Karlsruhe Institute of Technology

Photonics Lab II

Nanotechnology Lab

Organic Light Emitting Diodes

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1   Introduction

During the last two decades, organic light-emitting diodes (OLEDs) have attracted considerable interest owing to their promising applications in flat-panel displays by replacing cathode ray tubes (CRTs) or liquid crystal displays (LCDs). Electroluminescence is the emission of light from materials in an electric field, and in the 1960s [1] this phenomenon was observed from single crystals of anthracene. Despite the high quantum efficiency obtained with such organic crystals, no application has emerged owing to the high working voltage required as a result of the large crystal thickness and poor electrical contact quality. Nevertheless, these studies have led to a good understanding of the basic physical processes involved in organic electroluminescence, i.e. charge injection, charge transportation, exciton formation and light emission. A first breakthrough was achieved in 1987 by Tang and Van Slyke [2] from Kodak when they reported efficient and low-voltage OLEDs from p-n heterostructure devices using thin films of vapour-deposited organic materials. Another development of technological interest was the 1990 discovery of electroluminescence from polymers at the University of Cambridge [3]. The key advantages of OLEDs for flat-panel display applications are their self-emitting property, high luminous efficiency, fullcolour capability, wide viewing angle, high contrast, low power consumption, low weight, potentially large area colour displays and flexibility. Several approaches have been described to build full-colour displays [4], such as side-by-side patterning of discrete red (R), green (G) and blue (B) sub-pixels, RGB tuneable pixels, filtering of white OLEDs, down-conversion of blue emitting OLEDs or filtering of broad-band-emitting OLEDs.

2   Theoretical Background

This section intends to make an overview and general context about the physical principles behind the experiment done, with the purpose of making comprehensive the obtained results, analysis and conclusions.

2.1   Device Structure

The basic structure of an OLED consists of a thin film of organic material sandwiched between two electrodes, as depicted in Fig. 1. Organic electroluminescent (OEL) materials, based on π-conjugated molecules, are almost insulators, and light is produced by recombination of holes and electrons which have to be injected at the electrodes. The anode is transparent and is usually made of indium tin oxide

(ITO), while the cathode is reflective and is made of metal. The thickness of the organic layer is very thin, between 100 and 150 nm. When a voltage is applied between the electrodes, charges are injected in the organic material, holes from the anode and electrons from the cathode. Then, the charges move inside the material, generally by hopping processes and then two opposite charges (electron-hole pair) recombine to form excitons. The location of the recombination zone in the diode is a function of the charge mobility of the organic material as well as of the electric field distribution.
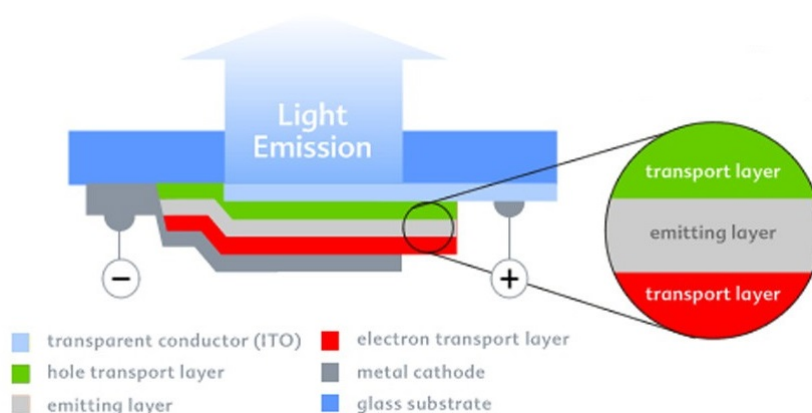

Figure 1: Basic structure of OLED Device. [8]

The colour of the photon is a function of the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of the electroluminescent molecule. For efficient hole injection from the anode, a low barrier is required in respect of the HOMO level of the organic material (typically 5–6 eV). ITO is usually used for the anode because of its high work function as well as its good transparency in the visible range. Hole injection is further enhanced by oxygen plasma treatment of the ITO [5, 6]. On the cathode side, a low barrier for electrons is needed in respect of the LUMO level of the organic material (typically 2–3 eV).

2.2   Functional Layers of the Device

Electroluminescence occurs as a consequence of charges – i.e. electrons and holes – being injected into a semiconductor material where they meet and recombine under the emission of photons. Originally observed in anthracene crystals 1, efficient EL has been reported by Tang and his coworkers [2]. Since then, highly efficient OLEDs have become complex multilayer systems, where various functions like charge

transport, recombination, among others. are separated to reach maximum device efficiency. Figure 2 illustrates a simple OLED sequence with its functional layers. A simple OLED with polymer emitter made of several thin films which are deposited on a glass substrate. It mainly consists of substrate, anode, hole transport layer (HTL), organic semiconductor emitting layer and cathode. Indium Tin oxide (ITO), is the anode of this organic device because ITO possesses a high work function of about 4.8 eV and it is not only highly conductive but also transparent. Elements with high work functions can help to inject holes. The ITO glass substrate is followed by a hole transport layer (HTL) which uses the water soluble PEDOT:PSS. PEDOT:PSS is an organic material and the HOMO level of PEDOT:PSS is between the HOMO level of emitting layer and the work function of ITO so that it can reduce the barriers to transport holes.
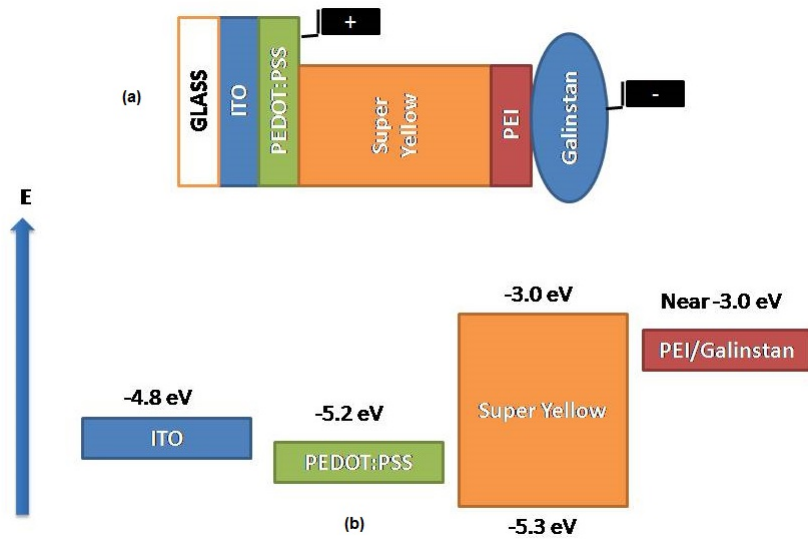

Figure 2: OLED structures and simple band diagram for OLED device functional layers.

The active layer is above HTL, works as an emitting layer. Electrons and holes are combined in this layer and emit light. This active layer is a toluene soluble layer of Super Yellow which is an organic material.

The layer of Polyethylenimine (PEI), which is a surface modifier used to reduce the work function of cathode Galinstan to a level closed to the LUMO level of Super Yellow [7]. It is on top of Super Yellow. Cathode Galinstan is a liquid metal alloy contains gallium and indium. Work function of cathode metal material is low so that electrons are easier to be injected from metal.

Anode injects holes while cathode injects electrons which are pushed to pass through layers to the middle emitting place by applied voltage. Other layers are designed to help transport these carriers. Electrons and holes recombine in emitting layer and create a photon whose frequency is determined by difference between LUMO and HOMO of the emitter. In this lab, Super Yellow emits light in mainly yellow spectrum. Light comes out in the direction from emitting layer to anode, as the cathode metal alloy galinstan is reflective.

2.3 OLED Characterization: Key Concepts

OLEDs are characterized in terms of physical and optical technical values which can be determined by analyzing calibrated emission spectrum of an OLED. For this purpose familiarization with the following photometric parameters is necessary.

1. **Luminous Intensity, I_v:** Luminous intensity is a measure of visible power per solid angle, expressed in candela (lumens per steradian).

2. **Luminance, L_v:** Luminance is a measure of the flux density per unit solid viewing angle expressed in cd/m^2.

3. **Luminous Flux, ϕ_v:** Luminous flux is a measure of the power of visible light. Photopic flux, expressed in lumens, is weighted to match the response of the human eye, which is most sensitive to yellow-green.

4. **Illuminance, E_v:** Illuminance is a measure of photometric flux per unit area, or visible flux density. Illuminance is typically expressed in lux (lumens per square meter) or foot-candles (lumens per square foot).

3 Experiment Procedure

This section goes into details of the architecture, fabrication and characterization steps of the OLED fabricated in this laboratory.

3.1 OLED architecture and fabrication

The architecture of the OLED built is shown in Figure 3. The first layer is the anode which was made with ITO (tin doped indium oxide), a highly conductive and transparent material with a work function of 4.8 eV. The ITO glass substrate of $25mm$x$25mm$ is then coated with two polymers, PEDOT:PSS and SY (Super

Yellow), the first one soluble in water and the second one in toluene, the different solubility of these two layers guarantee that they do not destroy each other during the coating deposition processes. The PEDOT:PSS layer acts as the hole transporter and the SY is the emitting polymer, thus, it acts as the active layer.
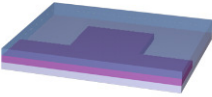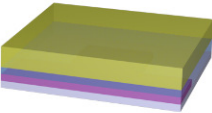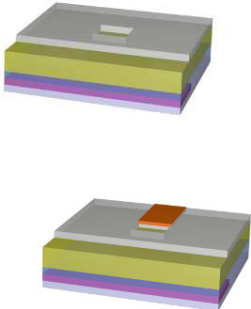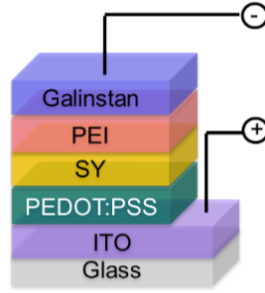

Figure 3: OLED architecture based on Super Yellow and PEDOT:PSS [14].

Afterwards, the second electrode, the cathode is built using a liquid metal at room temperature called Galinstan, however, one more layer called PEI (Polyethylenimine) is deposited before to decrease the work function of the Galinstan and to facilitate the transport of electrons to the active layer.

The fabrication of the OLED involved different steps, times and details are summarized and explained in Table 1.

Table 1: OLED Fabrication procedure (drawings taken from [14]).

Stage	Scheme	Description
1. Anode fabrication		• The ITO glass substrate is first etched with hydrochloric acid for 7 minutes, to define the surface of the electrode and active area. • Afterwards, the samples are cleaned 5 minutes in acetone (highly corrosive solvent) and 5 minutes in isopropanol, both using a ultrasonic basin. • Then the samples are dried with nitrogen gun and deposited into the plasma chamber to be treated with O2 plasma during 2 minutes.

2. Deposition of the PEDOT:PSS		• The samples are transferred to a glove box with Nitrogen atmosphere (the small chamber to insert the ITOs substrates into the box, was evacuated and filled 3 times with Nitrogen). • The solution mixture for the deposition of the first layer corresponds to $150\mu l$ of PEDOT:PSS diluted with ethanol with a proportion of 1:3. The deposition is done with a two-step process using a spin coater, first at $500rpm$ during 3s and afterwards $4000rpm$ during 30s. • Then, the samples are heated at $120°C$ to evaporate the residuals of water.
3-4. Deposition of SY and PEI		• The SY coating is deposited in a two step process using the spin coater, first at $1000rpm$ during 45s and then at $4000rpm$ during 3s , using a solution of $180\mu l$ with a concentration of $4g/l$ (this layer is a bit tricky because if the SY is not dropped over the whole sample's surface, there will be some areas without active layer after the spin coating). • Later, the sample is heated at $80°C$ during 10 minutes and the third layer (PEI) can be deposited using $150ml$ and $5000rpm$ during 30 seconds.
5. Fabrication of cathode (sticker, copper foil and deposition of Galinstan)		• An asymmetric sticker with a square hole ($5mm$x$5mm$) for the active area is fixed over the PEI layer. • Then a copper foil tape is pasted to create the contact with a drop of Galinstan on the active area
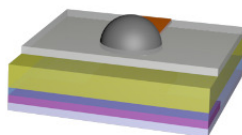
- The drop of Galinstan is distributed over the square by pressure using common tape.

- Afterwards the OLED can be tried with 5-6V.

4 OLEDs characterization

After the fabrication of OLED, it can be characterized immediately in a clean room. For this purpose a spectrometer placed inside a glove box was used. All three samples, one by one, were placed onto a plateholder designed specifically for the geometry of the device. In order to center the measurable area a pilot laser beam and motorized x-y control were used.

A swept of voltages was applied to the OLED, and the emitted light for each value was collected through an optical fiber. The data were recorded automatically through a computer software obtaining the spectrum of the device and the Energy density (W/m^3) vs. Voltage (V) data. The results and discussion are presented in the following sections.

4.1 Current density vs. voltage characteristics. Spectrum dependence on the applied voltage

Figure 4 shows the current density, J $[mA/cm^2]$ vs. Voltage, U $[V]$ for OLED1, OLED2 and OLED3, respectively. For all three samples not linear current dependencies on voltage are observed, this proves the semiconductor nature of the material. Therefore, to have any current running through the device, the voltage applied should be equal at least to the energy of the band gap given in the theoretical framework. According to the energy level diagram of the OLEDs layers given above, the theoretical value of the onset voltage should be slightly more than $3V$ (energy level of the PEI layer is not known exactly). While the characteristics show that this value is actually equal to approximately $4V$ for OLED1 or $4.5V$ for OLED2 and 3.
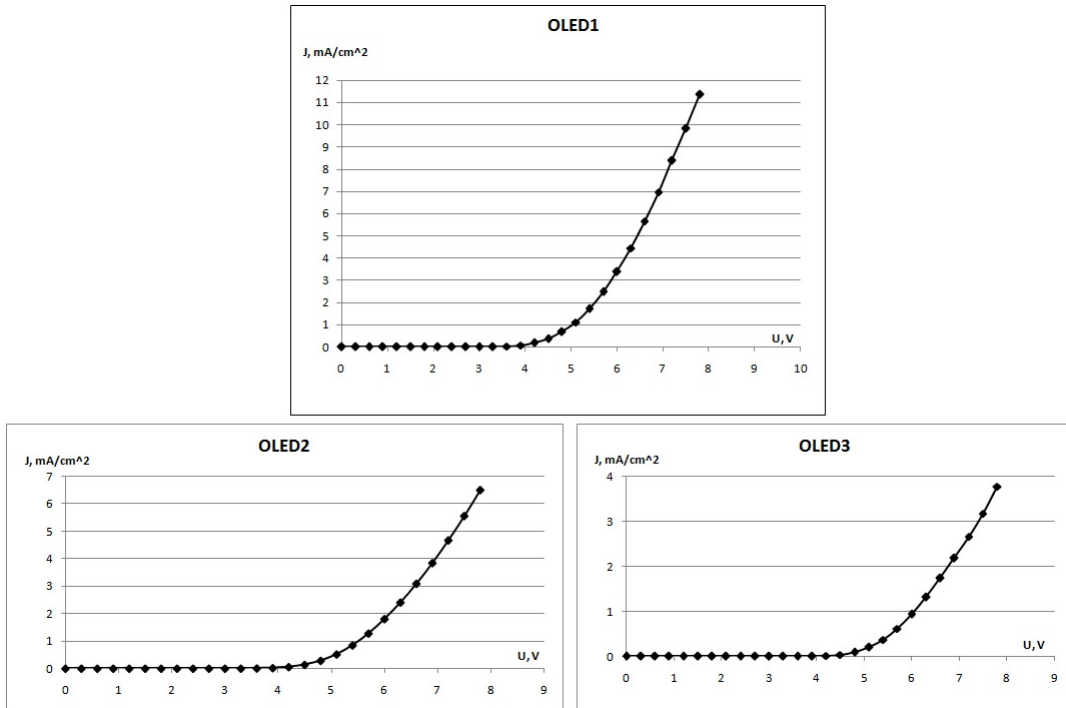
Figure 4: Current density-voltage characteristics.

4.1.1 Active area usage analysis

Figure 5 shows how fully the active regions of the manufactured OLEDs are used.
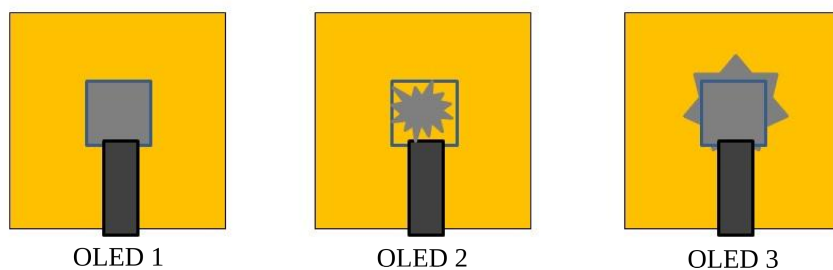

Figure 5: Active area usage for the fabricated OLEDs.

The square in the middle displays the active area region and light grey figures represent qualitatively the cathode material spread over it. Matching the current-voltage characteristics with the active area used in the corresponding OLED, one can see that the efficiency of the device in sense of brightness and the amount of luminous flux directly depends on the active volume usage (OLED1 vs. OLED2). It

says that it is quite important to spread a cathode all over the active area uniformly. However, even by carrying out this condition there are still other drawbacks exist (OLED1 vs. OLED3), which could be caused by different types of imperfections in the layers and between them.

4.2   Spectral energy density

Figure 6 shows a plot for the spectral energy density vs. wavelength from $350nm$ to $750nm$ for different voltages applied to OLED1. As the measured current density vs. voltage characteristics showed (Figure 9) there is no light emitted by the device below $4.5V$ is expected. And the spectrum measured below this voltage would represent none other than the noise of the device. From the theory one knows, that with increasing a voltage (and increasing a temperature, as well) the peak of the emission spectrum shifts from the long wavelength range to the visible range. However, the plotted curves of the OLED1 spectrum for different voltages have almost the same peak, which deviates around 552-558nm, while the intensity of the emission grows up with the increasing voltage.
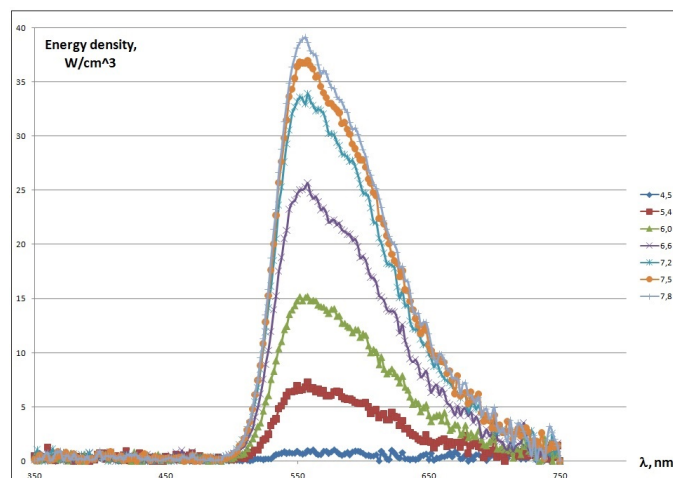

Figure 6: OLED1 spectrum for different applied voltages.

4.3   Eye sensitivity

The spectra curves for the three fabricated OLEDs with an applied voltage of $6.6V$, are displayed in Figure 7. The averaged measured value of the peak wavelength is $559nm$. While, according to the CIE coordinates the color perceived by a human

eye corresponds to approximately $575nm$ (Figure 8a). The difference between the observed and real wavelengths comes from a specific human eye sensitivity spectrum (Figure 8b). Historically a human eye evolved and adapted to the sunlight spectrum by a manner to be able to perform the highest sensitivity in a waverange, which is comfort for living. That is why one should always consider the eye sensitivity diagram for the perception correction when dealing with the light emission which is essential for human being. Nowadays, the maximum wavelength sensitivity of the eye falls at $555nm$ for a daylight and at $550nm$ for a nightlight, respectively [15].
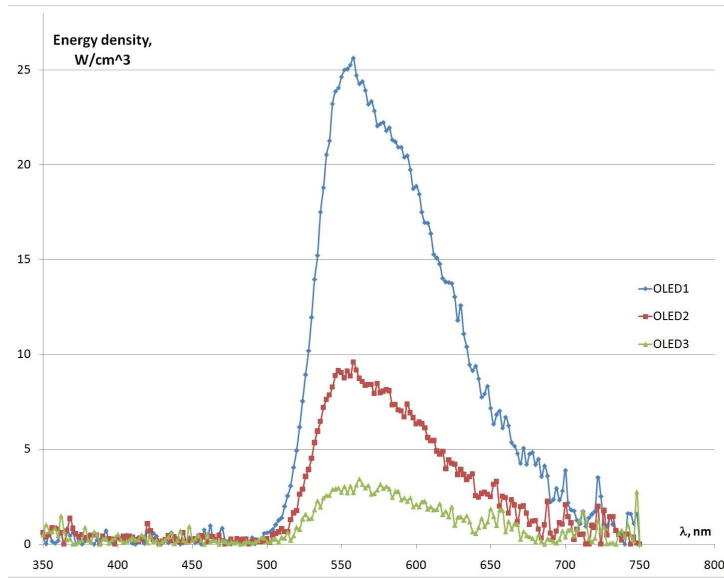

Figure 7: Spectrum of OLED1, 2, 3 at $6.6V$ of applied voltage.

Table 2: CIE measured coordinates for the manufactured OLEDs

	OLED 1	OLED 2	OLED 3	Average
CIE 1931 x	0,4733	0,4658	0,4779	0,4723
CIE 1931 y	0,5208	0,5264	0,5342	0,5271
CIE 1931 z	0,0059	0,0078	0,0121	0,0086
Peak wavelength (nm)	558	558	562	559

On the other hand, it can be noticed from Table 2 that the spectrum of manufactured OLEDs matches pretty high to the human eye spectrum, what says about the color effectiveness of such light sources.
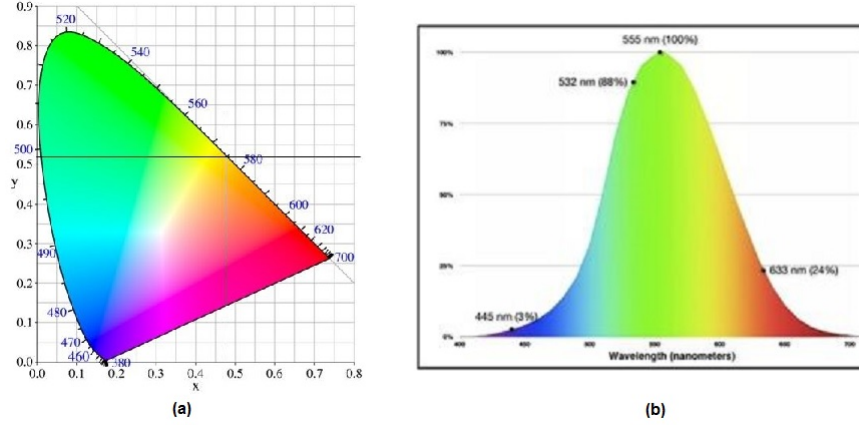
Figure 8: Human eye color sensitivity. (a) CIE diagram (Taken from [16] and (b) Eye sensitivity diagram (Taken from [15])).

4.4 Luminance, power efficiency, current efficiency calculation for spectrum of OLED1 at 6.6V

To calculate the luminance, power efficiency and current efficiency in the first step the luminous flux should be known. The luminous flux was calculated by the following formula:

$$\phi_v = KA \sum_{i=1}^{N=41} W(\lambda_i)V(\lambda_i)\lambda_i = 2.79 \times 10^{(}-2)lm \tag{1}$$

Where K is a constant, equals to 683 $[lm/W]$, A is an active area, 0.25 $[cm^2]$, W is a density of energy $[W/cm^3]$ for a given wavelength, λ $[nm]$, V (λ) is a human eye spectral sensitivity factor. The luminous flux was calculated for a wavelength range from $380nm$ to $780nm$ with a Δ λ step of 10 nm.

In this case the OLED was considered as a Lambertian source with the luminance independent on the viewing angle and thereby:

$$L_v = \frac{\phi_v}{\pi A} = \frac{2.79 \times 10^-2 lm}{3.14 \times 0.25 \times 10^-4 m^2} = 355 \frac{cd}{m^2} \tag{2}$$

The power efficiency is defined like a ratio between the obtained (luminous) power $[lm]$ and the applied (electrical) power $[W]$. Knowing the active area the power applied to the device can be found from the current density-voltage characteristics.
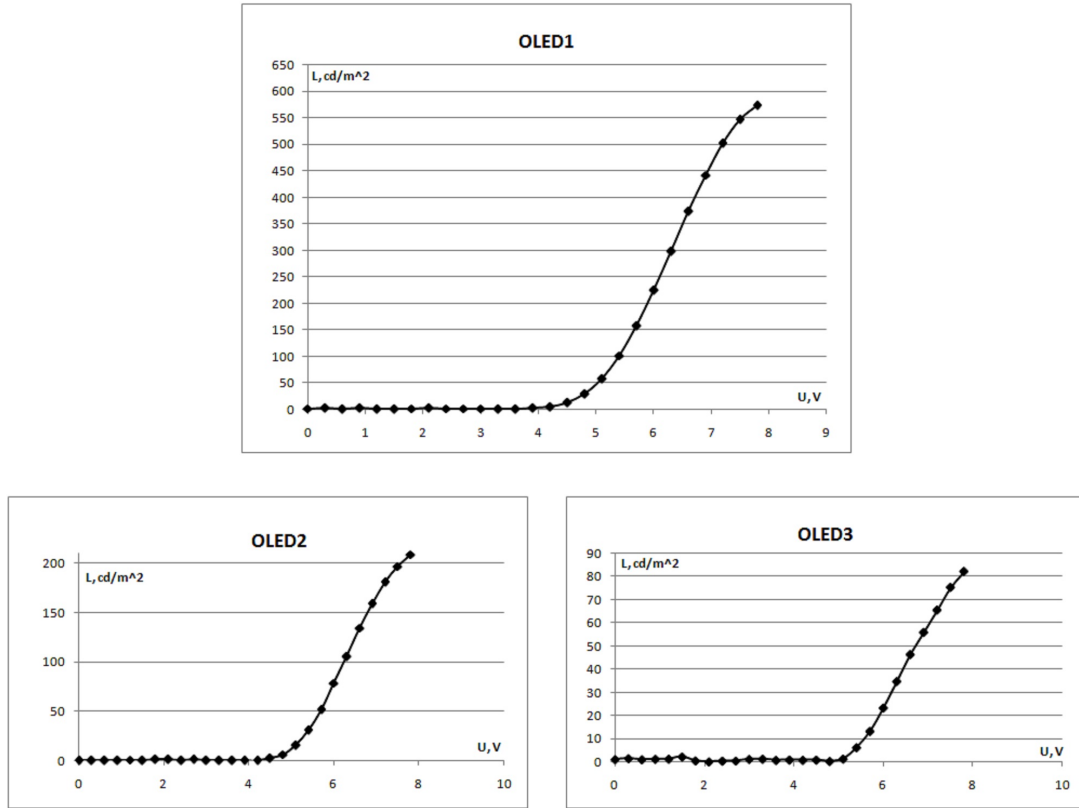
Figure 9: Luminance - voltage characteristics.

According to Figure 4, the current density value for OLED1, when the applied voltage is equals $6.6V$, is $5.658\ mA/cm^2$. And now one can calculate the power efficiency of the device for $6.6V$:

$$\eta_p = \frac{\phi_v}{\phi_e} = \frac{\phi_v}{JUA} = \frac{2.79 \times 10^{-2} lm}{5.658\frac{mA}{cm^2} \times 6.6V \times 0.25cm^2} = 2.98\frac{lm}{W} \tag{3}$$

While the current efficiency can be calculated from luminance-current density ratio:

$$\eta_c = \frac{L_v}{J} = \frac{355\frac{cd}{m^2}}{5.658\frac{mA}{cm^2}} = 6.27\frac{cd}{A} \tag{4}$$

4.5   Luminance vs. Voltage characteristics. Onset voltage.

Luminance of the device as well as the current density depends on the voltage. $10cd/m^2$ is a threshold value from which OLED is considered starting to shine on. The voltage related to this value is called the onset voltage and it can be determined from the luminance vs. voltage characteristic curves.

The averaged onset voltage found from the luminance vs.voltage characteristics for three samples is $4.5\ V$. It is certainly larger than the voltage corresponding to the energy barrier discussed in the beginning of this section. However, it should be remembered that the theoretical number is not precise, as the energy level of PIE is not known exactly, the only thing we know is that the minimum applied voltage should be no less than $3\ V$. Moreover, a real number is always larger due to different kind of imperfections in the device such as layers in-homogeneity, impurities in the layers, among others.

5   Conclusions

OLEDs were manufactured in the clean room by using the technique of spin coating for the deposition of the polymer layers. And it was learnt how sensible the cathode layer is for the final performance of the device.

We have understood the advantages of organic sources in comparison with other ones and the important photometric parameters to characterize such sources.

According to the luminance parameter OLED 1 has a better performance than the other ones.

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