, C2′) acetylacetonate (Ir(piq)2(acac)) (Luminescence Technology Corp., Taiwan), PVK (Scientific Polymer Products, Inc., NY), and PBD (Aldrich) were used as received. The WOLED devices were fabricated by first spin-coating a polymer layer of PVK/PBD/Ir(ppy) 3/Ir(piq)2(acac) onto PEDOT:PSS/ITO substrates, followed by thermal deposition of the oligoquinoline (B2PPQ) ETL and the LiF/Al cathode in a high vacuum chamber. The active area of the device was 0.2 cm2. The current–voltage characteristics were measured by using a HP4155A semiconductor parameter analyzer (Yokogawa Hewlett-Packard, Tokyo), and the luminance was using a HP4155A semiconductor parameter analyzer (Yokogawa Hewlett-Packard, Tokyo).

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