

A systematic doping strategy to control the emission spectrum of ternary luminescent polymer blends for white emission

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Abstract

In order to tune the emission color of a well-mixed ternary blend of organic luminescent materials with different bandgap energies, one should practice trial and error of varying the guest concentrations because the Förster-type energy transfer among the materials takes place so easily. In this work, we suggest a systematic doping strategy to control the emission color in ternary organic/polymer luminescent blends for white emission. The strategy comprises two steps: finding out the doping concentration of each guest in its binary blend with the host at which the emission intensities of the two components are comparable and then applying the predetermined doping concentrations of the two guests to the ternary blend system. The doping concentrations were as low as below 0.1 wt% of the host. Doping of a host chromophore with a very small amount of two emitting guests did not allow the excitation energy transfer among the guests although the partial energy transfer between the host and each of the guests occurred to give white electroluminescence.

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1. Introduction

Organic light-emitting diodes (OLEDs) based on small molecules or conjugated polymers have attracted much attention because of their diverse potential applications to large-area flexible or flat panel displays [1]. Although several approaches have been proposed for full-color organic displays [2], the white emission combined with color filter technique provides a relatively easy method. White organic electroluminescent devices also have attractive applications to the backlight of liquid crystal displays

and solid-state lightening [2]. Since white luminescence is usually obtained by mixing three primary colors (red, green, and blue), two or more emissive components are stacked in multilayer structure [3–6] or mixed within a single layer by doping or blending [7–10]. The latter approach is preferred because white OLEDs can be fabricated with a simpler structure and an easier process avoiding vacuum deposition (e.g. solution processing) for low-cost white electroluminescent elements. Even though the doping (or blending) of organic light-emitting materials with emissive dyes is also a simple and important technology for tuning emission colors, especially for white emission, it raises another technological issue on a precise control of the emission spectrum in multi-component systems because Förster-type energy transfer among the components takes places [8–11].

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In a molecularly intermixed blend of luminescent materials with different bandgap energies, the Förster-type energy transfer among the materials takes place so easily [12] that the narrowest bandgap material controls the emission wavelength. Therefore, it is very difficult to control the emission spectrum in well-mixed blends containing two or more guest components because the energy transfer is very sensitive to a slight change in the guest concentrations. As a result, without any guideline or strategy for designing white-emitting *multi-component blends (ternary or higher)*, one should practice trial-and-error experiments until the optimum composition is reached. And control of the emission spectrum becomes more complicated as the number of the components increases. The precise control of the excitation energy transfer among the guests has the key to a desired emission spectrum. Previously, a method to prevent energy transfer between the guests in a well-mixed blend has been proposed, which is to incorporate an insulating material such as poly(methyl methacrylate) as the energy transfer blocker [8]. Another method to control the energy transfer among the emitting guests for white emission is to employ a *poorly miscible or immiscible blend system*. In this system, each material not only emits its own color but also partially transfers its excitation energy to the narrower bandgap material within the limited region of Förster radius [10,11] such as the interfacial region of the blend. This partial energy transfer can broaden the emission spectrum to generate whitish light in such systems [10]. Both the approaches mentioned above, however, also require trial and error to get the best composition for white emission since it is very difficult to control the energy transfer between the host and the guests and that among the guests simultaneously.

In this work, we suggest a systematic doping strategy to control the energy transfer among the guests separately from the energy transfer between the host and the guests in molecularly-intermixed blend systems which will lead to a desired emission spectrum (especially white emission) from a multi-component blend of luminescent polymers and an organic dye. The key notion of this doping strategy is to *inhibit the energy transfer among the guests* by separating the guest molecules apart from each other beyond the Förster radius in the host matrix, which was accomplished by light-doping. We first determined the light doping concentration (0.005–0.7 wt%) of each guest in its binary blend with the host, with which the emission intensities of the host and the guest become comparable to each other. And then, we doped the host polymer with the predetermined small amount of two different emitting guests, which were small enough to prevent the excitation energy transfer between the guests. Although all the components are completely miscible with one another, white photoluminescence (PL) and electroluminescence (EL) are demonstrated by controlling the excitation energy transfer among them. In this case, we can control the emission spectrum of multi-component blends with *more than two guests*.

In organic dye-doped LEDs, Förster excitation energy transfer and carrier trapping are simultaneously involved in the EL processes. Therefore, it is important to control the two involved processes to obtain a desired emission color and high luminescence efficiency. In this work, we found that the relative concentration of the guests in the blend is an important factor to control the carrier trapping in the device. We will discuss the excitation energy transfer and the carrier trapping in the lightly-doped polymer/organic LEDs.

2. Experimental

Two fluorene-based light emitting polymers, poly(2,7-bis(*p*-styryl)-9,9'-di-*n*-hexylfluorene sebacate) (PBSDHFS) and poly(9,9'-di-*n*-hexyl fluorenediylvinylene-*alt*-1,4-phenylenevinylene) (PDHFPPV) were synthesized by Heck and condensation reactions as reported elsewhere [13]. PBSDHFS showed liquid crystallinity with the glass transition temperature of 48 °C and the nematic-to-isotropic transition temperature of 103 °C. We used a commercially available laser dye, 4-(dicyanomethylene)-2-methyl-6-(*p*-dimethylaminostyryl)-4H-pyran (DCM) from Aldrich Co. without further purification. The material structures are shown in Fig. 1.

For the precise doping of the host (PBSDHFS) with a very small amount of the guests (0.005–0.7 wt%) (PDHFPPV and DCM), we dissolved the guests homogeneously in chlorobenzene first and then took the precalculated portion of the solutions that we want to mix with the host chromophore.

The blends with several different compositions were spin-cast from the chlorobenzene solutions on clean glasses for PL spectrum measurement and also on O₂ plasma-treated indium–tin–oxide (ITO)-coated glass substrates for EL device preparation. The film thicknesses were averaged after measuring several times by a TENCOR P-10 surface profiler and controlled to be constant. Aluminum was

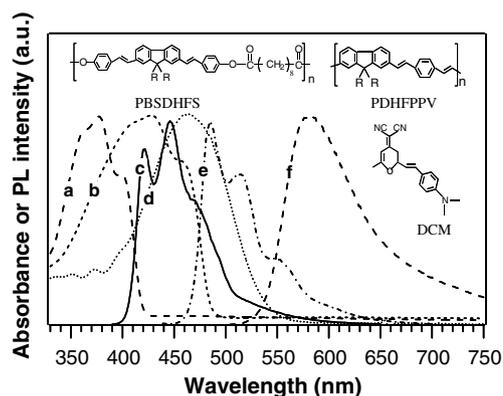


Fig. 1. UV/Vis absorption (Abs) and photoluminescence (PL) spectra: (a) Abs of the PBSDHFS film, (b) Abs of the PDHFPPV film, (c) PL of the PBSDHFS film, (d) Abs of DCM in dilute chlorobenzene solution, (e) PL of the PDHFPPV film, (f) PL of DCM in dilute chlorobenzene solution. All films were cast from the chlorobenzene solution. Inset shows the chemical structures of PBSDHFS, PDHFPPV, and DCM.

deposited on the top of the blend film under a high vacuum (10^{-6} torr) and used as the cathode. PL and EL spectra were measured using an ISS PC1 Photon Counting Spectrofluorometer.

3. Results and discussion

Two fluorene-based light emitting polymers, PBSDFHS and PDHFPPV, and a commercially available laser dye, DCM [13] were employed as the components of the white-emitting ternary blend system. The chemical structures and the normalized optical absorption and PL spectra of the materials are shown in Fig. 1.

Fig. 2 illustrates the energy levels of the component materials as well as the workfunctions of the electrodes. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of the materials were determined from the cyclic voltammograms and optical absorption spectra. The HOMO levels of PBSDFHS, PBDHFS, and DCM are -5.65 , -5.60 , and -5.07 eV, respectively and the LUMO levels are -2.72 , -3.04 , and -3.04 eV, respectively. From Fig. 1, we can clearly observe the spectral overlap between the emission of PBSDFHS and the absorption of PDHFPPV, and also the overlap between the emission of PDHFPPV and the absorption of DCM. The ternary blend system, therefore, meets the necessary condition of Förster-type energy transfer that the emission of the donor and the absorption of the acceptor should spectrally overlap with each other. We can expect the cascade energy transfer from PBSDFHS to PDHFPPV, and then to DCM when the polymers are molecularly intermixed within the Förster radius [11,14].

We examined the energy transfer from PBSDFHS to PDHFPPV and from PBSDFHS to DCM while changing the composition of each binary blend. First, we blended PBSDFHS and PDHFPPV in various ratios and we found out that the optimal composition for the most efficient energy transfer was 98:2 by weight. When we excited the binary blend film at 375 nm (the absorption peak wavelength of PBSDFHS), we observed a largely improved PL output (~ 13 times) at 475 nm compared with the pure PDHFPPV film [13]. Therefore, we confirmed an efficient

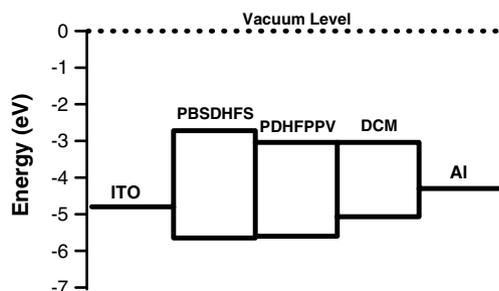


Fig. 2. The energy levels of PBSDFHS, PDHFPPV, and DCM in the EL devices.

energy transfer from PBSDFHS to PDHFPPV. Next, we blended PDHFPPV and DCM in the ratio of 98:2 by weight. We also confirmed the energy transfer from PDHFPPV to DCM because the emission spectrum of the blend is practically identical to that of the DCM solution (line f of Fig. 1). Finally, we blended PBSDFHS, PDHFPPV, and DCM in the 98:2:2 weight ratio but, upon exciting the ternary blend at 375 nm, we observed the emission from DCM only. This implies that a cascade energy transfer took place [14]. Therefore, it is clear that the control of the energy transfer among the components is important in tuning the emission spectrum for white emission, especially from a ternary blend system.

Color tuning by trial and error sometimes leads to an undesired result that the white PL can be obtained by controlling the doping ratio of the guests but the white EL cannot. We prepared a 98:2 binary blend of PBSDFHS and PDHFPPV first and then added increasing amount of DCM to the binary blend until white PL was observed. When 0.25 wt% of DCM was incorporated in the blend we observed white PL (CIE coordinates: $x = 0.33$, $y = 0.39$) as shown in Fig. 3a, however, EL spectrum of the ternary blend device was similar to that of the PDHFPPV single-component device as shown in Fig. 3b.

In the EL process of this ternary blend device, carrier trapping should also be considered in addition to the

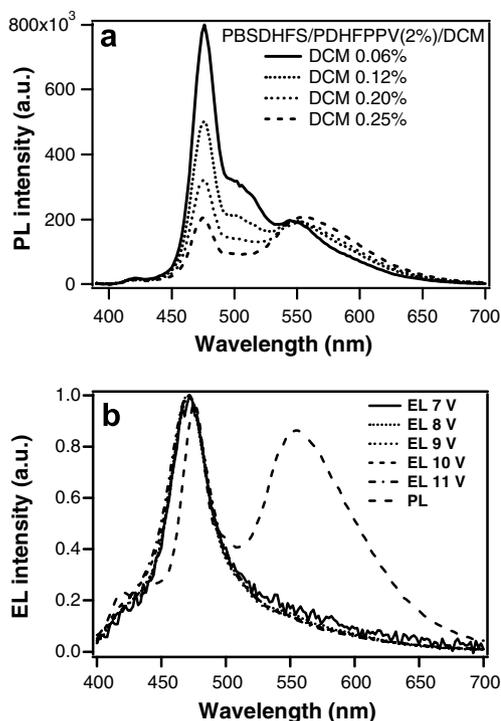


Fig. 3. (a) PL spectra of the ternary blends prepared by adding various amount of DCM into the 98:2 binary blend of PDBSHFS and PDHFPPV. (b) The solid film PL and the device EL spectra of the PBSDFHS/PDHFPPV/DCM blends with the 98:2:0.25 weight ratio. The device EL spectra were different from the PL spectrum and did not change with varying operating voltage.

energy transfer. In the case of general host-guest blend systems, as the guest dye easily traps the counter-charged carriers because of stronger Coulombic interaction, electron-hole pairs are generated on the guest dye and then the guest dye emits luminescence. The charge trapping is more favorable if the HOMO level of the acceptor is above (closer to vacuum level) that of the donor, and if the LUMO level of the acceptor is below (farther from vacuum level) that of the donor. Therefore, at a similar doping concentration level of the two different guests, the guest with the larger difference between the energetic levels of the donor (host) and the acceptor (guest) traps the carriers preferentially. However, since the concentration of PDHFPPV is much higher than that of DCM in this ternary blend device, PDHFPPV will trap the most of electronic carriers. As a result, DCM cannot contribute to the emission spectrum. It is also worthwhile to note that the excitation energy transfer from PDHFPPV (the first guest) to DCM (the second guest) in the EL device does not occur because of the low concentration of DCM. This device did not show any spectral change with increasing driving voltage. From these results, we can conclude that the carrier trapping process in the ternary blend depends on the relative concentration levels of the guests and is controlled by the guest of the higher concentration. Therefore, in tuning the emission color to prepare a white EL device using a ternary (or higher) polymer blend, it is recommended that each dopant should be incorporated on a similar *low* level of concentration, at which the cascade energy transfer is effectively suppressed.

In this respect, we tried to find out a more systematic method to obtain white PL and EL at the same time in a molecularly-mixed ternary blend. We first determined the doping concentrations of each guest in its binary blends with the host at which the host and the guest generate comparable emission intensities and the energy transfer between the guests (PDHFPPV/DCM) is mostly suppressed in the ternary blend.

Fig. 4a shows the PL spectra of the PBSDFHS film very lightly doped with PDHFPPV. The PL spectra demonstrated that the blue emission of the PBSDFHS/PDHFPPV binary blends centered at 475 nm gets stronger as the doping concentration of PDHFPPV increases. It is widely understood that the dilution of a chromophore enhances the luminous quantum yield because concentration quenching [15] and self-absorption are effectively suppressed. It is very interesting to observe that the emission intensity of PBSDFHS (from 400 to 450 nm) in the blends remains almost unchanged irrespective of the doping concentration, which implies that all excitation energy of the PBSDFHS host is not transferred to the guest. In other words, only the excitons generated within a certain boundary of the host surrounded by the guest molecules can transfer their energy to the guest. It is also very interesting to observe that the blend containing only 0.014 wt% of PDHFPPV gave the emission spectrum in which the emission intensity of PDHFPPV is comparable to that of PBSDFHS when excited at the absorption peak wave-

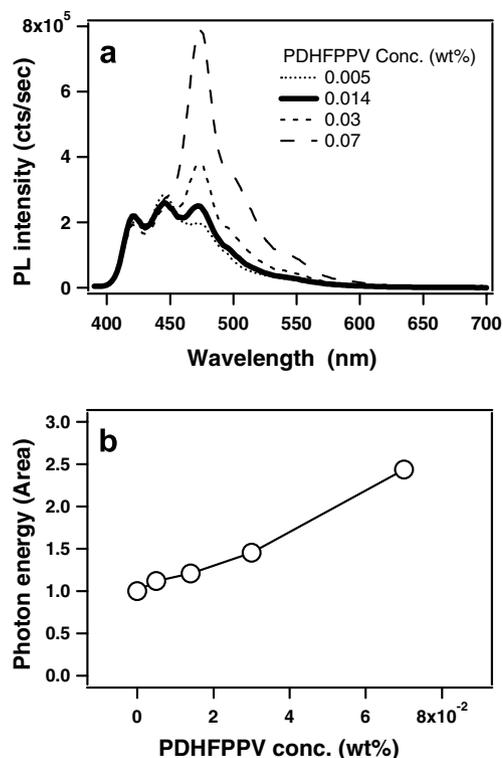


Fig. 4. (a) PL spectra of the PBSDFHS/PDHFPPV blends with different PDHFPPV concentrations, (b) The output photon energy of the PBSDFHS/PDHFPPV blends as a function of the PDHFPPV concentration.

length of PBSDFHS. If we assume that the PDHFPPV molecules are evenly distributed in a cubic lattice inside the PBSDFHS matrix and the density of the film is 1 g/cm^3 , at the concentration of 0.014 wt%, the PDHFPPV molecules would have a long separation of $\sim 18 \text{ nm}$ because of the high dilution in the PBSDFHS matrix. Fig. 4b shows the PL output energy of the highly diluted solid solution integrated over the whole wavelengths. Since the high dilution of the guest molecules (PDHFPPV) in the host (PBSDFHS) did not change the UV absorbance in the solid film, we can consider that the relative fluorescent yield increased as the doping concentration increases.

Fig. 5a shows the PL spectra of the binary blends of PBSDFHS and DCM. As the DCM concentration increases, the PL intensity in the emission band of DCM (500–700 nm) tends to increase. However, unlike the case of the PBSDFHS/PDHFPPV binary blends, the PL intensity in the emission band (400–500 nm) of PBSDFHS drastically collapsed and also the overall PL output energy gradually decreased with an increase of DCM concentration as depicted in Fig. 5b. These observations suggest that there are significant nonradiative energy transfer routes in addition to the radiative excitation energy transfer from PBSDFHS to DCM. This may be attributed to the charge separation of neutral excitations prior to the exciton migration to DCM because there exists a large difference ($\sim 0.6 \text{ eV}$) between the HOMO levels of PBSDFHS and

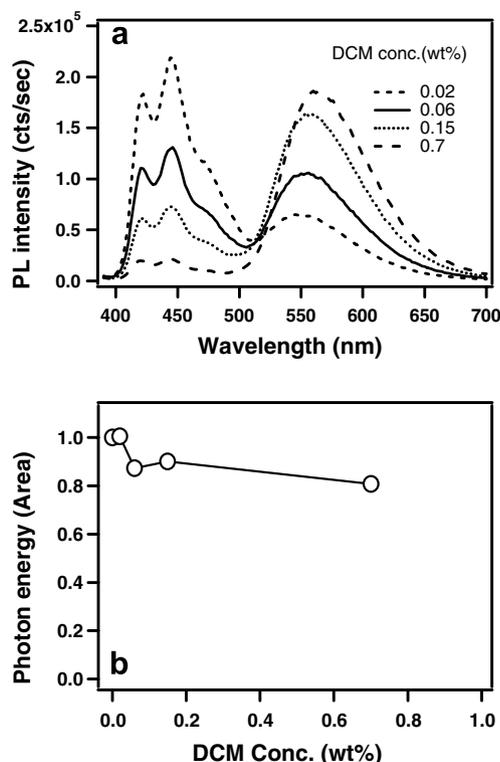


Fig. 5. (a) PL spectra of the PBS DHFS/DCM blends with different DCM concentrations. (b) The output photon energy of the PBS DHFS/DCM blends as a function of the DCM concentration.

DCM. When 0.06 wt% of DCM was incorporated in PBS DHFS, the emission intensity of DCM in the blend is almost equal to that of PBS DHFS. At the concentration of 0.06 wt%, the DCM molecules would have a separation of ~ 9.4 nm assuming that the DCM molecules are evenly distributed in a cubic lattice inside the PBS DHFS matrix and the density of the film is 1 g/cm^3 .

To obtain white PL emission we incorporated 0.014 wt% of PDHFPPV and 0.06 wt% of DCM into the PBS DHFS host. As a result, we observed white PL emission (CIE coordinates: $x = 0.29$, $y = 0.32$) from the blend as illustrated in Fig. 6a. The energy transfer from PDHFPPV to DCM is so weak that the cascade energy transfer from PBS DHFS to DCM can be avoided because the very low concentration of PDHFPPV and DCM in the host keeps the two guest molecules apart from each other.

Finally, we prepared an EL device employing the ternary blend as the emitting layer. Fig. 6b shows the EL spectra of the device measured at varying operating voltages. The emission color indices belonged to the white emission zone in the CIE chart when we drove the device above 16 V as shown in Fig. 7, which were very close to the PL CIE index. Fig. 8a shows the current–voltage–luminance characteristics of the ternary blend device and Fig. 8b demonstrates that the quantum efficiency of the ternary blend white EL device are hugely improved (~ 30 times) compared with that of the pure PBS DHFS device.

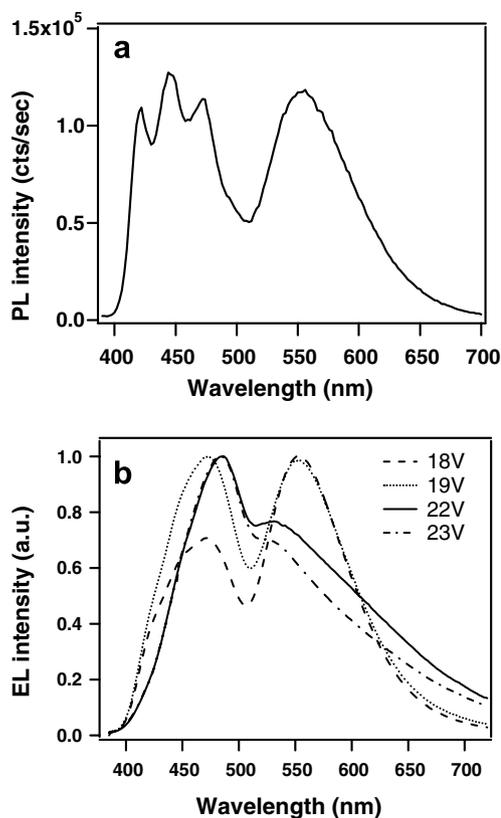


Fig. 6. (a) PL spectra of the PBS DHFS/PDHFPPV/DCM ternary blend with the 98:0.014:0.06 weight ratio (b) EL spectra of the ITO/(PBS DHFS/PDHFPPV/DCM ternary blend, 98:0.014:0.06 by wt%)/Al device obtained at different driving voltages.

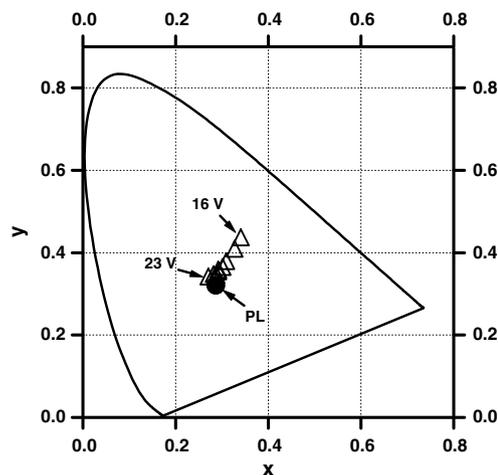


Fig. 7. CIE indices of the solid film PL and the device EL of the PBS DHFS/PDHFPPV/DCM ternary blend with the 98:0.014:0.06 weight ratio.

4. Concluding remarks

We propose a strategy to tune the emission color in a molecularly-intermixed ternary chromophore blend for white PL and EL. To design an organic dye-doped white EL device, carrier trapping as well as excitation energy

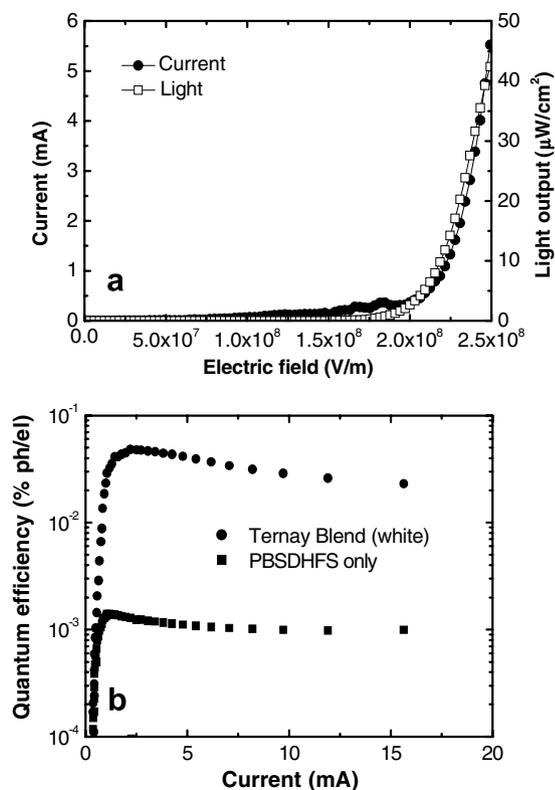


Fig. 8. (a) Current–voltage–luminance characteristics of the ITO/(PBSDHFS/PDHFPPV/DCM ternary blend, 98:0.014:0.06 by wt%)/Al (b) External quantum efficiencies of the ITO/(PBSDHFS/PDHFPPV/DCM ternary blend, 98:0.014:0.06 by wt%)/Al and the ITO/PBSDHFS/Al devices.

transfer should be considered in terms of the concentration of the guests. Since the guest with a higher concentration preferentially traps the charge carriers, it is recommended that the concentration levels of the guests should be similar and low enough to avoid the energy transfer between the guests for white emission. After we determined the doping concentration of each guest in the host at which the emission intensities of the dopant and the host in the binary blend are similar, we applied the same doping concentrations to the ternary blend, at which the energy transfer between the guests was prevented. The determined concentrations of the guests were very low (<0.1 wt%). This light-

doping keeps the intermolecular distances of the emitting guests out of their Förster radii to prevent the energy transfer between the guests, giving a combined PL or EL spectrum of the all guest chromophores, i.e. a white PL or EL. Although we used three different chromophores for white PL and EL, this doping strategy using the predetermined very low concentrations of each guest in the binary blends can be extended to design any desired emission spectrum by incorporating more guests.

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