Highly power efficient organic light-emitting devices enabled by phosphorescent and p-i-n technologies

Tobias W. Canzler*[a], Markus Burghart[a], Sven Murano[a], Jan Blochwitz-Nimoth[a], Brian D'Andrade[b], Michael Hack[b], Julie J. Brown[b]

[a]Novaled AG, Tatzberg 49, 01307 Dresden, Germany
[b]Universal Display Corporation, Ewing, NJ 08618, USA

ABSTRACT

Organic light-emitting devices (OLEDs) containing highly efficient phosphorescent emitters and highly conductive doped organic transport layers were studied. Saturated red devices with luminous efficiency of 15 cd/A operate at <4 V; hence, they have a record power efficiency of 12 lm/W at 1,000 cd/m^2.
Additionally, two high-efficiency red OLEDs were serially connected and vertically stacked to create a stacked OLED having a luminous and power efficiency (at 1,000 cd/m^2) of 28 cd/A and 12 lm/W, respectively. The electrical connection between the two OLEDs is enabled by molecular p- and n-type doped organic transport layers.
The single emissive layer red OLED has a projected lifetime (time to half initial luminance) of ~150,000 hrs from an initial brightness of 500 cd/m^2. The stacked device shows very similar lifetime characteristics when driven at similar currents, which results in significantly prolonged lifetime of ~260,000 hrs at an initial luminance of 500 cd/m^2.

Keywords: electroluminescence, OLED, phosphorescence, high power efficiencies, PIN, doped transport layers

1. INTRODUCTION

Organic light-emitting diode (OLED) technology still has to demonstrate further improvements to be competitive with existing display and lighting technologies. Two advancements required are low energy consumption in connection with long lifetimes and cost competitive manufacturing.
A major step in this direction was the invention of phosphorescent OLED (PHOLED™) [1]. PHOLED technology has the ability to achieve 100% internal quantum efficiency (number of photons out divided by the number of electrons into the device); whereas, fluorescent OLEDs are limited to an internal quantum efficiency of ~25%. The first generation of PHOLEDs contained a platinum complex (PtOEP) as the dopant, and a PHOLED with 6% external quantum efficiency was reported using this class of materials [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 22% [3], and red emitting PHOLEDs have shown external quantum efficiencies as high as 16.5%. Adjusting for optical effects such as outcoupling [4], the internal quantum efficiency of such devices has been estimated to be close to 100%. In terms of operational stability, green PHOLEDs have demonstrated lifetimes in excess of 40,000 hrs from an initial luminance of 1,000 cd/m^2 [5], and red PHOLEDs have exhibited even longer lifetimes of about 300,000 hrs projected from an initial luminance of 500 cd/m^2 [6].

* tobias.canzler@novaled.com; phone: +49-(0)351-7965823; fax: +49-(0)351-7965823; www.novaled.com

Organic Light Emitting Materials and Devices X, edited by Zakya H. Kafafi, Franky So,
Proc. of SPIE Vol. 6333, 633311, (2006) · 0277-786X/06/$15 · doi: 10.1117/12.679335

Universal Display's PHOLED™ technology offers up to 100% internal quantum efficiency, and this technology has been identified as a critical technology component for OLEDs to compete effectively on power consumption with conventional backlit active-matrix LCD displays.

Another major step to achieve the goals mentioned above was the development of conductivity doping for organic molecular materials. The basic principle of conductivity doping in organic semiconductors is similar to that in inorganic materials: One adds impurities that either transfer an electron to the electron conducting states (n-type doping) or remove an electron from the hole conducting states to generate a free hole (p-type doping). It has been shown that very high conductivities can be achieved when organic dyes with a weak donor character, such as phthalocyanines, are exposed to strongly oxidizing gases like iodine or bromine [7]. However, very small dopants can easily diffuse in the layers, so this technique is not suitable to prepare thermally stable bipolar devices such as pn- or pin-junctions. Similar considerations hold for doping by other small atoms like Lithium [8] or small molecules [9-12]. A better pathway to conductivity-doping for stable devices is to use large aromatic molecules that are strong π-electron donors or acceptors. Novaled has introduced the molecular dopant NDP-2 in 2004, and recently developed also the first molecular n-dopant NDN-1 [13], which both fulfill the OLED requirements as described above. The PIN OLED architecture refers to an OLED structure with a p-doped hole-transport layer, an intrinsically conductive emission zone and an n-doped electron-transport layer. The doped charge transport layers allow improved charge-carrier injection from contacts, and the voltage drop over the transport layers is negligible. Thus, Novaled's proprietary doping technology and materials can deliver highest power efficiency for a given emitter system. Since Novaled has successfully shown that high power efficiency and long lifetime can be combined, Novaled PIN OLED™ technology based on fully organic conductivity doping has reached a state where mass production is being pursued.

Here, PIN OLED and PHOLED technologies are combined to create a red PIN PHOLED device with a CIE of (0.65, 0.35), a peak external quantum efficiency of 16%, and a drive voltage of <4 V at 1,000 cd/m^2. These characteristics correspond to a luminous efficiency of 15 cd/A and a record power efficiency of 12 lm/W, at 1,000 cd/m^2. The red PHOLED device also has an excellent projected operational lifetime of ~150,000 hrs at an initial brightness of 500 cd/m^2.

In addition to low voltage devices, Novaled's p- and n-doped layers can be effectively used in a stacked OLED (SOLED^{TM}) [14,15] architecture, which consists of individual OLED units electrically connected and vertically stacked. The SOLED architecture offers at least two advantages over single OLEDs. Firstly, a SOLED can attain n (n = number of OLED units in SOLED) times the luminance of a single OLED; alternatively, a SOLED can attain the same luminance as a single OLED by driving each emissive unit of the SOLED at 1/n th the luminance of a single OLED. OLED power efficiency decreases with increasing luminance due to increases in voltage and reductions in quantum efficiency, so SOLEDs may have better power efficiency than single OLEDs when both are operated at the same luminance. Secondly, given that OLED operational stability typically has an inverse power law relationship to luminance [16], the operational stability of SOLEDs may potentially be significantly longer than single OLEDs when both SOLED and OLED are driven from the same initial luminance.

For most SOLEDs reported, the individual units are electrically connected using a variety of inorganic materials which act as charge-generation layer (CGL) [17-20]. Recently, the SOLED concept has received renewed attention because of the incorporation of p-n junction as CGL between two vertically stacked OLEDs with the p-n junction based on alkali-metal n-doping and $FeCl_3$ p-doping [21]. Here, the stacking is enabled by Novaled's fully molecular p- and n-type conductivity doping. These p-n junctions are compatible with small molecule OLED manufacturing technologies such as vacuum thermal evaporation, and this compatibility enables the junctions to be formed in the same chamber as the other layers in the OLED.

The SOLED device presented here has a current efficiency of 28 cd/A at an operating voltage of less than 7 V, and a power efficiency of 12 lm/W, all at 1,000 cd/m^2. The SOLED and OLED have identical lifetime behaviour when driven at the same current, so the SOLED has a much better lifetime than an OLED when both are operated from the same initial luminance. Hence, a significantly prolonged SOLED lifetime of ~260,000 hrs at an initial brightness of 500 cd/m^2 is projected.

2. EXPERIMENTAL

The devices presented in this report were fabricated in a single-chamber thin film vacuum deposition tool. All layers were deposited by thermal evaporation at a pressure below 5×10^{-7} mbar. The general structure of the single stacked devices is given here: substrate / anode / hole injection layer (HIL) / hole transport layer (HTL) / interlayer hole side (IL-H) / emission layer (EL) / interlayer electron side (IL-E) / electron transport layer (ETL) / electron injection layer (EIL) / cathode. The anode electrode is made from indium tin oxide (ITO); the cathode is made from Aluminium (Al). For the non-conductivity doped sample HIL004 and Lithium Fluoride (LiF) serve as HIL and EIL, respectively. 4,4-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (α-NPD) was used for HTL and/or IL-H and tris(8-hydroxyquinolinato)aluminum (Alq_3) for IL-E and/or ETL. EL consists of the emitter host BL42, doped with 12 wt.% of the phosphorescent sRGB-red emitter dopant RD07. P-doped HTL consists of the hole transport material NHT-5, featuring a high glass-transition temperature (T_{glass}) > 145°C, doped with the molecular p-dopant NDP-2, featuring a high evaporation temperature (T_{evap}) >150°C. N-doped ETL consists of the electron transport material NET-5 (T_{glass}>105°C) doped with molecular n-dopant NDN-1 (T_{evap} >200°C). For the double-stacked device the charge generation is established by a fully organic p-n junction based on Novaled's standard dopants NDP-2 and NDN-1.
OLED architectures are given in Fig. 1. The OLED in Fig 1(a) has an active area of 2 mm^2, and OLEDs in Figs. 1(b) and 1(c) have an active area of 6.35 mm^2. All devices were encapsulated under an inert gas atmosphere in a glove box. The spectral measurements were carried out using an Instrument Systems CAS 140 spectrometer with a calibrated measurement head. Power efficiencies are calculated assuming Lambertian emission and were confirmed by measurements using an integrating sphere with a diameter of 50 cm. For integrating sphere measurements, the OLED backside and the edges of the glass substrate were optically sealed to ensure that only light emitted in forward direction was taken into account. No out-coupling enhancement measures have been taken for the results presented here. Measurements of device operational stability were carried out with the encapsulated OLED devices at room temperature and driven by a constant DC current without any initial burn-in periods.

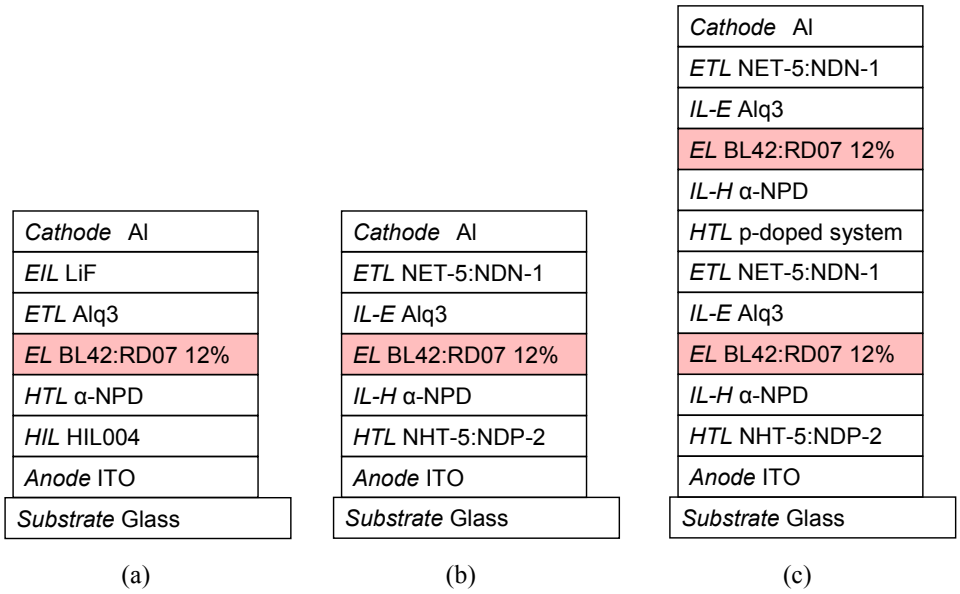

Fig. 1. Phosphorescent OLED structures: (a) single stack without conductivity doping, i.e. III OLED, (b) single stack applying conductivity doping, i.e. PIN OLED, (c) double stack applying conductivity doping, i.e. stacked PIN OLED.

3. RESULTS

The demonstration of high efficiency red PHOLEDs by Forrest group in 1998 generated intense research interest with the potential for 100% internal quantum efficient devices [2]. To go beyond 100% internal quantum efficiency, SOLED architectures have proven to be a suitable and reliable path to successfully achieve this goal. SOLEDs consisting of separate OLED units stacked upon each other have demonstrated their potential to achieve high quantum and current efficiencies due to so-called "multiphoton emission". The working principle of such a layout is a series connection of several OLEDs that allows the same current to flow through all OLED units. This increases the current and quantum efficiencies, and it also increases the operating voltage.

In addition to quantum efficiency, power consumption is a critical parameter of OLED performance. Often, the power efficiency of devices at useful brightness is limited by having operating voltages that are much greater than the thermodynamic threshold voltage, which is set by the wavelength of the emitted photon. The highest power efficiency ever achieved for a LED is 150 lm/W at a brightness of 100 cd/m^2, and 140 lm/W at 1,000 cd/m^2. These record values were achieved recently by Novaled scientists using an $Ir(ppy)_3$ based bottom-emitting phosphorescent PIN OLED applying out-coupling enhancement . For this purpose, a glass lens is attached to the glass substrate. Measurements were carried out in a calibrated integrating sphere. The edges of the substrate were covered, excluding the substrate modes that escape the substrate through the edges. The used out-coupling approach is not suitable for e.g. large-area lighting applications but gives an upper-limit indication of power efficiency achievable from a certain device.

However, luminous power efficiency is strongly depended on emission spectrum as it is a photometric unit based on human-eye sensitivity. For converting radiometric and photometric quantities, the radiation luminous efficacy K_r is defined:

$$K_r = K_m \frac{\int_{380nm}^{770nm} \Phi_e(\lambda) V(\lambda) d\lambda}{\int_0^{\infty} \Phi_e(\lambda) d\lambda}, \qquad (1)$$

where Φ_e is the radiant flux in Watts, $V(\lambda)$ is the photopic spectral luminous efficiency function standardized by the International Lighting Commission (CIE) in 1924, and K_m = 683 lm/W is a conversion constant. The radiation luminous efficacy is not an efficiency, but gives the effectiveness of a beam of radiation in stimulating the perception of light in the human eye. Typical values of K_r are about 500 lm/W for green light emission, e.g. $Ir(ppy)_3$ based emission, about 125 lm/W for deep red, and about 75 lm/W for deep blue, (for an overview about this topic see reference [22]). For RD07 with a CIE of (0.65, 0.35) we find K_r = 170 lm/W. Thus, power efficiency values of different OLEDs can not be compared directly, and emission spectrum or at least colour coordinates are necessary for interpretation.

Figure 2 gives a comparison of voltage reduction applying conductivity doping: For non-conductivity doped device (a) about 9 V has to be applied to reach a luminance of 1,000 cd/m^2. Applying conductivity doping (b) only 4 V are necessary for the same luminance. For the double stacked device, less than 7 V are necessary to reach 1,000 cd/m^2, which demonstrates that virtually no electric power is lost by directly stacking two PIN OLEDs on top of each other.

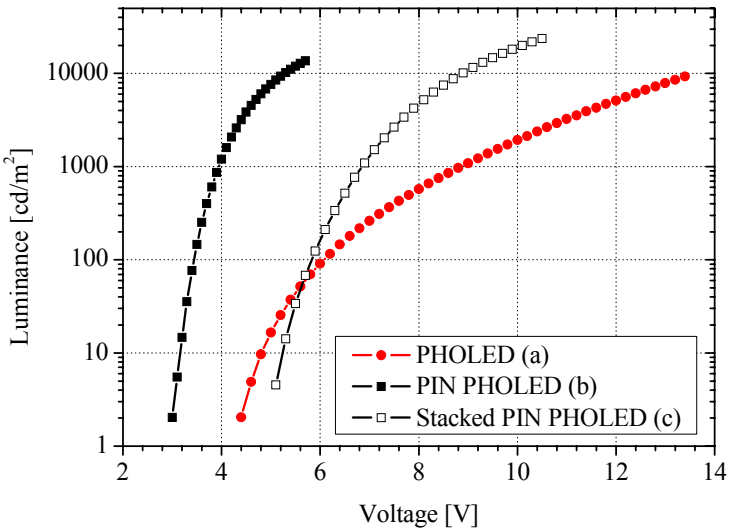

Fig. 2. Luminance vs. applied voltage for the RD07 based devices.

Quantum efficiencies for devices (a) and (b) are similar, as shown in Fig. 3. RD07 shows external quantum efficiency of about 13% for device (a) and 14% for device (b), all at 1,000 cd/m^2. Minor deviations in the efficiency characteristics can be attributed to different charge-carrier balance within the devices. The double-stacked pin device exhibits significant improvement of external quantum efficiency with a maximum of ~25% as compared to the single stacked devices with a maximum of ~16%. In principle, a SOLED consisting of two OLED units should have double the quantum efficiency of a single unit.

Figure 4 shows power efficiency of investigated OLED structures. Here, the effect of conductivity doping effectively translates into increased power efficiency: While undoped device (a) exhibits a power efficiency of about 5 lm/W at 1,000 cd/m^2, the pin device (b) shows about 12 lm/W. The double stacked pin device (c) shows similar power efficiency as the comparable single stacked pin device (b).

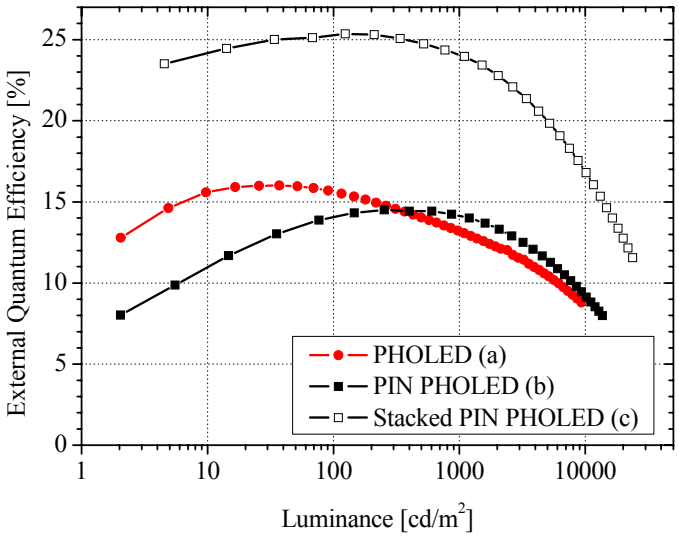

Fig. 3. External quantum efficiency for the RD07 based devices.

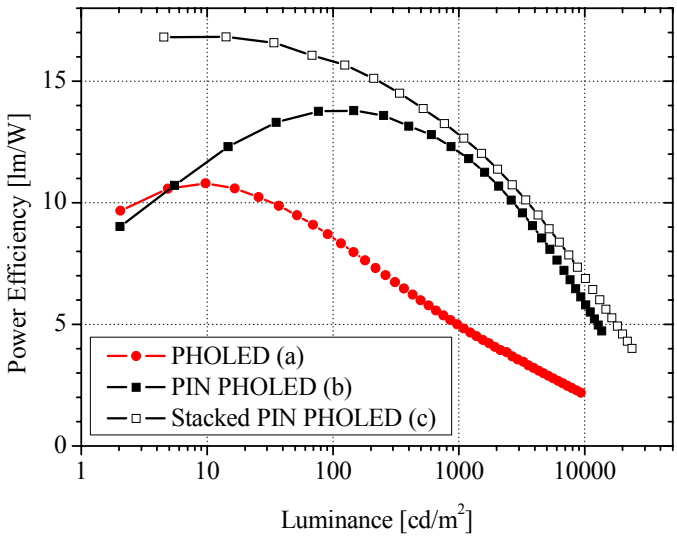

Fig. 4. Power efficiency for the RD07 based devices.

The operational stability of the red devices is very high, and lifetimes of more than 150,000 hours at 500 cd/m^2 are possible for PIN OLEDs based on RD07. Here, lifetime is defined as the time for the luminance to drop to 50% of the initial value at constant driving current. As 100,000 hrs is equivalent to more than 10 years, it becomes apparent that it is not possible to measure a device over the entire time span with the desired initial luminance. Therefore, OLED degradation is accelerated at higher brightness and lifetimes at display luminance levels are determined from extrapolations. To determine lifetimes, 4 identical OLEDs of a given architecture were operated at different DC currents for about 2,700 hrs. If luminance decay has not reached half initial luminance, the lifetime constant $\tau_{1/2}$ is fit to a single exponential decay. Exemplarily, we have shown measurement data for OLEDs driven at 20 mA/cm^2 in the inset of Fig. 5. As starting luminance is normalized here, one can readily see that luminance decay for the stacked device is comparable to the single device for the same current density. Values of $\tau_{1/2}$ are then given in the main plot. Assuming an empirical lifetime acceleration function:

$$L_0^n \cdot \tau_{1/2} = const\,, \tag{2}$$

where L_0 is the initial luminance and n is the lifetime acceleration constant, we are able to predict lifetimes at any given initial luminance. Figure 5 summarizes lifetime measurements; the dotted lines show lifetime extrapolation applying Eq. (2). At 500 cd/m^2 we estimate lifetimes of $\tau_{1/2}$ ~150,000 hrs with n = 1.9 for device (b) and ~ 260,000 hrs with n = 1.8 for device (c). Operational stability is therefore not limited by the organic materials used to form the electrical connection of the two OLED units.

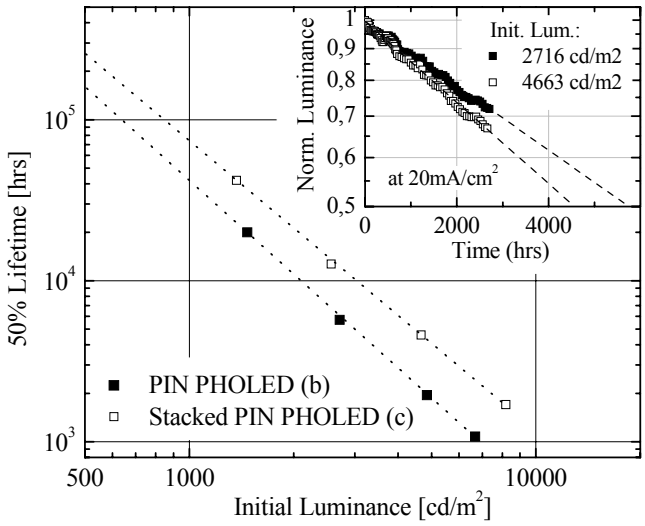

Fig. 5. Operational stability for the RD07 based devices after 2,700 hrs. For a given structure, lifetimes (time to half initial luminance) at 4 different initial luminance values are shown. The dotted lines are guides to the eye for estimating lifetimes at 500 cd/m^2 assuming a lifetime acceleration constant $n \approx 1.8$-1.9. The inset shows exemplarily luminescence decay at a driving current of 20 mA/cm^2. The logarithmic scale of luminance axis allows for linear extrapolation to half initial luminance (dashed lines) assuming single exponential decay.

4. SUMMARY

The combination of PIN OLED and PHOLED material strengths has enabled the power efficiency of red PHOLEDs to attain new record performance levels. A red PIN PHOLED was demonstrated with the following characteristics: CIE of (0.65, 0.35), a peak external quantum efficiency of 16%, and a drive voltage of <4 V at 1,000 cd/m^2, which corresponds to a luminous efficiency of 15 cd/A and a record power efficiency of 12 lm/W. The red PHOLED device was also shown to have a projected operational lifetime of ~150,000 hrs at an initial brightness of 500 cd/m^2.
Additionally, a red SOLED, consisting of two stacked red PIN PHOLEDs electrically connected by molecular p- and n-type doped layers, was shown to have a current efficiency of 28 cd/A, an operating voltage of <7 V, and a power efficiency of 12 lm/W at 1,000 cd/m^2. The SOLED and OLED have identical lifetime behaviour when driven at the same current, resulting in a significantly prolonged SOLED lifetime of ~260,000 hrs at an initial brightness of 500 cd/m^2.

REFERENCES

1. M.A. Baldo, D.F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M.E. Thompson, S.R. Forrest, "Highly Efficient Phosphorescent Emission from Organic Electroluminescent Devices", Nature **395**, 151 (1998).
2. D.F. O'Brien, M.A. Baldo, M.E. Thompson, S.R. Forrest, "Improved Energy Transfer in Electrophosphorescent Devices", Appl. Phys. Lett. **74**, 442 (1999).
3. V.A. Adamovich, R.C. Kwong, M.S. Weaver, M. Hack, J.J. Brown, "Maximizing the Efficiency Lifetime Product for Phosphorescent OLEDs", Proceedings of Asia Display/Int. Meeting on Information Display 2004, 272 (2004).
4. A. Chutinan, K. Ishihara, T. Asano, M. Fujita, and S. Noda, Org. Electron. **6**, 3 (2005).
5. M.S. Weaver, R.C. Kwong, V.A. Adamovich, M. Hack, J.J. Brown, "Recent Advances in Phosphorescent OLEDs for Small and Large Area Displays", Proceedings of SID Eurodisplay 2005, 188 (2005).
6. M.S. Weaver, Y.-J. Tung, B. D'Andrade, J. Esler, C. Lin, P.B. Mackenzie, J.-Y. Tsai, C.S. Brown, R.W. Walters,

V. Adamovich, S.R. Forrest, M.E. Thompson and J.J. Brown, "Advances in Blue-Phosphorescent OLEDs" Presented at the SID International Symposium. San Francisco, CA. Jun. 6th 2006.
7. Y. Yamamoto, K. Yoshino, Y. Inuishi, J. Phys. Soc. Jpn. **47**, 1887 (1979).
8. G. Parthasarathy, C. Shen, A. Kahn, S.R. Forrest, J. Appl. Phys. **89**, 4986 (2001).
9. D.R. Kearns, G. Tollin, M. Calvin, J. Chem. Phys. **32**, 1020 (1960).
10. M. Maitrot, G. Guillaud, B. Boudjema, J.J. Andre, J. Simon, J. Appl. Phys. **60**, 2396 (1986).
11. J.J. Andre, J. Simon, R. Even, B. Boudjema, G. Guillaud, M. Maitrot, Synth. Met. **18**, 683 (1987).
12. J. Kido, T. Matsumoto, Appl. Phys. Lett. **73**, 2866 (1998).
13. J. Birnstock et al. SID 05 Digest (2005) 40; J. Birnstock et al. Proceedings of Eurodisplay 2005, 192 (2005).
14. P.E. Burrows, S.R. Forrest, S.P. Sibley, M.E. Thompson, Appl. Phys. Lett. **69**, 2959 (1996).
15. Z.L. Shen, P.E. Burrows, V. Bulovic, S.R. Forrest, and M.E. Thompson, Science **276**, 2009 (1997).
16. P. Wellmann, M. Hofmann, O. Zeika, A. Werner, J. Birnstock, R. Meerheim, G. F. He, K. Walzer, M. Pfeiffer, and K. Leo, J. Soc. Inf. Disp. **13**, 393 (2005).
17. G. Gu, G. Parthasarathy, P. Tian, P.E. Burrows, and S.R. Forrest, J. Appl. Phys. **86**, 4076 (1999).
18. T. Matsumoto, T. Nakada, J. Endo, K. Mori, N. Kawamura, A. Yokoi, and J. Kido SID 03 Digest, 979 (2003).
19. H. Kanno, R.J. Holmes, Y. Sun, S. Kena-Cohen, and S.R. Forrest, Adv. Mater. **18**, 339 (2006).
20. J.X. Sun, X.L. Zhu, H.J. Peng, M. Wong, and H.S. Kwok, Appl. Phys. Lett. **87**, 093504 (2005).
21. L.S. Liao, K.P. Klubek, and C.W. Tang, Appl. Phys. Lett. **84**, 167 (2004).
22. W.R. McCluney. Introduction to radiometry and photometry. Artech House, Boston, London, 1994.