Efficient multilayer red fluorescent polymer light-emitting diodes by host and guest blend system

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ABSTRACT

Efficient red light polymer light-emitting diodes are obtained by energy transfer from host and guest blend system. Two kinds of blend systems, SPB02:(10-(2-benzothiazolyl)-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1H,5H,11H-[1] benzopyrano [6,7,8-ij]quinolizin-11-one)(C545T):4-(dicyanomethylene)-2-t-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTB) and SuperYellow (SY):poly(3,3'''-didodecylquaterthiophene) (PQT-12), are used as the active layers. C545T is a green emitter, acting as an assistant dopant to improve the energy transfer from blue SPB02 host to red DCJTB. The efficiency can achieve to 3.3 cd/A for DCJTB and 3.5 cd/A for PQT-12 system by multilayer device structure with 2,2''-(1,3,5-phenylene)-tris(1-phenyl-1H-benzimidazole) (TPBi) as electron transport layer. The SuperYellow:PQT-12 device shows great luminance of 16,930 cd/m^2.

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Polymer light-emitting diode (PLED) is regarded as the candidate for the next generation light source and flat panel display. It attracts great interest because of their potential in solution process for large-area fabrication and rich colors by easily change the blending ratio of red, green, and blue emitters in solution. Compared with blue and green emitters, the red ones somehow show weak progress. The most common way to achieve red fluorescent PLED is to synthesize red copolymer [1–4]. The efficiency of red copolymer achieves 1.0 cd/A with corresponding external quantum efficiency (EQE) of 3.0 % [2]. However, the progress of red copolymer is slow due to its complicated synthesis. In addition, low bandgap polymer will result in low PL quantum efficiency. The other way to achieve red light is blending red emitters into green or blue host. In this way a host material with good electroluminescent efficiency and a red dopant with high photo-luminescent (PL) efficiency are required. Efficient red light PLED can be obtained through efficient energy transfer from proper host to the red dopant. The efficiency of red PLED based on host–guest system could be enhanced to 3.1 cd/A with corresponding EQE of 5.2 % by blending the red emitter into green host [5]. In this way there is no need to synthesize the red emitter to have both good carrier transport and high PL effi-

ciency for high electroluminescent efficiency. Moreover the device efficiency can be further improved by multilayer device structure, which combines hole transport layer (HTL), emissive layer (EML), and electron transport layer (ETL) [6]. The multilayer device structure can provide the carrier confinement effect and improve the device efficiency. There is no report about high efficient red PLED achieved by the host–guest emissive layer combined with multilayer device structure. In this work two approaches of blend system are applied to red PLED. One is polymer host with small molecular red emitter, and the other is polymer host with polymer red emitter. In two cases, we combine highly efficient host with red dopants with high PL efficiency to achieve efficient red PLEDs through good energy transfer from host to guest. Both the host and the guest emitters are commercial materials. For the multilayer device structure, there is no need to use the low work function cathodes such as Ca, Ba, or CsF/Al. The cathode can be LiF/Al, which is the same as that in common small molecular organic light-emitting diodes. Efficient red PLED of multilayer device structure with efficiency up to 3.5 cd/A is achieved with blend systems without synthesis of new red emitters.

In this work two blend systems are applied to achieve efficient red light PLED. One is s small molecular red dopant, 4-(dicyanomethylene)-2-t-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTB, purchased from Luminescence Technology Corporation) in blue host SPB02 (purchased from
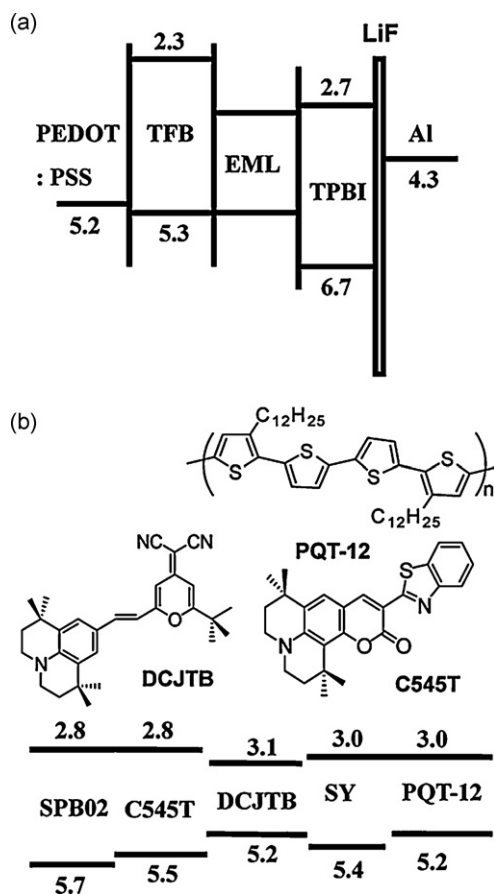
Fig. 1. (a) Schematic energy diagram of multilayer device structure. (b) Chemical structures and the electron affinity as well as the ionization potential of the materials used in this work. The numbers are in eV.

Fig. 2. PL and absorption spectra of the (a) SPB02, C545T, DCJTB, (b) SY, and PQT-12.

Merck) and the other is a red polymer dopant, poly(3,3-didodecylquaterthiophene) (PQT-12, purchased from American Dye Source) in yellow host, SuperYellow (SY, purchased from Merck) [7]. For SPB02 and DCJTB system, a green dopant, (10-(2-benzothiazolyl)-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1H,5H,11H-[1] benzopyrano [6,7,8-ij]quinolizin-11-one) (C545T) is added to improve the energy transfer from the blue host to the red dopant. Three kinds of devices are made to study the multilayer device structure, which are ITO/PEDOT:PSS/EML/Cathode (single layer device), ITO/PEDOT:PSS/HTL/EML/Cathode (double layer device), and ITO/PEDOT:PSS/HTL/EML/ETL/Cathode (trilayer device). ITO is indium tin oxide and PEDOT:PSS is poly-(3,4-ethylenedioxythiophene):poly-(styrenesulfonate) (CLEVIOS^{TM} P VP CH 8000, purchased from HC Starck). Fig. 1 shows the schematic energy diagram and the chemical structures of the materials used in this work [8–10]. PEDOT:PSS is spin coated to form a 40 nm thin film on pre-cleaned the ITO substrate and then is baked at 200° C for 15 min. Before depositing the emissive layer, poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,4′′-(N-(4-secybutylphenyl))diphenylamine)] (TFB, purchased from American Dye Source) with 1 wt% in toluene is blade coated on the PEDOT:PSS layer and annealed at 180° C for 40 min. The TFB layer is then spin-rinsed by toluene to remove the dissolvable part [11]. This step make the TFB layer are insoluble with subsequent layers. The blends for emissive layers, SPB02:DCJTB (100:2), SPB02:C545T:DCJTB (80:20:2), are dissolved in toluene and then blade coated on top of TFB layer to form 40 nm thin films. The SY:PQT-12 (6:1) are dissolved in chlorobenzene and blade coated to form a 40 nm thin film. All the EMLs are then annealed at 120°
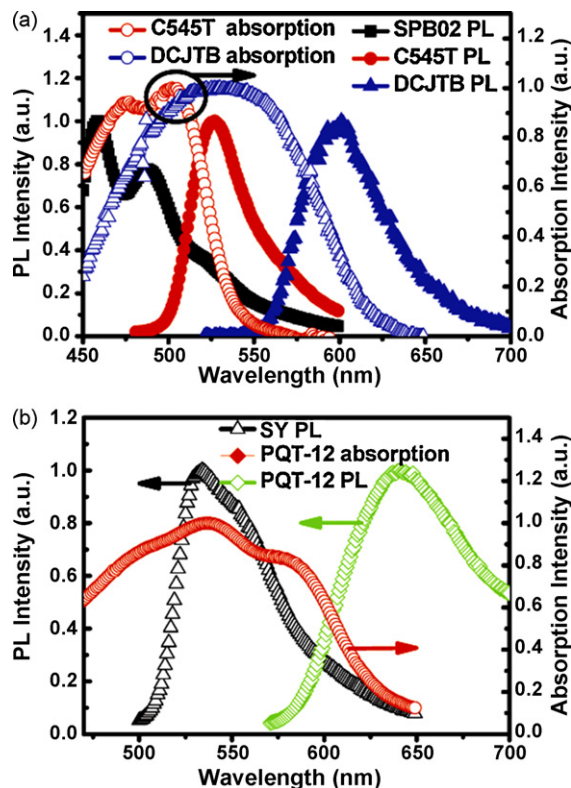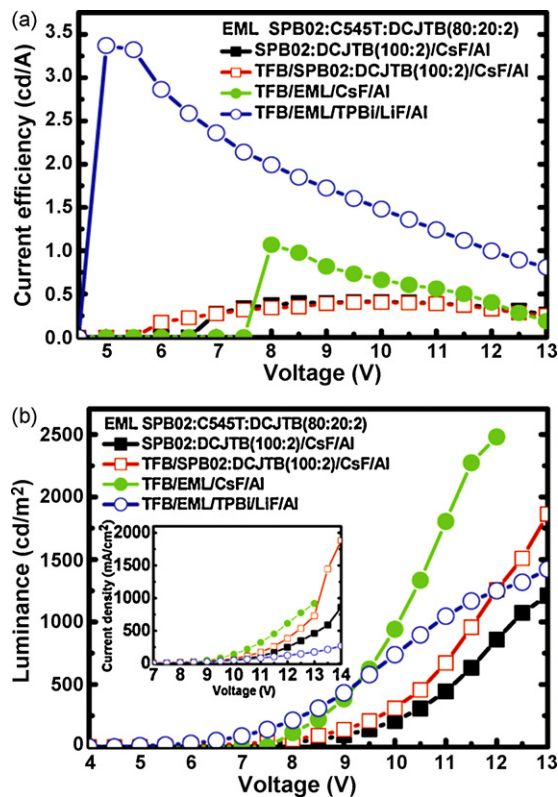

Fig. 3. Device performance of the SPB02:DCJTB device in single layer (solid square) and SPB02:C545T:DCJTB devices in single layer (empty square), double layer (solid circle), and trilayer (empty circle) device structure. (a) The current efficiency and (b) the luminance. Inset is the current density.

C for 20 min. Finally 2,2,2''-(1,3,5-phenylene)-tris(1-phenyl-1H-benzimidazole)) (TPBi, purchased from Luminescence Technology Corporation) dissolved in methanol with 0.5 wt% is blade coated to form a 20 nm ETL on top of EML. There is no anneal process of the ETL to prevent that from crystallization since TPBi is the small molecule. Three kinds of cathodes are chosen for different kinds of devices, which are CsF (2 nm) / Al (100 nm) for the EML based on SPB02 as host for single layer and double layer devices, Ca (35 nm) / Al (100 nm) for the EML based on SY as host for single layer and double layer devices, and LiF (1 nm) / Al (100 nm) for all the trilayer devices. All the fabrication processes, including the blade coating, annealing, and evaporation are carried out in a glove box with nitrogen atmosphere. Both the humidity and oxygen are less than 5 ppm. The emitting area of the devices is 4 mm^2. The film thicknesses are measured by a Kosaka ET4000 Surface Profiler. The electroluminescence (EL) spectra and current–luminance–voltage (I–L–V) characteristics are measured by a Photo Research PR650 spectrophotometer integrated with Keithley 2400 multi-meter. Ionization potential is measured by cyclic voltammetry and electron affinity is calculated by ionization potential plus band gap determined by the ultraviolet absorption spectrum. The uniformity and reproducibility of the film prepared by blade coating method are good. On the same substrate, the film thicknesses are similar. As for the average thicknesses on different substrate, the average thicknesses are also similar.

Fig. 2 shows the PL and the absorption spectra of the materials used in this work. The efficient Förster type energy transfer requires the overlap between the PL spectra of the host and the absorption of the dopant [12,13]. As can be seen there is not good overlap between the PL of SPB02 and absorption of DCJTB.

This implies that in the case of DCJTB doping into SPB02, the Förster energy transfer should be inefficient. In case of assistant dopant C545T, a better spectral overlap between PL of SPB02 and absorption of C545T, PL of C545T and absorption of DCJTB can be observed. Therefore we expect that there is an efficient Förster energy transfer from SPB02 to C545T and then to DCJTB, leading to efficient emission from DCJTB. For the case of SY:PQT-12, there is good overlap between PL of SY and absorption of PQT-12. Now we turn to the device performance. Fig. 3 shows the results of the four kinds of red PLEDs based on DCJTB dopant. The device structures are ITO/PEDOT:PSS/SPB02:DCJTB/CsF/Al (A-1), ITO/PEDOT:PSS/TFB/SPB02:DCJTB/CsF/Al (A-2), ITO/PEDOT:PSS/TFB/SPB02:C545T:DCJTB/CsF/Al (A-3), and ITO/PEDOT/TFB/ SPB02:C545T:DCJTB/TPBi/LiF/Al (A-4). The maximum efficiency are 0.5 cd/A (0.22 %) for single layer device(A-1), 0.5 cd/A (0.22 %) for double layer structure (A-2). The current of the single layer device (A-1) and double layer device (A-2) are low that may be attributed to the poor energy transfer from SPB02 to DCJTB. The current efficiency can be improved to 1.1 cd/A (0.45 %) for the double layer device (A-3) with the assistant dopant, C545T, due to the better energy transfer through SPB02 to C545T and C545T to DCJTB. The efficiency is further improved to 3.3 cd/A (1.5 %) for the trilayer device (A-4). In the trilayer device (A-4) TPBi layer provides not only efficient electron injection but also hole blocking effect to achieve high device efficiency. The maximum luminance are 1210 cd/m^2 for single layer (A-1), 1862 cd/m^2 for double layer device without C545T (A-2), 2480 cd/m^2 for the double layer device with C545T (A-3), 1422 cd/m^2 for the trilayer device (A-4). Fig. 4 shows the EL spectra of the double layer device (A-1) without C545T and double layer device (A-3) with C545T. It can be seen that when only DCJTB doped in SPB02, a huge peak at 476 nm is observed
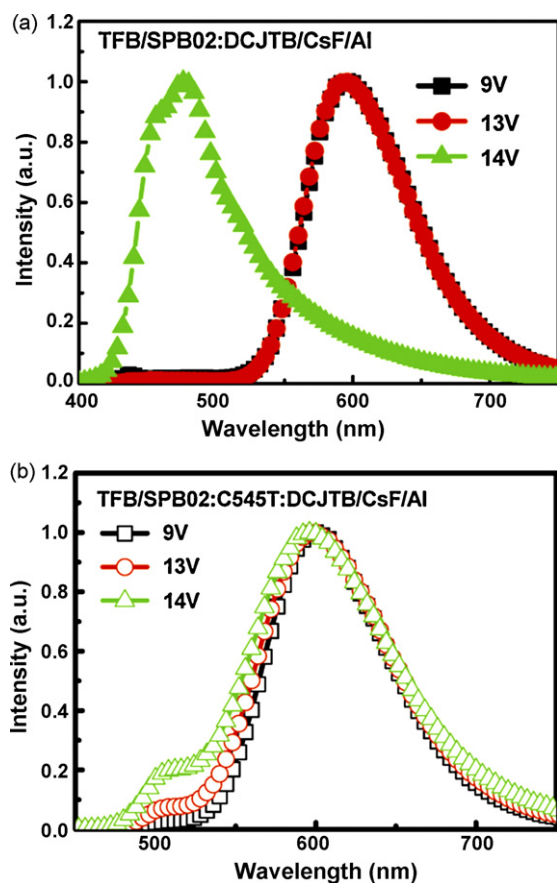

Fig. 4. EL spectra of (a) SPB02:DCJTB and (b) SPB02:C545T:DCJTB devices under 9 V (square), 13 V (circle), and 14 V (triangle).
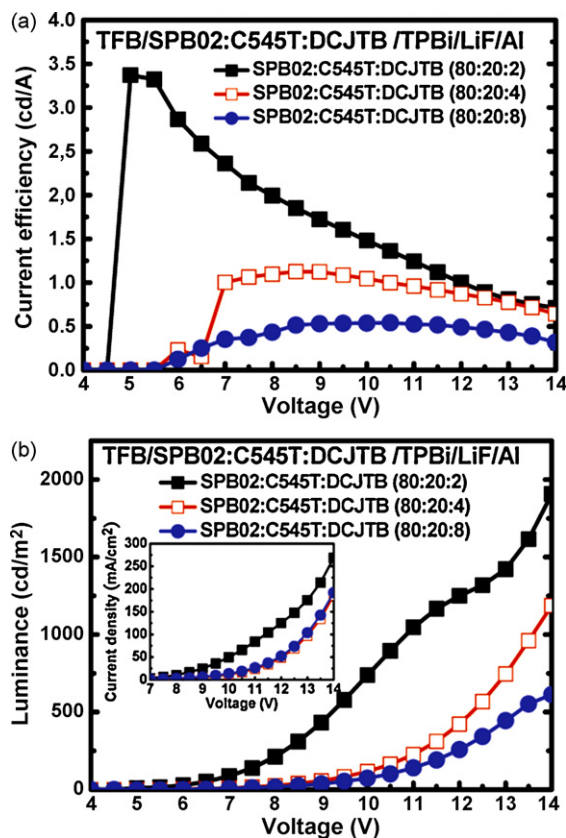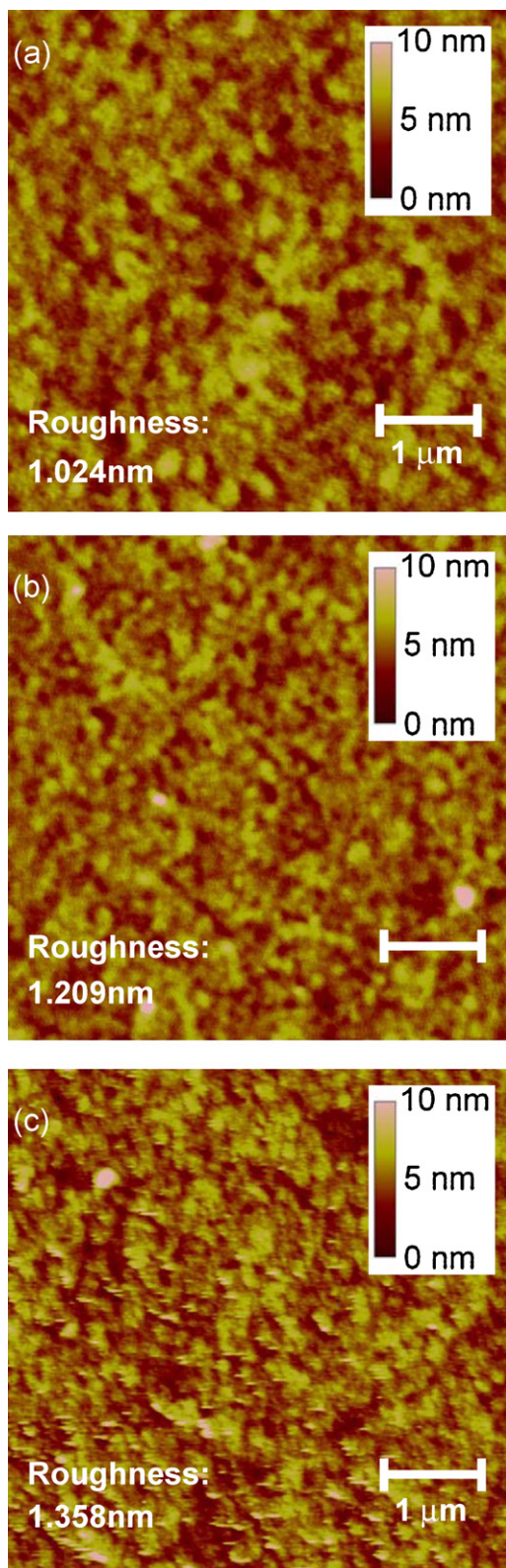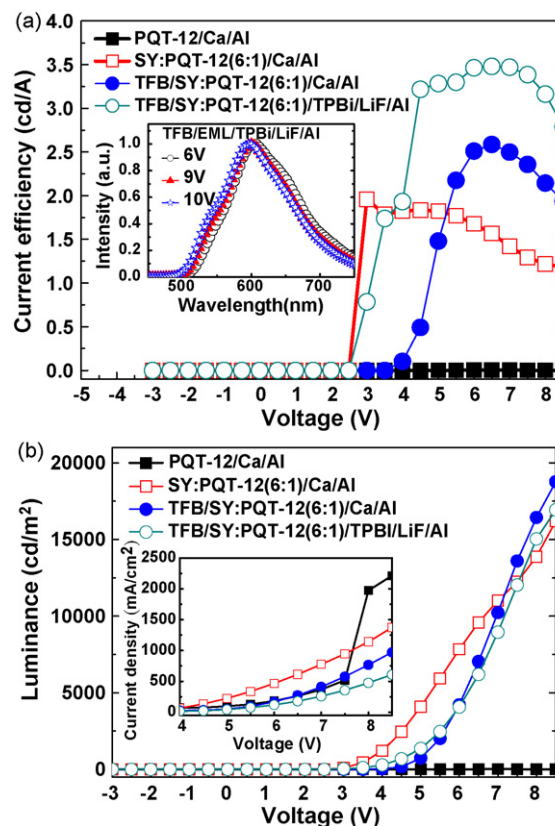

Fig. 5. The device performance of the trilayer SPB02:C545T:DCJTB devices with different ratios of 80:20:2 (solid square), 80:20:4 (empty square), and 80:20:8 (solid circle). (a) The current efficiency and (b) the luminance. Inset is the current density.

Fig. 6. Atonic force images of the films contain different amount of red dopant. The ratios of the SPB02:C545T:DCJTB blend are (a) 80:20:2, (b) 80:20:4, and (c) 80:20:8.

Fig. 7. The device performance of the PQT-12 (solid square) in single layer, SY:PQT-12 (6:1) devices in single layer (empty square), double layer (solid circle), and trilayer (empty circle) device structure. (a) The current efficiency and (b) the luminance. Inset is the current density.

at 14 V. Obviously, the huge blue peak originates from the self emission of SPB02 due to incomplete energy transfer from SPB02 to DCJTB. This inefficient energy transfer phenomenon is due to the poor spectral overlap between the emission spectrum of SPB02 and the absorption spectrum of DCJTB. In order to realize better

energy transfer, we have used C545T as an assistant dopant into the SPB02:DCJTB system. By doping C545T into SPB02:DCJTB, it completely eliminates the self emission of SPB02. Based on the good device performance of the trilayer device (A-4), we further increase the amount of red dopant in the blend. Three trilayer devices with different ratios of the SPB02:C545T:DCJTB blend are compared, which are 80:20:2 (A-4), 80:20:4 (A-5), and 80:20:8 (A-6). Fig. 5 shows the results. The maximum efficiency are 1.1 cd/A (0.45 %) for the trilayer device A-5 and 0.54 cd/A (0.25 %) for the trilayer device (A-6) , which are lower than that of the trilayer device (A-4). The decrease of efficiency with increase of red dopant results from the aggregation of the DCJTB as shown in Fig. 6. The DCJTB has poor solubility and may not be dispersed very well in the blend, thus reducing the device efficiency.

As the mentioned above, aggregation of small molecule dopants will restrict the performance of devices due to the poor solubility of the small molecular dopant without side chains. Therefore, we introduce a red polymer dopant, PQT-12, which has better solubility. Four devices based on PQT-12 as the dopant with different device structures are studied, which are ITO/PEDOT:PSS/PQT-12/Ca/Al (B-1), ITO/PEDOT:PSS/SY:PQT-12/Ca/Al (B-2), ITO/PEDOT:PSS/TFB/SY:PQT-12/Ca/Al (B-3), and ITO/PEDOT/ TFB/SY:PQT-12/TPBi/LiF/Al (B-4). Fig. 7 shows the results. The maximum efficiency are 0.004 cd/A (0.001 %) for the single layer device without SY as the host material (B-1) and 2 cd/A (1.18 %) for single layer device with SY as the host material (B-2). The luminance are 9.8 cd/m^2 for single layer device without SY as host material (B-1) and 16,190 cd/m^2 for single layer device with SY as the host material (B-2). The efficiency and luminance of device with pure PQT-12 are very low but increase dramatically with S-Y:PQT-12 as the emissive layer, indicating the efficient
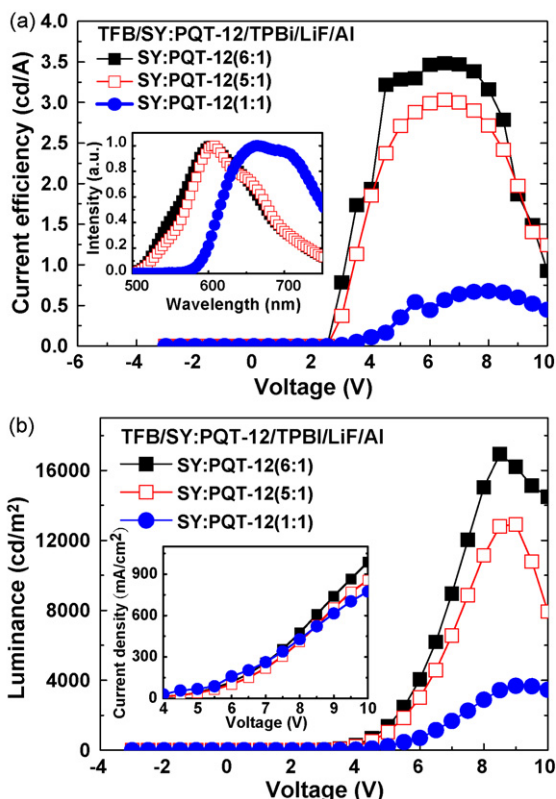
Fig. 8. The device performance of the trilayer SY:PQT-12 devices with different ratios of 6:1 (solid square), 5:1 (empty square), and 1:1 (solid circle). (a) The current efficiency and (b) the luminance. Inset is the current density.

energy transfer from S-Y to PQT-12. Although the PQT-12 is not a good red emitter due to its poor carrier transport properties, it can be blended in to the highly efficient host and has good device performance through efficient energy transfer. The efficiency can be further improved to 2.6 cd/A (1.54 %) for double layer device (B-3) and 3.5 cd/A (2.07 %) for trilayer device (B-4). The maximum luminance are 18,760 cd/m^2 for double layer device (B-3) and 16,930 cd/m^2 for trilayer device (B-4). The device with trilayer structure (B-4) has the carrier confinement effect to balance the carriers and get high device efficiency. The ratio of SY:PQT-12 of the single layer, double layer and trilayer device is 6:1, which is much higher than that of trilayer device (A-4), indicating the difference of solubility between polymers and small molecules. The polymer-based

PQT-12 has higher solubility and not east to aggregate, thus achieving high efficiency and luminance. We further increase the amount of PQT-12. Three trilayer devices with different ratios of SY and PQT-12 are compared, which are 6:1 (B-4), 5:1 (B-5), and 1:1 (B-6), shown in Fig. 8. The maximum efficiency are 3.5 cd/A (2.07 %) for device B-4 , 3.0 cd/A (1.78 %) for device B-5 , and 0.6 cd/A (1.52 %) for device B-6. The maximum luminance are 16,930 cd/m^2 for device B-4, 12,920 cd/m^2 for device B-5, 3686 cd/m^2 for device B-6. Both efficiency and luminance decrease with the PQT-12 increases. This may be attributed to the concentration quenching effect since the ratio of the PQT-12 is too high [14]. On the contrary, when the dopant of PQT-12 decrease the yellow emission will originates from the self emission of SY.

In conclusion efficient red PLEDs are achieved through efficient energy transfer by blending red emitters into blue or green host as emissive layer. Two commercial available red emitters, small molecular DCJTB and polymer-based PQT-12, are used in this work. Better device efficiency and luminance can be achieved by PQT-12 due to its good solubility. The device performance is further improved by multilayer device structure. This result provides a general way to achieve high PLED performance by combining the advantages of energy transfer and multilayer structure.

Acknowledgments

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