Maximizing the Efficiency Lifetime Product for Phosphorescent OLEDs

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Abstract
Great strides in organic light emitting device (OLED) technology have resulted in a number of commercial products. To continue this growth into large area displays, for example televisions, an understanding of the mechanisms that drive the OLED device efficiency and lifetime performance is critical. In this work, we consider maximizing the efficiency lifetime product based on phosphorescent OLED (PHOLED™) technology. We report green PHOLEDs with luminous efficiency of 82 cd/A, 5.7 V and 10,000 hours lifetime at 1,000 cd/m², red PHOLEDs with CIE of (0.67,0.33), 11 cd/A and 35,000 hours lifetime at 500 cd/m² and recent progress in blue demonstrating efficiencies of 18 cd/A at 200 cd/m².

Introduction
Since the first report of efficient fluorescent OLEDs in the early 1980's [1], research efforts worldwide have focused on understanding the basic operational principles of OLEDs. Much of this research work has been directed towards maximizing the overall device power efficiency by achieving 100% internal quantum efficiency, minimizing drive voltages and enhancing the light extraction. Specific work has included the advent of phosphorescent emitters [2], optical outcoupling enhancements [3,4], top emission architectures [5,6], and reduction in operating voltages [7]. Such work has spanned the field of low molecular weight and polymeric based OLEDs [8]. In this work we focus on the importance and recent advancements for PHOLED device performance. The combination of PHOLEDs with outcoupling enhancement techniques and top-emission architectures may be necessary for OLEDs to achieve the demanding requirements for full-color large area display applications.

Low power consumption is a key display requirement for mobile applications in order to extend the battery life of the portable products. Display power efficiency, however, is possibly even more critical to large area displays to meet the display lifetime requirements at high brightness for large area displays. Highly efficient OLEDs, which require low drive currents, will be necessary to meet commercial product requirements. The lifetime enhancement with increasing efficiency is easily understood by the relationship between drive current and OLED pixel lifetime coupled with a reduction in Joule heating from the power dissipated along a drive line impedance, and TFT backplane. Therefore, by incorporating PHOLEDs and maximizing the OLED efficiency, the overall display temperature is reduced and lifetime enhanced. The focus of this work is to demonstrate the potential of PHOLED technology to maximize the efficiency lifetime product and thereby open up the potential for demanding applications such as OLED TVs.

Phosphorescent OLEDs
In a small molecule OLED, approximately 25% of the generated excitons are in the singlet state, and 75% are in the triplet state. In conventional fluorescent small-molecule OLEDs [3], light emission occurs as a result of the radiative decay of singlet excitons, and the internal quantum efficiency is limited to approximately 25%. In the phosphorescent [4] OLED system, all singlet excitons may be converted into the triplet state through inter-system crossing via the presence of a heavy metal atom. The triplet states can emit radiatively, enabling extremely high conversion efficiencies. The development of PHOLEDs based on phosphorescent heavy metal complexes as the dopant emitters has accelerated quickly since the initial work with platinum 2, 3, 7, 8, 12, 13, 17, 18-octaethyl-12*H*, 23*H*-porphyrin (PtOEP) red devices in 1997 [2]. Second and third generation materials for full color RGB systems soon followed. High efficiencies and long operational lifetimes have now been demonstrated. For example, PHOLEDs employing heavy metal complexes exhibiting green, orange-red, and red phosphorescent emission with maximum external quantum efficiencies of 19%[9]. 14% and 12%, respectively, have been demonstrated. Since these reports, continued progress in PHOLEDs has been made [18]. As the work now is aimed at meeting product specifications for full-color displays, a fundamental understanding on efficiency and lifetime combined performance and the design requirements for each individual color – chromaticity, and the product of efficiency and lifetime is the focus here.

Maximizing the Efficiency Lifetime Product
The demonstration of high efficiency red PHOLEDs by Baldo et. al. in 1998 generated intense research interest with the potential for 100% internal quantum efficient devices. This paper reported a red organic phosphor 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphyrin platinum(II) (PtOEP) doped into a single heterostructure OLED with 4% EQE [12]. Here PtOEP was doped into an electron transporting host tris(8-hydroxyquinoline) aluminum(III) (Alq_3). Even higher efficiency (~6% EQE) PtOEP PHOLED was shortly realized with a 4,4'-N-N'-dicarbazolyl-biphenyl (CBP) host and an additional 2,9-dimethyl-4,7-diphenylphenanthroline (BCP) layer after the emissive layer. Following this PtOEP PHOLED, this group of researchers found, by utilizing a green organic phosphor *fac-tris(2-phenylpyridine)iridium (* $Ir(ppy)_3$), peak device efficiencies of 8% EQE and 31 lm/W could be achieved. Further work resulted in $Ir(ppy)_3$ based PHOLEDs with maximum external quantum efficiencies of 19-20%[9,10,13]. In both the PtOEP and $Ir(ppy)_3$ PHOLED devices, the organic layer structure is α NPD/Dopant:Host/BCP/Alq_3 where α-NPD is 4,4'-bis[N-(1-napthyl)-N-phenylamino]biphenyl and BCP is 2,9-dimethyl-

4,7-diphenylphenanthroline. Here the BCP layer was inserted to perform the function of exciton and charge carrier confinement or blocking. The efficiency results obtained with this structure were very exciting, however, the initial results obtained for the long term stability of the devices was limited to < 2,000 hours. One model to explain the short lifetime was the morphological instability of the BCP layer. Hence work to solve the lifetime issue was launched.

A first step was reported by Burrows et. al. of long-lived red PHOLEDs based on the phosphorescent material, PtOEP [14]. They reported after a 50 hour burn-in, 3000 hours of continuous operation at 35 cd/m^2 resulted in a 5% loss of initial. luminance. The enhancement of lifetime was attributed to removing the layer of BCP from the device. Based on this work, the next challenge was to replace the unstable BCP layer with a more stable material. Two groups then reported achieving > 10,000 hour operational lifetime at starting luminances of 600 cd/m^2 for Ir(ppy)$_3$-based green PHOLEDs using more stable metal quinolate materials such as BAlq$_2$ [15,16,17,18] as the blocking layer. The external quantum efficiency and luminous efficiency of these devices was demonstrated to be ~ 6% and ~ 25 cd/A, respectively. The demonstration of high efficiency PHOLEDs with long operational stability disproved the speculations that PHOLEDs, due to the relatively long triplet exciton lifetimes, would be more unstable than singlet emitters. In order to achieve maximum efficiency lifetime product simultaneously in the same device and across the full color spectrum, however, more work was needed. Such a study is the focus of this work in which we present results to demonstrate the affect of dopant and other associated materials in addition to device optimization on the efficiency lifetime product.

Experimental Results

For the devices reported in this paper, the basic structure includes an indium tin oxide (ITO) anode with a series of thin film organic materials deposited by vacuum thermal evaporation and completed with a cathode of lithium fluoride (~10Å) and Al (~1000-2000Å). The organic materials are deposited in OLED equipment manufactured by Kurt J. Lesker Company in addition to a second system by Tokki Corporation. Both systems are evacuated to a base pressure < 5 x 10^{-7} Torr prior to organic film deposition. The PHOLED device structure contains an optional first layer of hole injecting material (~100Å) followed by a hole transport material (~300-500Å). The emissive layer is then typically a mixture of a charge conductive host and phosphorescent dopant. The range of doping levels is in the range of 3.5% to 12% measured in weight percent. The device is then completed with an optional blocking (~50-150Å) layer and electron transport layer (~300-500Å). The devices are all characterized by a custom built luminance-current-voltage tester and life test system. The lifetime testing is performed on packaged devices under conditions of constant current drive of 1.5 mA/cm^2 to 40 mA/cm^2 at both room temperature and 60°C.

Green PHOLED Performance

A comparison of the efficiency and device lifetime of green PHOLEDs with GD29 (or Ir(ppy)$_3$) as compared to an improved green phosphorescent material, referred to as GD33, is shown in Figure 1 [18]. An enhancement in external quantum efficiency from 6 to 8% and luminous efficiency from 25 to 28 cd/A at 1000 cd/m^2 is achieved. Possibly even more important is the increase in room and elevated temperature device stability. A room temperature lifetime improvement from 10,000 hours to > 25,000 hours and an improvement from several 1000s of hours to > 5,000 hours at 60 °C is reported (Figure 2). This improvement in lifetime was obtained by a combination of molecular design, improved material purity levels (> 99.5% as measured by HPLC), and device layer structure optimization (i.e. doping percentage and emissive layer thickness).

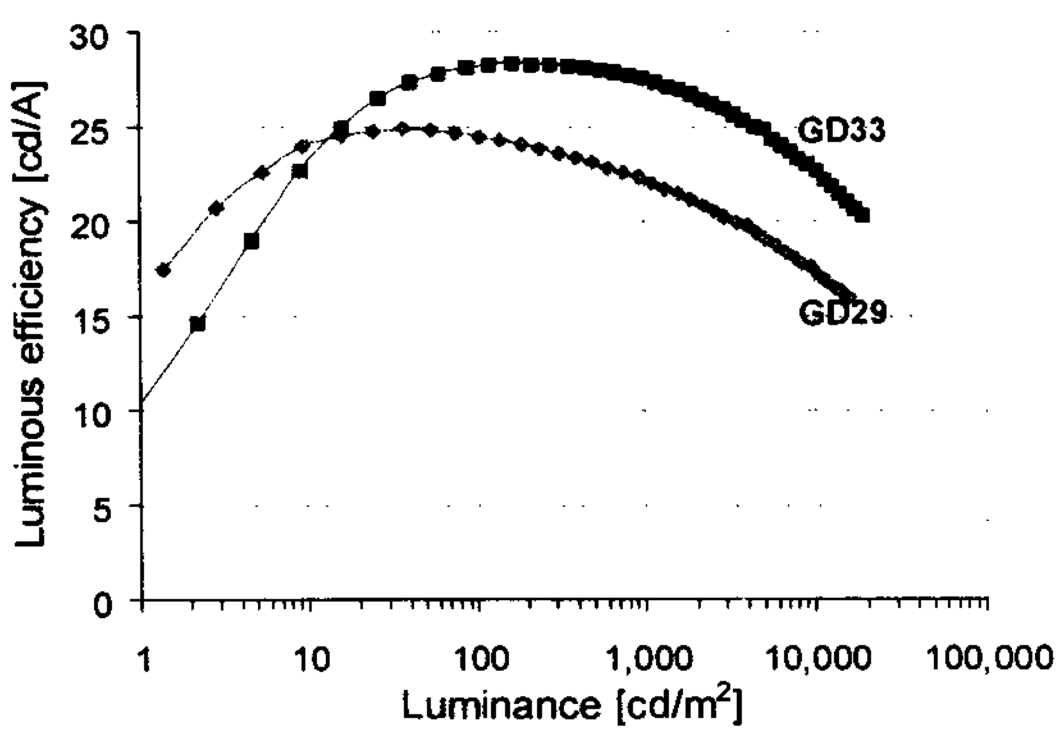


Figure 1: Luminous efficiency (cd/A) versus luminance (cd/m^2) for green PHOLED devices with GD29 (Ir(ppy)$_3$) and GD33 dopants. The CIE coordinates for both devices are (0.30, 0.63).

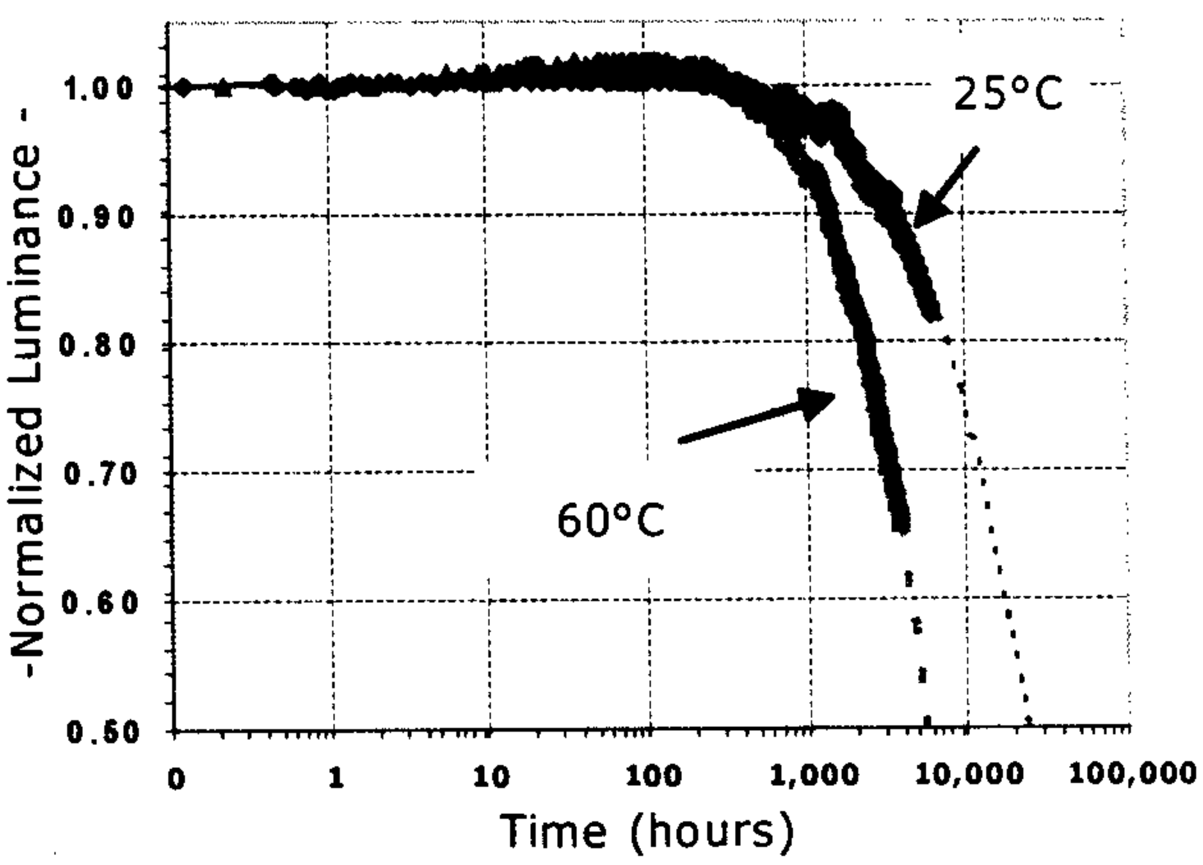


Figure 2: Operational lifetime performance for GD33-based green PHOLED operated under constant DC current drive. The initial luminance is 1000 cd/m^2 and the packaged device is tested at both room temperature (25°C) and elevated temperature of 60°C. A lifetime, defined at 50% of the initial luminance, is > 20,000 and 5,000 hours for RT and 60°C, respectively.

The next improvement is obtained by introducing a new charge transporting layer. By replacing the metal quionolate based blocking layer, the GD33 PHOLED device performance is shown in Figure 3. Here we refer to this as GD33-G2 device structure. This new material was designed to have a deeper HOMO level, higher triplet energy and higher glass transition temperature as compared to the metal quinolate compound. In this new design, both luminous efficiency, power efficiency and device lifetime are all improved within the same device structure. For example, an improvement in luminous and power efficiencies from 25 cd/A to 37 cd/A and from 9.5 lm/W to 15 lm/W at 1000 cd/m^2, respectively, is obtained. Particular note that the overall device operating voltage decreased by ~ 1 V. Furthermore the device lifetime is in excess of 15,000 hours at initial luminance of 1,000 cd/m^2.

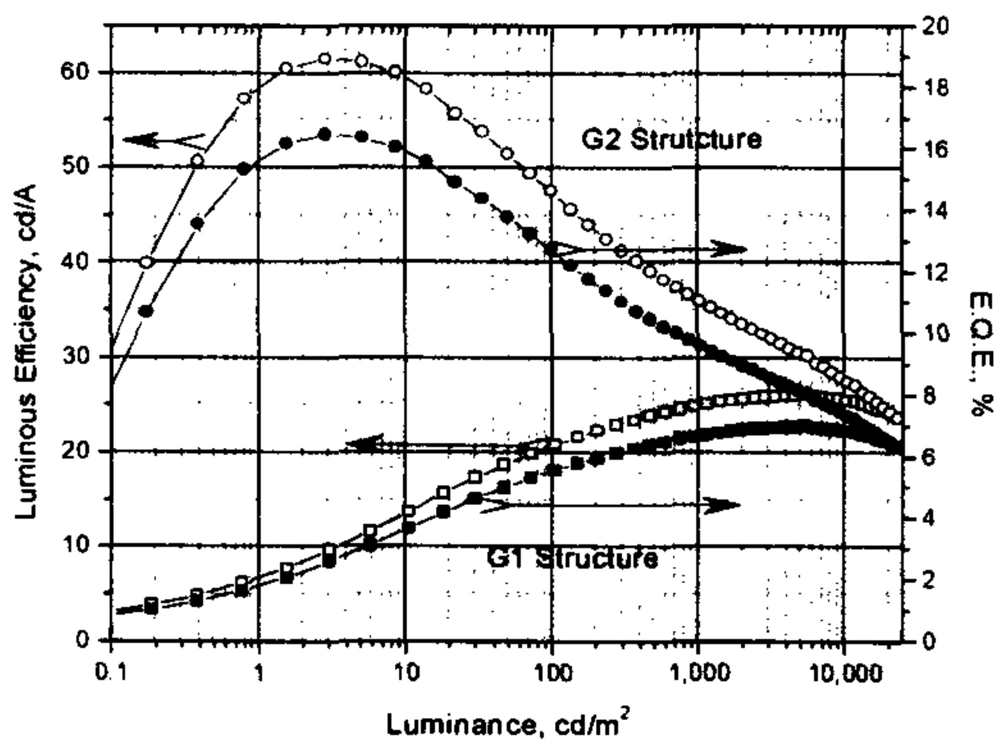


Figure 3 Luminous efficiency (cd/A) and external quantum efficiency (EQE) versus luminance (cd/m^2) for green GD33 PHOLED devices with two different blocking layers. The top two curves are for the G2 device structure and the bottom two curves for the G1 device structure.

Most recently, further improvements in the phosphorescent emitter design and overall device architecture has resulted in a long lifetime green PHOLED device performance with approximately 100% IQE. Furthermore, the device operating voltage is reduced by an additional 1-2 V as compared to GD33-G2. This result is shown in Figure 4. An efficiency of 82 cd/A at 1,000 cd/m^2 has been demonstrated which corresponds to over 22% EQE, translating to about 100% of internal quantum efficiency. Moreover, the operating voltage of these devices is ~5.7 V at 1,000 cd/m^2. This gives about 45 lm/W at 1,000 cd/m^2 luminance. Preliminary results demonstrate a device lifetime in excess of 10,000 hours at initial luminance of 1000 cd/m^2. This most recent advancement is a strong motivation to now replace green fluorescent OLEDs with green PHOLEDs for both active and passive matrix applications.

Red PHOLED Performance

Due to the low photopic response of the human eye to red, and the relatively large contribution of red in brightness for a balanced white, the red component constitutes a large portion of the total power consumption for a full-color display. Hence, a central focus for PHOLED development has been on red devices. Following the early reports of PtOEP-based red PHOLEDs, the next family of emitters were an orange-red PHOLED based on iridium (III)bis(2-phenylquinolyl-N,C2')acetylacetonate(PQ$_2$Ir(acac)) with reported $T_{1/2}$ of ~ 5000 hours at initial luminance levels of 300 cd/m^2. The limitation of this device was the chromaticity of (0.61,0.38). In order to develop red emitters with deeper color saturation and a combined high efficiency and lifetime, we directed our research into new classes of phosphorescent molecular designs. Furthermore these, the PtOEP PHOLED exhibited

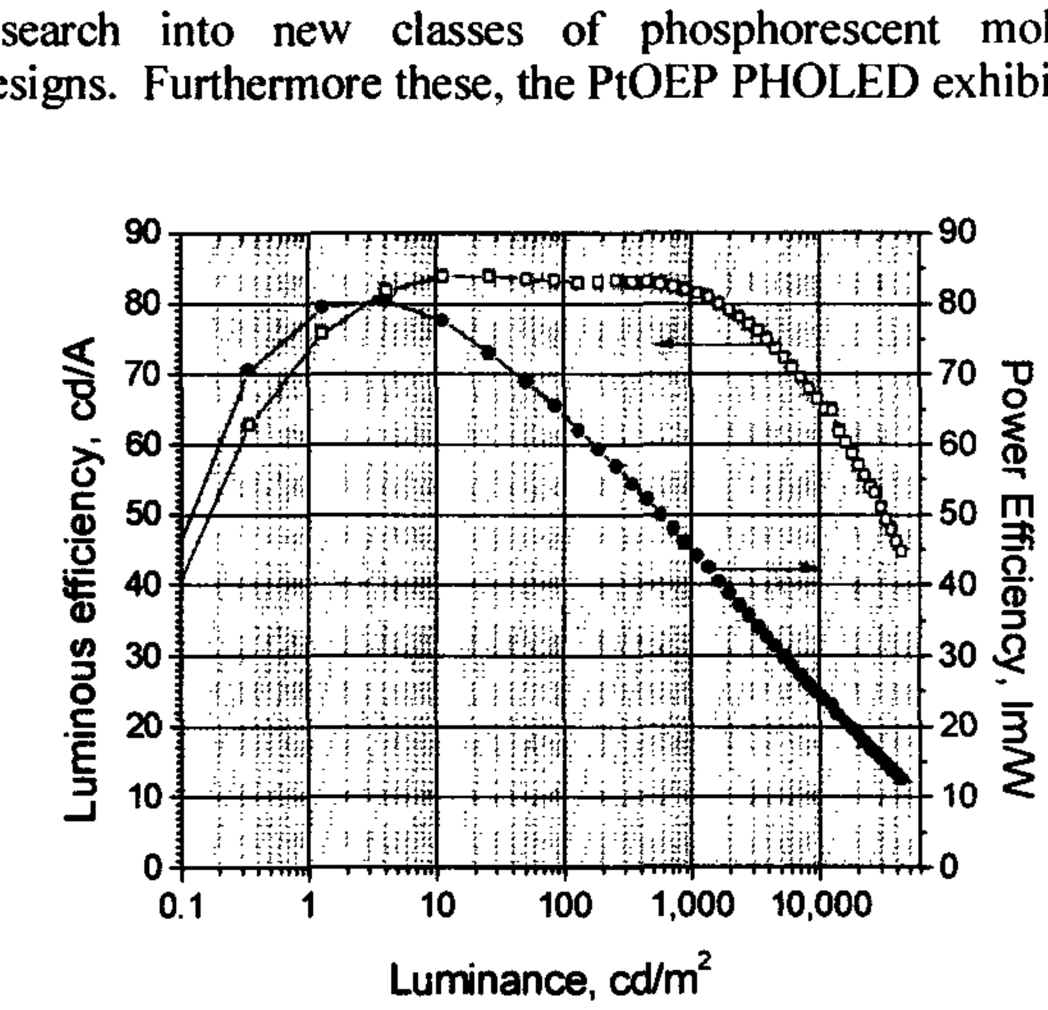


Figure 4: Luminous efficiency (cd/A) and power efficiency (lm/W) versus luminance (cd/m^2) for green PHOLED devices with G2 device structure (see Figure 3) and improved green phosphorescent dopant.

significant efficiency roll-off with increasing current drive. This also has been addressed in our new material and device designs.

We have previously reported highly efficient red PHOLEDs RD07 and RD15 with color coordinates of (0.65,0.35) and (0.67,0.33), respectively. The RD07 device meets sRGB color standards and RD15 satisfies another important color standard for NTSC standards. The efficiency performance of these two devices is shown in Figure 5. Both devices have external quantum efficiencies of greater than 13%. In earlier reports for RD15 red PHOLEDs, the luminous efficiency was ~8 cd/A over the operating range of 100 to 1000 cd/m^2. Here we report an improved efficiency to > 10 cd/A over this same luminance range. This improvement can be attributed to both the host material selection and layer design optimization. Furthermore. a similar improvement in RD07 efficiency is obtained.

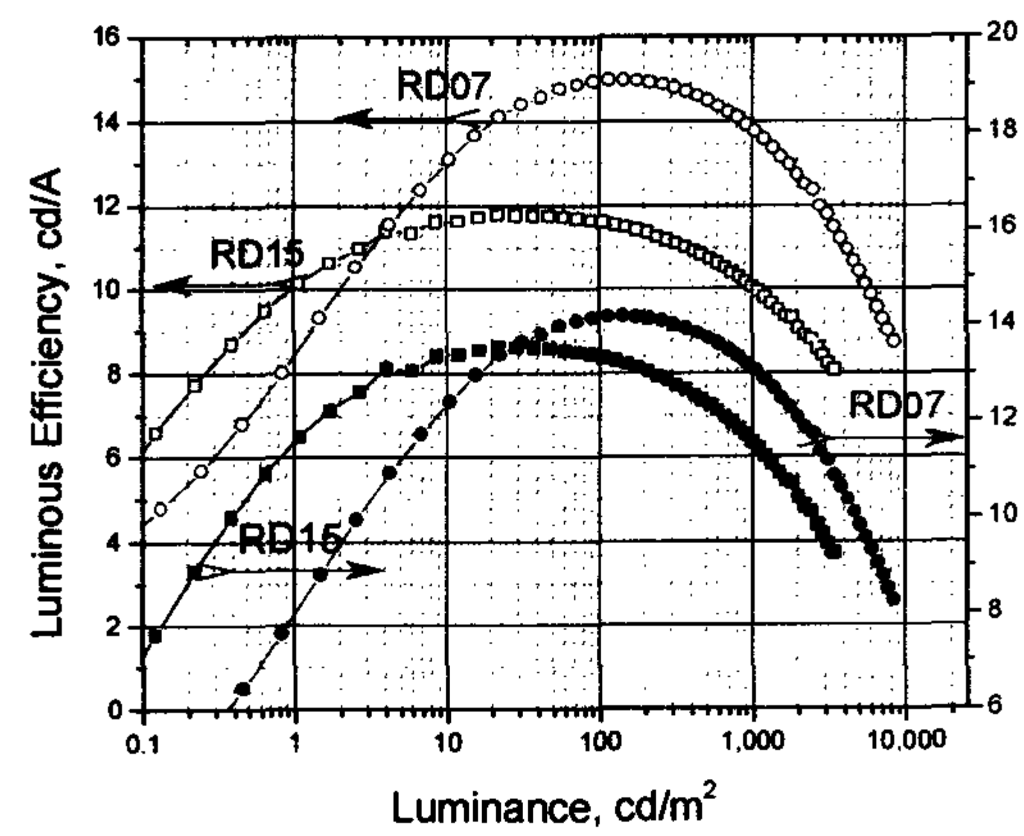
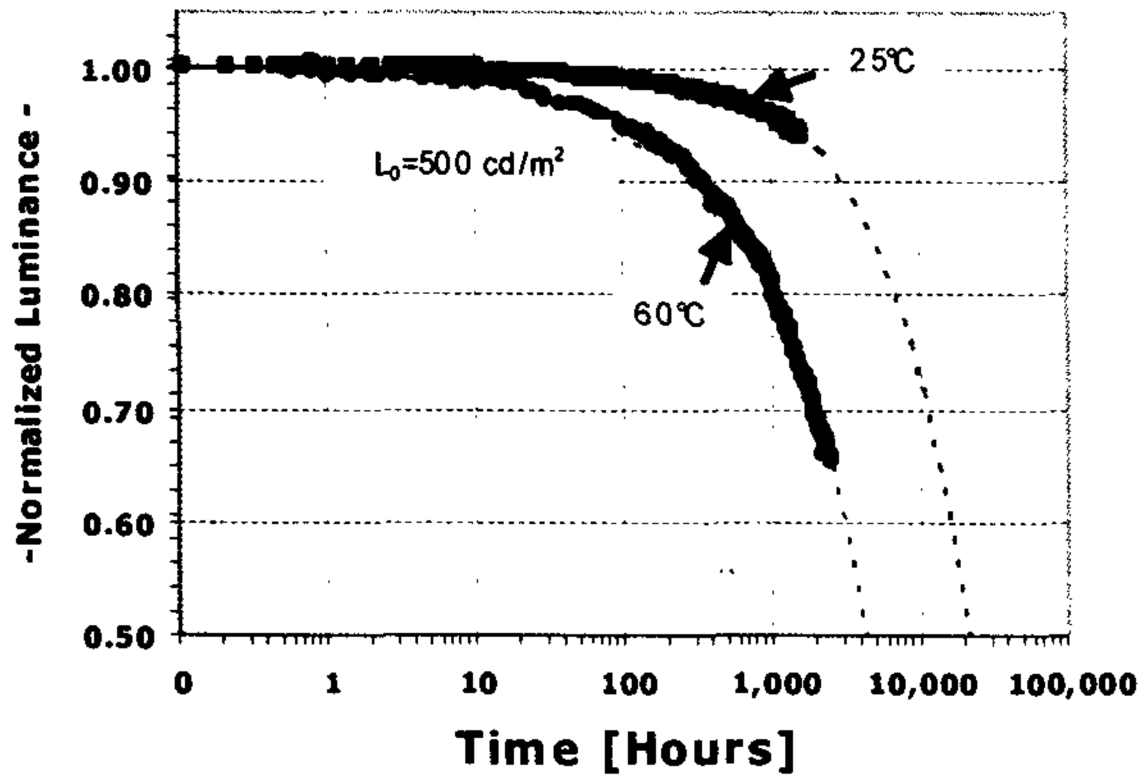


Figure 5: Luminous efficiency (cd/A) and external quantum efficiency (EQE) versus luminance (cd/m^2) for red RD07 and RD15 PHOLED devices. The CIE coordinates for the RD07 and RD15 PHOLEDs are (0.65, 0.34) and (0.67, 0.33), respectively.

We have fully characterized the lifetime performance for the red PHOLEDs at both room temperature and an elevated temperature of 60°C. The test results are given in Figures 6 and 7. For the deeper red device, RD15, the luminance decay is not observed until an excess of 1000 hours of drive at initial luminance of 500 cd/m^2. This stability is important in reducing the affects of differential color aging in a display. Based on our learnings here we will continue to apply this knowledge to both green and eventually blue PHOLEDs.



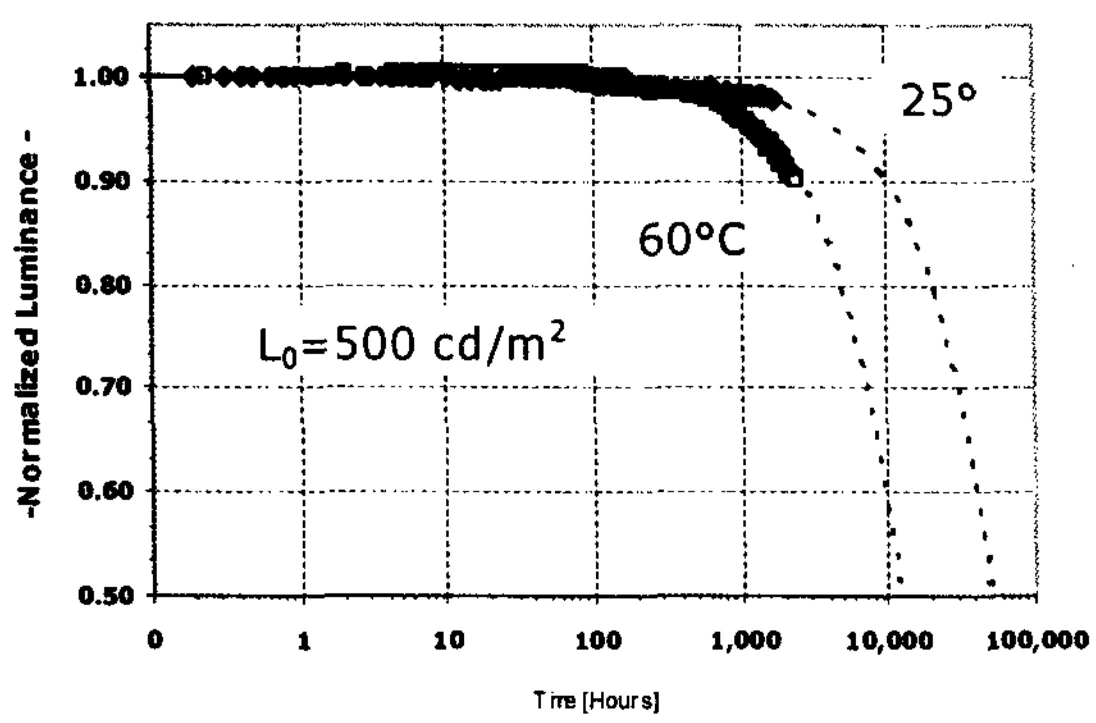


Figure 7: Operational lifetime performance for RD15-based red PHOLED operated under constant DC current drive. The initial luminance is 500 cd/m^2 and the packaged device is tested at both room temperature (25°C) and elevated temperature of 60°C. A lifetime, defined at 50% of the initial luminance, is > 35,000 and 10,000 hours for RT and 60°C, respectively.

Blue PHOLED Performance

The design of efficient PHOLED devices begins with the selection of materials, that when combined, allows for exothermic energy transfer between a conductive host and phosphorescent guest. Unlike the design of red and green PHOLEDs, the challenge to achieving exothermic energy transfer for blue was met by Holmes et. al. [19] with the combination of N,N'-dicarvaolylly-3,5-benzene (mCP) and iridium(III)bis[(4,6-difluorophenyl)-pyridinato-N,C2']picolinate (FIrpic). A peak EQE of 7.5% and power efficiency of 9 lm/W was obtained for the mCP:FIrpic devices. The emission spectrum of this device is blue-green with CIE coordinates of (0.16,0.37). Early studies of the inherent stability of FIrpic pointed to a potential instability in this design. Based on this finding we have developed improved material systems and achieved an incremental improvement in stability and greater than 2 fold increase in efficiency along with deeper color saturation.

Most recent results for blue PHOLEDs demonstrate a spectral response peaked at 480 nm with CIE coordinates of (0.14, 0.21) (Figure 8). Initial device efficiency performance with this dopant:host system was limited to < 8-9 cd/A at a luminance of 200 cd/m^2. With further device work and inserting the new blocking layer material, the efficiency performance has increased to a peak EQE of 13% (Figure 9) which correspond to luminous efficiency of 18 cd/A at 200 cd/m^2. Achieving long term stability is ongoing.

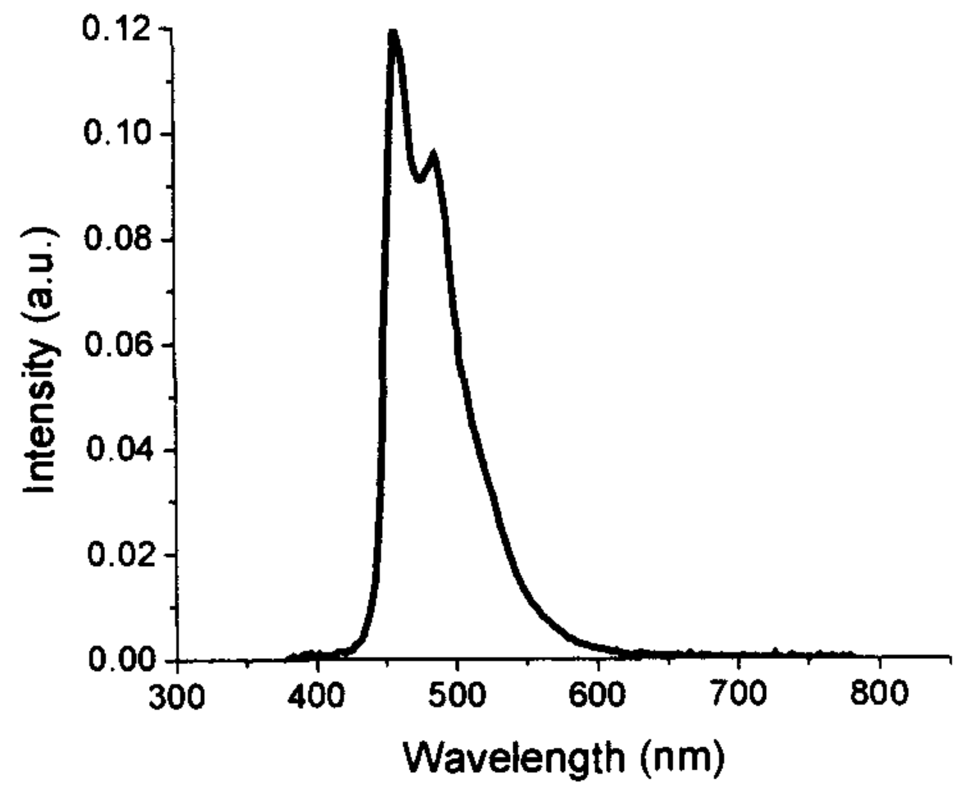


Figure 8: Electroluminescent response for blue PHOLED device. CIE coordinates are (0.14 0.21).

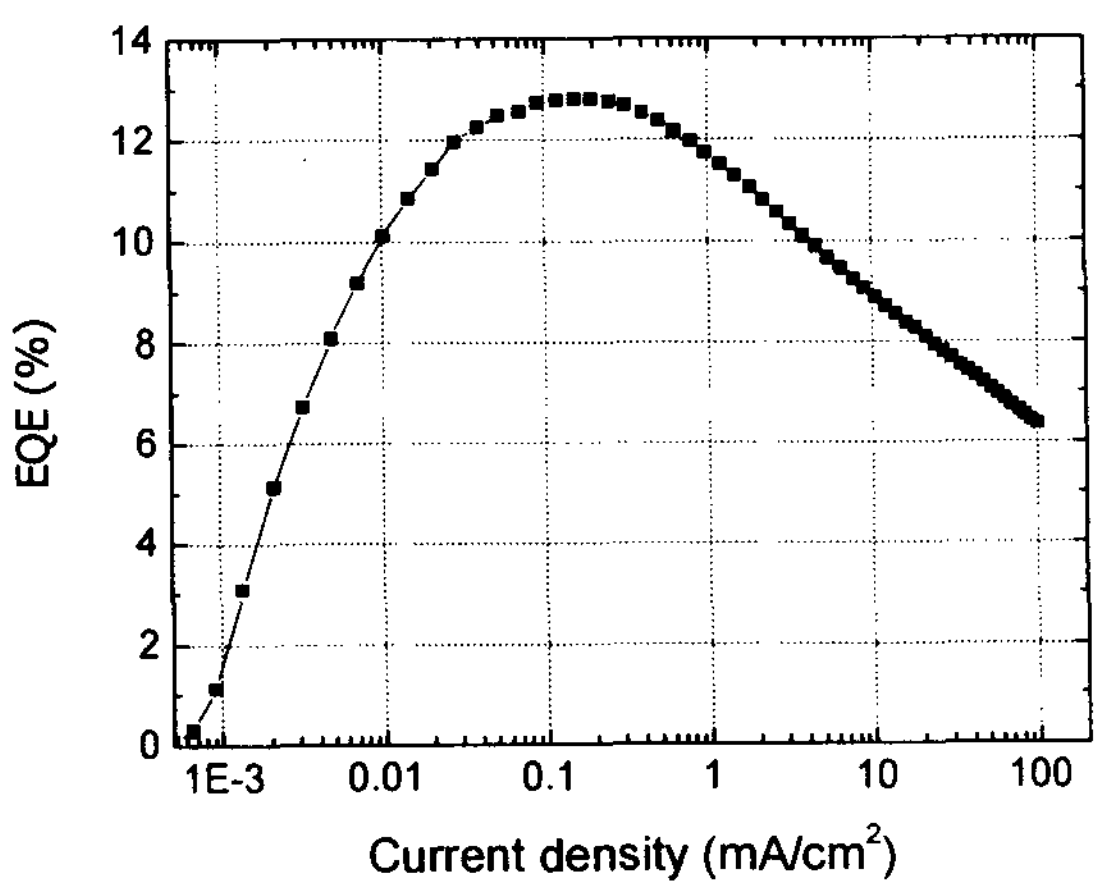


Figure 9: External quantum efficiency versus current density for blue PHOLED (Figure 8).

Conclusions

The progress achieved, to date, for red and green PHOLEDs is summarized in Table 1. For initial commercial products this performance meets many different product demands. In order to achieve performance for large area such as OLED TVs, we will focus on extending this product of efficiency and device lifetime. With recent strides in understanding the operational mechanisms for efficiency and stability of blue PHOLEDs, it is promising a solution for obtaining long lifetime will be achieved. The combination of all phosphorescent OLED display has the potential to achieve the demanding requirements for small area to large area full-color flat panel displays.

Color	CIE	λ_{max}, nm	LE cd/A	E.Q.E. %	Lifetime (hours) at 25°C	
					L_o, cd/m^2	$L_{50\%}$, hrs
Red R1	0.65 0.35	616	15	14	500	>22,000
Red R2	0.67 0.33	622	11	13	500	>35,000
Green G1	0.31 0.34	520	25	7	1,000	>20,000
Green G2	0.31 0.34	520	37	10	1,000	>15,000
Green G3	0.30 0.64	520	82	22	1,000	>10,000

Table 1: Summary of current performance of a selection of red and green PHOLEDs. The luminous efficiency (LE), external quantum efficiency (EQE) and power efficiency (lm/W) are reported at a luminance of 500 cd/m^2 and 1000 cd/m^2 for red and green, respectively. The lifetime data is extrapolated from actual test times of >> 1,000 hours.

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