

OPTICAL PROPERTIES OF FLEXIBLE ORGANIC LIGHT EMITTING DIODES UNDER MECHANICAL STRAIN

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Abstract. In this work a detailed opto-electrical study of flexible organic light emitters is presented. Devices have been made with *m* - MTDATA [4, 4', 4'' - tris (3 - methyl - phenylphenylamino) triphenylamine], NPB [N, N' - bis - (1 - naphthyl) - N, N' - diphenyl - 1, 1' - biphenyl - 4, 4'' - diamine] and Alq3 [aluminium - tris (8 - hydroxyquinoline on polyester (PET) film. The electroluminescence (EL) spectrum shows a main emission centered in green region (near 520 nm) in a broad band. Using DCM [4 - dicyanomethylene - 6 - (p - dimethylaminostyryl) - 2 - methyl - 4H - pyran] as dopant, a red electroluminescence has been obtained (band peaked at 630 nm). The driving voltage is less than 9 V. The optical output at the EL band maximum (single spectrum line) is near 3 μ W (1 mW in whole band). Under mechanical strain (under a curvature with a central angle up to 45°, or if the device is twisted along an axis in a turn less than 30°) the EL response remains unchanged. By Time of Flight, effective mobilities near 10^{-4} $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ (hole transport layers) and near 10^{-8} $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ (electron transport layer) is obtained. A correlation between the carrier transport and efficiency is discussed. The device lifetime is low when exposed to air (less than six hours under continuous operation), requiring an encapsulation reducing the flexibility. The applicability will be discussed.

Keywords: OLED, optical properties, electrical properties, mechanical strain

1. Introduction

Since the discovery of the Organic Light Emitting Diodes (OLED's), the research in this field has been strongly increased in order to produce more efficient and reliable devices. (Heeger *et al* 2000, Brütting *et al* 2001, Hung and Chen, 2002; Lee *et al* 2003) Although the main goal for applications is the displays, the recent development of emitting devices in flexible substrates opened new areas of applications (Xie *et al* 2003, Borchard, 2004, Yu *et al* 2005). One of the most important is in biological systems, either for photobiomodulation or tunable sources (it is very easy to produce all the visible spectrum using appropriate organic compounds or dyes) either for specific treatments in medical contexts (for a general information see e.g. Eells *et al* 2003 and Kimberly *et al* 2004). Simultaneously, there are many important problems to be overcome, namely the optical power, device modularity as well the device lifetime. In many cases, the complete understanding about the carrier transport phenomena can help in the device fabrication. The goal is to produce a reliable device to be used in medical context. The device must exhibit a relative high optical output, a low driving voltage, an appropriate lifetime and must be extremely flexible. Also, it is important to obtain devices emitting in different colors, as the output spectrum energy must be easily adjusted to the requested color depending on specific application (see e.g. Pfeiffer *et al* 2003 and references therein).

In this work a detailed optical and electrical study of flexible OLED's (green and red emissions) is presented. The optical output and external efficiency are correlated with the electrical carrier transport. Also, its dependence on mechanical strain (curvature and / or twisted angles) is studied. Finally, the flexibility vs. device lifetime is showed. With all these data, the question about the applicability of this kind of light emitting devices is discussed.

2. Experimental

Organic hole transport and emissive materials were deposited sequentially on patterned ITO polyester (PET) film (0.2 mm thick) by thermal evaporation. Two hole transport layers have been used, the *m* - MTDATA [4, 4', 4'' - tris (3 - methyl - phenylphenylamino) triphenylamine] with a thickness of 450 Å and NPB [N, N' - bis - (1 - naphthyl) - N, N' - diphenyl - 1, 1' - biphenyl - 4, 4'' - diamine] with a thickness of 50 Å. For electron transport layer the Alq3 [aluminium - tris (8 - hydroxyquinoline)] is used (thickness of 500 Å). This multilayer device appears to be much more efficient than the conventional two layer configuration (Silva and Pereira, 2000). On the top of organic conductivity layer an aluminium electrode has been evaporated. The final device has six OLED's each one with 5 mm² of emitting area. For red emission, the Alq3 has been doped with DCM [4 - dicyanomethylene - 6 - (p - dimethylaminostyryl) - 2 - methyl - 4H - pyran] with a concentration of 4% in mass. The deposition rate was about 5 Å/s. The thickness of the organic and metal layers is monitored by a quartz crystal oscillator thickness monitor. The chemical structures of the used molecules and the OLED structure are shown in Fig. 1.

The electroluminescence spectra have been collected on a Spex 1703 / 04 Spectrometer with a resolution of 0.1 Å. The electrical measurements were obtained with a Keithley 2410 SourceMeter with a resolution of 10 pA. For Time of Flight measurements, a Lecroy 9140 Digital Oscilloscope have been used (time resolution up to 1 ns). The optical power has been measured with an Ophir Optonics PD300-SH PowerMeter with a resolution of 0.1 μW. All measurements were performed at room temperature.

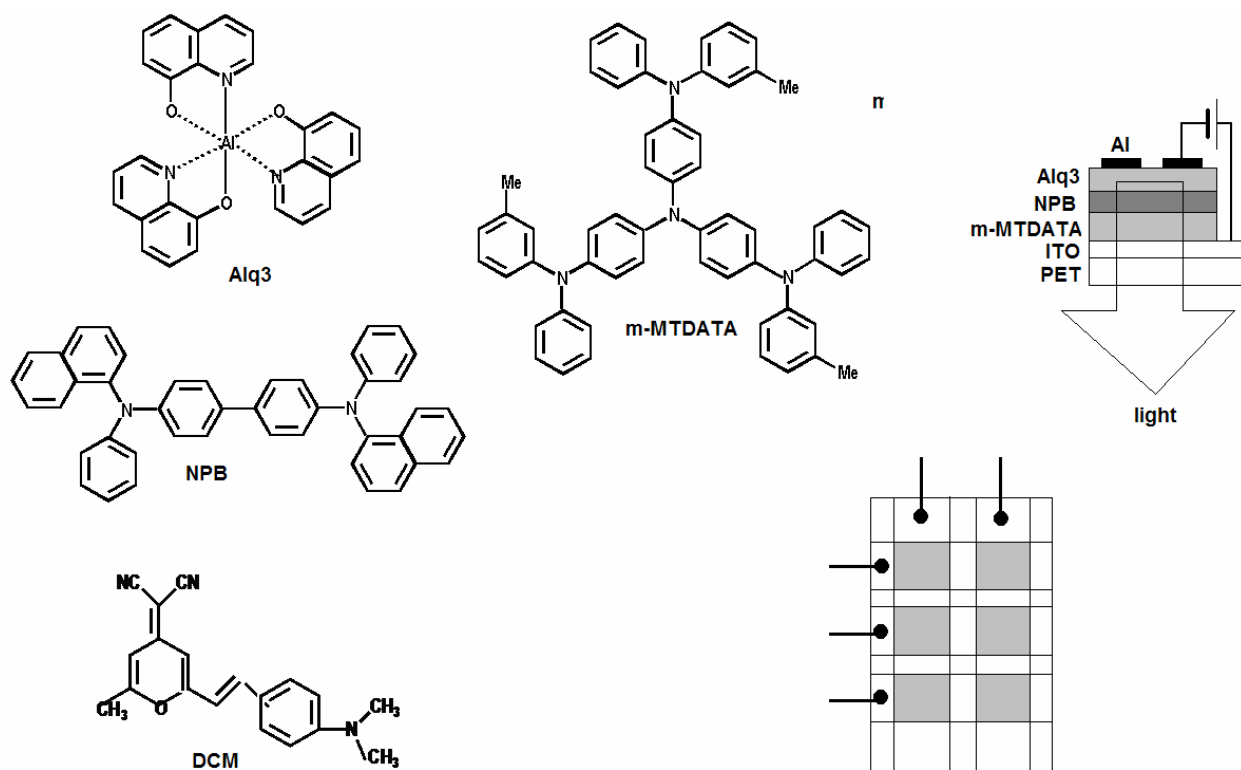


Figure 1. Chemical structure of the organic compounds and scheme of the OLED device

3. Results and discussion

3.1. Electroluminescence

The final devices exhibits clear distinct emission colors: green from undoped and red for DCM doped. The electroluminescence spectrum (EL) of the two kinds of devices is shown in Fig. 2. Both EL intensities are in same scale and the experimental data has been corrected for the optical setup response.

For undoped samples the peak of EL band is near 530 nm while for DCM doped the peak is near 630 nm that is the maximum values of the photoluminescence bands for Alq3 and DCM respectively (Mori *et al* 1995, Zungang and Nazaré, 2000).

Considering that the theoretical probabilities for electroluminescence bands give a Gaussian mathematical model, a numerical fit can be done on our data. In Fig. 2, it is possible to view that the EL bands are composed by three overlapped bands. For undoped samples, a small blue band appears (peaked at ~ 430 nm) followed by the major green band (representing over 70% of the total EL emission) and finally a broad orange band (peaked at ~ 585 nm) is showed. As a final result, a light green emission is produced. A little different behavior is observed in the red emission: due to the new energy levels introduced by the DCM, no more blue emission contribution is found. A small green band (arising from some electronic transition inside pure Alq3) is observed (peaked at ~ 510) and two large red bands control the optical emission (one peaked at ~ 610 nm and the second at ~ 660 nm). The final emission is clearly red. Although both kinds of devices have the same applied voltage, (10 V) the red emission is weaker than the original green from undoped sample, indicating a lower efficiency.

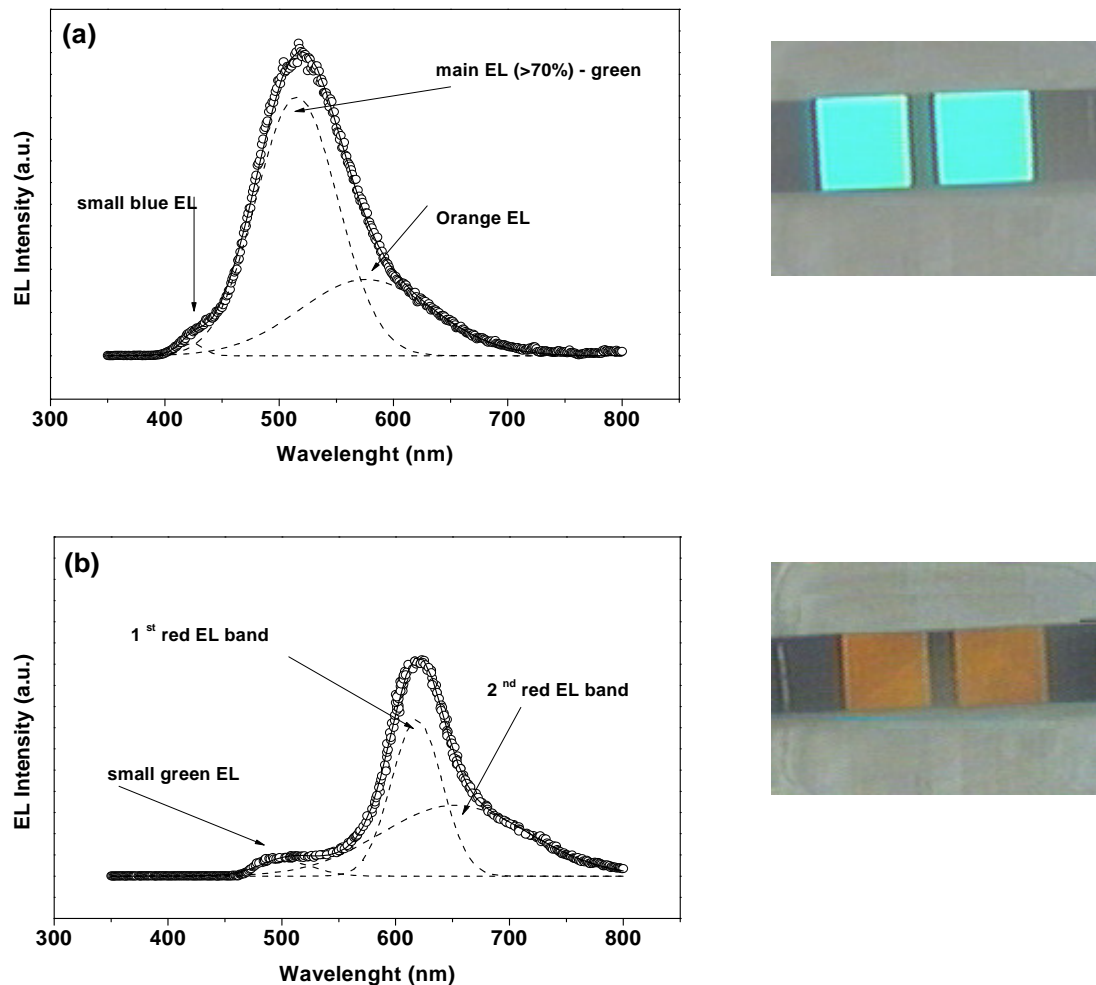


Figure 2. Electroluminescence spectra of the OLED devices: (a) green and (b) red (DCM-doped). (o) Experimental data and (--) theoretical bands obtained from numerical fit. The pictures shows the typical color emission

3.2. Electrical current and optical power with applied voltage

Figure 3 shows the current vs. applied voltage ($I - V$) and Optical Power vs. Applied voltage ($\Phi - V$) for the green device (output @ 520 nm). The red device exhibits a similar behavior (output @ 625 nm) although the optical power is lower.

The optical emission is strongly dependent on the device electrical behavior. For an efficient electron – hole recombination, it is necessary to have an excess of carriers near the interface between the hole and the electron transport layers. This situation only occurs when an electrode can inject more carriers than the semiconductor volume can transport. When this occurs, a carrier accumulation inside the semiconductor volume appears, leading to a space charge limited conduction. Also, some energy states arising from semiconductor intrinsic or extrinsic defects can influence this charge accumulation, acting as traps for the carriers. In general, at high applied voltages we expect a bulk limited conduction that can be trap-limited or trap-free. The electrons injected from Al electrode are trapped in Alq3 and recombine with the holes injected from the m-MTDATA / NPB layers. The electrical conduction is controlled by the energy states in the semiconductor bulk. This can be treated in Space Charge Limited Conduction (SCLC) or hopping / Poole-Frenkel (PF) frameworks (Berleb *et al* 2000, Brütting *et al* 2001). Independently on the specific model, and following the Child Law (for a complete description see e.g. Lampert, 1956 and Lampert, 1961), it is expected that at low applied voltages the $I - V$ data follows an ohmic behavior with $I \propto V$; if shallow traps are present and increasing the applied voltage, the currents shows an $I \propto V^2$ dependency and finally $I \propto V^n$ (with $n > 2$); for deep traps, the second and third region changes.

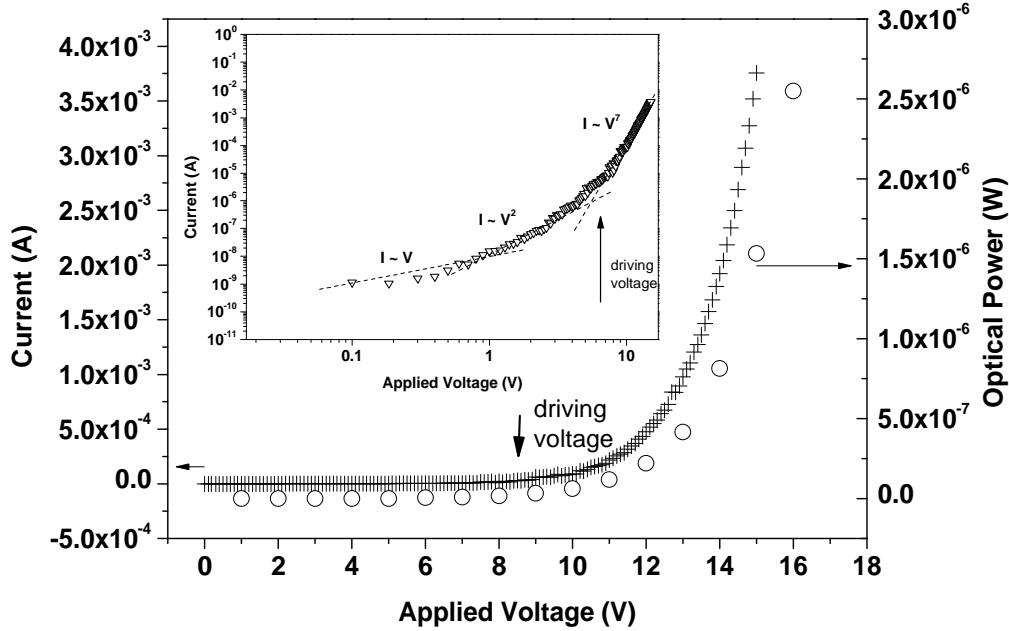


Figure 3. (+) Current – Voltage ($I - V$) and (O) Optical Power – Voltage ($\Phi - V$) for the green EL OLED. Inset: the log $I - \log V$ plot showing the relationship between the driving voltage and SCLC behavior

Then, it is expected that the driving voltage (the applied voltage at the device starts emitting) represents a voltage when the charge accumulation inside the semiconductor volume becomes important. Usually this appears in the region when the electrical behavior leaves the ohmic region of applied voltage. This is confirmed by the data shows in the inset of Fig. 3. The ideal situation is lowering as much as possible this driving voltage. The electrical behavior of multilayer OLED's is known to have a strong dependence on Alq3 due to its mobility. Using the Time of Flight technique, we measured effective mobilities of near $10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ (hole transport layers) and near $10^{-8} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ (electron transport layer) that is not much dependent on electrical field. Although these very low values (and in agreement with the literature) it is possible to build an OLED device with low driving voltage.

The external efficiency η can be obtained from the relationship between electrical current (I) and optical power (Φ), as the $\Phi = \eta I$ where q is the electronic charge. Figure 4 shows the data for both kind of OLED's.

Accordingly to the EL band spectra (showed in Fig. 2) the emitted optical power for the red OLED (for same current) is lower than the obtained for the green one, resulting in a low external efficiency (0.1 % vs. 0.06 %). These values for η are usual in this kind of electroluminescence device. In a conventional OLED on a glass substrate, the maximum values of η are near 0.2 %. The total output optical power (integrated over the entire EL spectrum) gives values in the range of mW , which is, in principle, good enough for displays, but can be insufficient for some more specific applications.

In order to increase the output optical power, working with the η values above, more electrical current must flow throughout the device. Although this seems to be simple (Φ vs. I is a linear function) there is a maximum value for Φ . Increasing more the current, the optical power remains constant when all available energy states in the hole and electron interface layers are involved in the recombination process. Moreover, the high values for current leads to a fast organic semiconductor degradation and must be avoided. Our samples show a maximum of allowed current near 10 mA, corresponding to an optical output (@ band maximum) near $9 \mu W$. In contrast, our previous work on OLED's made on glass substrate, shows nominally, in same conditions, an output power near $30 \mu W$ for approximately 20 mA (Silva and Pereira, 2005). One explanation for this big difference may reside in the PET-ITO interface that exhibits an high resistivity when compared to the equivalent glass-ITO. One workaround is the use of different HTL materials. This is currently on progress.

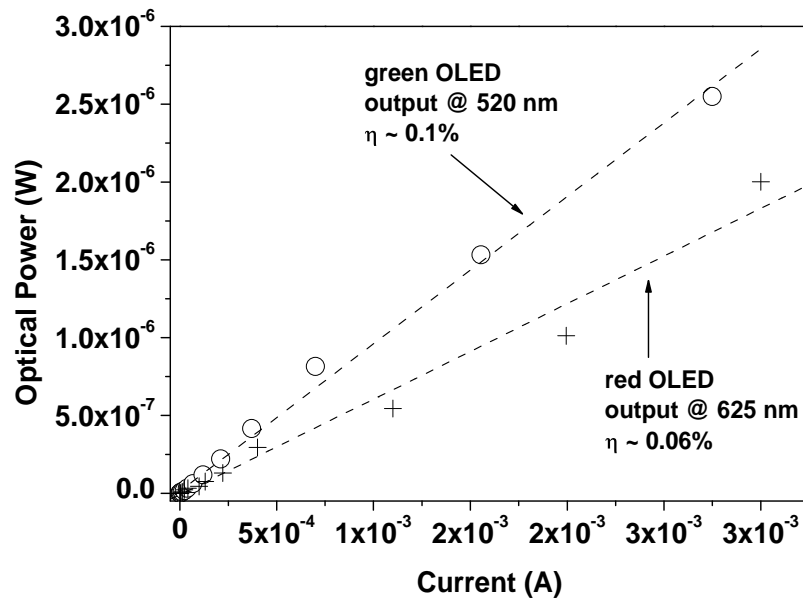


Figure 4. Optical Power – Current ($\Phi - V$) for the green (O) and red (+) OLED, obtained at the respective EL maximum bands (~ 520 nm and ~ 625 nm)

3.3. Efficiency and mechanical strain

Thinking in the potential applications, the advantages of OLED's in flexible areas are enormous. But these advantages are constrained by the OLED structural resistance and by its capability to stay working under some extreme mechanical forces. Our devices are a thin film with a total thickness about 0.2 mm and can be subjected to different torsions. In order to study the working limits for the mechanical constrains of this emitters, the optical power and efficiency has been measured under two different situations. One is the central curvature of the film and other is a twisted along a central axis. In both situations, the electro-optical data has been taken. Both kind of devices shows (at owns scale) the same behavior. The results for green OLED is shown in Fig. 5.

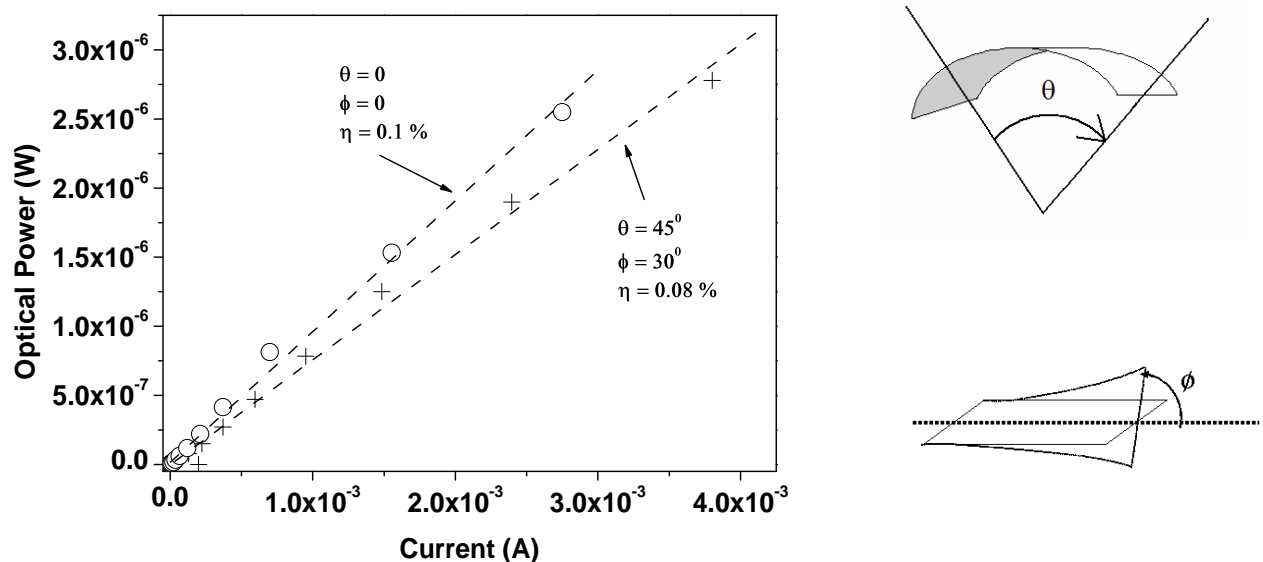


Figure 5. Optical Power – Current ($\Phi - V$) for the green OLED, obtained at the respective EL maximum; (O) with θ and ϕ equal to zero; (+) with $\theta = 45^\circ$ or $\phi = 30^\circ$ (see scheme)

At the limit of mechanical torsion, the optical power is about 20% less than in planar configuration. As in the red device this decrease is the same, we think that this reduction is much more related with the dispersion of the emitted light near the PowerMeter, due to the difficulty in optical alignment to take a measure. Above these limit angles it is practically impossible to taken any data from PowerMeter, although the devices still emitting. Furthermore, we have a good reproducibility of these results, as the decrease in EL with time is due to the organic layer degradation and does not depend on many times the device is curved and / or twisted.

The physical degradation of OLED's is known and becomes the most important problem to be solved (Lin *et al* 2002, Ni *et al* 2004). In fact, after some time working, the organic semiconductor tends to degraded, losing its efficiency and stops emitting. When build on rigid substrates like glass, the encapsulation is the most common solution, as the principal agent for degradation is the chemical reaction between the organic semiconductor and the conventional atmosphere (Yamashita *et al* 2001). The lifetime can be increased up to several thousands of hours and the device becomes useful. In the opposite situation are the devices build on flexible substrates. The great flexibility showed in this work is not available when an encapsulation is performed (another PET layer is used making a "sandwich" structure on inert atmosphere). The flexibility is drastically reduced (as the new PET layer can damage the organic semiconducting layers) although the lifetime increases more than ten times. In the devices not encapsulated (like the used in this work) the lifetime is less than six hours under continuous operation: encapsulated, can achieve sixth or more hours depending on the current density. As an interesting result, these lifetimes are completely independent on the mechanical strain applied to the devices (curvature and / or twisted).

With these data, two questions must be addressed in order to make flexible OLED's competitive: one is a most efficient hole injection from ITO on the PET substrate: a solution is checking new hole transport layers; other is obtained a good insulating material that is simultaneously very flexible and do not interact with the organic semiconductor: this remains an open question.

4. Conclusion

Flexible OLED's has been build by thermal evaporation and characterized in order to get information about their optical and electrical properties under mechanical strain. Two kind of devices has been made: the conventional m-MTADATA / NPB / Alq3 (with green emission) and the m-MTADATA / NPB / Alq3 (DCM doped) in order to get the red emission. The devices have been built on PET substrate with ITO transparent electrode. The total devices thickness is near 0.2 mm (1000 Å for the total of organic layers). Considering the nature of the substrate, some differences with the equivalent devices on glass substrate are expected. The electroluminescence spectrum is very similar to the expected, showing larges green (undoped Alq3 layer) and red (DCM doped Alq3 layer) bands. These emissions are composed for three overplayed bands. The green emission is composed by a small blue, a large green and a medium orange emissions; the red emission is more weak and composed to a small green and two large red emissions. The external efficiencies are about 0.1 % and 0.06 % for the green and red emissions respectively. The optical power at band maximum (ca 520 nm for green and ca 630 nm for red) for an applied voltage of 12 V is about 3 µW and 1.6 µW for the green and red emission respectively. The electrical current at this condition is near 3.5 mA. When take into account the mechanical strain applied to flexible devices, it is surprising to observe that, even under extreme conditions, the devices still working. Curving the flexible device up to a central angle of 45° or twisted the device in a central rotation up to 30°, their still working with a similar efficiency than the obtained under planar configuration. This data opens news possibilities for applications of this kink of flexible electronics.

5. References

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6. Responsibility notice

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