Tandem white organic light-emitting diodes adopting a C_{60}:rubrene charge generation layer*

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Organic bulk heterojunction fullerence (C_{60}) doped 5, 6, 11, 12-tetraphenylnaphthacene (rubrene) as the high quality charge generation layer (CGL) with high transparency and superior charge generating capability for tandem organic light emitting diodes (OLEDs) is developed. This CGL shows excellent optical transparency about 90%, which can reduce the optical interference effect formed in tandem OLEDs. There is a stable white light emission including 468 nm and 500 nm peaks from the blue emitting layer and 620 nm peak from the red emitting layer in tandem white OLEDs. A high efficiency of about 17.4 cd/A and CIE coordinates of (0.40, 0.35) at 100 cd/m^2 and (0.36, 0.34) at 1000 cd/m^2 have been demonstrated by employing the developed CGL, respectively.

Keywords: tandem white organic light-emitting diodes, organic bulk heterojunction, charge generation layer, current efficiency

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1. Introduction

White organic light-emitting diodes (WOLEDs) have drawn much attention due to their applications in solid-state lighting and as the backlight for liquid-crystal displays.[1–5] In the conventional OLEDs, the luminance increases with increasing current density, however the operational lifetime decreases because of the degradation of the organic material due to the charge passing through the organic layer.[6] A tandem OLED generally consists of two or more electroluminescence (EL) units, in which the current efficiency scale is almost linear with the number of EL units.[7] The charge generation layer (CGL) located between the EL units plays a crucial role on the device performance. In addition to the efficient injection of oppositely charged carriers into the adjoining organic layers, the CGL must also possess a high optical transparency. Up to now, some kinds of CGLs in tandem OLEDs have been tried, such as Bphen:Li/MoO_3[7] and BPhen:Cs/NPB:2, 3, 5, 6-tet -rafluoro-7,7,8,8-tetracyanoquinodimethane (F_4-TCNQ).[8] Since all those units consist of reactive metals or metal oxides, therefore, their fabrication requires high temperature deposition, which inevitably increases the manufacturing cost. Another potential problem in those doped organic systems is that the diffusion of some metal dopants (e.g., Li) alters the electrical conductivity of the organic layers.[9–12] In addition, the organic bulk heterojunction CGL increases the area of the exciton separation interface compared to the bilayer organic heterojunction CGL to a large extent. Under the application of an electric field, the intensities of blue and red light emission spectra will be lopsided with the increase of the voltage in tandem WOLEDs; the transparency of the CGL with metal or metal oxide dopants is also lower than that of the organic heterojunction CGL at the same thickness, thus resulting in a very strong optical interference and microcavity effect in tandem OLEDs.

In this article, we successfully demonstrate a CGL of fullerene (C_{60}):5, 6, 11, 12-tetraphenylnaphthacene (rubrene) organic bulk heterojunction consisted in tandem OLEDs. This CGL can work well for both the tandem blue fluorescent and tandem white fluorescent OLEDs with two EL units, whose current efficiency equals to the sum of those of the two single-unit devices. It is found that, with C_{60}:rubrene-based CGL, the charge carriers for recombination are well balanced and the CIE coordinates are (0.36, 0.34) at the luminance of 1000 cd/m^2 in tandem WOLEDs. In addition, this CGL shows excellent optical transparency about 90%, which can reduce the optical interference effect formed in tandem OLEDs.

2. Experiment

All devices were fabricated on indium-tin-oxide (ITO) coated glass. The ITO surface was cleaned by ultrasonication

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in acetone and isopropyl for 15 min before it was loaded into the BOC Edwards Auto-500 type thermal evaporation system in a glove box of M. Braun. All layers were deposited by thermal evaporation in a high vacuum system with a base pressure of less than 5×10^{-4} Pa without breaking the vacuum. The photoelectric characteristics of all devices were measured using a Keithley source measurement unit (Keithley 2400 and Keithley 485) and a PR 650 spectral scan spectrometer. All the measurements were carried out in an ambient atmosphere at room temperature except for the lifetime tests.

3. Results and discussion

Firstly, C_{60}:rubrene was used as the CGL in tandem blue fluorescent OLEDs and then the ratio of C_{60}:rubrene was optimized. The structures of tandem blue fluorescent OLED devices are shown as follows:

device A: ITO/NPB (50 nm)/MADN:DSA-ph (3 wt.%, 30 nm)/Bphen (30 nm)/LiF (0.8 nm)/Al (120 nm);

device B: ITO/NPB (90 nm)/MADN:DSA-ph (3 wt.%, 30 nm)/Bphen (30 nm)/LiF (0.8 nm)/C_{60}:rubrene (1:1) (30 nm)/NPB (50 nm)/MADN:DSA-ph (3 wt.%, 30 nm)/Bphen (30 nm)/LiF (0.8 nm)/Al (120 nm);

device C: ITO/NPB (90 nm)/MADN:DSA-ph (3 wt.%, 30 nm)/Bphen (30 nm)/LiF (0.8 nm)/C_{60}:rubrene (1:2) (30 nm)/NPB (50 nm)/MADN:DSA-ph (3 wt.%, 30 nm)/Bphen (30 nm)/LiF (0.8 nm)/Al (120 nm);

device D: ITO/NPB (90 nm)/MADN:DSA-ph (3 wt.%, 30 nm)/Bphen (30 nm)/LiF (0.8 nm)/C_{60}:rubrene (2:1) (30 nm)/NPB (50 nm)/MADN:DSA-ph (3 wt.%, 30 nm)/Bphen (30 nm)/LiF (0.8 nm)/Al (120 nm).

The emitting layers of the tandem blue fluorescent OLEDs (devices B–D) are the same as that of the single-unit device (device A), in which p-bis(p-N, N-diphenyl-amino-styryl) benzene (DSA-ph) doped 2-methyl-9,10-di (2-napthyl)anthracene (MADN) is used as the blue emitting layer and 1,3,5-tri (phenyl-2-benzimidazole) benzene (Bphen) is used as the electron transporting layer (ETL).

Figure 1 shows the luminance–current density–current efficiency characteristics of the tandem blue OLEDs with different ratios of C_{60} and rubrene in the CGL. As shown in Fig. 1, the current efficiency of device D (29.98 cd/A) is about two times that of the single-unit device A (13.47 cd/A), which is higher than the other two tandem devices. This result demonstrates that the optimized ratio of C_{60}:rubrene is 2:1 in the CGL for tandem OLEDs. An incorrect ratio between C_{60} and rubrene results in a low probability of charge transfer and imbalanced charge transport, leading to poor device performance.[13]

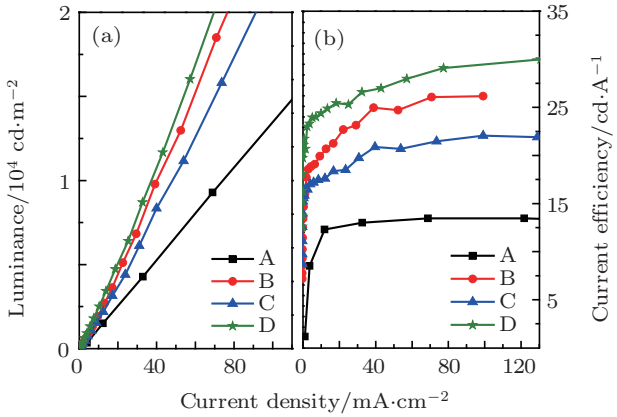


Fig. 1. (color online) (a) Luminance–current density and (b) current efficiency–current density characteristics of the devices.

Moreover, in order to prove the performance of the CGL in detail, a CGL-only device was designed and the dependencies of the current density on the driving voltage were measured as shown in Fig. 2. From this figure, it can be found that the current density of the CGL-only device shows a rapid growth when the voltage is above 10 V. Meanwhile, it can be obviously seen in the inset of Fig. 2 that C_{60}:rubrene (2:1, 30 nm) as the CGL exhibits a better transmittance of over 90% in the blue–red region of 400–700 nm, making it suitable for red OLEDs as the top unit in the tandem OLEDs with lower absorption loss.

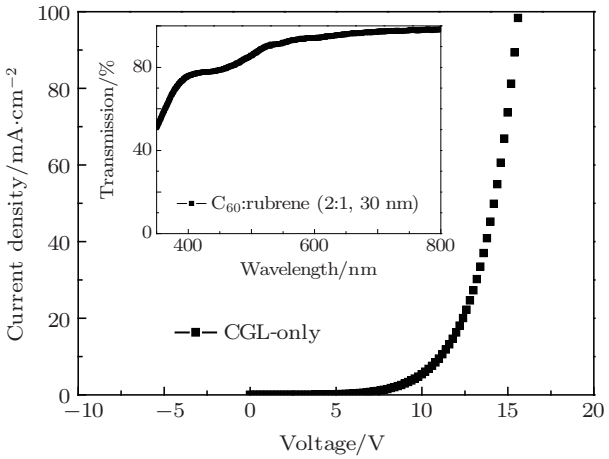


Fig. 2. Current density–voltage characteristics of the CGL-only device and transmittance spectrum of C_{60}:rubrene thin film (inset). The CGL-only device is ITO/Bphen (100 nm)/LiF (0.5 nm)/C_{60}:rubrene (2:1, 30 nm)/NPB (100 nm)/Al.

Next, another type of tandem white fluorescent OLEDs with C_{60}:rubrene as the CGL and two single-unit devices were fabricated, respectively. The structures of the two single-unit devices are shown as follows:

device E: ITO/m-MTDATA:F_4-TCNQ (30 nm)/NPB (20 nm)/MADN:DSA-ph (30 nm)/Bphen (30 nm)/LiF (0.8 nm)/Al (120 nm);

device F: ITO/m-MTDATA:F_4-TCNQ (30 nm)/NPB

(20 nm)/Alq_3:DCJTB (30 nm)/Bphen (30 nm)/LiF (0.8 nm)/Al (120 nm);

device G: ITO/m-MTDATA:F_4-TCNQ (30 nm)/NPB (50 nm)/MADN:DSA-ph (30 nm)/Bphen (30 nm)/LiF (0.5 nm)/C_{60}:rubrene (2:1, 30 nm)/MoO_3 (3 nm)/NPB (50 nm)/Alq_3:DCJTB (30 nm)/Bphen (30 nm)/LiF (0.8 nm)/Al (120 nm).

Here, 4-(dicyanomethylene)-2-tert-butyl-6-(1,1,7,7-tetramethyljulolidin-4-yl-vinyl)-4H-pyran (DCJTB) as the red emission material and DSA-ph as the blue emission material are used. Furthermore, the p-type doping m-MTDATA:F_4-TCNQ is used as the hole buffer layer to reduce the driving voltage in the three devices.[14] Figure 3 shows the energy level diagram of device G. It is noteworthy that the CGL possesses the functionality of the effective charge generation in device G. The accumulation of free electrons and holes in the bulk heterojunction can be caused by the charge transfer processes from the highest occupied molecular orbital (HOMO) level of rubrene to the lowest unoccupied molecular orbital (LUMO) level of C_{60} in the CGL. Under an external electric field, the bounded electron–hole pairs can be separated into free electrons and holes. Then these free electrons will immediately be driven away from the interface by the external electric field and injected into the emission layer. The free holes left in the HOMO level of rubrene are injected into the emission layer of its own emission unit in the same way.[15–17]

Figure 4 demonstrates the luminance–current density–current efficiency characteristics of devices E, F and G. The results indicate that the maximum luminance of device G is

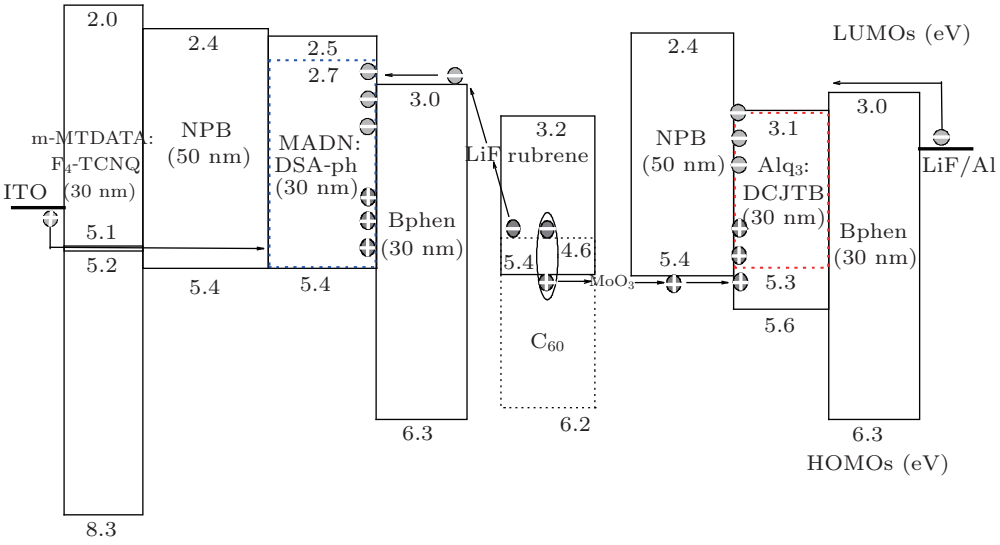


Fig. 3. (color online) Energy level diagram of device G.

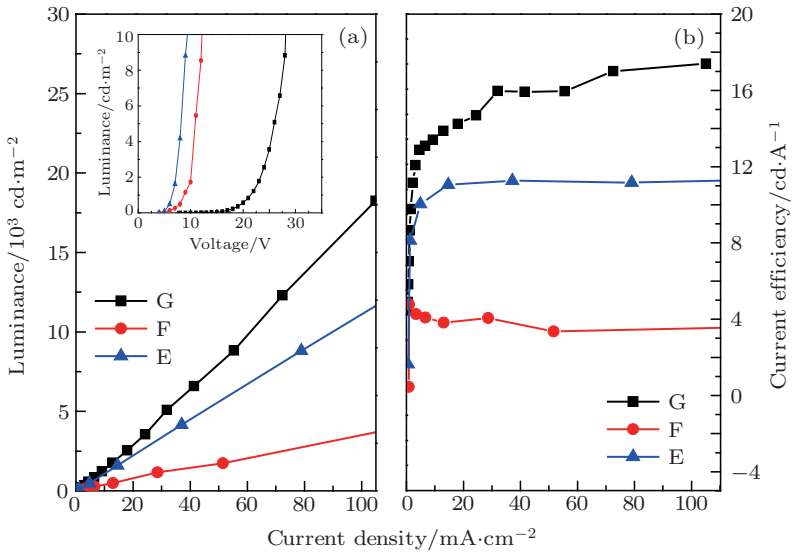


Fig. 4. (color online) (a) Luminance–current density and (b) current efficiency–current density characteristics of device E, F and G and the dependency of luminance on voltage (inset).

basically equal to that of device E and F, but the luminance of device G is much higher than that of device E and F under the same current density. The maximum current efficiency of device G reaches 17.4 cd/A at a current density of 104.92 mA/cm^2 in Fig. 4. The current efficiency basically equals the sum of those of device E and F, where the maximum current efficiency of device E is 11.38 cd/A at a current density of 143.6 mA/cm^2 and that of device F is 4.78 cd/A at a current density of 0.73 mA/cm^2. This result indicates that C_{60}:rubrene functions as an effective CGL in tandem WOLEDs.

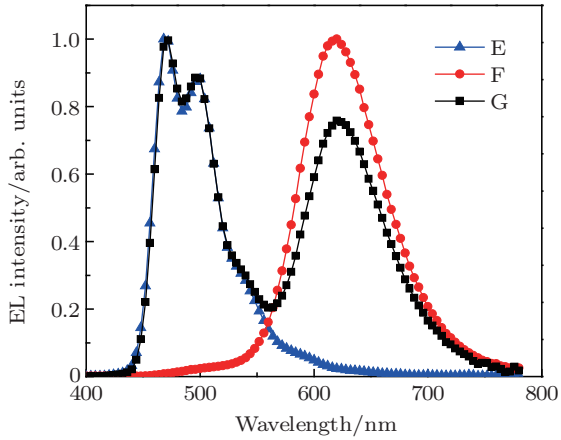


Fig. 5. (color online) EL spectra of device E, F and G.

Figure 5 shows the EL spectra of the blue OLEDs (device E), red OLEDs (device F) and tandem WOLEDs (device G). It is clearly seen that the EL spectrum of the tandem WOLEDs, which covers a wide range of the visible region with three peaks at 468 nm, 500 nm and 620 nm corresponding to the emissions from DSA-ph and DCJTB, respectively, is also consistent with the superposition of the spectra of device E and F; its CIE coordinates are (0.36, 0.34). Figure 6 shows the EL spectra of the tandem WOLEDs at the luminance of 100 cd/m^2 and 1000 cd/m^2. As shown, when the luminance increases from about 100 cd/m^2 to 1000 cd/m^2, the CIE coordinates of device G slightly change from (0.40, 0.35) to (0.36, 0.34). In device G, the relative intensity of the blue emission is slightly increased and no unexpected peak shift is observed. We attribute this slight spectral change to the minor optical interference and the microcavity effect in the multilayer device, which has been reported in congener tandem OLEDs.[18] This apparent resistance to color change under various driving current densities suggests that the charge carriers for recombination are well balanced in device G.[19,20] It is obvious in Fig. 7 that the EL spectrum of device G gradually exhibits a stable white EL emission along with the increase of the working time.

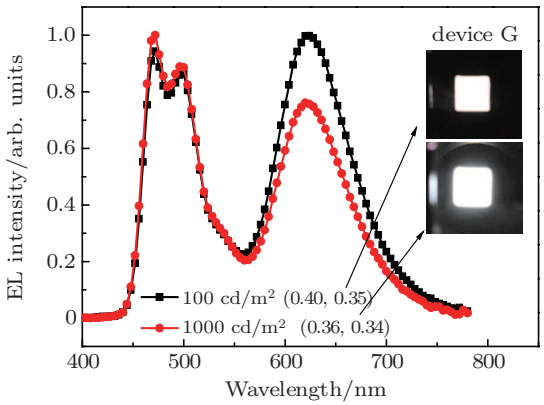


Fig. 6. (color online) EL spectra of device G at the luminance of 100 cd/m^2 and 1000 cd/m^2.

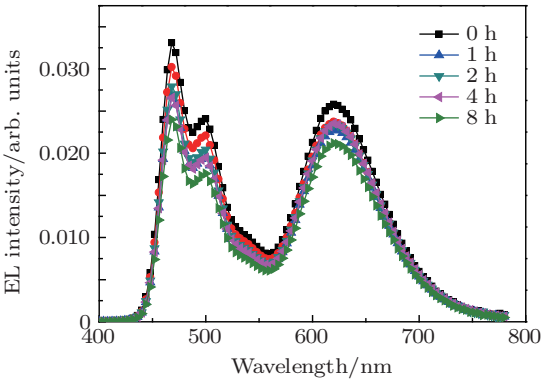


Fig. 7. (color online) Dependencies of EL spectra of device G on working time. The initial luminance of device G is 3000 cd/m^2.

4. Conclusion

In summary, we have demonstrated an effective charge generation layer based on the C_{60}:rubrene organic bulk heterojunction, which has been used in both tandem blue OLEDs and tandem WOLEDs. The current efficiencies of the two types of tandem OLEDs can be greatly enhanced. The charge carriers for recombination in the tandem WOLEDs are well balanced and the CIE coordinates are (0.36, 0.34) at the luminance of 1000 cd/m^2. We note that the combination of an effective charge generation layer is important to realize the tandem OLEDs with high performance.

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