

Simple color tuning of phosphorescent dendrimer light emitting diodes

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A simple way of tuning the emission color in solution processed phosphorescent organic light emitting diodes is demonstrated. For each color a single emissive spin-coated layer consisting of a blend of three materials, a *fac*-tris(2-phenylpyridyl)iridium (III) cored dendrimer (Ir-G1) as the green emitter, a heteroleptic [bis(2-phenylpyridyl)-2-(2'-benzo[4,5- α]thienyl)pyridyl] iridium (III) cored dendrimer [Ir(ppy)₂btp] as the red emitter, and 4,4'-bis(*N*-carbazolyl) biphenyl (CBP) as the host was employed. By adjusting the relative amount of green and red dendrimers in the blends, the color of the light emission was tuned from green to red. High efficiency two layer devices were achieved by evaporating a layer of electron transporting 1,3,5-tris(2-*N*-phenylbenzimidazolyl)benzene (TPBI) on top of the spin-coated emissive layer. A brightness of 100 cd/m² was achieved at drive voltages in the range 5.3–7.3 V. The peak external efficiencies at this brightness ranged from 31 cd/A (18 lm/W) to 7 cd/A (4 lm/W). © 2005 American Institute of Physics. [DOI: 10.1063/1.1899256]

Organic light emitting diodes (OLEDs) are of great interest for flat panel displays.^{1–4} Phosphorescent materials based on iridium (III) complexes, e.g., *fac*-tris(2-phenylpyridyl)iridium (III) [Ir(ppy)₃] are particularly attractive because both singlets and triplets can be harvested for light emission, giving higher efficiency.² Devices made from Ir(III) complexes usually consist of many layers deposited sequentially under high vacuum by thermal evaporation. Solution-processing techniques^{3,4} such as spin-coating or inkjet printing provide much simpler ways to fabricate OLEDs. We have therefore pursued the development of solution-processible electrophosphorescent dendrimers based on iridium (III) complexes.^{5–7} Light-emitting dendrimers consist of a core, dendrons, and surface groups. They have shown great promise, with efficiencies of 55 cd/A (40 lm/W) at 4.5 V and 400 cd/m² reported for two layer green emitting OLEDs⁶ while in single layer devices a maximum power efficiency of 12.8 lm/W at 8.1 V and 550 cd/m² has been observed for the same dendrimer.⁷ The dendrimer technology has not only been successful for green emission, and a power efficiency of 4.5 lm/W at 80 cd/m² and 5 V has been reported for a red phosphorescent dendrimer in a bilayer device structure.⁸

In OLEDs, the efficient tunability of the emission spectrum to a desired color is an important consideration when designing materials. One way of tuning color is to change the molecular structure. However, if the required chromophore for a particular color is not easily available then to be able to blend two colors to give the required emission would be advantageous. Blending materials that emit different wavelengths of light to tune emission color has been demonstrated for devices prepared by evaporation of small molecules⁹ and solution processed polymer guest/host combinations.^{10,11}

Kawamura *et al.*¹⁰ demonstrated color tuning in a blend of cyclometalated Ir(III) complexes doped into poly(9-vinylcarbazole). The devices showed modest efficiencies and consisted of two organic evaporated layers on top of a spin-coated light emitting layer and a PEDOT:PSS hole injection layer. Recently, we have shown color tuning over a limited range from blue to blue-green by blending fluorescent dendrimers.¹² However, fluorescent dendrimers tend to be less efficient than phosphorescent dendrimers and in this letter we show that phosphorescent dendrimers can be blended to obtain color tuning in solution processed OLEDs with a simple (two organic layer) structure. We demonstrate color tuning from green to red by adjusting the relative amounts of red and green emitting dendrimers in a blend and show that high efficiencies are achieved across the color range.

The materials used were the green emitting *fac*-tris(2-phenylpyridyl) iridium (III) cored dendrimer (Ir-G1), the red emitting [bis(2-phenylpyridyl)-2-(2'-benzo[4,5- α]thienyl)pyridyl]iridium (III) cored dendrimer [Ir(ppy)₂btp], 4,4'-bis(*N*-carbazolyl)biphenyl (CBP), and 1,3,5-tris(2-*N*-phenylbenzimidazolyl)benzene (TPBI). The devices were formed by spin-coating dendrimer blends from chloroform solution onto oxygen plasma ashed indium tin oxide coated glass substrates. The total concentration of the CBP and dendrimers in solution was 20 mg/ml of which 80 wt % was CBP. The compositions used ranged from 0:20:80 wt % Ir(ppy)₂btp:Ir-G1:CBP (pure green) through 1:19:80, 4:16:80, 9:11:80, to 20:0:80 (pure red). An electron transporting TPBI layer of 70 nm thickness was evaporated on the top of the spin-coated films. The cathode consisted of lithium fluoride (LiF) 0.4 nm, calcium (Ca) 15 nm and aluminum (Al) 100 nm layers.

Figure 1 shows the absorption and photoluminescence (PL) spectra of the dendrimers. The absorption of both dendrimers in the 350–500 nm wavelength range is due to MLCT transitions and the absorption in the UV region peak-

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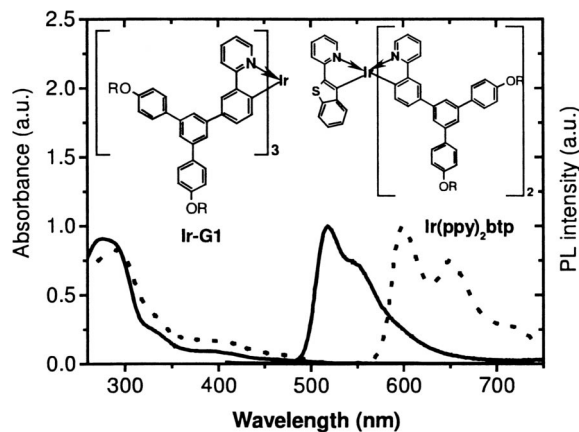


FIG. 1. Chemical structures of Ir-G1 and Ir(ppy)₂btp with R = 2-ethylhexyl. The lower panel shows the absorption spectra of neat films of Ir-G1 (solid lines) and Ir(ppy)₂btp (dotted line); photoluminescence spectra of 20:80 wt % Ir-G1:CBP blend film (solid line) and 20:80 wt % Ir(ppy)₂btp:CBP blend film (dotted line). Excitation wavelength 325 nm.

ing at ~ 290 nm is assigned to the biphenyl dendrons and ligands.^{5,8,13} Although the difference in absorption is small, there is a substantial difference in the PL spectra, due to a difference in the triplet energy levels of the two materials. The PL spectra of a 20:80 wt % Ir-G1:CBP blend film exhibits a peak at 518 nm with a shoulder at 545 nm. For a 20:80 wt % Ir(ppy)₂btp:CBP blend film the PL shows peaks at 600 and 652 nm, with a shoulder at 720 nm. The emission from both dendrimers is phosphorescence.^{5,8}

Figure 2 shows the electroluminescence (EL) spectra and Commission Internationale de L'Éclairage (CIE) coordinates of each device. The EL spectra of the 0:20:80 and 20:0:80 wt % Ir(ppy)₂btp:Ir-G1:CBP devices are very similar to the PL spectra of the same blends indicating that the emission is from the same phosphorescence transitions. The CIE coordinates for 20:0:80 and 0:20:80 wt % Ir(ppy)₂btp:Ir-G1:CBP devices were (0.64, 0.36) and (0.36, 0.60) indicating pure red and green colors respectively. For three component 1:19:80, 4:16:80, and 9:11:80 wt % Ir(ppy)₂btp:Ir-G1:CBP devices we observed EL emission from both dendrimers with the contribution of the red emission (which peaks at 600 nm) increasing as the concentration of the Ir(ppy)₂btp increases. It is important to note that no CBP emission was detected from any of the devices. The CIE coordinates of the 1:19:80, 4:16:80, and 9:11:80 wt % Ir(ppy)₂btp:Ir-G1:CBP devices were (0.42, 0.54), (0.52,

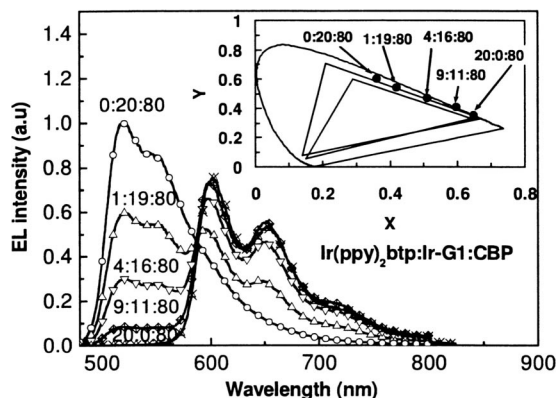


FIG. 2. EL spectra of Ir(ppy)₂btp:Ir-G1:CBP blend devices. Inset shows CIE coordinates of each device.

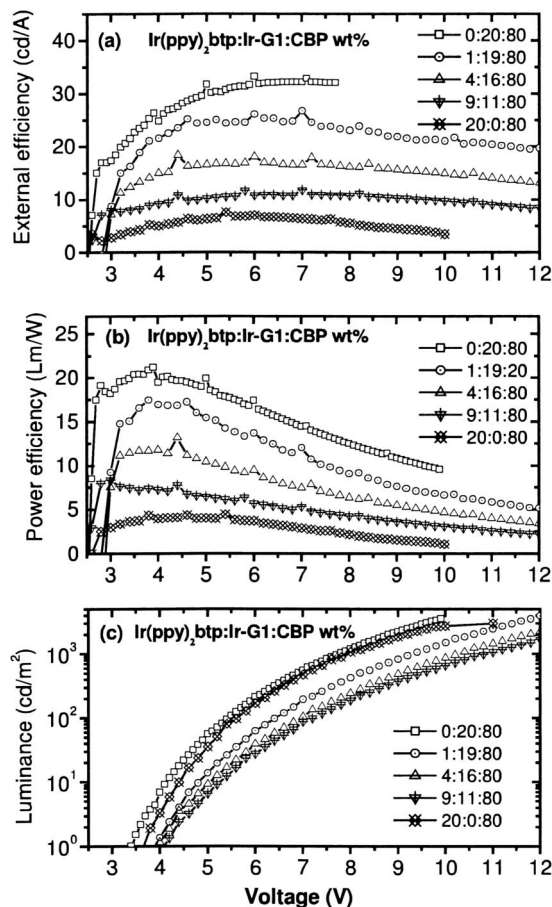


FIG. 3. (a) External quantum efficiency cd/A; (b) power efficiency lm/W; (c) luminance (cd/m²) for Ir(ppy)₂btp:Ir-G1:CBP devices as function of voltage.

0.46), and (0.60, 0.40), respectively. These points lie on the line joining green to red in the CIE color diagram, showing that blending provides a simple way of tuning color over a wide range. The color of emission from the blends does not change significantly in the brightness range studied of 10–1000 cd/m².

Figures 3(a)–3(c) show the external efficiency, power efficiency, and luminance of the devices as a function of voltage. For two component 0:20:80 and 20:0:80 wt % Ir(ppy)₂btp:Ir-G1:CBP blends efficiencies of 31 cd/A (18 lm/W) and 7 cd/A (4.0 lm/W) were obtained at 100 cd/m², respectively. For three component blends 1:19:80, 4:16:80, and 9:11:80 wt % Ir(ppy)₂btp:Ir-G1:CBP, efficiencies of 25 cd/A (12.4 lm/W), 17 cd/A (7.5 lm/W), and 11 cd/A (4.8 lm/W) respectively were obtained at 100 cd/m².

These efficiencies are very much higher than our earlier work¹² on blending blue and blue-green fluorescent dendrimers (1.5 lm/W). They are also much higher than the values reported by Kawamura *et al.*¹⁰ for phosphorescent small molecules blended with poly(9-vinylcarbazole) as a host. At 100 cd/m², our efficiencies (in lm/W) are approximately three times higher in the green and ten times higher in the red region of the spectrum. The higher efficiency in the dendrimer devices is due to a combination of lower operating voltage and higher quantum efficiency. It is also achieved in a simpler device structure (two organic layers instead of four).

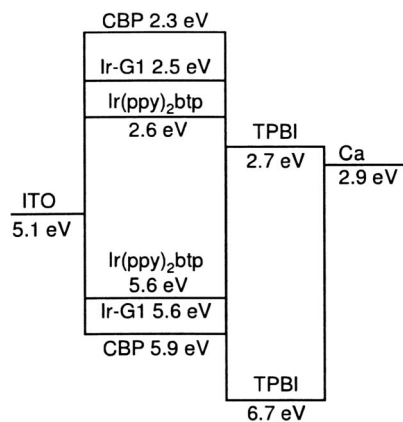


FIG. 4. Energy level diagram for the materials used.

An important observation was that in all devices the high efficiency was maintained across a large range of voltages indicating good charge balance is achieved in the bilayer device structures. The decrease in the efficiency with increasing concentration of Ir(ppy)₂btp is mainly due to the change in the emission color combined with the eye's lower sensitivity to red light than green light. For the EL spectra reported here, the eye's sensitivity is a factor 2.5 lower for red than for green. The light turn-on voltage (1 cd/m²) for all devices was in the range 3–4 V and the operating voltage at 100 cd/m² was in the range of 5.3–7.3 V. Hence the electrical properties are insensitive to the blend composition, and good performance is achieved for all the devices.

In order to understand the possible mechanism of color tuning in the device, we need to consider both charge trapping and energy transfer. Under electrical excitation, both energy transfer and charge trapping can play a crucial role in EL emission. Figure 4 shows the HOMO and LUMO energy levels for the constituent materials. Where possible both energy levels were deduced from cyclic voltammetry, though for the Ir(ppy)₂btp only the HOMO could be determined from cyclic voltammetry and so the absorption spectrum was combined with this value to estimate the position of the LUMO. The cyclic voltammetry measurements are reported in our earlier work.^{13,14} The HOMO levels of Ir-G1 and Ir(ppy)₂btp are 0.3 eV above those of CBP, implying that holes are readily trapped on both.^{6,14} Figure 4 also suggests that electrons will be trapped on the dendrimers. Hence excitons are expected to form directly on the dendrimers, and this is supported by the absence of CBP emission. For three component Ir(ppy)₂btp:Ir-G1:CBP devices we expect energy transfer between the different dendrimers and charge trapping to occur concurrently. Since the HOMO and LUMO energy levels for both dendrimers are similar we expect direct excitation of red and green dendrimers by charge trapping, leading to exciton formation proportional to the concentration of green and red dendrimers. Energy transfer from

green to red dendrimers will then occur by the Förster mechanism at a rate related to the overlap of the absorption spectrum of Ir(ppy)₂btp with the PL spectrum of Ir-G1. Figure 1 shows that this overlap is relatively weak. The transfer rate also depends on distance R between Ir-G1 and Ir(ppy)₂btp molecules and is given by $k_T = (1/\tau) \cdot (R_0/R)^6$ where τ is the excited state lifetime of the donor Ir-G1 dendrimer, and R_0 is the Förster radius. From the overlap of the absorption and emission spectra¹⁵ we obtain a value of $R_0 = 23 \pm 2$ Å. This fairly small value of R_0 means that color tuning requires a substantial concentration of the red dendrimer. In contrast if R_0 were large, small concentrations would be needed which could be harder to weigh out accurately.

In conclusion, we have demonstrated a simple and efficient way of color tuning from green to red using solution processible electrophosphorescent dendrimers in a two-layer device structure. We have shown that the good color tuning is due to weak energy transfer and efficient charge trapping. Our results show that blending of dendrimers is a convenient way of tuning the properties of solution processed optoelectronic devices.

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