The prospects of highly power efficient OLEDs using molecular dopants for display and lighting applications

Ansgar Werner, Jan Blochwitz-Nimoth, Jan Birnstock, Philipp Wellmann, Tilmann Romainczyk, Andrea Lux, Michael Limmert, and Olaf Zeika

Novaled AG, Dresden, Germany

Phone:+49-351-7965838, E-mail: ansgar.werner@novaled.com

Abstract

Dopant and host molecules for charge transport layer in OLED have been developed. They enable implementation of the PIN OLED technology in mass production. We review the status of PIN OLED with main focus on top-emission structures and operation stability at elevated temperatures.

A green phosphorescent top-emission device with 2.5 V operating voltage and 90 lm/W at 1000 cd/m^2 is presented. For a red top-emission device, lifetime exceeding 100,000 h at 500 cd/m^2 initial brightness is reported. Operational stability at 80°C has been investigated. A lifetime of 17,000 h at 500 cd/m^2 has been achieved.

Finally, we comment on further reduction of the operating voltage in OLED.

1. Introduction

After years of growth in the field of passive matrix displays, OLED technology now sets to enter the market for active matrix displays. Established technologies, such as LCD, at the same time, proceed to improve in technological and price competitiveness. Therefore, market success for OLED relies on cost reduction as well as on convincing performance on the display level. Further improvements in power efficiency and lifetime will contribute to this task.

Today's displays contain OLEDs pixels comprising the classical stack of insulating organic layers. Such OLEDs exhibit rather high operating voltage due to the low conductivity of the layers used. A significant reduction in the operating voltage can be achieved using dopant species considerably increasing conductivity. Initially, premature dopants such as F4TCNQ or cesium have been used to demonstrate the strong reduction of the operating voltage of OLED, and hence increase in power efficiency. Today, the availability of molecular dopants allows transferring this concept to mass production.

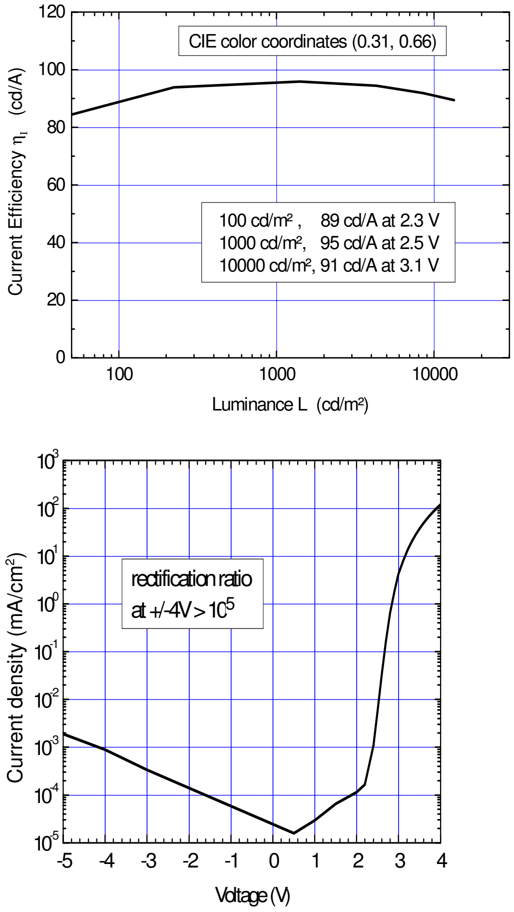

Figure 1: *Performance data of a deep green top-emitting PIN-OLED comprising the phosphorescent emitter Ir(ppy)$_3$ and Novaled proprietary charge carrier transport materials.*
Top Graph: Current efficiency vs. Luminance graph,
Bottom Graph: Corresponding I-V-curve

In this paper, we discuss the current status of PIN OLED. We demonstrate the extension of the PIN OLED concept to application requiring high temperature stability. Finally, we comment on new developments to be expected in the future.

2. Results

The bottom emission OLED is the classical design of an OLED device. Injection of holes takes place from conductive oxides such as ITO, and low work-function metals such as aluminum are used as cathode. It has soon been realized that injection and transport of charge carriers contribute dominantly to the total operating voltage.

This unwanted power dissipation can be reduced by doping special dopant molecules into the hole and electron transporting layers. This approach is commonly abbreviated as the PIN approach referring to the structure consisting of the *p*-doped hole transport layer, the undoped (intrinsic) emitter layer and the *n*-doped electron transport layer [1].

More advanced is the top emission concept. In such structures, a transparent or semi-transparent top electrode is provided to allow for light emission away from the substrate. The top-emission design is attractive especially for active-matrix applications. Here, part of the substrate is opaque due to the presence of the pixel driver. Consequently, the aperture ratio for light emission is more favorable for top-emission.

Top-emission has long been considered as inherently more difficult to achieve due to the difficult processing of the transparent top-electrode and difficulty to inject charge carriers efficiently. We have shown earlier, that the use of dopants, again, allows to much more flexibility in the choice of the electrode materials and for wider process windows. Consequently, top-emission OLED with comparable performance and lifetime to their bottom-emission counterpart are available [2].

This is illustrated in Figure 1. It summarizes the performance of a top emission OLED using Novaled´s proprietary molecular dopants NDP-2 and NDN-1 and the the phosphorescent emitter Ir(ppy)$_3$. Very high current efficiencies have been achieved exceeding 90 cd/A. The power efficiency has been determined in an integrating sphere in order to account for potential deviations from Lambertian emission characteristics. For the device, we obtain a power efficiency of 90 lm/W at 1000 cd/m^2; the voltage is 2.5 V at this brightness. Obviously, some deviation from Lambertian emission is observed due to effects of the cavity. Falsely neglecting these

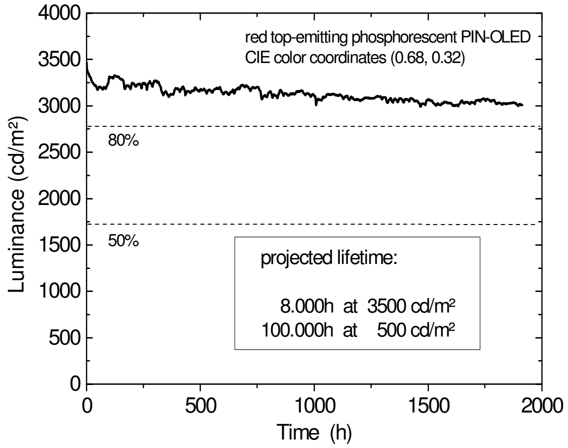

***Figure 2:** Lifetime graph of a deep red top emitting PIN-OLED. After 2000 h of operation under room temperature at a starting brightness of 3500 cd/m², luminance is still above 85% of the initial value. The projected lifetime (down to 50% initial luminance) is 8000 h. This corresponds to 100,000 h at 500 cd/m² initial brightness.*

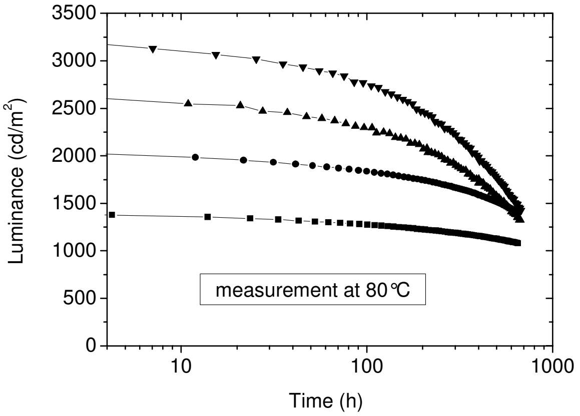

***Figure 3:** Lifetime graph of a deep red bottom emitting PIN-OLED. 4 Diodes on one substrate are driven with 4 different initial luminances at a temperature of 80 C. All diodes are encapsulated and DC-driven. A lifetime of 17,000 hours at an initial brightness of 500 cd/m² is predicted.*

effects, one would calculate 113 lm/W, i.e. overestimate the power efficieny by 25%.

With respect to operational stability, major progress has been achieved too. Figure 2 gives the result of a lifetime experiment for a red phosphorescent OLED. Current extrapolation yields a lifetime around 100,000 h at 500 cd/m^2. This is not only an excellent lifetime as such, but also comparable to the typical lifetime of bottom emission structures based on the same emitter.

Temperature stability is a major requirement for most OLED products. Process steps following the deposition of the OLED may require durability of the device at elevated temperature, too. Among others effects, morphological changes in the organic layers are known to have a detrimental influence on the lifetime of the devices. This stimulated major efforts to improve the morphological stability of the organic layers as well as the interfaces to the contacts.

In the case of PIN-OLEDs there were many concerns if high temperature stability can be reached at all. Dopants have been suspected to diffuse within the OLED stack giving rise to quenching in the emitter layer. Such beliefs have been spurred by the rather instable examples used in the early days of doping technology such as F4TCNQ:MeO-TPD or Cs:BPhen. In these systems, the low morphological stability of the host material is combined with the small dimensions of the dopants.

In the meantime, major progress has been made. The classical p-dopant F4-TCNQ is succeeded by the new material NDP-2. NDP-2 exhibits a stronger intermolecular interaction making it more stable. This is demonstrated by the evaporation temperature of 150°C, in contrast to below 100°C for F4TCNQ. In addition to this, the doping strength of NDP-2 is higher than that of F4TCNQ. As a host, we use NHT-5, a hole transporting layer with a Tg higher than 140°C.

According to our investigations [4], OLED comprising Cs:Bphen exhibit a very low thermal stability. Above 60°C, a fast degradation mechanism limits operational lifetime to a few hours. Shelf lifetime is strongly compromised as well.

Therefore, for electron transport, the molecular n-dopant NDN-1 has been developed. As a next step, an electron transport materials suitable as a host for NDN-1 has been developed. We found that Alq$_3$ is not sufficiently doped by NDN-1 due to its low electron mobility. Thus, we designed a molecular structure featuring a structural motif to allow for high electron mobility as well as high morphological stability. In result we obtained a new electron transport material NET-5 with a Tg exceeding 105°C and high electron mobility. Further studies lead to host materials with even higher stability. For example, NET-9 has a Tg greater than 165°C. This host provides sufficient thermal stability even for automotive applications operated in harsh environment.

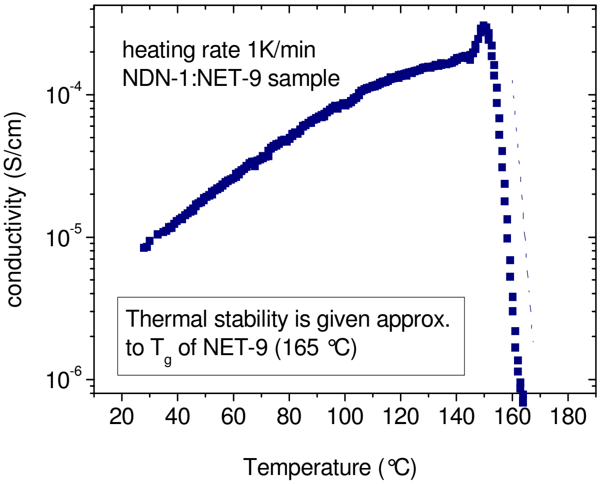

Figure 4: *Conductivity of an n-doped transport layer in dependence on the temperature. Approximately at the T_g of NET-9, the conductivity collapses.*

Having established this new set of transport materials, we studied their influence on the thermal stability of PIN OLED. As an emitter system, we have chosen a red phosphorescent emitter system from Merck OLED Materials (former Covion) known to give excellent lifetimes at room temperature [3].

Figure 3 shows the operational stability of such OLED operated at 80°C. Extrapolation using the empirical law $L_0 t_{0.5}^n=1$ yields a lifetime of 17,000 h at 500 cd/m^2. This value is by far the highest ever reported for a PIN-OLED at this temperature and belongs to the best lifetimes at elevated temperatures known in the OLED community. The OLED exhibits a small dependence of efficiency from the operating temperature. From room temperature to 80°C, the efficiency changes only by 5%.

To get a deeper insight into the various parameters influencing operational stability, we were interested in the stability of the doping effect itself vs. heat. As a measure we used the conductivity of the doped layer

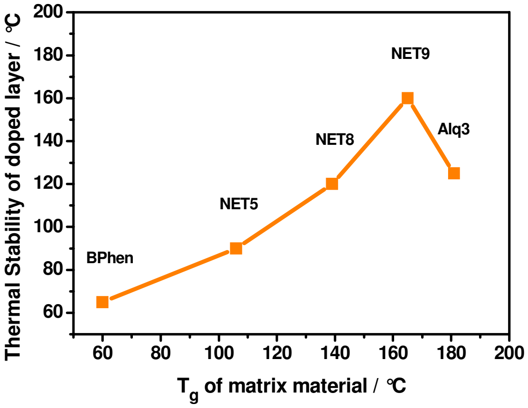

Figure 5: *Comparison of thermal stability of the doping effect an the* T_g *of the host molecule. For the various material classes BPhen, NET and* Alq_3*, no general correlation is found. In tendency, a higher* T_g *gives rise to higher thermal stability.*

in dependence from temperature. Figure 3 shows a typical example for such a measurement. Shown is the conductivity of the NDN-1:NET-9 layer during an heating phase. The heating rate was 1K/min. Increasing the temperature starting from room temperature, we observed an increasing conductivity of the layer. This we attribute to an increasing mobility of the charge carriers due to thermally activated hopping processes. The change in conductivity is reversible. For very high temperatures, finally, we observe a maximum at about 150°C in the conductivity followed by a decrease for further heating. Approaching the maximum, the conductivity changes become irreversible.

The close relationship between the temperature of the conductivity maximum and the Tg of the host lead us to study further hosts. All host molecules have been doped using NDN-1. Figure 5 summarizes our findings by comparing the thermal stability of the doping effect to the Tg of the host. Not for all electron transport materials that were investigated, this pronounced relation between Tg and thermal stability could be confirmed. Prominent example is NDN-1:Alq with has actually a lower thermal stability than NDN-1:NET-9 despite the higher Tg of the host. Other parameters that are not yet revealed seem to play an important role as well.

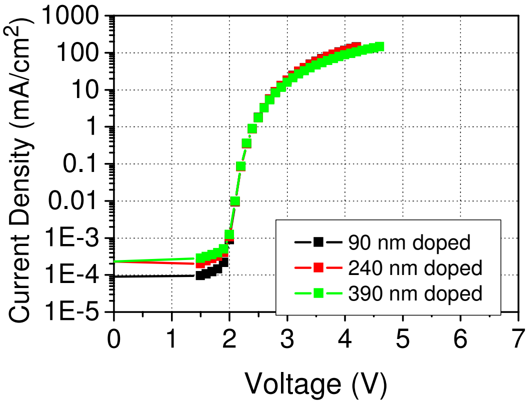

Figure 6: *Variation of current-voltage characteristics with variation of transport layer thickness. All OLED exhibit virtually the same operating voltage despite a variation in the thickness of the doped charge transport layers by a factor of four.*

Although it is now well established that PIN OLED technology give rise to very low operating voltages, it is still worthwhile to study, which voltage losses remain in the OLED structure. As a first step, it is instructive to rule out losses in the doped charge transport layers. Figure 6 shows the current-voltage characteristics of PIN OLEDs where the thickness of the doped charge transport layers have been varied. The remaining layers, including the emitter layer, are identical. One can see that despite the strong variation in layer thickness, the driving voltage is almost the same for all devices. Of course this is due to the doping effects caused by the molecular p-type and n-type dopants. The IV curve is characterized by a steep rise in current density over 4 orders of magnitudes in the voltage range of 2 V to 2.5 V. This is the characteristic feature of the p-n junction formed in the device and is due to the compensation of the built-in voltage by the bias. For higher bias, however, one observes a less steep rise. The current flow must be limited by some resistance giving rise to an increasing voltage drop.

At first, a series resistance in the contacts, especially in the ITO layer, can be expected. In this respect, it is convenient to compare the IV characteristics of a usual bottom-emission device to a device having metal electrodes as cathode and a anode. The comparison reveals that the additional voltage drop caused by the ITO sheet resistance is about 0.2 V at 100 mA/cm^2.

It is easy to see that this series resistor has not a major influence on the IV characteristics. The deviations from the exponential behavior below this limit must be attributed to another part in the OLED structure. We assume that no injection barriers are present in a sophisticated PIN OLED stack, as it is evident from the steep exponential rise of the IV characteristics. Thus, it must be the charge transport in the undoped layers, especially of the emitter layer, which gives rise to additional resistance. This is reasonable because charge transport takes place by space charge limited currents in these layers. For this reason, development of emitter materials needs to be directed towards providing high mobility host materials to reduce operating voltage.

On the other hand, it may be beneficial to reduce the influence of space charges as much as possible. Therefore, we tested mixed host systems such as Alq$_3$ and Rubrene mixtures known as host combination for red fluorescent emitters. Here, Rubrene is considered as a molecule facilitating energy transfer from Alq$_3$ to the emitter dopants thus increasing current efficiency. In addition, we speculate that the combination of electron and hole transporting properties of Alq$_3$ or Rubrene, respectively, will allow for an overlap to the negative space charge injected into Alq$_3$ with the positive space charge injected into Rubrene. Consequently, the net charge of the layer is reduced and less voltage is needed to maintain the high charge carrier density injection level.

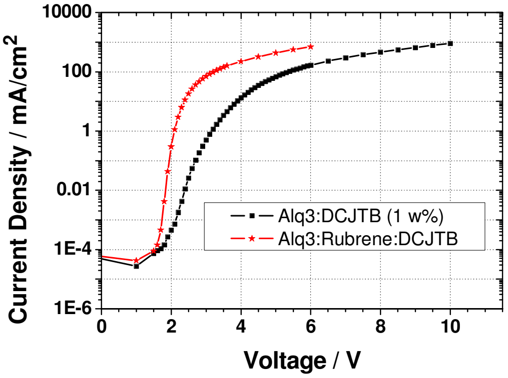

Figure 7: *Current voltage characteristics of red devices with Alq$_3$ and a mixture of Alq$_3$ and Rubrene as a host for DCJTB. The mixed host yields a strong reduction of operating voltage. Note the very low voltage of only 3 V to drive 100 mA/cm^2.*

In Figure 7, the IV characteristics of PIN OLED comprising DCJTB:Alq$_3$ is compared to the three component system DCJTB:Rubrene:Alq$_3$. It is obvious that the latter system requires less driving voltage for the reason given above. The use of bipolar emitter systems will be a route to improve the power efficiency of PIN OLED in the future even more.

3. Conclusion

PIN OLED technology is the major prerequisite for low voltage and high power efficiency OLED solutions. Highly efficient and very stable PIN OLEDs have been demonstrated. Further, the PIN approach enables to fabricate top-emission OLED with identical performance compared to a similar bottom-emission counterpart. This opens the way to further improve active matrix displays.

With the availability of dopant and host materials designed for high thermal stability, operational stability of PIN OLED can be ensured even at elevated temperatures needed for automotive applications.

In the future, bipolar host-emitter systems allowing transport of both types of charge carriers may enable to further reduce the operating voltage of OLED.

4. Acknowledgements

This work was supported in parts by financial funding from the Free State of Saxony and the European Union.

5. References

[1] J. Huang, M. Pfeiffer, A. Werner, J. Blochwitz, S. Liu, and K. Leo, Appl. Phys. Lett. 80, 139 (2002)

[2] A. Werner, J. Birnstock, M. Hofmann, S. Murano, M. Vehse, A. Lux, M. Limmert, A. Grüßing, and J. Blochwitz-Nimoth, Proc. 12th Intern. Display Workshops (IDW/AW) Book 1, 581 (2005)

[3] J. Birnstock, A. Lux, M. Ammann, P. Wellmann, M. Hofmann, and T. Stübinger, Society of Information Display (SID), Digest of Technical Papers Vol. 37, Book 1, p. 1866 (2006).

[4] J. Birnstock, P. Wellmann, A. Werner, T. Romainczyk, M. Hofmann, M. Limmert, A. Gruessing, J. Blochwitz-Nimoth, Eurodisplay 2005, Proceedings, pp. 192-194 (2005).