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Efficient tandem organic light-emitting device based on photovoltaic-type connector with positive cycle

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We designed a tandem organic light-emitting device based on an organic photovoltaic-type charge generation connector (CGC) of fullerene carbon 60/copper(II) phthalocyanine. The CGC can absorb a portion of photons radiated from emission zone and form excitons which disassociated into free charges at PN junction interface without energy barrier, leading to low driving voltage and better charge balance. The efficiency increases remarkably with increasing current density, even beyond two folds compared with single unit device under higher current density, meaning slower roll-off. The whole process is a positive cycle, and actually enhances the utilization of internal radiation and the overall performance of tandem device. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4773591>]

Over the past twenty years, organic light-emitting devices (OLEDs) have been attracting more and more attentions and recently entering the era of industrialization. But as a new information display technology, OLEDs still meet a lot of difficulties need to solve, such as bi-exciton formation, polaron-exciton interaction, and Joule heating in conventional OLEDs, especially in the phosphorescent devices under high current density, which lead to a lower efficiency level and a shorter operational lifetime.^{1,2} Additionally, how to increase the light extraction efficiency has also always been an attractive topic, because, generally, in OLEDs only about 20% of radiation from recombination zone can be out-coupled, and the remaining 80% is wasted through waveguide mode, substrate mode, and surface plasmonic mode.^{3,4}

Tandem OLEDs can be selected as an alternative to avoid such disadvantages mentioned above, because tandem OLEDs can offer the same luminance with much lower current density compared with single emissive unit device.^{5,6} As the key point of tandem OLEDs, the charge generation connectors (CGCs) actually were PN junctions structured with pristine or doped films. For P-type layers, the toxic transition metal oxides or p-type molecules, such as tungsten oxide (WO₃), molybdenum oxide (MoO₃), and doped 4,4',4''-tris(N-3-methylphenyl-N-phenyl-amino)triphenylamine (m-MTDATA) were most used candidates.⁷⁻⁹ Most reported n-type layers were organic films doped with active metal such as lithium, cesium, and magnesium, which will diffuse into recombination zone and lead to emission quenching.^{7,8,10-12} Additionally, in order to reduce the wastage caused by the absorption of CGC in tandem OLED, usually used candidates were wide band gap materials, such as 4,7-diphenyl-1,10-phenanthroline (Bphen) and m-MTDATA.^{5,8,11-13}

Obviously, the conventional pristine organic heterojunction CGCs are advantageous in handling and device stability. In this work, we thought outside the box and designed a special CGC which can absorb internal radiation partially but favors charge generation, leading to enhancement of the electroluminescence (EL) performance.

In our work, an organic photovoltaic (OPV) type combination of fullerene carbon 60 (C60)/copper(II) phthalocyanine (CuPc) was selected to constitute the CGC of tandem device. Additionally, in order to make the generated charges inject the adjacent emissive units more easily, at two sides of C60/CuPc CGC (see Fig. 1), we added p-type and n-type buffer layers which can modify the interface energy alignment. The p-type and n-type buffer layers are m-MTDATA doped with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-quinodimethane (F4-TCNQ) and 1,3,5-tris(1-phenyl-1H-benzimidazol-2-yl) benzene (TPBi) doped with cesium carbonate

FIG. 1. The schematic energy diagram of EL unit (left) and the structure of device II (right).

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(Cs_2CO_3), respectively. In consideration of the absorption spectrum of CuPc, the red phosphorescent material bis(1-phenyl-isoquinoline)(acetylacetonato)iridium(III) ($\text{Ir}(\text{piq})_2\text{acac}$) was selected as emission dopant.

The schematic energy diagram of EL unit and the structure of tandem device are illustrated in Fig. 1. Device I is the contrast device with single emissive unit, and device II is the tandem device with the CGC mentioned above. For the emission layer, we used a cohost composed of 4,4',4''-tri-9-carbazolyltriphenylamine (TCTA) and TPBi with a 1:1 weight ratio and the doping concentration of $\text{Ir}(\text{piq})_2\text{acac}$ was about 7 wt. %. The device structures are as below: Device I: ITO/NPB (50 nm)/TCTA (10 nm)/TCTA:TPBi: $\text{Ir}(\text{piq})_2\text{acac}$ (7 wt. %, 20 nm)/TPBi (30 nm)/TPBi: Cs_2CO_3 (10 wt. %, 20 nm)/Al (100 nm),

Device II: ITO/NPB (50 nm)/TCTA (10 nm)/TCTA:TPBi: $\text{Ir}(\text{piq})_2\text{acac}$ (7 wt. %, 20 nm)/TPBi (20 nm)/TPBi: Cs_2CO_3 (10 wt. %, 10 nm)/C60 (20 nm)/CuPc (20 nm)/m-MTDATA:F4-TCNQ (20 wt. %, 10 nm)/NPB (40 nm)/TCTA (10 nm)/TCTA:TPBi: $\text{Ir}(\text{piq})_2\text{acac}$ (7 wt. %, 20 nm)/TPBi (30 nm)/TPBi: Cs_2CO_3 (10 wt. %, 20 nm)/Al (100 nm), here NPB is 4,4'-bis-(1-naphthyl-N-phenylamino)-biphenyl. All chemicals in our work are commercially available. The OLEDs were thermal evaporated onto pre-cleaned ITO glass with sheet resistance of $20 \Omega/\text{sq}$ at a base vacuum pressure less than 3×10^{-4} Pa. The evaporating rates were kept at $1\text{--}2 \text{ \AA}/\text{s}$ for the organic layers and $10 \text{ \AA}/\text{s}$ for the Al cathode, respectively. The absorption and transmission spectra of CuPc film were measured by UV-Vis-NIR scanning spectrophotometer UV3101 (SHIMADZU). The photoluminescence (PL) spectrum of TCTA:TPBi: $\text{Ir}(\text{piq})_2\text{acac}$ (7 wt. %, 30 nm) film was recorded with Hitachi F-4500 Fluorescence Spectrophotometer. The luminance-current-voltage (I - V) characteristics of all devices were measured with Keithley 2400 power source meter combined with Photo Research PR 655 spectrometer simultaneously. All measurements were carried out in air ambient at room temperature.

As expressed in Fig. 2, there is great overlap between the absorption spectrum of CuPc thin film and PL spectrum of $\text{Ir}(\text{piq})_2\text{acac}$ molecules. Because the distance between CuPc layer and emission layer is far beyond the radius of Förster and Dexter energy transfer process, the quenching of

$\text{Ir}(\text{piq})_2\text{acac}$ molecules emission deduced by relaxed CuPc molecules is negligible.¹⁴ The photons radiated from $\text{Ir}(\text{piq})_2\text{acac}$ molecules could be absorbed by CuPc layer and finally generate charges from CGC. It seemed that the light absorption of CuPc layer might weaken the overall efficiency, considering the high transmittance of 20 nm thick CuPc film (Fig. 2) and normally 20% extraction efficiency of radiation in OLEDs, although about 75% radiation in the tandem device crossed the CuPc layer, the wastage caused by CGC absorption would be negligible.

In order to prove the CGC dose generate charges by absorbing the photons radiated from $\text{Ir}(\text{piq})_2\text{acac}$, we did the measurement as below. Under irradiation of 650 nm light emitting diode (LED) lamp, we found that the driving voltage of device II decrease dramatically to two times of device I comparing with the case without irradiation, as shown in Fig. 3. CuPc molecules in CGC absorbed the photons from LED lamp and form excitons, as indicated in Fig. 4(a), which will be dissociated at C60/CuPc interface through charge transfer and followed by charge transport. These are the precisely processes contained in OPV except charge collection.¹⁵ Differing from other normal CGCs, it is noted that there is no energy barrier in charge generation process for device II, therefore, under high current density, the driving voltage of device II is even lower than two times of device I (see Fig. 3). Additionally, as presented in Fig. 4(a), the applied electrical field favors the charge dissociation and charge transport in CGC, just like the case of organic photodetector device, thus, the quantum efficiency should be much higher than that of C60/CuPc OPV device.^{16,17} In the case of without irradiation, under low driving current density, there is hardly any excitons in CuPc layer, so the charge generation must be carried out through electron transfer from the highest occupied molecular orbit (HOMO) of CuPc to the lowest unoccupied molecular orbit (LUMO) of C60. Because there is a high energy barrier to overcome, as shown in Fig. 4(b), a high electrical field is required to assist charge transfer to take place. As a result, the driving voltage of device II without irradiation is much higher than two times of device I at low current density area. We know in OLED the luminance approximately increases with increasing current

FIG. 2. Absorbance and transmittance spectra of 20 nm CuPc film and PL spectrum of TCTA:TPBi: $\text{Ir}(\text{piq})_2\text{acac}$ (7 wt. %, 30 nm) film deposited on quartz substrates.

FIG. 3. Plots of current density as a function of voltage of all devices.

FIG. 4. Charge generation processes in connector interface with (a) and without (b) light irradiation.

density linearly, so under high current density the component of the light radiated from OLED increases and the influence of the light from LED lamp becomes relatively weaker. As shown in Fig. 3, as current density increases, the two I-V curves of device II with and without LED irradiation are getting closer.

From Fig. 5, it is noted that at low current density, the current efficiency of device II is a little higher (smaller than two times) than that of device I, while as current density increases, the current efficiency of device II increases faster below 1 mA/cm^2 and drops slower above 1 mA/cm^2 than that of device I. The maximum current efficiency of device II is larger by about two times than that of device I. This result is consistent with the general concept that the tandem OLEDs with two EL units show the current efficiency of about two times larger than the non-tandem OLEDs.¹⁸ This indicates that the present OPV-type layers work as CGC. As presented in inset of Fig. 5, the current efficiency ratio of the two devices increases monotonically with increasing driving current, even going beyond two folds. We thought that there should be two probable reasons which lead to such strange feature. First, at low current density, the charges were generated through charge transfer from CuPc HOMO to C60 LUMO, which need a high assistant electrical field, as shown in

FIG. 5. Dependences of current efficiency on current density of devices I and II. Inset: The current efficiency ratio between device II and device I.

Fig. 4(b). The generated charges are too less to balance the charges injected from electrodes in recombination zone, leading to low current efficiency at last. Additionally, the ground state CuPc molecules absorb the photons radiated from emission zone, which further weaken the current efficiency. As current density and luminance increase, more and more CuPc molecules in CGC absorb photons radiated from Ir(piq)₂acac and form excitons, leading to the amount of generated charges through exciton dissociation at interface increases remarkably, resulting in better balance with charges injected from electrode in recombination zone. Second, under high current density, a large number of CuPc molecules were in the excited state after absorbing the photons radiated from Ir(piq)₂acac and could not absorb photons anymore, so the wastage caused by absorption of CuPc layer dropped to a negligible level. It is noted that such features of tandem device II are favorable to enhancing the contrast ratio of OLED display. Even though the CuPc molecules in CGC absorbed the photons radiated from Ir(piq)₂acac relaxation, the current efficiency of tandem device II was still higher than twice of single unit device I, thus, we thought the special tandem device actually use the 80% internal radiation which should be wasted through various channels in normal devices.

Based on the discussion above, the work process of tandem device II can be separated into two steps, as shown in Fig. 6. The first step is device startup process. Under electrical field assisting, the CGC generates charges which recombine with the charges injected from electrodes in recombination zone and eventually radiate photons. And then a portion of such photons are absorbed by ground state CuPc molecules in CGC and form excitons, which is actually to prepare for the second step—positive cycle process, meaning that the current efficiency at low current density is relative lower. In the second positive cycle process at high current density, through CuPc excitons dissociation at C60/CuPc interface with no energy barrier, the CGC spouts a huge number of charges which recombine with the charges injected from electrodes in recombination zone and eventually radiate photons, and then a portion of such photons will be absorbed by relaxed CuPc molecules in CGC and form excitons again. In this cycle, a large number of CuPc

FIG. 6. The scheme of work process in device II. Step 1 is the startup stage of device at low current density, and step 2 is the positive cycle stage at higher current density.

molecules are in excited state, so the wastage caused by absorption of ground state CuPc molecules is negligible.

In our tandem device, although CuPc molecules absorb a portion of photons radiated from emissive zone, the current efficiency is still going beyond two times of single emissive unit device. Clearly, the special tandem device based on such OPV type CGC actually enhances the utilization of internal radiation and retards the current efficiency drop at high current density through a positive cycle process. This device model can be proposed as an alternative to enhance contrast ratio and overall performance of phosphorescence OLED.

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