High-efficiency Red Organic Light Emitting Diodes Incorporating 1,3,5-Tris(1-pyrenyl)benzene as the Host Material

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We have developed high-efficiency red organic light emitting diodes (OLEDs) incorporating 1,3,5-tris(1-pyrenyl)benzene (TPB3) as the host material and 4-(dicyanonaphthalene)·2-tert-butyl-6-(1,1,7,7-tetramethyljulolidyloxy)-9-epoxy (DCJTB) as the dopant. The highly efficient energy transfer, which arose as a result of (i) perfect overlap between the photoluminescence spectrum of TPB3 and the absorption spectrum of DCJTB and (ii) the high fluorescence quantum yield of TPB3, allowed us to fabricate red OLEDs exhibiting improved efficiency. A device having the configuration of indium-tin oxide/1,3,5-tris(1-pyrenyl)benzene/N,N′-bis(1-naphthyl)-N,N′-diphenylyl-1,1′-biphenyl-4,4′-diamine/TPB3:DCJTB (9%/LiF/Al) exhibited a maximum luminance at 13.5 V of 70,600 cd/m², ca. four times higher than that of the device incorporating Alq3 as the host material at the same potential. The device’s current efficiency was 4.38 cd/A; its power efficiency was 2.12 lm/W at 20 mA/cm². The current and power efficiencies were greater than 4 cd/A and 1 lm/W, respectively, over a large range of potentials (3.5–13.5 V), with good Commission Internationale de l’Eclairage coordinates of (0.63, 0.37). These results indicate that searching for a suitable host material is a promising approach toward achieving high-efficiency red OLEDs.

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Although organic light emitting diodes (OLEDs) 1 are used widely in flat-panel displays because of their superior brightness, high contrast, wide viewing angle, rapid response, and low production cost, the poor color purity and low efficiency of red OLEDs have limited the development of full-color organic displays. A doping system 2–10 is often required in red OLEDs to obtain higher efficiencies and to prevent concentration quenching. 6 Several red fluorescent dyes, including 4-(dicyanonaphthalene)-2-methyl-6-p-(dimethylaminostyryl)-4H-pyran (DCM), 4-dicyanonaphthalene-2-methyl-6-(2,3,6,7-tetrahydro-1H,5H-benzo) [ii]-quinoxalin-8-y]-4H-pyran (DCM2), 4-(dicyanonaphthalene)-2-methyl-6-(1, 1, 7, 7'-tetramethyljulolidyloxy)-9-epoxy (DCJTB), and 4-(dicyanomethylene)-2-tert-butyl-6-(1,1,7,7-tetramethyljulolidyloxy)-9-epoxy (DCJTB) 6, 8–11 have been studied as red dopants for OLED applications, usually in conjunction with tris[8-hydroxyquinolinato] aluminum (Alq3) as the host material because of its high stability and good carrier-transport properties. Nevertheless, energy transfer from the Alq3 host to, for example, DCJTB, is not optimal because of poor overlap between the photoluminescence (PL) spectrum of the former and the absorption spectrum of the latter. As a result, the efficiency of such a doping system is too low for practical applications. Although the use of rubrene as an assistant dopant 12–17 aids the energy transfer from Alq3 to DCJTB and improves the optical and electrical properties of the resulting red OLEDs, the preparation of such devices requires the vaporization of all three materials simultaneously, which can be difficult to control. Chen et al. 18 and Qui et al. 19 found that use of tris(8-hydroxyquinoline)gallium (Gaq3) and bis(salicylidene-o-aminophenolato)bis[8-quinolinonato]bisgallium(III) [Ga2(saph)2], respectively, as host materials improved the efficiency relative to that of the doped Alq3 device. Although the development of these host materials is a promising approach toward improved performance, their current and power efficiencies at 20 mA/cm² are less than 3 cd/A and 1 lm/W, respectively, which, for red OLEDs, is unsatisfactory. The main issue in those systems is incomplete energy transfer from the host to the dopant.

There are, however, several red phosphorescent emitters, including iridium 20, 21 and platinum porphyrin 22, 23 complexes, that provide high efficiency and brightness, but they perform well only in devices operated at low current densities. In most cases, the long lifetimes of triplet-state excitons lead to triplet–triplet annihilation. As a result, the emission is quenched even at medium current densities. Red OLEDs fabricated with such emitters usually fall short of the efficiency and chemical stability required for commercial applications, even though the current efficiency can reach as high as 29 cd/A. 20 Recently, an osmium complex has been reported for use in red-emitting phosphorescent devices exhibiting a high current efficiency (29.9 cd/A) with Commission Internationale de l’Eclairage (CIE) coordinates of (0.64, 0.36). 24 The current efficiency of fluorescent red OLEDs based on Alq3 and 2-methyl-9,10-di(2-naphthyl)anthracene (MADN) as cohost and DCJTB as the doped material reaches 5.42 cd/A at 20 mA/cm² with CIE coordinates of (0.63, 0.37); 25 this device is one of the best fluorescent red OLEDs reported to date. There is still, therefore, much room for improvement in the efficiency of fluorescent red OLEDs. To do so, the host and doped materials must have good carrier-transport properties and undergo efficient energy transfer, which arises as a result of (i) perfect overlap between the PL spectrum of the host material and the absorption spectrum of the doped material and (ii) a high fluorescence quantum yield of the host material.

In this study, we describe the use of 1,3,5-tris(1-pyrenyl)benzene (TPB3) as a host material that undergoes efficient energy transfer to the red dopant DCJTB. We fabricated a red OLED based on the single host, having the configuration of indium-tin oxide (ITO)/N,N′-bis(1-naphthyl)-N,N′-diphenylyl-1,1′-biphenyl-4,4′-diamine (NPB) (65 nm)/TPB3:DCJTB (2 wt %, 40 nm)/Alq3 (30 nm)/LiF (0.8 nm)/Al (200 nm) that exhibited a maximum luminance at 13.5 V of 70,600 cd/m², ca. four times higher than that of the device incorporating Alq3 as the host material at the same potential. The doped TPB3 device displayed a high current efficiency of 4.38 cd/A and a power efficiency of 2.12 lm/W at 20 mA/cm²; these efficiencies remained higher than 4 cd/A and 1 lm/W, respectively, over a wide range of potentials (3.5–13.5 V), with good CIE coordinates of (0.63, 0.37).

Experimental

Figure 1 presents the molecular structures of TPB3, which was prepared according to published procedures 26 and DCJTB. The devices were fabricated on glass substrates layered with 130 nm ITO having a sheet resistance of ca. 13 Ω/□. The substrates were cleaned through ultrasonication in isopropyl alcohol and deionized water, followed by treatment with oxygen plasma. All of the organic
layers and the LiF/Al layers were evaporated onto the substrates at $10^{-6}$ Torr without breaking the vacuum. The rates of evaporation and thicknesses of the organic and metal layers were monitored using quartz oscillators. The device structure was ITO/NPB (65 nm)/TPB3:DCJTB (1,1,5,2,2.5, or 3 wt %, 40 nm)/Alq3 (30 nm)/LiF (0.8 nm)/Al (200 nm). NPB and Alq3 were used as hole and electron transporting layers, respectively. As a reference, a device was prepared incorporating Alq3 as the host material; its configuration was ITO/NPB (65 nm)/Alq3:DCJTB (2 wt %, 40 nm)/Alq3 (30 nm)/LiF (0.8 nm)/Al (200 nm). The emission layer was fabricated through coevaporation of DCJTB with the host material; the concentrations (wt %) of the dopant material were estimated from the ratio of the evaporation rates. ITO and LiF/Al were employed as the anode and cathode, respectively. The thickness was measured using a Dektak 150 surface profiler. The PL and absorption spectra were measured using a Perkin–Elmer FL LS55 fluorescence spectrophotometer and a Perkin–Elmer Lambda35 UV-visible spectrometer, respectively. The energy levels were determined using a Riken KeiKi AC-2 photoelectron spectrometer. The electroluminescence (EL) spectra and CIE coordinates of the devices were measured using a PR650 spectrometer. The fluorescence quantum yield was measured using a Hamamatsu C9920-02 absolute PL quantum yield measurement system. The luminance–current–density–voltage characteristics were recorded simultaneously with the EL spectra by combining the spectrometer with a Keithley 2400 programmable voltage–current (V–I) source after the devices had been sealed in a nitrogen-filled glove box. All measurements were recorded at room temperature under ambient conditions. The active area of the device was 3 mm².

Results and Discussion

Photophysical properties.—In this study, we used TPB3 as a host material for two reasons: (i) most triarylbenzenes and tetraarylbenzenes have high glass transition temperatures ($T_g > 130^\circ$C); among them, TPB3 possesses particularly good thermal stability ($T_g = 165^\circ$C); (ii) the fluorescence quantum yield of TPB3 (0.8) is four times that of Alq3 (0.2). In addition to these two factors, another critical issue is the effect of energy transfer from the host material to the dopant.

One method of determining the effect of energy transfer is through calculating the Förster radius ($R_0$), defined as the distance between the host material and the dopant material at which the probability of relaxation of the host material via energy transfer equals that through other processes. A large Förster radius indicates efficient energy transfer. The Förster radius can be calculated using the equation:

$$R_0^6 = \frac{0.5291k^2\phi_D}{n^2N} \int_0^\infty F_D(v)\varepsilon_D(v)\frac{dv}{v^2}$$

where the value of $\kappa$ depends on the relative orientation of the host and dopant materials' dipoles ($\kappa^2 = 2/3$ for randomly oriented dipoles), $n$ is the refractive index of the medium, $N$ is Avogadro’s number, $\phi_D$ is the fluorescence quantum yield of the host material, $F_D(v)$ is the normalized emission spectrum of the host material, $\varepsilon_D(v)$ is the molar extinction coefficient of the dopant material, and $v$ is the energy, expressed in wavenumbers.

From Eq. 1, it is clear that good overlap between the emission spectrum of the host material and the absorption spectrum of the dopant material is an important factor affecting efficient energy transfer, as is a high fluorescence quantum yield of the host material. Figure 2 displays the optical absorption spectrum of DCJTB and the PL spectra of TPB3 and Alq3. There is a much better overlap between the PL spectrum of TPB3 and the absorption spectrum of DCJTB than that between the PL spectrum of Alq3 and the absorption spectrum of DCJTB. The fluorescence quantum yield of TPB3 (0.8) is four times of that of Alq3 (0.2). Table I. The calculated Förster radius between TPB3 and DCJTB (63 Å) is larger than that between Alq3 and DCJTB (47 Å) because of the improved spectral overlap of the former pair and the high quantum yield of TPB3.
TPB3. Thus, the material properties of TPB3 and Alq3 (Table I) suggest that energy transfer might occur more efficiently from TPB3 to DCJTB than from Alq3 to DCJTB.

**EL properties.**—Figure 3 presents the energy diagrams of the doping system in this study, fabricated in the configuration ITO/NPB (65 nm)/TPB3:DCJTB (1.1, 1.5, 2, 2.5, or 3 wt %, 40 nm)/Alq3 (30 nm)/LiF (0.8 nm)/Al (200 nm). We adopted TPB3 as the host material because of its good thermal stability, high fluorescence quantum yield, and excellent carrier-transport properties; DCJTB was used as the red dopant. A photoelectron spectrometer was used to determine the highest occupied molecular orbital (HOMO) energy levels of the various components; the lowest unoccupied molecular orbital (LUMO) energy levels were calculated by subtracting the optical bandgaps from the HOMO energy levels. Accordingly, the HOMO and LUMO energy levels of DCJTB were revealed to fall between those of TPB3. Therefore, energy can easily be transferred from TPB3 to DCJTB. The Alq3:DCJTB doped system is currently one of the most efficient red OLEDs; therefore, we used this doped system as a reference. In a previous study,28 we observed that when the concentration of DCJTB was greater than 2 wt %, the intensity of the Alq3 green emission peak of Alq3 appeared in addition to the red peak of DCJTB, suggesting incomplete energy transfer. When the concentration of DCJTB at 2 wt % and prepared a reference device with DCJTB was 2.5 or 3.0 wt %, the intensity of the TPB3 peak decreased, and the intensity of the DCJTB peak reached its maximum. This behavior is consistent with more complete energy transfer from TPB3 to DCJTB. When the concentration of DCJTB was 2.5 or 3.0 wt %, the intensity of the TPB3 peak decreased, and so did the intensity of the DCJTB peak because of concentration quenching. Thus, the use of TPB3:2 wt % DCJTB provided the optimized doped device. Figure 6 displays the CIE coordinate–voltage characteristics of the TPB3:2 wt % DCJTB-doped device. The CIE coordinates changed only slightly over a wide range of potentials (3.5–13.5 V), thereby revealing the color stability of the TPB3:DCJTB-doped devices.

Figure 7 displays the luminance–voltage (B-V) characteristics of the devices doped with TPB3 and Alq3. At a given voltage, the doped TPB3 device exhibited a much higher luminance than did the doped Alq3 device. The maximum luminance of the doped TPB3 device (70,600 cd/m² at 13.5 V) was ca. four times higher than that of the doped Alq3 device at the same potential. Figure 8 presents the current efficiency–current density and power efficiency–current density curves of the two devices. The current and power efficiencies of the doped TPB3 device were more than double those values of the doped Alq3 device at any given current density. Table II summarizes the EL characteristics of the devices; using TPB3 as the host material resulted in much better performance relative to that of Alq3 in terms of the maximum luminance, current efficiency, and power efficiency.

**Table I. Material properties of TPB3 and Alq3.**

<table>
<thead>
<tr>
<th>Material</th>
<th>$\lambda_{max}$ (nm)</th>
<th>$\lambda_{max}$ (PL) (nm)</th>
<th>HOMO/LUMO</th>
<th>$d_p$ (Å) with DCJTB</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPB3</td>
<td>354</td>
<td>518</td>
<td>5.63/2.53</td>
<td>0.8 63</td>
</tr>
<tr>
<td>Alq3</td>
<td>388</td>
<td>526</td>
<td>5.6/2.8</td>
<td>0.2 47</td>
</tr>
</tbody>
</table>

Figure 3. Schematic energy-level diagram of the red OLED.
Conclusion

The PL spectrum of TPB3 exhibits perfect overlap with the absorption spectrum of the red dopant material DCJTB; in addition, TPB3 possesses a high fluorescence quantum yield. A red-doped OLED system having the configuration ITO/NPB (65 nm)/TPB3:DCJTB (2 wt %, 40 nm)/Alq3 (30 nm)/LiF (0.8 nm)/Al (200 nm) exhibited a maximum luminance of 70,600 cd/m² at 13.5 V, CIE coordinates of (0.63, 0.37), and high current and power efficiencies of 4.38 cd/A and 2.12 lm/W, respectively, at 20 mA/cm². Our findings suggest that searching for a suitable host material can be a fruitful approach toward fabricating red OLEDs exhibiting high performance; in this case, TPB3 is a suitable host material for red OLED applications when paired with DCJTB as the dopant.

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