Efficiency and Aging Comparison Between N,N′-Bis (3-methylphenyl)-N,N′-diphenylbenzidine (TPD) and N,N′-Di-[(1-naphthalenyl)-N,N′-diphenyl]-1,1′-biphenyl-4,4′-diamine (NPD) Based OLED Devices

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Summary: In this paper we present and discuss experimental results to evaluate performances and aging behaviour of two Hole Transporting Material (HTM), TPD and NPD, in Organic Light Emitting Device (OLED) with structure: ITO/HTM/Alq3/Al. For each of these HTMs, devices with several thicknesses have been built, to measure and emphasize behaviours of material-geometry combinations. Electro-optical properties have been measured to estimate and compare brightness, power efficiency and aging decays.

Keywords: aging; NPD; OLED; power efficiency; TPD

Introduction

Since their first realization,[1] multilayer organic light-emitting devices (OLED) have attracted the efforts of display industries and research foundations to improve their optical and mechanical features and exploit the advantages in cost-competitive, flexible, low power and high brightness flat displays and lighting applications. Different items have yet to be optimized to completely take these advantages. For instance, to improve the carrier transport action and the device stability under usage stress, specific materials can be used, not only for the emissive layer (EML), but also for the charge's transport layers.

In this paper, we report our tests and comparison between two of the most used small molecules hole transport materials: TPD (N,N′-Bis (3-methylphenyl)-N,N′-diphenylbenzidine) and NPD (N,N′-Di-[(1-naphthalenyl)-N,N′-diphenyl]-1,1′-biphenyl-4,4′-diamine).

OLEDs with these two materials have been fabricated with three different thicknesses, to find out which configuration gives the best results in terms of capability to: (a) improve the device efficiency, (b) lower the threshold voltage (the voltage at which the OLED starts to emit), (c) extend the lifetime of the device.

For each device, we have measured: the current-voltage characteristics, the power efficiency (lumen per watt vs. voltage), the electroluminescence vs. time at constant current, and the electrically induced thermal stress, imaging the infrared (IR) emission of the devices under high voltages and currents.

In the following, we refer to the devices through the thicknesses of their hole transport layer (HTL) and electron transport layer (ETL), i.e. 20/30 means that the HTL is 20 nm thick and the ETL is 30 nm thick.

Devices Manufacturing

We have fabricated our devices on Corning 1737 glass, deposited with commercial ITO layer 150 nm thick, with a sheet resistance of 10 Ω/□. The substrates were cleaned

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with deionised water, detergent and ultrasounds and dried in oven at 115 °C for 2 hours.

The anodes were patterned through inverse photolithography and HCl-based solution etching; soon after it, the deposition of organic and cathode layers was carried out in an high vacuum evaporator. The base vacuum was always lower than 10^{-6} mbar; the HTL and the ETL were thermally evaporated sequentially without patterning; the growth rate was kept constant at about 1 Å/s. Then, the aluminium cathode was also deposited by thermal evaporation, through shadow mask; the growth rate was about 3 Å/s. All the deposition processes were done at room temperature. No encapsulation was adopted to enclose the finished OLEDs.

The thicknesses of the devices layers are shown in Table 1. Figure 1 is a picture of a working device. On each substrate there are 12 devices.

We have measured current-voltage characteristics and absolute electroluminescence light emission of devices soon after their fabrication, to analyse an unstressed behaviour.

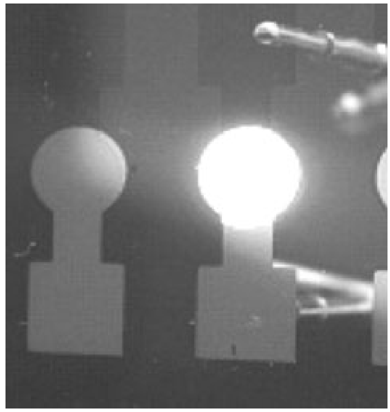

Figure 1.
A working OLED, showing the layout of devices. The light emission is green (Alq3, wavelength 535 nm).

Electrical Characterization

The electrical measurements have been done with a Keithley 2400 Power Supply SourceMeter. Figure 2 shows the J-V characteristics, plotted in log-log scales, of the first measurement for each device, showing a peculiar peak at low voltages[7] not related however to light emission. The log-log representation helps us to identify the threshold voltage,[4] where the J-V curve changes its slope; in these measurements, the initial peak evidently does not hide the threshold. The threshold values are reported in Table 2.

At first glance, the behaviour of these devices seems not clearly predictable, but in general, the device showing lower currents before threshold, shows also a lower threshold. For most of them, this happens for TPD devices; the situation is instead reversed for 40/60 devices: NPD device shows higher subthreshold currents but lower threshold.

The TPD devices, with the exception of that one with the thickest HTL, show better J-V characteristics than NPD ones: lower subthreshold currents and higher currents in the active region.

Power Efficiency Comparison

The optical quantities have been measured through an integrating sphere, linked by an optical fibre to an Optronics Laboratories OL770 spectroradiometer, to obtain calibrated values of total luminous flux (TLF) in the visible region. The instrument

Table 1.
Thicknesses of OLED layers.

ITO anode thickness [nm]	HTL thickness TPD or NPD [nm]	ETL thickness Alq3 [nm]	Al cathode thickness [nm]
150	20	30	200
150	20	60	200
150	40	60	200
150	75	60	200

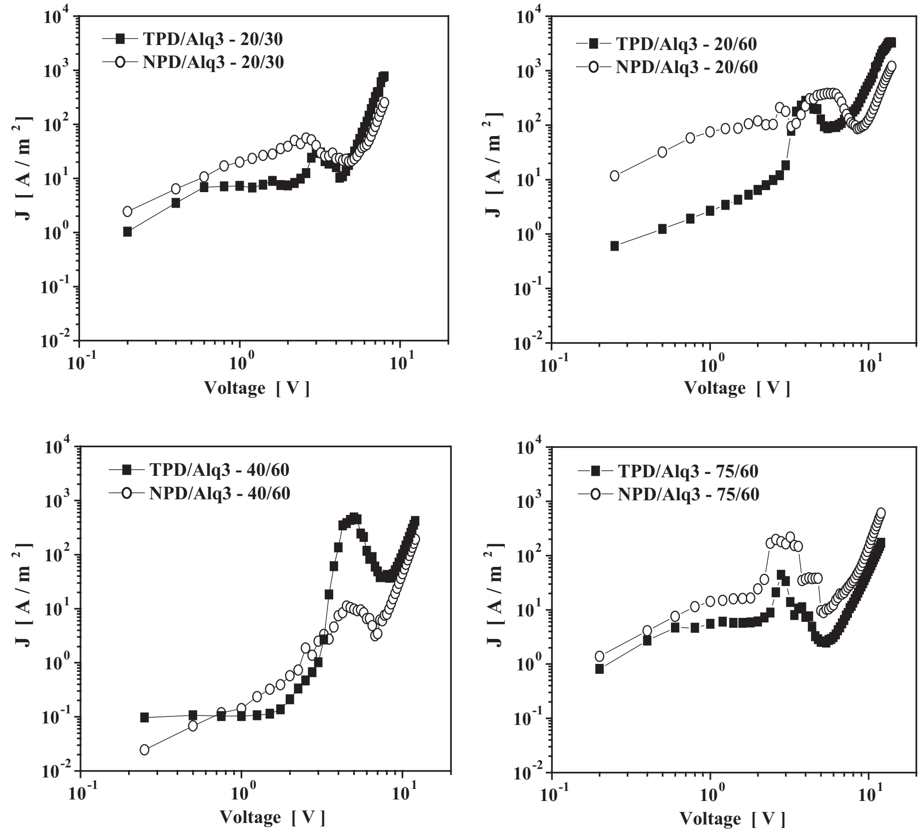

Figure 2.
Example of the J-V characteristics of OLEDs made with various thicknesses of TPD and NPD as HTL (the plots are all in the same scale).

supplies voltage to the device and records the resultant absolute luminescence.

Here, we are comparing different materials in the same operating conditions, not looking for the device with the highest absolute performances, so we compare power efficiency. Data for the fabricated devices are shown in Figure 3.

Lumen per watt vs. voltage plots are represented in the same scale for voltages and efficiencies and are obtained from the electroluminescence vs. voltage characteristics, with the aim to emphasize device-dependant operating conditions for radiative recombination.

Operating voltage ranges are not always the same: this is due to the failure limits of the devices, related to the thickness and hence to the maximum acceptable electric field inside the organic layers. As expected, thicker layers can sustain higher voltages.

The best power efficiency has been achieved by the 20/60 combination, both for TPD and NPD. The 40/60 devices reach a higher absolute TLF, but the current is so high to push the OLED in an operating region of reduced efficiency.

From plots, it is not difficult to see that TPD hole transport layer has to be

Table 2.
Threshold voltages of devices.

Thickness HTL/ETL [nm]/[nm]	V_{th} TPD [V]	V_{th} NPD [V]
20/30	4.67	5.95
20/60	5.49	6.69
40/60	7.75	6.75
75/60	5.98	6.13

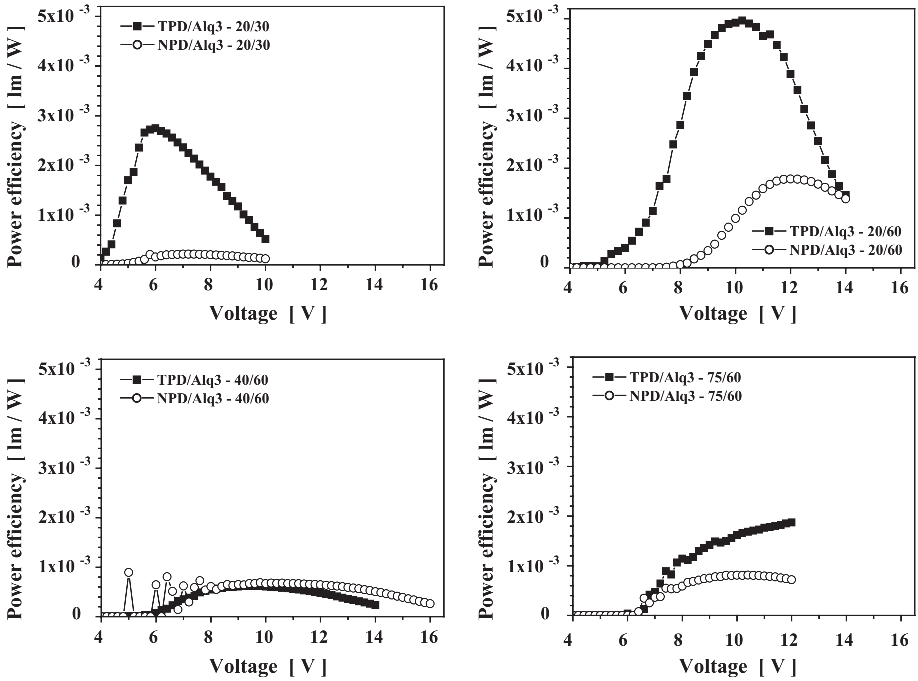

Figure 3.
Power efficiency of devices vs. voltage (the plots are all in the same scale).

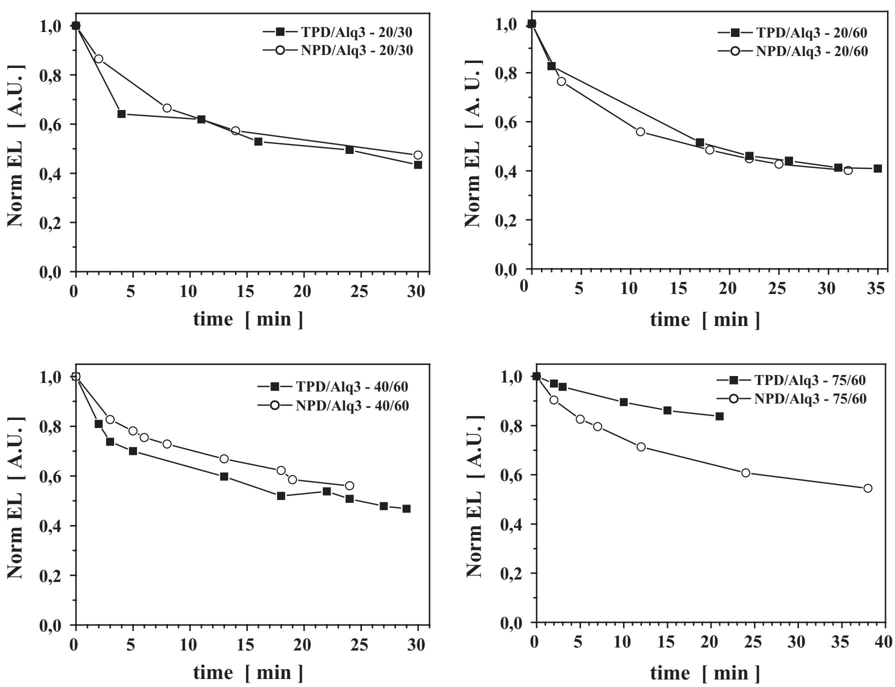

Figure 4.
Normalised electroluminescence vs. time, to show the aging decay of the devices.

Table 3.
Glass transition temperature of TPD, NPD and Alq3 [4].

Material	TPD	NPD	Alq3
T_g [°C]	65	95	>170

preferred because of the higher efficiency. Moreover, the ''thin'' TPD devices show an efficiency peak at lower voltages than NPD ones, in agreement with the threshold voltages found from the J-V characteristics.

Aging Decay Comparison

Aging measurements have been performed at the same fixed constant current[6] for all the devices. Current density needs to be high enough in order to have light emission from the devices, but also low enough to minimize the accumulation of Alq3 cathions at HTL/EML interface[10] (the higher is the driving current density, the faster is the luminance decay) and to reduce the electrical induced thermal damage. In Figure 4, the electroluminescence vs. time is reported in a normalized scale, to make considerations independent from the initial brightness value. In this way, we can evaluate the intrinsic decay process alone. Devices are not encapsulated, so the environment-induced degradation is the same for all of them.

For devices with thinner HTLs, aging degradation is comparable and has similar time constants. Thicker devices exhibit a longer lifetime than thinner ones, and TPD shows a more stable behaviour and a slower degradation. In thicker HTLs, there are less available holes at the HTL/ETL interface because of higher non-radiative recombination in the HTL, slowing the formation of Alq3 cathions, and therefore reducing the degradation.

Thermal Stress Damage and Aging Effects

Until now, we have analysed the behaviour of the devices in conditions of ''normal operation'' (no ''hard'' thermal and electrical stress conditions). To investigate limits for the two types of fabricated devices, we made measurements also reaching their electrical, optical and thermal ''breakdowns'' and in the same time we have recorded their thermal maps using an IR camera (AVIO neo-thermo TVS-700).[8]

The heating produced by Joule effect in an OLED can damage it by strain driven surface stress and by material degradation.[4,5] These effects depend mostly by the glass transition temperature (T_g) of organic materials. The HTL can be considered the main responsible for this aging mechanism, because the T_g of Alq3 is much higher (Table 3).

The electroluminescence (Figure 5) and thermal (Figure 6 and Figure 7) responses of two devices are reported as an example. In these curves, we can see how IR measurements show material limitations on the highest operating temperatures and

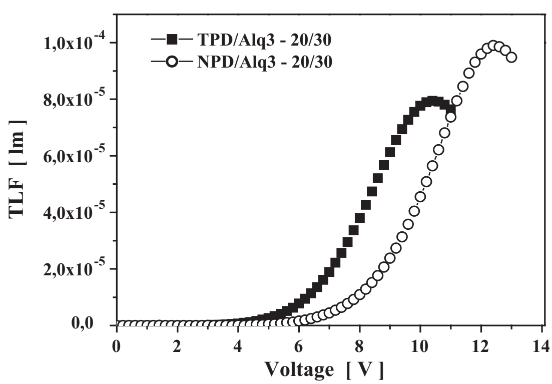

Figure 5.
Total Luminous Flux (TLF) vs. voltage of 20/30 devices.

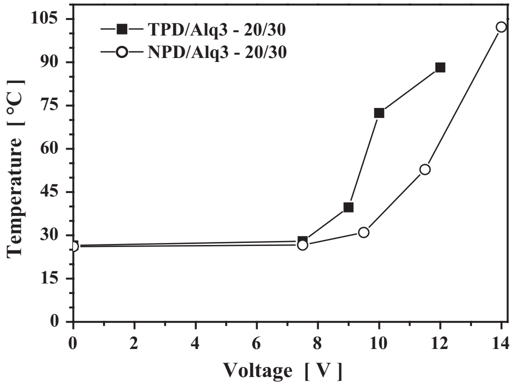

Figure 6.
Thermal behaviour of 20/30 devices driven by voltage.

on the highest operating currents and voltages. In fact, the reduction of the total luminous flux (TLF) at higher voltages (Figure 5) means that degradation of the device is already started, and this effect begins for the TPD devices at lower voltages than for NPD ones. This is confirmed also by the temperature plots (Figure 6) and the IR images (Figure 7): the TPD curve seems starting to saturate, because the material is already at or higher than its T_g, changing its solid structure to a more rubbery phase,[9] while NPD curve is still increasing at higher voltages. The NPD, because of its higher T_g (Table 3), can sustain more intense electrically induced thermal stress than TPD, without damaging the device.[2,4]

Conclusions

We have presented the electrical, optical and thermal behaviours of small molecules

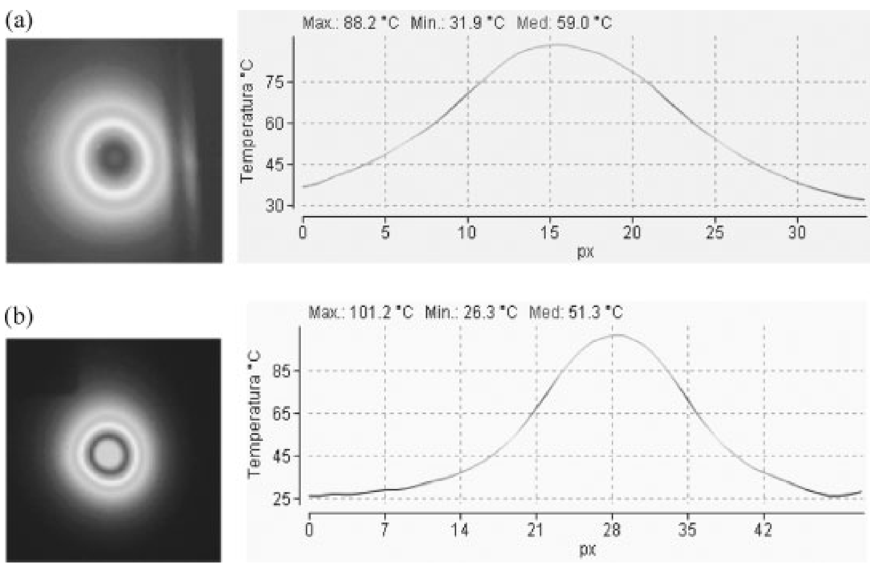

Figure 7.
IR images of the two devices of Figure 6, driven (a) at 12 V for the TPD and (b) at 14 V for the NPD, with the temperatures observed along a section through the centre of the devices (px: pixels of the IR image).

OLEDs, fabricated with two hole transport materials, TPD and NPD, and the influence of these materials and materials thickness on the devices efficiency and aging decay.

At low thicknesses, TPD devices present higher currents above threshold and, in general, better power efficiency; at low current/low electroluminescence regime, the aging process shows the same trends in time for both the materials, while thicker HTLs shown the best aging performances, with a longer lifetime for TPD. NPD devices can sustain higher thermal stress electrically induced.

Further investigations are in progress, including encapsulated devices, to better understand the material-geometry correlation.

[1] C. W. Tang, and S. A. Van Slyke, "Organic electroluminescent diodes", *Appl. Phys. Lett.* **1987**, *51*, 913.
[2] X. Zhou, J. He, L. S. Liao, M. Lu, X. M. Ding, X. Y. Hou, X. M. Zhang, X. Q. He, and S. T. Lee, *Adv. Mater.* **2000**, *12*, 265–269.
[3] C. Giebeler, H. Antoniadis, D. D. C. Bradley, and Y. Shirota, "Influence of the Hole Transport Layer on the Performance of Organic Light-Emitting Diodes", *J. Appl. Phys.* **1999**, *85*, 608–615.
[4] D. F. O'Brien, P. E. Burrows, S. R. Forrest, B. E. Koene, D. E. Loy, M. E. Thompson, "Hole Transporting Materials with High Glass Transition Temperatures for Use in Organic Light-Emitting Devices", *Advanced Mater.* **1998**, *10*, 14, 1108–1112.
[5] P. Fenter, F. Schreiber, V. Bulovic, S. R. Forrest, *Chem. Phys. Lett.* **1997**, *277*, 521.
[6] C.-H. Tsai, C.-H. Liao, M.-T. Lee, and C. H. Chen, "Highly stable organic light-emitting devices with a uniformly mixed hole transport layer", *Appl. Phys. Lett.* **2005**, *87*, 243505.
[7] V. A. Kolesnikov, V. I. Zolotarevsky, and A. V. Vannikov, "Anomalous current-voltage characteristics of thin polymer films", *Phys. Stat. Sol. A*, **2003**, *200*, No. 2, 388–392.
[8] G. Nenna, G. Flaminio, T. Fasolino, C. Minarini, R. Miscioscia, D. Palumbo, M. Pellegrino, "A study on thermal degradation of Organic LEDs using IR imaging", in this same Macrom. Symp. issue.
[9] L. E. Nielsen, "*Mechanical properties of polymers and composites*" Vol. *1*, Marcel Dekker inc., New York (in press).
[10] D. Y. Kondakov, J. R. Sandifer, C. W. Tang, and R. H. Young, *J. Appl. Phys.* **2003**, *93*, 1108.

