New Hole Transport Materials for Solution Processing and Vacuum Deposition

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ABSTRACT

In this paper, the authors describe latest results in the development of new hole transport layer (HTL) materials for OLEDs. Basically there are two fundamentally different techniques to apply the HTL: Either via solution processing techniques such as spin-coating, slot-dye coating and ink-jet printing or via vacuum deposition techniques such as thermal evaporation or organic vapor phase deposition. For both types of deposition techniques new materials will be introduced.

1. INTRODUCTION

Nowadays AMOLED displays are widely used in mobile phones, cameras and smaller tablet PCs. In addition, first TVs are introduced to the market. The most crucial performance parameters of the OLED itself are certainly efficiency, lifetime, driving voltage and temperature stability. An important role in the improvement of those parameters is played by the hole transport layer and its interaction with the anode and the neighboring emission layer. In most relevant OLED stacks, the HTL is the thickest layers. Therefore its conductivity is important for the driving voltage of the device as well as for the charge carrier balance and therefore for efficiency and lifetime.

Currently the two fundamentally different techniques to apply the HTL are solution processing and vacuum deposition. Whereas vacuum deposition is very well established in the production, also solution processing might offer certain advantages such as lower tact time or better conformal coating of defects in the underlying layer.

In this paper, new materials for both types of deposition techniques are described, starting with materials for the vacuum deposition. In both cases p-doped materials will be used in order to minimize the ohmic losses in the HTL and the injection losses between the anode and the organic stack.

2. NEW HTL MATERIAL FOR VACUUM DEPOSITION

In general, the lifetime and efficiency of the blue pixel is considered to be the bottleneck in an AMOLED display. Therefore the qualification of new HTL materials is usually done in a typical blue pixel structure. The blue pixel comprises a highly reflective bottom anode which is made of silver. This metal is the interface to the organic stack. Since the stability of the interface between the anode and the organic material is crucial for the stability of the whole device, e.g. what the voltage increase during lifetime is concerned, a p-doped HTL was chosen for all experiments. Such p-doped HTLs are known to give very low and very stable OLED driving voltage. The p-dopant used is the well-known material NDP-9.

As a newly developed hole transport material in Novaled, NHT-90 is capable for further improvement of OLED device performance with an enhanced p-doped ability. Compared with NHT-51, an earlier and well established hole transport material, NHT90 was tested as both p-HTL and HTL in a top blue-emission OLED device, as shown in Figure 1.

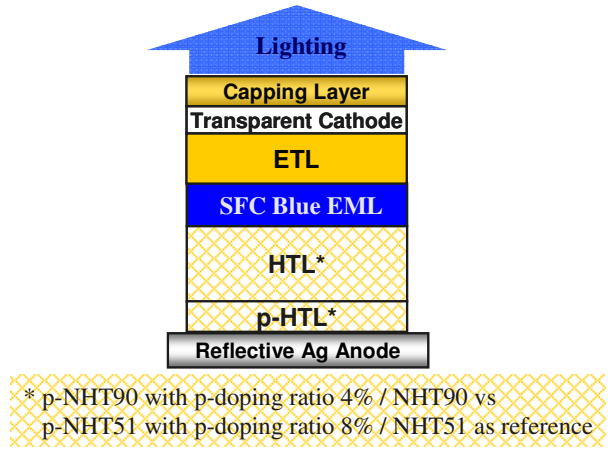

Figure 1. Top emitting fluorescent blue OLED structure

The p-doping ratio in p-NHT-90 layer is only half of that in p-NHT-51 layer. However, as shown in Figure 2a, the device with NHT-90 presents a slightly lower driving voltage compared to that of the device with NHT-51. This lower driving voltage is mainly attributed to the improved p-doped ability and conductivity of NHT-90. Meanwhile, Figure 2b shows that the efficiency of the device with NHT-90 at 10 mA/cm^2 is around 11% higher than that of the device with NHT-51 since NHT-90 can offer better hole injection into EML. Note that NHT-90 and NHT-51

have nearly the same HOMO level, NHT90 is speculated to offer more suitable sterical configuration between molecules which results in enhanced p-doped ability and hole injection.

We conclude that NHT90 can obviously enhance the device efficiency while keeping the low driving voltage even by using the low p-doping ratio. By means of molecular design and engineering, further series of hole transport materials compatible for different emitter systems while keeping the efficient p-doped capability will be developed.

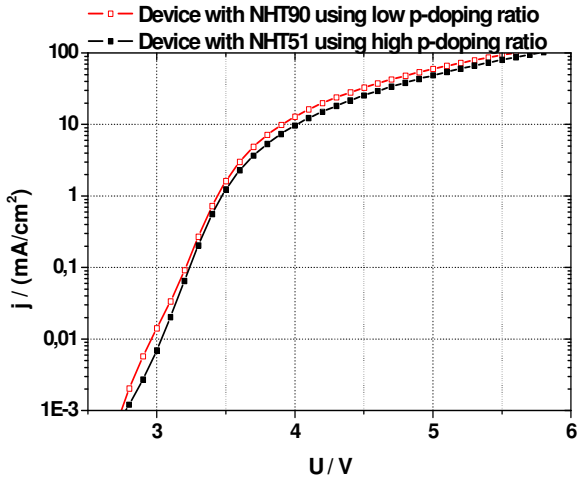

Figure 2a. J-V characteristics of blue top emitting OLED

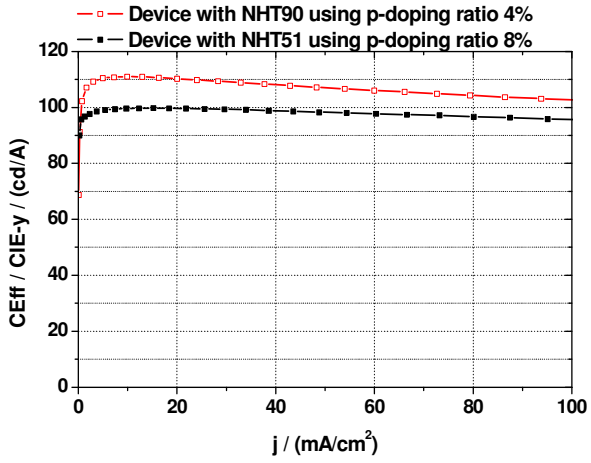

Figure 2b. CEff/CIE-y vs J characteristics of blue top emitting OLED

3. INTRODUCTION OF TRIPLET BLOCKING MATERIALS

Phosphorescent organic light-emitting diodes use organic metal complexes to allow harvesting of both singlet and triplet excitons for 100% of internal quantum efficiency. Practically, this will lead to higher efficient devices. However, the external quantum efficiency is reduced due to exciton quenching at the interface of the emitting layer and the hole transport layer. To minimize this efficiency loss in phosphorescent devices, high triplet materials as blocking layers are investigated.

In so-called “hole only” devices newly developed Novaled high triplet materials NHT-121 (triplet gap 2.59 eV) and NHT-129 (triplet gap 2.58 eV) are compared with NHT-51 (triplet gap 2.4 eV). NHT-121, NHT-129 and NHT-51 show voltages of 2.7 V, 2.6 V and 2.4 V, respectively, at 8% NDP-9 doping at 10 mA/cm². Reduced NDP-9 doping concentration (3%) results in voltages of 2.8 V (NHT-121) and 3.2 V (NHT-129) at 10 mA/cm². Here, the increased p-dopability of NHT-121 is attributed to a 0,12 eV higher HOMO level in comparison to NHT-129. The HOMO level was derived from CV measurements vs. Ferrocene in Dichloromethane. Sterical effects are supposed to further affect p-dopability.

In another experiment, phosphorescent green OLED devices were processed. Both materials NHT-121 and NHT-129 are used as triplet exciton blocking layers between the HTL and the emission layer. In comparison to NHT-51, efficiencies are increased by 15% due to their higher triplet levels. The 95% lifetimes at 15 mA/cm² are ~90 h for both NHT-51 and NHT-121. NHT-129 demonstrates an increased lifetime of almost 120 h which is not yet fully understood (see figure 3). Investigations on the influence of chemical structure on lifetime are ongoing.

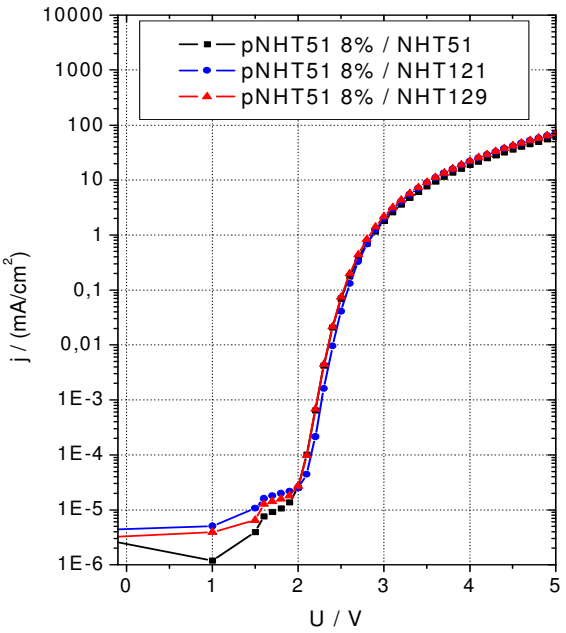

Figure 3a. J-V characteristics of green phosphorescent bottom emitting OLEDs with different blocking layers

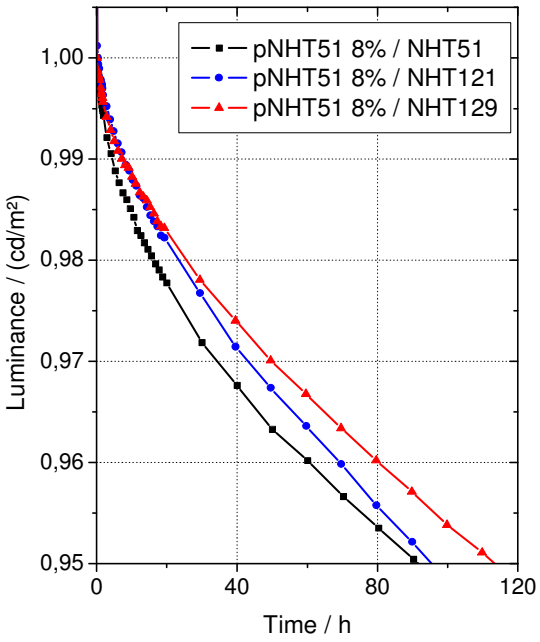

Figure 3b. Lifetime measurement at 15 mA/cm² of green phosphorescent bottom emitting OLEDs with different blocking layers

4. NEW HTL MATERIAL FOR SOLUTION PROCESSING

The manufacturing of printed OLED involves the deposition of a multi-layer stack of functional materials, sequentially deposited from organic solvent-based inks. This bears the challenge that the deposition of the subsequent layer must not alter thickness or composition of the underlying layer. Novaled has developed material set that can be deposited by industry-relevant printing techniques like ink jet printing or slot die coating onto a standard TCO substrate. Key of the concept is the use of a one-step thermal in-situ conversion of the printed film into an insoluble film in the presence of a redox-dopant. The new material, S-NHT-PL4, was tested in blue hybrid OLED devices (Figure 4).

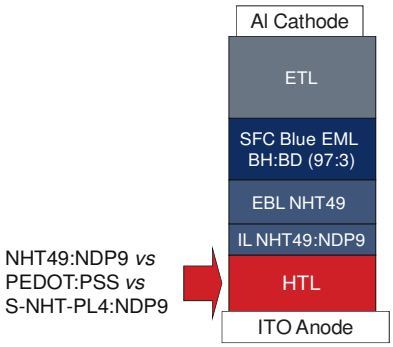

Figure 4. Test OLED structure for comparison of solution processed and evaporated HTLs

Based on blue hybrid OLED the structure was optimized. Thus, OLED with promising initial performance were achieved (Figures 5a-c). Benchmarks were on the one hand a blue reference OLED using solution deposited PEDOT:PSS, on the other hand a high-performance blue OLED made by evaporation process. Compared to the references, very comparable initial voltage and efficiency have been achieved. No big differences between hybrid OLEDs with solution processed S-NHT-PL4 vs. vapor deposited reference were seen. The blue hybrid OLED with the new NHT material S-NHT-PL4 give slightly higher efficiency than the vapor deposited reference.

The lifetime LT95 of the blue hybrid OLED with S-NHT-PL4 is lower than that of the vapor deposited reference, but significantly improved compared to the device with PEDOT:PSS (see figure 5d.). The future development will focus on improving this and on extending this concept to fully printed OLED.

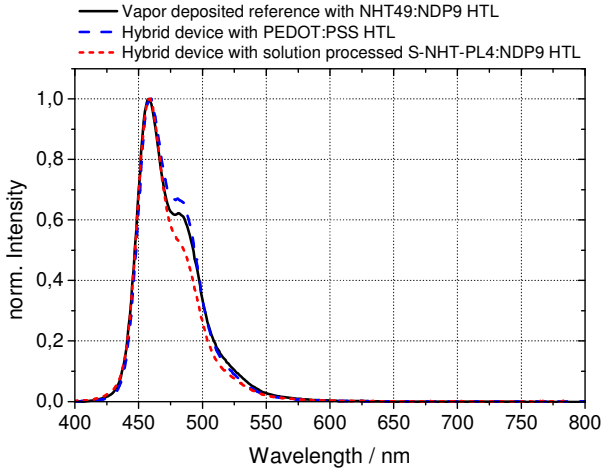

Figure 5a. Spectrum of the blue OLEDs

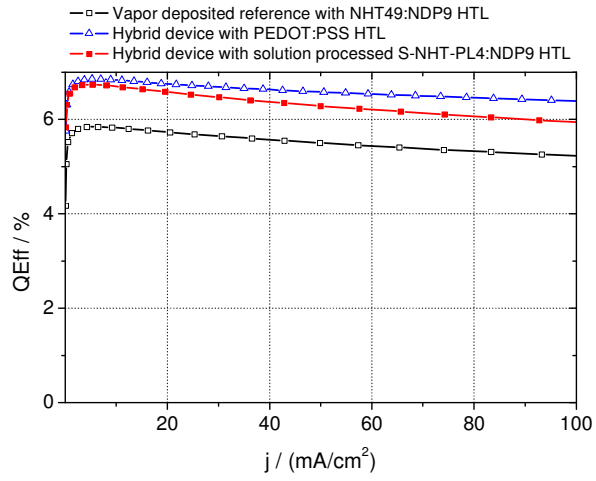

Figure 5b. Quantum Efficiency

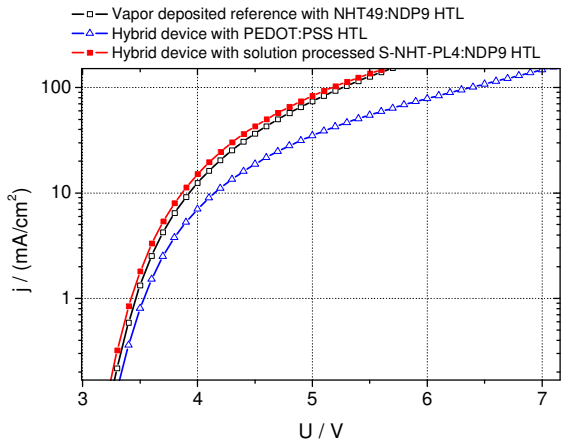

Figure 5c. J-V-curve

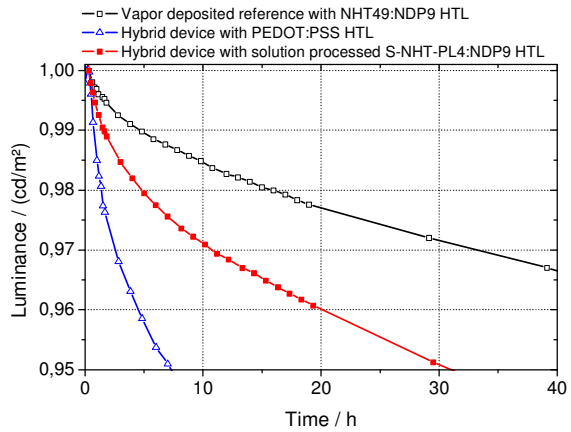

Figure 5d. Lifetime measurement

5. SUMMARY

It could be shown that the HTL material is crucial for the OLED performance even if the same emission layer and electron transport layer is used and the HTL material has the same HOMO level and is p-doped. The sterical configuration of the host and dopant molecules of the p-doped HTL is suspected to be the reason for the behavior and will be investigated further. Apparently slight changes in the charge carrier balance can have rather drastic effect on the OLED performance of the blue pixel.

In addition a new solution processed HTL material has been introduced that uses a one-step thermal in-situ conversion of the printed film into an insoluble film in the presence of a redox-dopant. Using this material, OLEDs have been produced that clearly outperform reference OLEDs that contained PEDOT:PSS as HTL.

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