11.1: *Invited Paper:* Advances in Blue Phosphorescent Organic Light-Emitting Devices

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Abstract

This paper discusses the latest developments towards a commercial blue phosphorescent organic light emitting device (PHOLED™) technology. Progress towards achieving a high efficiency, long-lived saturated blue PHOLED is discussed. First, a high efficiency (20% EQE, 45 cd/A), light blue (0.17, 0.39) PHOLED is presented. Next, long-lived blue PHOLEDs having chromaticity co-ordinates (0.17, 0.38) and (0.16, 0.29) are estimated to degrade to half their initial luminance of 200cd/m^2 after >100,000 hrs and 17,500 hrs, respectively. Finally, results from PHOLEDs designed to increase blue color saturation and lifetime are presented.

1. Introduction

In phosphorescent organic light emitting devices (PHOLEDs) [1], the singlet excited state (S_1) excitons may be converted into the triplet excited state (T_1) through inter-system crossing via the presence of a heavy metal atom. In these devices, the triplet states can emit radiatively (T_1 to S_0), enabling record high conversion efficiencies. The first generation of PHOLEDs contained platinum 2,3,7,8,12,13,17,18-octaethyl-12H,23H-porphyrin (PtOEP) as the dopant phosphor. An impressive external quantum efficiency, at the time, of 6% was reported [2].

Later generations of PHOLEDs improved considerably upon the early promise of PtOEP. PHOLEDs incorporating phosphorescent organometallic iridium compounds have exhibited green electroluminescence with maximum external quantum efficiencies of 23% [3]. Red emitting PHOLEDs have shown external quantum efficiencies as high as 16.5% [4]. Adjusting for optical effects such as outcoupling [5,6], the internal quantum efficiency of such devices has been estimated to be close to 100%. Green PHOLEDs have demonstrated lifetimes in excess of 40,000 hrs from an initial display luminance L_0=1000 cd/m^2 [7]. Red PHOLEDs have exhibited even longer lifetimes with more than 100,000 hrs projected from an initial luminance of 500 cd/m^2 [8].

Efficient blue electroluminescence from an Ir3+ organometallic compound was first demonstrated [9] in 2001. Figure 1 shows the electroluminescence spectrum and efficiency characteristics of a PHOLED containing the electrophosphorescent dopant iridium (III)(bis)(4,6-di-fluorophenyl)-pyridinato-N,C$^{2'}$)picolinate (FIrpic). This device showed sky blue electroluminescence with an onset of emission at 442 nm, a peak wavelength of 472 nm with 1931 Commission Internationale d'Éclairage (CIE) color co-ordinates of (0.16, 0.37), and a peak external quantum efficiency of 6.1%. The PHOLED was fabricated on transparent 120 nm ITO coated 0.7 mm soda lime glass. The device was constructed by sequentially depositing layers of copper phthalocyanine (CuPc) [10 nm], 4,4'-bis[N-(1-napthyl)-N-phenyl-amino] biphenyl (α-NPD) [30 nm], 4,4'N,N'-dicarbazole-biphenyl (CBP) [30 nm] doped with FIrpic at a concentration of 6 wt.%, and aluminum(III)bis(2-methyl-8-quinolinato)4-phenylphenolate (BAlq) [40 nm]. The structure was completed with a 1 nm layer of LiF and a 100 nm layer of Al as the cathode contact. The organic and metal layers were thermally deposited at 0.2–4 Å/s in a vacuum of <10^{-7} Torr to yield devices with an active area of 5

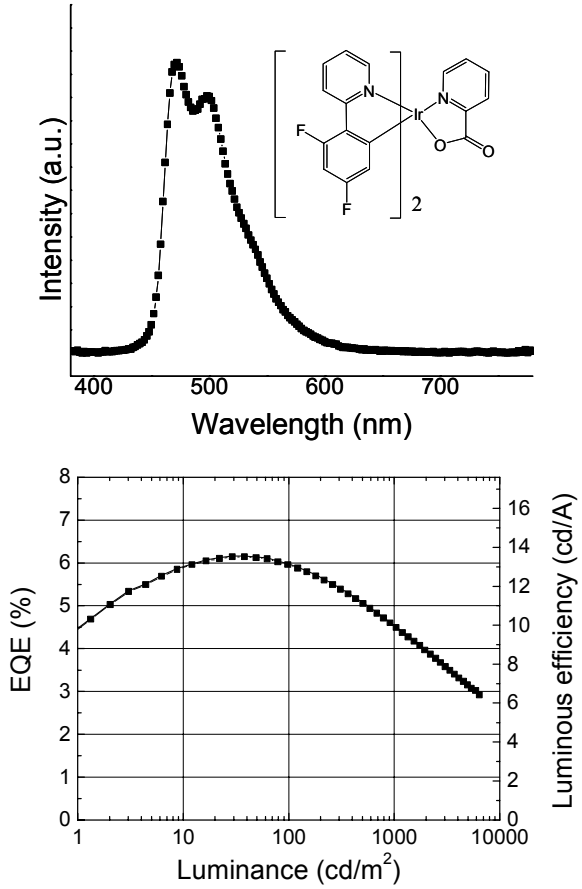

Figure 1. The electroluminescence spectrum and efficiency vs. luminance characteristics of a FIrpic doped PHOLED. Inset: chemical structure of FIrpic

mm^2. The PHOLEDs were encapsulated in a dry nitrogen atmosphere (<1 ppm H_2O and O_2) using a glass lid and a UV

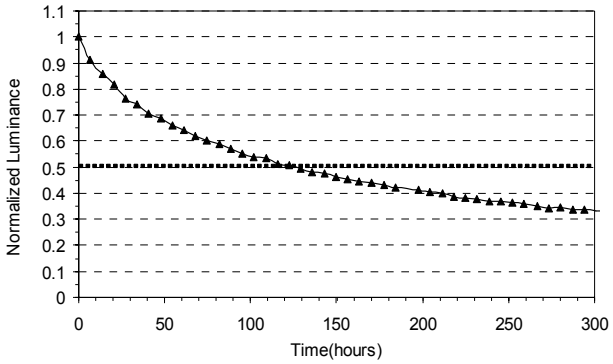

Figure 2. The typical lifetime characteristic of the FIrpic PHOLED device from Figure 1. The device was tested at a constant DC current drive from an initial luminance L_0=100 cd/m^2.

cured epoxy edge seal. A CaO getter was inserted inside the package to absorb byproducts of the cured epoxy and any residual water present within the encapsulated volume. All subsequent devices in this paper were fabricated using the same deposition rates, vacuum levels, encapsulation conditions and cathode.

The efficiency of PHOLEDs containing FIrpic have since improved to near theoretical maximum values with the use of high energy host materials and transport layers [10,11], but operational lifetimes have remained low. Figure 2 shows a typical lifetime characteristic of the FIrpic device from Figure 1. The device was tested at a constant DC current drive from an initial luminance L_0=100 cd/m^2. In addition to the inadequate lifetime, the color saturation of FIrpic devices is insufficient for most display applications. In order to realize commercial blue PHOLEDs, high efficiency values, long lifetimes (>10,000hrs) and good color saturation (a CIE y color co-ordinate <0.2) must be achieved in combination. This paper describes some of the latest developments in realizing efficient, long-lived, color saturated blue PHOLEDs.

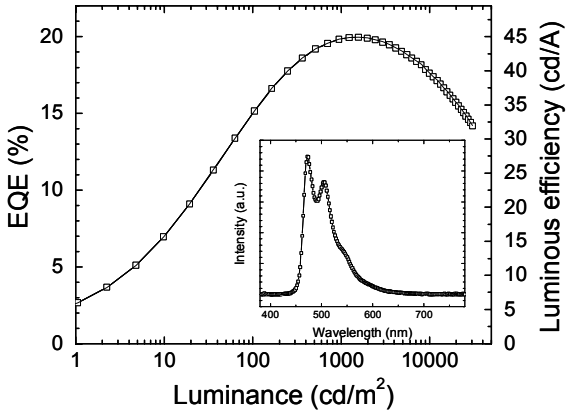

Figure 3. The efficiency vs. luminance characteristics and electroluminescence spectrum (inset) of a light blue PHOLED.

2. High Efficiency Blue PHOLEDs

Figure 3 shows the electroluminescence spectrum and efficiency characteristics as a function of luminance of a light-blue PHOLED developed for high efficiency at active matrix OLED (AMOLED) luminance levels. The device structure was ITO (80 nm)/hole injection layer (HIL)/ α-NPD/ hole transport layer 2 (HTL2)/emissive layer (EML) containing a host doped with a light-blue electrophosphorescent dopant/BAlq/electron transport layer 2 (ETL2)/LiF/Al. Here the HIL material was supplied by LG Chemical. The onset of emission occurs at 444 nm and has a peak wavelength of 472 nm. The CIE co-ordinates of this particular device are (0.17, 0.39). The PHOLED has a peak external quantum efficiency of 20% (equivalent to 45 cd/A luminous efficiency) at 1580 cd/m^2. External quantum efficiencies >20% without outcoupling enhancement, have now been demonstrated for a wide range of PHOLEDs spanning the entire visible spectrum.

3. Long-lifetime Blue PHOLEDs

In order to realize the efficiency benefits of PHOLEDs in a commercial application, lifetimes in excess of 10,000 hrs at luminance levels > 500 cd/m^2 (depending on the application) must

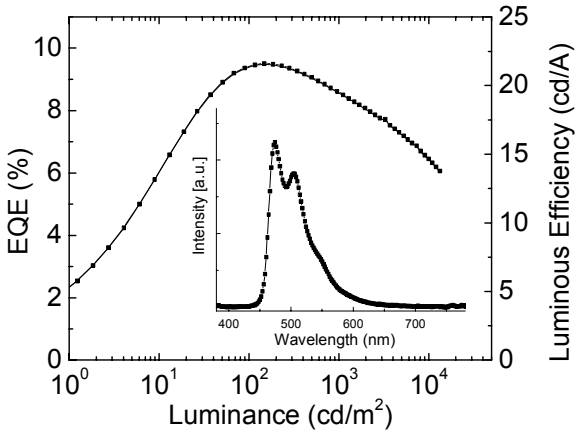

Figure 4. The efficiency vs. luminance characteristics and electroluminescence spectrum (inset) of a sky-blue PHOLED.

be demonstrated. Recently a sky blue PHOLED with a CIE of (0.16, 0.37) having a lifetime of 15,000 hrs from an initial luminance of 200 cd/m^2 was reported [4]. The device structure was ITO (80 nm)/hole injection layer (HIL)/ α-NPD/ EML containing a host doped with a sky-blue electrophosphorescent dopant /tris-(8-hydroxyquinoline) aluminum (Alq_3)/LiF/Al. Figure 4 shows the electroluminescence spectrum and efficiency characteristics of this device. The onset of emission occurs at 446 nm and has a peak wavelength of 474 nm. The maximum external quantum efficiency of this device was 9.5%, which corresponds to a luminous efficiency of 22 cd/A. Efficiencies from PHOLEDs with similar CIE co-ordinates of (0.17, 0.38) have been improved

CIE	External Quantum efficiency [%]	Luminous efficiency [cd/A]	Lifetime [hrs] to 50%, L_0=200cd/m^2 (extrapolated)
(0.16, 0.29)	11%	21	17,500
(0.17, 0.38)	14%	32	100,000

Table 1. Stable blue PHOLED performance.

to 14% EQE (32 cd/A) and lifetime has been increased to 100,000 hrs, driven constant current DC from a starting luminance L_0 = 200 cd/m^2 or 20,000 hrs at L_0 = 500 cd/m^2.

Figure 5 shows the electroluminescence spectrum of a new blue PHOLED, which has an onset of electroluminescence at 432 nm, a first emission peak wavelength of 460 nm, and CIE coordinates of (0.16, 0.29). The external quantum efficiency of this particular blue PHOLED is 11% or 21 cd/A at 200 cd/m^2. The device has a lifetime of 17,500 hrs driven constant current DC from a starting luminance L_0= 200 cd/m^2. The above lifetimes are, to the best of the authors' knowledge, the highest ever reported for blue PHOLEDs and represent a significant breakthrough towards the realization of commercial blue PHOLEDs and an all phosphorescent commercial OLED display. Table 1 summarizes the stable blue PHOLED performance to date.

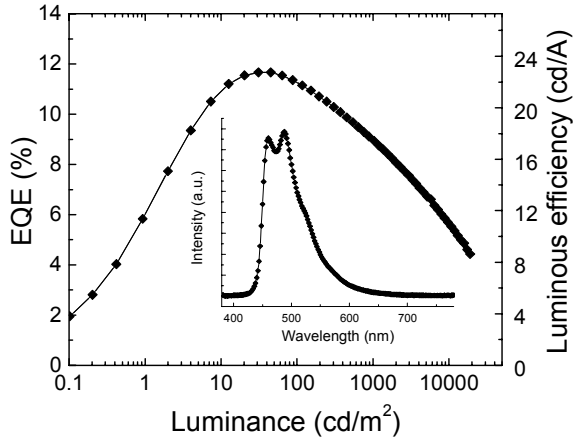

Figure 5. The efficiency vs. luminance characteristics and electroluminescence spectrum (inset) of a blue PHOLED.

4. Saturated Blue PHOLEDs

By changing the ITO layer thickness (200 nm) and organic layer thicknesses of the PHOLED shown in Figure 5 the electroluminescence spectrum can be further saturated without significant changes to the radial emission characteristics. Using this approach the CIE coordinates can be shifted from (0.16, 0.29) to (0.17, 0.25). Figure 6 shows the resulting electroluminescence spectrum. The onset of emission remains the same at 432 nm and the peak wavelength is only slightly blue shifted by 2 nm to 458 nm. However the major change in the electroluminescence spectrum with respect to the previous device is the increase in the height of main emission peak with respect to the first vibronic peak and a narrowing of the full width half maximum (FWHM) from 75 nm to 58 nm. This type of subtle device optimization is an effective strategy for tailoring the CIE coordinates of a particular dopant. However in order to make a more significant change in the CIE coordinates, i.e. produce a spectrum with an NTSC blue point, three other possible strategies can be used.

A first approach to producing a saturated blue emission spectrum from a pixel element is to apply a color filter to the OLED. The emission spectrum from most organic materials tends to be broad (>50 nm FWHM) with a long tailing edge of emission at longer wavelengths (> 500 nm). In blue OLEDs, this tail plays a large role in reducing the saturation of the CIE coordinates. For example, if all emission at wavelengths longer than 520 nm was

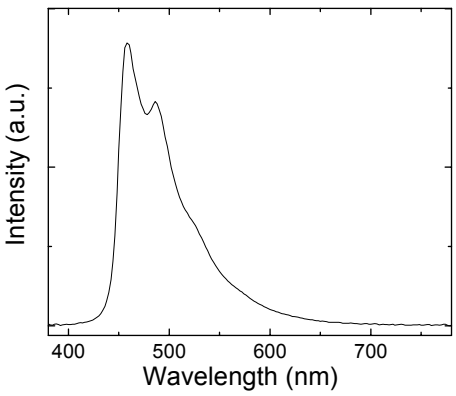

Figure 6. The electroluminescence spectrum of a blue PHOLED, CIE (0.17, 0.25), with device layers optimized to reduce the CIE y coordinate.

filtered or suppressed for the device shown in Figure 5, the resulting device would have CIE coordinates of (0.11, 0.17) and a luminous efficiency of 9 cd/A (8% external quantum efficiency). When considering schemes such as white OLEDs with color filters for displays, the above approach to achieving deep color saturation may be a consideration.

A second approach to achieving a more saturated blue color is to develop materials where the emission spectrum is further blue-shifted. Recently, deeply saturated blue PHOLEDs based upon Ir-carbene complexes were developed [12,13] that emit in the near-UV with a peak wavelength of 386 nm, having CIE coordinates of (0.16, 0.07). In this case, although the blue CIE meets the NTSC requirement, the emission spectrum of this Ir-carbene complex is not ideally suited for display applications, since much of the photon energy lies outside the visible wavelengths. To maximize luminous efficiency, blue PHOLEDs with a peak emission wavelength in the visible spectrum that can also achieve the requisite CIE coordinates are preferred.

A third approach to achieving a desired color saturation without sacrificing efficiency is to narrow the intrinsic emission characteristics of the emissive material. Figure 7 shows an

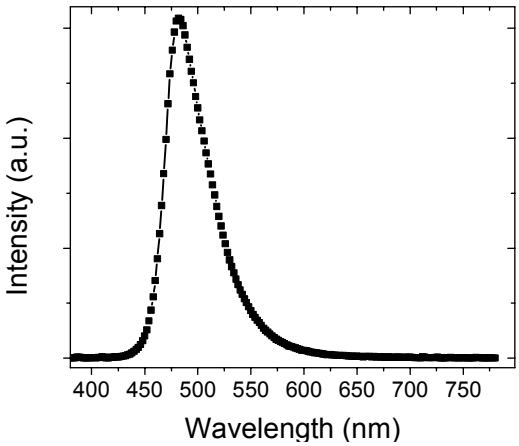

Figure 7. The electroluminescence spectrum of a narrow emission PHOLED having CIE (0.14, 0.35).

example of such an approach. The device structure was ITO (80 nm)/CuPc / α-NPD/EML containing a host doped with an electrophosphorescent dopant /a hole blocking material (BL41)/ $BAlq_2$/LiF/Al. The electroluminescence spectrum has an onset of emission at 444 nm, a peak at 482 nm, and most importantly a FWHM of only 48 nm. The CIE coordinates are a modest (0.14, 0.35) for this PHOLED. However, the important point is that this material has been engineered to have a narrowed emission spectrum. This benefit is best illustrated by example: the device shown in Figure 4 has a peak wavelength of 474 nm, which is 8 nm blue-shifted from the 482 nm spectral peak here in Figure 7; however, the color saturation for the device in Figure 4 is in fact worse, being *less saturated* by +0.02 in both the x and y coordinates due to the long emission tail.

5. Summary

We have demonstrated that, as for red and green PHOLEDs, external quantum efficiencies as high as 20% are achievable for blue PHOLEDs. However, in order to capitalize on this extremely high efficiency for commercial display applications, saturated emission color and long-lifetimes are necessary. In this paper, we have demonstrated two blue PHOLEDs having CIE co-ordinates (0.17, 0.38) and (0.16, 0.29), which are estimated to degrade to half their initial luminance of 200 cd/m^2 after >100,000 hrs and 17,500 hrs, respectively. In addition, we have outlined possible strategies for achieving saturated blue emission with examples of PHOLEDs emitting at UV energies and a PHOLED having a narrowed emission line-width, e.g. a FWHM <50 nm. In conclusion, we believe the results outlined above represent important milestones towards achieving efficient, long-lived saturated blue PHOLEDs.

6. Acknowledgements

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7. References

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