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## Scientific Report

**ESF ORGANISOLAR exchange grant number 2010**

**June 2008 – September 2008**

Exchange between Hasselt University (IMO), Belgium and

Universitat de Valencia (ICMol), Spain with the purpose to

”Apply Functionalized Poly(3-alkylthiophene)s in Organic Solar Cells”

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## Introduction

In the field of plastic electronics, the development and use of conjugated polymers has, since the end of the 1970's, lead to the first commercially available applications today, for example the XEL-1 OLED-TV by Sony. Conjugated polymers combine all the advantages of the polymer-class materials such as light weight, high mechanical strength and flexibility with semi-conductive properties. This opens a broad spectrum of new possibilities for electronic applications.

Poly(3-alkylthiophene)s (P3AT)s are soluble conjugated polymers which are also semiconductors in their undoped state. These polymers are applied as hole conducting or p-type material in the active layer of the bulk heterojunction plastic solar cells. Especially poly(3-hexylthiophene) (P3HT) is one of the workhorse materials, together with the soluble C<sub>60</sub> derivative, i.e. Phenyl-C<sub>61</sub>-Butyricacid-Methylester ([60]PCBM), used as electron acceptor or n-type material, fig.1. The synthesis of P3ATs is well documented and can be achieved using various synthetic routes<sup>1-4</sup> (oxidative polymerization in presence of FeCl<sub>3</sub>, Rieke, McCullough, GRIM method, Suzuki or Stille couplings). Experience in the field of synthesis of functionalized P3HT has been gathered at the University of Hasselt.

The polymers made at the UHasselt are novel functionalized polythiophene copolymers with 3HT, produced using the Rieke method<sup>5,6</sup>, yielding materials with regio-regularity over 90%. Such materials have a tendency to crystallize upon annealing, favouring high energy conversion efficiency in solar cells<sup>7</sup>. The regio-regular (RR) crystalline material displays superior properties compared to regio random polymers. The functionalized polymers have the same degree of regio-regularity compared to P3HT synthesized with the same method, so that the material properties and hopefully also the performance in organic solar cells of the novel PTs are minimally degraded due to insertion of functional groups.

At the UHasselt it is possible to synthesize copolymers of P3HT containing ester, acid, or alcohol functionalities in the side chain. The acid and alcohol functionalities can be coupled to complementary functional groups using well documented chemical reactions. This way RR P3ATs functionalized with a variety of molecules can be obtained, which leads to a broad spectrum of possibilities to engineer the molecular structure towards different properties. Introduction of functional groups on the polymer side chains allows to explore the possibilities of several secondary functionalities on this material.

The purpose of the visit to Valencia is the application of the produced polymers in plastic solar cells and OLEDs, using the expertise present at the ICMol in the preparation of molecular opto-electronic devices. This way we mean to determine the influence of inserted functionalities on the performance of RR P3AT in several devices.

## Outline

### 1. Production of plastic solar cells using functionalized poly(3-alkylthiophene)s

The production of plastic solar cells using novel functionalized copolymers of poly(3-hexylthiophene) (P3HT, fig. 1) has been evaluated. This will allow us to determine the influence of several functionalities introduced into RR P(3AT)s on the production and characteristics of devices, prepared with these materials. The purpose is to make solar cells using materials with a certain percentage of ester, alcohol or acid functions in the polymer side chains. This percentage may vary from 10% to 50%. Results from the novel copolymers will be compared to the results of reference P3HT. With the obtained information a prediction can be made of the behaviour of functionalized polymers in a device, and the properties of these devices.

Additionally, an attempt is made to introduce additional absorbing groups via postpolymerization functionalization in the side chain of the novel copolymers using covalent linkage.

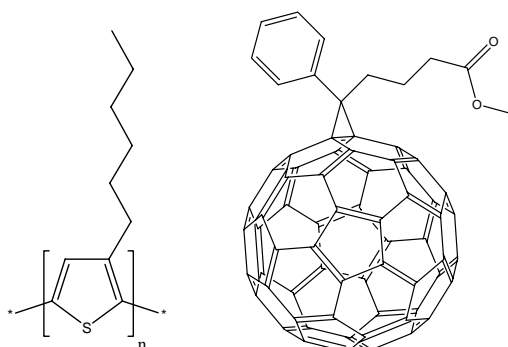


Figure 1: P3HT (left), PCBM (right)

### 2. Enhanced attraction between a functionalised polymer and metal oxide electrodes

The effects of a possible enhanced attraction between the copolymers having a percentage of polar side groups (as acid groups) and the electrodes will be investigated. These materials will be grafted on metal oxide planar surfaces that function as electrode.

### 3. Production of plastic solar cells using ionized poly(3-alkylthiophene)s

Copolymers where the acid functionalities are converted to a salt can be used in its ionized form. These compounds can be processed from aqueous solutions, allowing the use of a “green solvent” in the production of solar cells. An ionized polymer is useful as a polymeric electrolyte in a dye sensitized solar cell. Also, the ions could cause an improved electrical contact between polymer and a metal oxide cathode. Ions near the electrode create a large electric field, which should lead to a higher charge injection from the electrodes to the material directly or via the formation of p- and n-doped regions near anode and cathode. Therefore, salt-containing polymer will be applied as charge-injecting layer.

## Obtained results

### 1. Application of functionalized poly(3-alkylthiophene)s in organic solar cells

To determine the influence of a certain percentage of functionalized side chains, which we introduced into the P3HT structure, we compare the characteristics of devices with these materials to a reference P3HT/PCBM solar cell. This solar cell has an often used configuration, shown in Figure 2. All copolymers are applied in solar cells, prepared according to the same method, with the same characteristics as the one depicted.

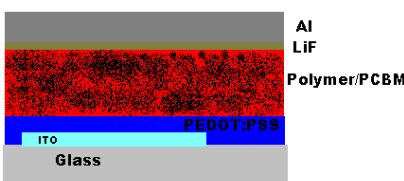


Figure 2: Plastic solar cell configuration ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al

#### 1.1 Reference solar cell with P3HT:PCBM

The solar cells in this report are prepared according to a standardized method. Following to the cleaning procedure of the ITO-patterned glass substrate, this is treated with UV/O<sub>3</sub> for 15 minutes. PEDOT-PSS is spin-coated from an aqueous solution and heated for 10 minutes on 130°C. The blend is deposited by spin coating from a polymer/PCBM (1/1 w/w%) solution in chlorobenzene, which is stirred overnight on elevated temperature previous to filtration over a PTFE filter. LiF and Al or Ba and Ag are evaporated under high vacuum ( $<3.10^{-6}$  mbar) to act as a cathode.

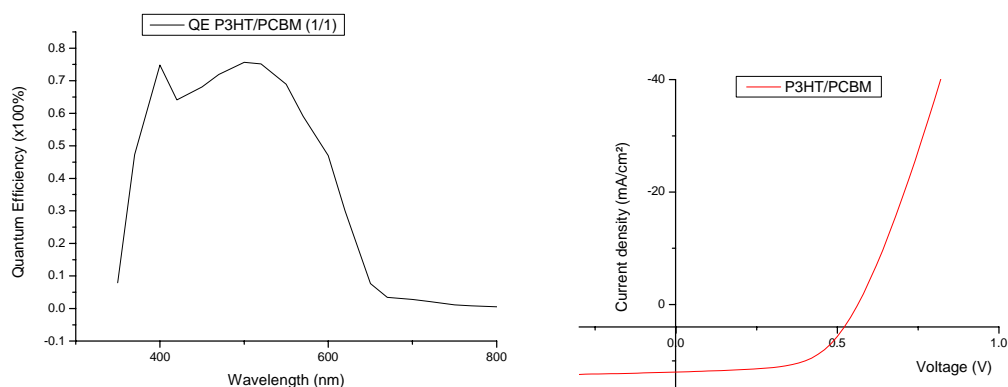


Figure 3: EQE and J-V curve of /PEDOT:PSS/P3HT:PCBM/LiF/Al solar cell

The device characteristics for this solar cell with an active layer of 150nm P3HT/PCBM (1/1) are shown in table 1, 2 and 3 to compare the solar cells made with copolymers containing functional groups in the side chains. To evaluate device performance, external quantum efficiencies (EQE) and current density (J) – voltage (V) curves are measured.

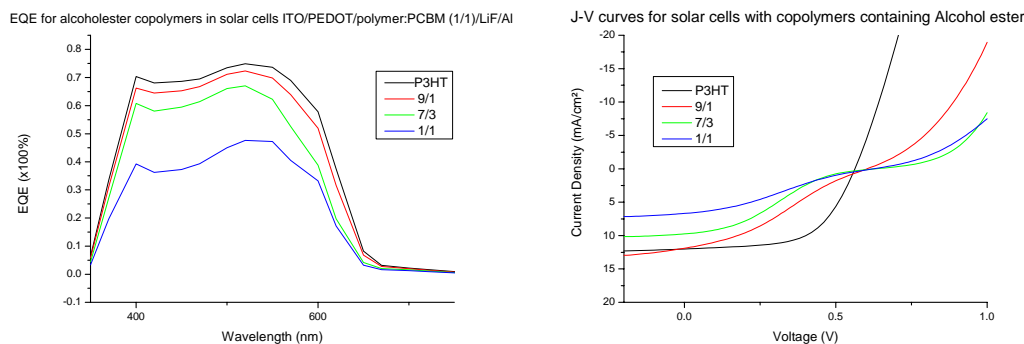
## 1.2 Solar cells made from copolymers containing several ratios of alcohol esters functions

Device characteristics of solar cells made with copolymers (COPO) containing an increasing percentage of alcohol ester functions (m/n ratio, n being the alcohol ester fraction) are shown in Table 1. The measured EQE and J-V curves are depicted in Figure 4. The 9/1 copolymer contains 1 repeating unit with an ester in the side chain for 9 hexylthiophene units. In total this copolymer contains 10% ester side chains. The 7/3 copolymer contains 30% and the 1/1 copolymer 50% of ester side chains.

Solar cells with the copolymers COPO/PCBM showed a J-V curve with S-shape, causing a low fill factor and a drop in efficiency compared to the reference P3HT/PCBM.  $J_{sc}$  is decreasing with the increased content of alcohol ester functional groups compared to the reference P3HT/PCBM. Some conclusions may be drawn from these measurements. With an increasing ratio of ester groups in the side chains the EQE and short circuit current ( $J_{sc}$ ) drop to a lower level, while the open circuit voltage ( $V_{oc}$ ) rises very slightly. This study results in a series of solar cells with less efficiency compared to the pristine P3HT solar cells. However, the copolymer with 10% ester shows only a slightly lower EQE: due to a layer thickness of 200nm, compared to the 150nm of the P3HT/PCBM solar cell, a higher  $J_{sc}$  is measured.

**Table 1: Performance of devices containing alcohol-ester m/n-copolymers**

COPO (m/n)	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF (%)	Eff (%)
P3HT	0.56	10.13	59	<b>3.38</b>
9/1	0.60	10.81	29	<b>1.88</b>
7/3	0.63	8.45	27	<b>1.45</b>
1/1	0.63	6.06	28	<b>1.05</b>



**Figure 4: EQE and J-V curve of /PEDOT:PSS/copolymer:PCBM/LiF/Al solar cell**

### 1.3 Solar cells made from copolymers containing various ratios of acid esters

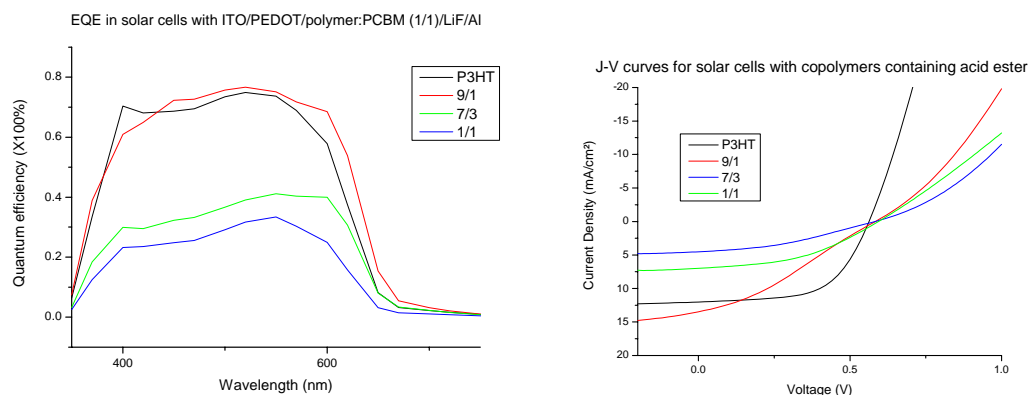
**Table 2: Performance of devices containing acid-ester m/n-copolymers**

(Co-)Polymer (m/n)	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF (%)	Eff (%)
P3HT	0.56	10.13	59	<b>3.38</b>
9/1	0.58	12.07	30	<b>2.17</b>
7/3	0.59	6.21	49	<b>1.80</b>
1/1	0.58	4.25	36	<b>0.90</b>

As for devices with alcohol esters in the side chains, described in §1.2, EQE and J-V curves are measured for devices made with copolymers containing esters of acid. Characteristics of solar cells made with these copolymers are shown in Table 2.

Here, the presence of 10% ester side chains has a beneficial influence on the EQE, resulting in a higher  $J_{sc}$ , measured for a layer thickness of 170nm. For copolymers with 30 or 50% of ester side chains EQE and  $J_{sc}$  drops to about half the value of the 10% copolymer.

An increase of ester groups above 10% causes the EQE and  $J_{sc}$  to drop to a lower level, while the open circuit voltage ( $V_{oc}$ ) is quite constant. The solar cells with these copolymers also show a low fill factor, causing a low efficiency (Table 2).



**Figure 5: EQE and J-V curve of /PEDOT:PSS/copolymer:PCBM/LiF/Al solar cell**

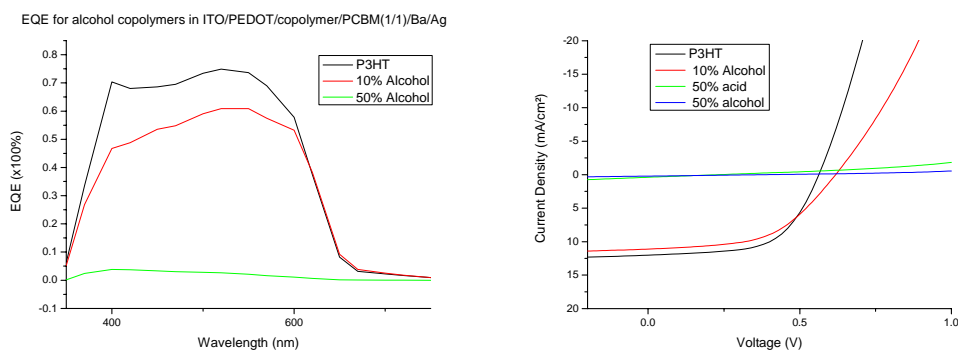
### 1.4 Solar cells made from copolymers containing free alcohol or acid groups

With the conversion of esters in the side chains of the copolymers to the corresponding acid or alcohol, the solubility of the materials is strongly affected. For this reason the copolymers with 50% acid and 50% alcohol are processed in a THF solution. This apparently affects the system so strongly that  $J_{sc}$  drops dramatically and efficiency is brought down to about 0.05% (Table 3).

A copolymer with 10% of alcohol is still soluble in chlorobenzene when it is stirred at a higher temperature. In devices made with this copolymer, the EQE and  $J_{sc}$  decrease, but the  $V_{oc}$  is affected positively, resulting in an efficiency of 2.8% compared to 3.4% for P3HT/PCBM.

**Table 3: Performance of devices with copolymers containing free alcohol and acid functions**

(Co-)Polymer (m/n)	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF (%)	Eff (%)
P3HT	0.56	10.13	59	<b>3.38</b>
9/1 alcohol	0.62	8.73	52	<b>2.82</b>
1/1 alcohol	0.39	0.54	26	<b>0.06</b>
1/1 acid	0.25	0.96	25	<b>0.06</b>



**Figure 6: EQE and J-V curve of /PEDOT:PSS/copolymer:PCBM/LiF/Al solar cell**

## Summary

In the section on the preparation of solar cells using functionalized copolymers we noticed that an increasing percentage of functionalities in the side chains cause a drop in EQE and  $J_{sc}$ . Also, due to a low FF, no optimal efficiency is obtained. It is possible to conclude that the introduced functionalities are the cause of drop in  $J_{sc}$ , probably due to a loss in crystallinity of the polymers. This may hamper the hole conductivity in the material, or may have the consequence that the ideal morphology is not obtained. Trying a range of solvents or different annealing steps could influence the degree of crystallinity and the morphology in the active layer, so that higher  $J_{sc}$  and efficiency could be reached. It is clear that 10% of side chains can be introduced without severely influencing the device performance. The influence depends on the nature of the functional group in the side chain, but for small ester- or alcohol groups, the influence on  $J_{sc}$  is limited. When introducing more than 10% of functionalities, the  $J_{sc}$  drops to a significant lower level. With optimization of processing conditions for materials containing higher ratios of functionalities, it may be possible to obtain better EQE and  $J_{sc}$  as we found here. In general, we need better fill factors to obtain higher efficiencies.

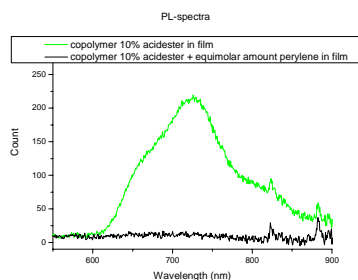
## 1.5 Perylene substituted polythiophenes

A possible way to increased efficiency in plastic solar cells is to broaden the absorption window of the polymer material. Since P3HT absorbs light with wavelengths ranging from



400-600 nm, the addition of a molecule absorbing in the 600-700 nm region on the polymer structure will cause an increased absorption of energy from the sunlight. This could lead to a higher photocurrent in a solar cell and an increased efficiency.

Perylenes are a class of light absorbing molecules, which also can be used as electron acceptor, as evidenced by the quenching of photoluminance of P3HT (Figure 7) in a film when a certain amount of perylene is added.

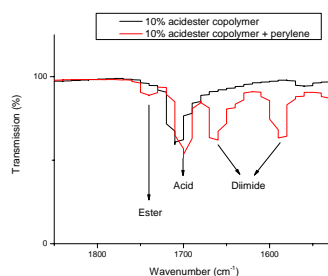


**Figure 7: PL-spectra of a copolymer film and a copolymer/perylene blended film**

The group of organic chemistry at the Universidad Miguel Hernandez in Elche, Spain provided a functionalized perylene compound. Depending on the structure of the perylene, the For this reason we tried to attach covalently a perylene to a functionalized polythiophene

When the crude product is analyzed, the absorption of a C=O of an ester is visible on the Infra red spectrum around  $1740\text{ cm}^{-1}$  (Figure ). As the C=O absorption of the acid function is still present at  $1700\text{ cm}^{-1}$ , some perylene is covalently bonded to the polymer, but no complete functionalization of the available acid functions is obtained.

Due to an elaborate purification required for the perylene compound, this product was not available in large quantities. Together with a limited solubility of the starting copolymer, the small excess of reagent in which the perylene-OH was added, even in the presence of the coupling reagents, was not sufficient to drive post-functionalisation to completion.



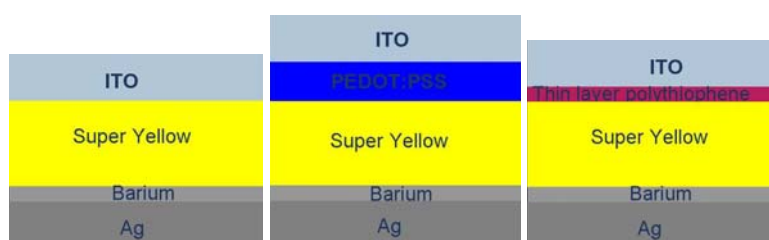
**Figure 8: FT-IR spectra of copolymer**

The crude product was purified using a soxhlet extraction with pentane to remove any remnants of non reacted perylene. Unfortunately, after purification the product could not be extracted due to solubility problems, and so it was impossible to apply this product in any device for evaluation.

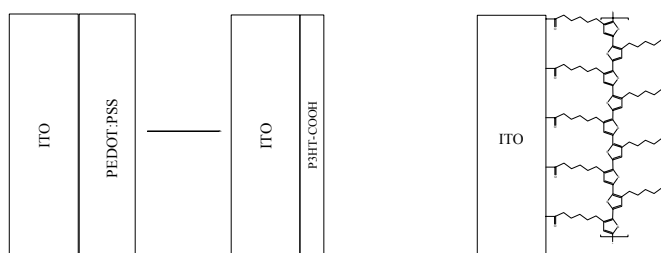
## 2 Enhanced attraction between a functionalised polymer and metal oxide electrodes

### 2.1 OLEDs with a thin layer of P3HT-COOH grafted to the ITO surface

One application of acid-functionalized polythiophenes is the grafting of these materials on metal oxide planar surfaces. The additional polythiophene layer can improve the electrical contact between the metal oxide and the polymer and therefore enhance charge injection (Figure 9, right). To be able to judge the influence of this layer, a series of OLEDs with Super Yellow (SY) as light emitting polymer and different configurations is prepared (Figure 9). OLEDs with SY have high light output, so any changes would be readily measurable.

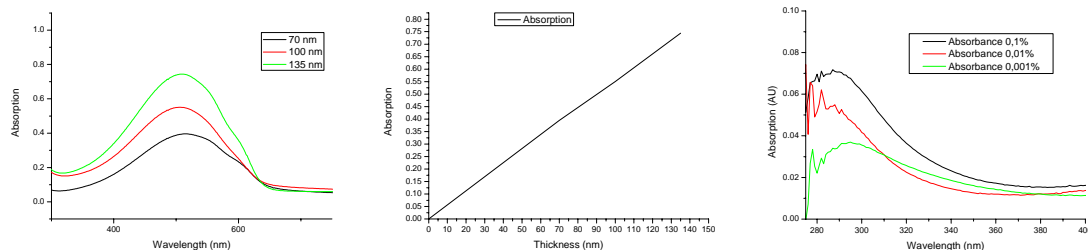


**Figure 9: OLED ITO / SY/ Ba/ Ag (left), PEDOT:PSS as charge injecting layer (mid), polythiophene as charge injecting layer (right)**

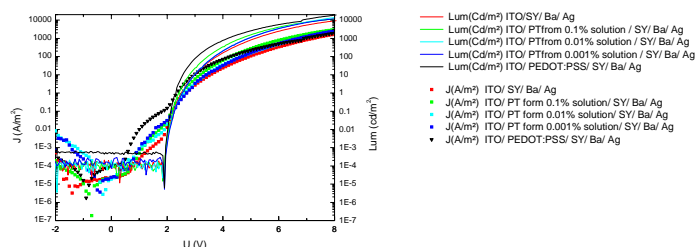


**Figure 10: Changing of charge-injecting layer (left), idealized representation of contact between ITO and grafted polymer (right)**

Devices are prepared after standard cleaning of the substrate. PEDOT-PSS is spincoated from an aqueous solution. The thin layer of acid functionalized P3HT is grafted or physically adsorbed to the metal oxide by putting a glass substrate with Indium Tin Oxide (ITO) or ZnO in a THF solution of the 1/1 copolymer. This substrate is left overnight in this solution and rinsed excessively with THF and acetone. The thickness of the deposited polythiophene layer is depending on the concentration of the polymer solution. The SY layer is then spin-coated at 1000 rpm to obtain a layer thickness of about 60 nm. The Ba/Ag cathode is evaporated in high vacuum ( $<3 \cdot 10^{-6}$ ). Current density ( $J$ , A/m<sup>2</sup>) and luminance ( $L_{um}$ , Cd/A) of these devices are displayed in Figure 12. The thickness of the thin layer of polymer is determined using absorption spectroscopy. The absorption of films with a varying thickness (70, 100, 135 nm) is measured, where there is a linear increase of absorption for thicker films at 510 nm, the wavelength for maximal absorption ( $\lambda_{max}$ ). For the thin films the absorption can be measured, but  $\lambda_{max}$  is shifted to 290 nm. From the absorption maxima, a thickness of 12.5 nm from a 0.1% solution, 9 nm from 0.01% and 6 nm from a 0.001 w% solution can be determined.

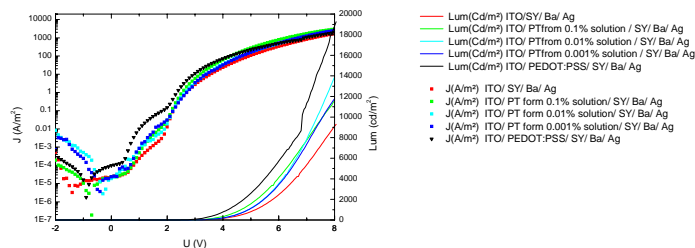


**Figure 11: Absorption of films with varying thickness (left), linear increase of absorption with film thickness (middle), absorption of thin films adsorbed to the ITO substrate from solutions with different concentrations.**



**Figure 12: Logarithmic plot of  $J(\text{A/m}^2)$  and  $\text{Lum}(\text{Cd/m}^2)$  for the series of OLEDs with SY**

In the logarithmic plot (Figure 12) it is visible that the device prepared with PEDOT:PSS as charge-injecting layer emits most light, also this device displays the highest efficacy (Figure 4), improving significantly the device, compared to the one where no charge injecting layer is present.



**Figure 13: Linear plot of  $\text{Lum}(\text{Cd/m}^2)$  for the series of OLEDs with SY**

For the devices made with the grafted layer of acid functionalized polythiophene, we see that there is a beneficial influence of the polythiophene layer in Figure 13, where all devices with the polythiophene layer emit more light compared to the reference device. At high luminance, there is also a slight increase of efficacy, for the polythiophene layer deposited from a 0.01% solution in THF (Figure 14).

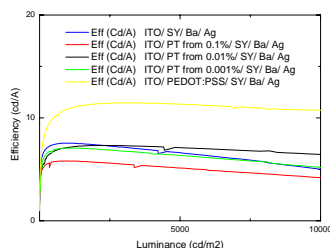


Figure 14: Efficacy (Cd/A) for OLEDs with SY depicted in figure

## 2.2 HyLED with P3HT-COOH grafted to ZnO surface

A hybrid light emitting device (HyLED) uses an inverted device configuration, where ZnO is used as a cathode, and a gold contact is evaporated to be used as an anode. The light emitting polymer is here P3HT. With P3HT-COOH as contact improving layer we see a clear turn-on voltage around 2V (Figure 15), which is similar to an OLED with P3HT as LEP.

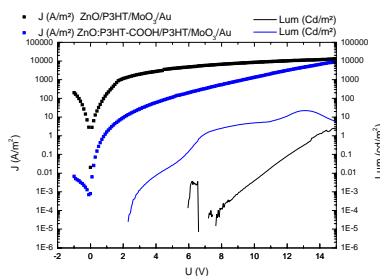


Figure 15: J-Lum-V of P3HT HyLED with and without P3HT-COOH grafted layer

## 3 Production of plastic solar cells containing ionized poly-3-alkylthiophenes.

### 3.1 Salt formation of a 1/1 acid copolymer and use as a charge injecting layer

The 1/1 acid copolymer, where 50% of the side chains on the polymer contain an acid function is only soluble in THF. Upon addition of an aqueous solution of tetrabutylammonium (TBA) hydroxide, the acid functions in the side chain of the polymer form a salt. This polyelectrolyte forms a bright red solution in water, methanol, ethanol and acetone.

After filtration of a 1w% aqueous solution, a 20nm layer is spin-coated onto a cleaned ITO substrate. After spincoating a 60nm layer of SY and vacuum deposition of a Ba/Ag, no light is observed. In a solar cell with P3HT/PCBM and Ba/Ag blend a maximum efficiency of 0.02% and EQE of 0.1% is observed. The salt layer seems to act as an isolating layer, rather than as a charge-injecting one. Attempts to deposit a thinner polyelectrolyte layer, what might diminish the isolating effect, were unsuccessful.

## Future collaboration with host institution

In the future, we will continue developing materials for electronic applications at the Hasselt University. The Universidad de Valencia is one of the partners to apply the produced materials in actual devices. Results concerning electrical characterisation and device performance are a necessary feedback on the material design and may lead to new insights about promising structures for certain applications, leading to a future collaboration with mutual benefits.

## Publications of the results obtained during this grant period

Publications concerning the application of regio-regular functionalized poly-3-alkylthiophenes in plastic solar cells and the grafting of acid functionalized P3HT to metal oxide electrodes are being prepared as a result from this exchange grant.

## Personal benefit of the exchange grant

As a general comment, this exchange period (long stay and work in another European country) was an enriching experience, both scientifically and personally. Hopefully, these experiences will contribute to a higher level of personal and cultural development of me and to a broadening of my view on life and the world. Also, the contribution to my know-how on device preparation and scientific knowledge is valuable, which can affect positively the coming work for my PhD research and hopefully also the results coming from this study.

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