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Electrodeposition of PEDOT perchlorate as an alternative route to PEDOT:PSS for the development of bulk heterojunction solar cells

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Abstract

Bulk heterojunction (BHJ) solar cells were fabricated employing different PEDOT buffers: one deposited by electrochemical potentiostatic synthesis (perchlorate as counter-ion) and the other by casting a commercial polymer (polystyrene sulfonate, PSS, as counter-ion) on Indium Tin Oxide (ITO) electrodes. The experimental conditions to electrosynthesize the PEDOT film and control its thickness were successfully investigated. The blend consisted of [6,6]-phenyl-C₆₁ butyric acid methyl ester (PCBM) as electron acceptor and either the regioregular poly(3-hexylthiophene) (P3HT) or a polythiophene copolymer, functionalized with a porphyrin derivative to improve the absorption of the layer in the visible range, as electron donor.

The morphologies of the PEDOT and the photoactive layers were extensively investigated by atomic force microscopy. The performances of all devices were tested evaluating the power conversion efficiencies which resulted comparable when either PEDOT:ClO₄ or PEDOT:PSS was used as buffer layer.

That proves electrochemical deposition of PEDOT can represent a good alternative to casting for the production of solar cells, since it is less expensive and permits an excellent control of the thickness of the layer.

Keywords: Bulk heterojunction (BHJ) solar cells, electrochemical PEDOT deposition, AFM morphology, PEDOT perchlorate, PEDOT:PSS.

1. Introduction

In the last decades, conductive polymers have been studied due to their interesting characteristics and increasing applications in electronic devices such as sensors, light emitting diodes and organic photovoltaic devices (OPVs) [1]. Polymeric solar cells offer considerable promise for large-scale power generation based on flexible, lightweight material properties and low-cost fabrication.

A solar cell operates through four main steps. The first two consist of the absorption of a photon by the active layer which can promote an electron from the valence to the conducting band and the diffusion of the resulting exciton towards an interface between the donor and the acceptor materials. In the third step the separation of the charge pair at the interface occurs and finally the free generated charges are collected at the electrodes.

The simplest structure of an OPV is a bilayer of donor and acceptor, i.e., the organic active layers are sandwiched between two electrodes with different work functions [2]. One electrode must be transparent, and ITO (indium tin oxide) is usually used for this purpose, the other is very often aluminium which is stable in air. The active layers are generally composed of a conducting polymer (donor material which forms the hole-transport network) and fullerene or its derivatives (acceptor material which constitutes the electron-transport network). In such cells the exciton is separated when the charge carrier moves from HOMO of donor to LUMO of acceptor. However, this device is inefficient, due to short diffusion range of excitons.

Bulk heterojunction (BHJ) cells, consisting of conducting polymer and fullerene blended together, were developed to improve the performances of the OPVs by permitting a better charge transport and reduce the loss of efficiency due to hole-electron recombination processes. In such devices the interface between the donor and the acceptor is enlarged, thus excitons have more chances to diffuse into an internal field and get separated [3]. Moreover, BHJ solar cells are particularly simple to manufacture since the critical interfacial morphology is formed spontaneously by self-assembly during coating.

The active layer of such cells should be more than 100 nm thick in order to absorb most of the light (from 60 to 90%). The donor nanodomains should be of the same size as the exciton diffusion length, which is about 10 nm in organic materials [3], and so the nanomorphology of the photoactive layer is a key factor: the donor and the acceptor materials should form a continuous network to guarantee the collection of the charges at the electrodes. That is favoured by the presence of crystalline domains; therefore the regioregularity of the donor polymer is also an essential element.

BHJ solar cells based on the conjugated regioregular poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C₆₁ butyric acid methyl ester (PCBM) blend have been demonstrated to achieve up to 5% solar power conversion efficiency (PCE) [4,5] which is proposed to be due to a microcrystalline lamellar stacking in the solid state packing [6].

The photocurrent generation efficiency is directly related to the fraction of light absorbed by the photoactive layer, which is function of the absorption strength. An efficient solar cell should have a wide absorption spectrum, so as to create as many excitons as possible. In particular, the absorption of polymer/fullerene devices, primarily governed by the band gap of the semiconducting polymer component, reduces significantly at wavelengths above 600 nm.

One way to overcome the spectral limitation involves the incorporation into the device of additional chromophores with absorption spectra complementary to that of the usual polymer-fullerene binary blend. It has been demonstrated that the NIR absorption of the P3HT/PCBM blend system can be improved significantly by using small dyes like, for example, phthalocyanines [7,8]. Recently, porphyrins have been considered as potential light harvesters for photovoltaic applications because of their key role in photosynthesis, in exciton transport and separation, and in charge transport [9]. Our group has synthesized three regioregular thiophenic copolymers bearing different amounts of a porphyrin moiety in the side chain (poly[3-(6-bromohexyl)thiophene-co-(3-[5-(4-phenoxy)-10,15,20-triphenylporphyrinyl]hexylthiophene)]) obtaining very soluble and easily filmable materials. Their performances as the active layers in bulk heterojunction solar cells were tested and the highest photovoltaic performances were obtained in the presence of the highest porphyrin content, probably because the material exhibits a wider and more intense absorption in the UV-Vis region [10].

The fabrication of an OPV is usually carried out by coating the ITO glass with a thin film (~50 nm) of poly(3,4-ethylenedioxythiophene), PEDOT, an important conducting polymer with a relatively low band gap (1.6-1.7 eV) and a high degree of visible light transmittivity [11, 12], which is known to be efficient for injection of holes. PEDOT displays also good film-forming properties so that it is easily applied on ITO by Doctor blade equipment using the commercially available product which contains poly(styrene-4-sulfonate) (PSS) as the counter ion.

However, the electrochemical polymerization of EDOT in NaPSS polyelectrolyte aqueous solution has been successfully attempted [12] also investigating the physico-chemical processes which take place during the PEDOT growth. Furthermore, the Authors pointed out the correlation existing between the morphological features of the polymer films obtained under different experimental conditions (potentiostatic and potentiodynamic syntheses).

More recently a study on the morphology and conductivity of PEDOT layers produced by different electrochemical routes using NaPSS as the supporting electrolyte [13] has reported that the thickness and the roughness of the deposited layer are strictly related to the intrinsic conductivity.

The electrochemical synthetic approach allows the rapid (order of min) obtainment of PEDOT films directly on the electrode surface with tunable electroactivity and thickness. Besides, very low amounts of monomer are consumed and it is possible also to insert different anionic species, compensating the positively charged PEDOT, in dependence on the electrolyte used for the electrosynthesis.

The electrochemical polymerization of PEDOT allows the introduction of a wide range of counterions since they can be added as supporting electrolytes to the reaction solution and their choice is limited by their solubility and stability under the reaction conditions [14]. The effect of the electropolymerization conditions in the presence of anions different from PSS on the electrochemical, morphological, and structural properties of PEDOT films has been published by Melato et al. [15]. From their results the best properties of PEDOT, as to its application in organic solar cells as hole extracting layer, were obtained in the presence of LiClO_4 as the supporting electrolyte. In fact, this salt leads to higher electropolymerization efficiency and to an increase of electroactivity and crystallinity of the polymers. Furthermore, LiClO_4 favours the formation of a more compact morphology of the polymeric film.

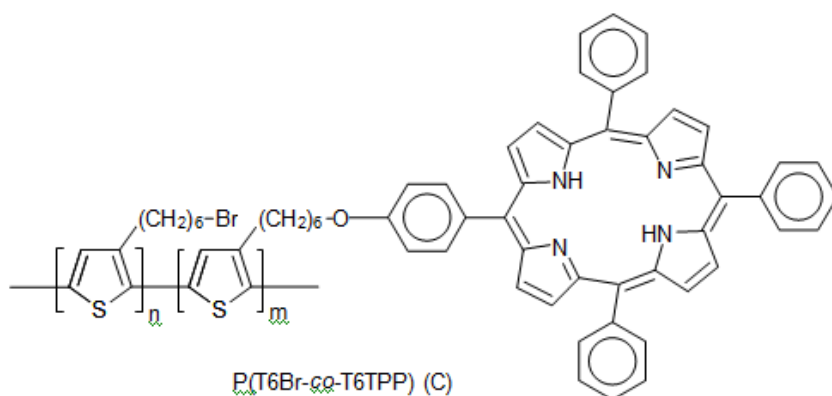
To our knowledge, the researches on electrochemical deposition in the field of BHJ cells are still quite limited [16, 17]. On the basis of the rather satisfactory results obtained with the regioregular thiophenic copolymers bearing the porphyrin moiety as to the fabrication of BHJ solar cells and considering the advantages of the electrochemical approach, we attempted to prepare solar cells *via* electrochemical deposition of both PEDOT and polymeric component of the blend, carrying out a deep study on the best operative conditions to perform the electrosynthesis. Unfortunately, we were not able to electrodeposit the copolymer containing porphyrin.

For these reasons we focused our attention on the comparison of the performances of the OPVs where PEDOT was either electrochemically synthesized in the presence of perchlorate or the commercially available PEDOT:PSS. The comparison was made using either the previously synthesized copolymer (rr-P(T6Br-co-T6TPP)) or the more commonly employed P3HT, taking into account the photoefficiency values.

2. Material and methods

2.1 Materials

ITO coated glass slides ($R_s = 4-8 \Omega\text{cm}^{-1}$, size $2.5 \text{ cm} \times 0.8 \text{ cm}$, thickness 1 mm) were purchased from Delta Tech. PCBM (99% pure) was supplied by SES Research Texas. 3,4-Ethylenedioxythiophene (EDOT), HCl (33% w/w), hydrogen peroxide (35% w/w) were purchased from Aldrich. Poly(3,4-ethylenedioxythiophene-poly(styrene sulfonate)) (PEDOT:PSS) (2.8% w/w, dispersion in water, PEDOT content 0.14%, PSS content 2.6%, M_w (PEDOT) $1000-1500 \text{ g mol}^{-1}$) was also obtained from Aldrich and diluted 1:1 with isopropyl alcohol. Acetonitrile (99.8% pure), purchased by JT Baker, was previously dried in calcium hydride and distilled under N_2 atmosphere. Ammonium hydroxide (33% w/w) was purchased from Normapur. The supporting electrolytes, lithium perchlorate ($\geq 99.0\%$ pure) and tetrabutylammonium hexafluorophosphate (TBAPF6, $> 99.0\%$ pure), were provided by Fluka. Chlorobenzene (99% pure) was purchased from Carlo Erba. P3HT was synthesized by us using the McCullough procedure [18] (98% HT dyads content, $51.000 \text{ g mol}^{-1}$). Poly[(3-(6-bromohexyl)]thiophene)-*co*-(3-[5-(4-phenoxy)-10,15,20-triphenylporphyrinyl]hexylthiophene)] (rr-P(T6Br-*co*-T6TPP)) was synthesized in our laboratory [9]. The chemical formula of the copolymer rr-P(T6Br-*co*-T6TPP) is shown below.



2.2 Chemical equipment

The electrochemical deposition and characterization were performed by using a PGSTAT 20 Autolab potentiostat (Ecochemie) controlled by a personal computer via GPES 4.9 software (Windows operating system).

The electrochemical depositions were carried out using a single compartment, three-electrode cell. A platinum wire (Sigma Aldrich) was used as counter electrode, a saturated calomel electrode (SCE, by Amel Instruments) as reference and ITO as working electrode. The redox behavior of PEDOT:PSS and PEDOT: ClO_4 was studied by cyclic voltammetry (CV); prior to the electrochemical measurements, the solution was purged by bubbling N_2 for 20 minutes and a nitrogen atmosphere was maintained over the solution during the experiments. The electrochemical characterizations were performed at room temperature, using a single compartment, three electrode cell in acetonitrile solution with 0.1 M TBAPF6 as supporting electrolyte. The working electrode was a Pt disk, 2 mm diameter, sealed inside a Teflon support, the counter electrode was a Pt wire and the reference electrode an aqueous saturated calomel electrode (SCE). The working electrode was polished carefully with alumina slurry and cleaned in an ultrasonic bath before the experiments. The CV curves were recorded at a potential scan rate of 0.5 V/s and five voltammograms were sequentially recorded.

Bandelin Sonorex Super Sonicator (RK 510 H) was used for the cleaning of the ITO electrodes.

Doctor blade equipment (Sheen Instruments Model S265674) was used as film applicator to coat ITO with PEDOT:PSS in order to obtain the desired layer thickness ($\sim 50 \text{ nm}$). UV-Vis-NIR spectra were recorded with a HP 8453 diode array

spectrophotometer (Agilent). Morphological studies were performed by Atomic Force Microscope (AFM) using a Solver Pro P47-Hand and an Axiolab A optical microscope (ZEISS). AFM characterizations were performed in standard semi-contact mode simultaneously acquiring both height and phase signal.

Büchi B-580 evaporator was used to dry the polymeric films after deposition. Aluminum cathode was vacuum deposited in an Edwards coating system E306A.

The J/V characteristics of the fabricated devices were measured under 1000 Wm^{-2} white light illumination from a standard AM 1.5 Solar Simulator lamp (Abet Technologies LS 150-Xe) and recorded using a Keithley Instruments 2400 source meter. J/V curves were recorded to test the devices operability as diodes and as solar cells, measuring current with a potential sweep from -3 V to $+3 \text{ V}$ and from -0.1 to $+0.6 \text{ V}$, respectively. To evaluate the reproducibility of cells fabrication three independent devices were prepared for each experiment.

2.3 ITO electrode preparation

To remove the ITO film from the edge of the electrodes in order to avoid short circuit, a chemical etching was done using a 10% (w/w) HCl solution, at $60 \text{ }^\circ\text{C}$. Then ITO coated glasses were soaked in sequence in aqueous detergent solution, acetone and isopropyl alcohol for 15 min, under sonication, and then dried. The substrate as such were employed for the PEDOT electrodeposition, whereas a further cleaning procedure was applied in order to activate the hydroxyl groups of the electrode surface before PEDOT:PSS casting. The glasses were immersed in a solution consisting of 20 ml of distilled water and 1 ml of 33% (w/w) aqueous NH_3 which was heated to $60 \text{ }^\circ\text{C}$, then 4 ml of 35% (w/w) H_2O_2 were added and the solution was kept at the mentioned temperature for 20 minutes.

2.4 Fabrication of the OPV devices

The ITO anode was coated with the hole transporting layer PEDOT, either by casting (PEDOT:PSS) or by electrochemical synthesis (PEDOT: ClO_4). The polymeric film was dried under nitrogen gas stream. Then the PEDOT modified electrodes were annealed at $120 \text{ }^\circ\text{C}$ under vacuum for 2 hours using a Büchi glass oven and stored under vacuum.

The photoactive layer, i.e. the blend constituted of the copolymer (rr-P(T6Br-co-T6TPP)) or P3HT:PCBM was deposited, after filtration on a Teflon septum ($0.2 \text{ } \mu\text{m}$ pore size), by casting onto the ITO/PEDOT electrode (thickness $\sim 150 \text{ nm}$). The blend was prepared by dissolving 20 mg of rr-P(T6Br-co-T6TPP) or P3HT and 20 mg of PCBM in 1 ml of chlorobenzene. The film was dried under nitrogen gas stream and stored in vacuum. After the blend deposition the cells were annealed at $150 \text{ }^\circ\text{C}$ for 30 minutes.

Finally, an aluminum cathode (150-200 nm thick) was deposited onto the composite film by vapor deposition under vacuum (pressure of about $1 \cdot 10^{-4} \text{ Pa}$). The active area of the cell was fixed to be 0.25 cm^2 by an aluminum mask. The cells structure is schematically shown in Fig. 1.

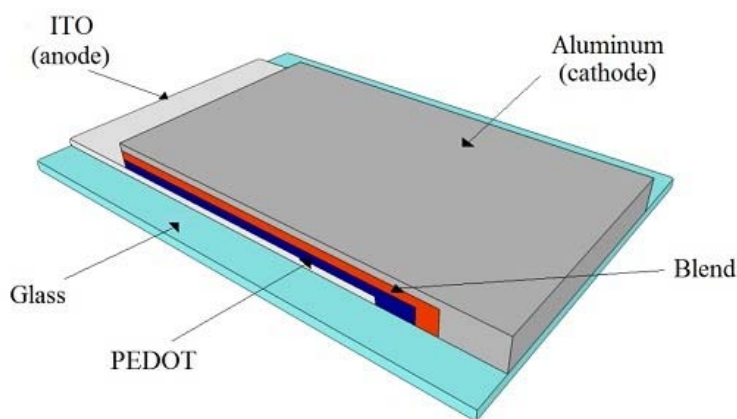


Figure 1 - Solar cell structure

2.5 Synthesis of PEDOT: ClO_4

The PEDOT layer was polymerized from $5.0 \cdot 10^{-3}$ M EDOT aqueous solution in the presence of 0.1 M $LiClO_4$ as supporting electrolyte. The oxidative polymerization was carried out applying a constant potential of +1.05 V vs SCE for 10 s. The obtained film was thinned applying 25 potential cycles at $0.05 V s^{-1}$ from 0 V to +1.3 V in the solution containing only the supporting electrolyte in order to obtain a film thickness of about 50 nm, which is the ideal value required for traditional cells. The film thickness was checked before and after the application of potential cycles by AFM. Finally PEDOT modified ITO electrodes were washed in distilled water and dried in nitrogen gas stream.

3. Results and discussion

3.1 Electrochemical synthesis of PEDOT: ClO_4

To fabricate the electrochemical cells different approaches were tried in order to obtain the desired characteristics for PEDOT: ClO_4 film. Many experiments were done to find the better conditions to deposit the PEDOT layer on ITO; the applied techniques were chronoamperometry (CA) and cyclic voltammetry (CV). The PEDOT film synthesized by CA (Figure 2) resulted more stable, so this technique was chosen for the electrodeposition. Furthermore, the potentiostatically deposited film resulted more homogeneous as inspected by optical microscopy. The lowest concentration of EDOT to obtain a homogeneous film was found to be $5 \cdot 10^{-3}$ M.

The thickness of the film obtained by the potentiostatic synthesis was too high (~ 200 nm) to be used for the fabrication of the BHJ cells. Therefore, a thinning procedure consisting of 25 CV cycles in distilled water containing only the supporting electrolyte was applied to ITO glasses after the electrodeposition of PEDOT. This treatment guaranteed a homogeneous degradation of the layer, permitting the reduction of the thickness (~ 50 nm) without creating uncovered zones.

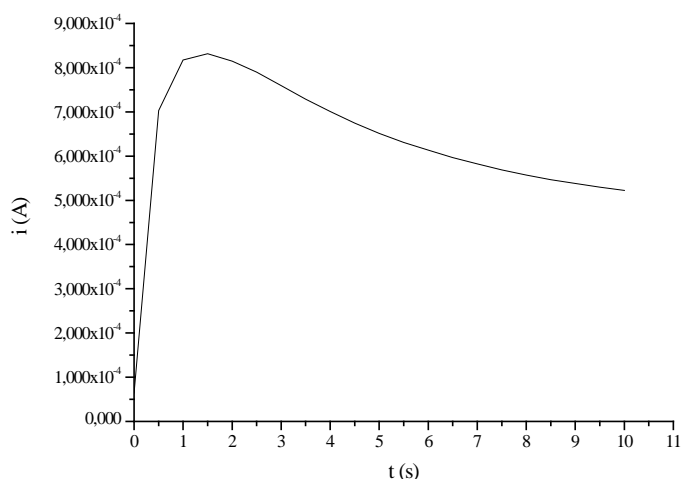


Figure 2 - Potentiostatic deposition of PEDOT:ClO₄ on ITO starting from a solution containing 5 mM EDOT and 0,1 M LiClO₄, applying +1,05 V for 10 s.

3.2 Electrochemical characterization of PEDOT:PSS and PEDOT:ClO₄ films

The commercial PEDOT:PSS and the electrosynthesized PEDOT:ClO₄, were electrochemically characterized by cyclic voltammetry (CV). The CV curves (Figure 3) were recorded in acetonitrile containing TBAPF₆ as supporting electrolyte, using a Pt electrode coated either with PEDOT:PSS or PEDOT:ClO₄.

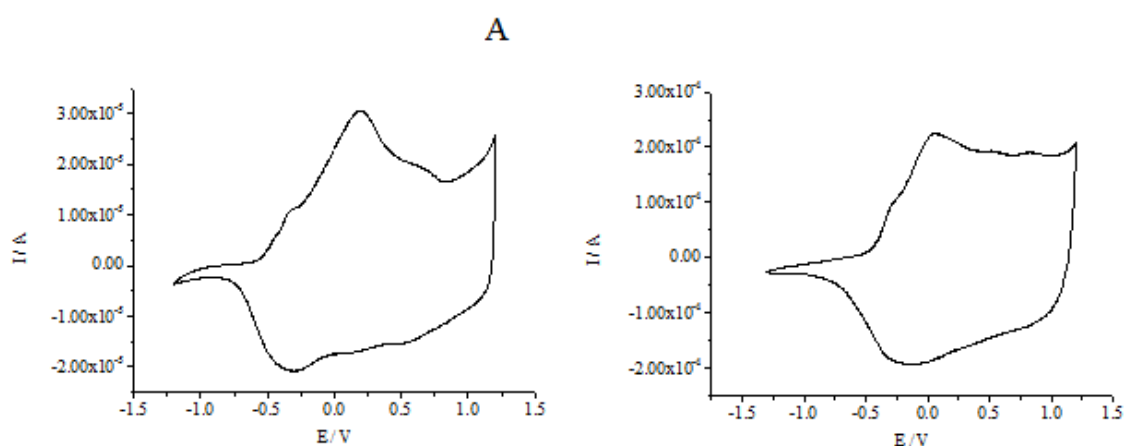


Figure 3-CV curves (fifth cycle) recorded in 0.1 M TBAPF₆ acetonitrile solution at the scan rate of 0.5 V/s for a Pt electrode coated with a thin film of PEDOT:ClO₄ (A) and PEDOT:PSS (B).

It can be seen that the electrochemical behaviour is similar for both polymers since they acquire conductive character at very low potential (about -0.5 V), even if for PEDOT:ClO₄ the oxidative doping process starts at less anodic potential (about 50 mV). Furthermore, the electrochemical characterization of PEDOT:PSS displays a more capacitive behaviour. Obviously, the recorded currents are not comparable since the procedure to coat the Pt surface with PEDOT:PSS involves a higher deposited amount of polymer. For both polymers the CV responses evidence two oxidation steps which correspond to the formation of polarons and bipolarons typical of the conductive mechanism of this polymer [19].

3.3 UV-Vis characterizations

Figure 4 shows the absorption spectra recorded for both PEDOT polymers using ITO as a support. Again the absorption values are different due to the different deposited amounts. Nevertheless, it is possible to examine the shape of the spectra in order to obtain some information about the oxidation degree of the material in the pristine state.

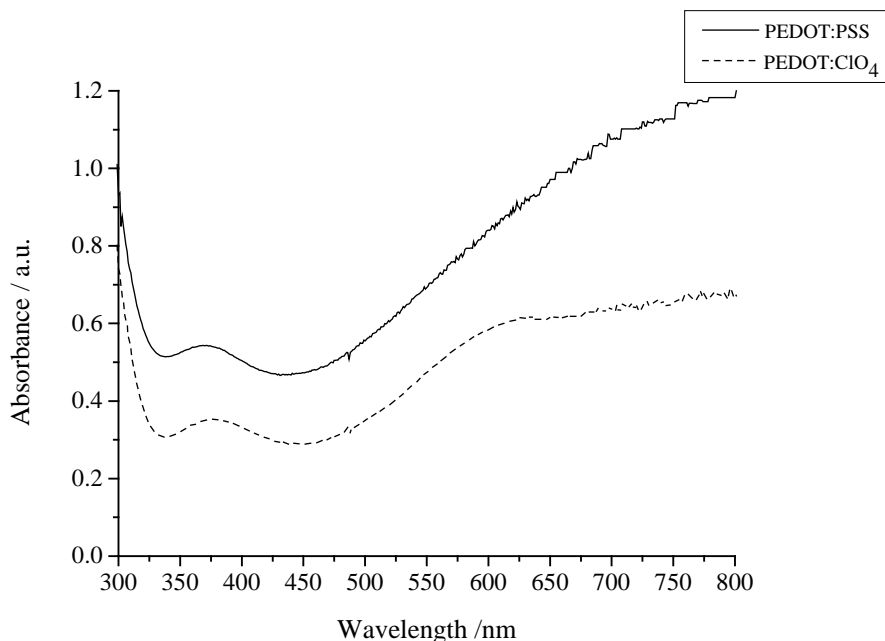


Figure 4 – Absorption spectra of PEDOT:PSS (solid line) and PEDOT:ClO₄(dashed line) coated ITO.

In the range between 300 and 600 nm the two spectra display the same trend. On the contrary, the shapes are different in the range between 600-800 nm, wherein the absorption of polaron occurs [20], with a maximum at about 900 nm. Unfortunately, a high noise affects the absorbance over 800 nm for both spectra. The recorded spectra suggest that the pristine PEDOT:PSS is in a middle-oxidized state. On the other hand, in the 600-800 nm range the PEDOT:ClO₄ spectrum displays a plateau that is consistent with a high oxidation degree of the material and so, with the formation of bipolarons maybe ascribable to the potentiostatic electropolymerization.

3.4 Annealing treatments

The relatively high efficiency of P3HT:PCBM devices has been attributed partly to the ability of P3HT to self-organize into a two-dimensional lamellar structure in a process mediated by the interpenetration of the side groups of adjacent polymer chains. In this ordered structure, the distance between adjacent planes of polymer chains is very small (3.8 Å) [21,22] and P3HT as such is characterized by both strong interchain interactions and high charge mobility for a conjugated polymer.

In addition, the annealing techniques can improve the OPV efficiency [23] by favouring the phase separation and a better charges transport. A higher crystallinity of P3HT:PCBM films is observed upon annealing, which leads to the formation of P3HT long fibrils and enhances the hole mobility by an order of magnitude [24,25] while micrometric PCBM aggregates can form thanks to diffusion and crystallization of PCBM [26]. Annealing not only causes recrystallization but also reduces the free volume and the density of defects at the interfaces [27]. All the BHJ cells investigated in this work were fabricated submitting both the PEDOT layer and the blend film to a proper annealing

treatment. In particular, PEDOT films were annealed at 120 °C under vacuum for 2 hours and after the blend deposition the cells were again annealed at 150 °C for 30 minutes. These conditions were chosen on the basis of both the literature data [28] and the expertise acquired by our group in the fabrication of devices constituted of commercial PEDOT:PSS and P3HT:PCBM blend.

3.5 Performances of the BHJ cells

The most commonly used parameters to test the performances of the OPV devices were measured, i.e. the short circuit current density J_{SC} , the open circuit voltage V_{OC} and the fill factor FF .

J_{SC} is determined by the efficiency of the charge generation, separation and collection. V_{OC} is related to gap between LUMO of acceptor and HOMO of donor. Fill factor (FF) is defined as the ratio of the actual maximum obtainable power to the product of the open circuit voltage and short circuit current. Fill factor is governed primarily by cell resistances, i.e., internal shunt (parallel) and series resistances. In an ideal cell, parallel resistances would be infinite and series resistances would be negligible. Such a cell would be an ideal diode, for which the J/V plot follows an exponential curve and has a fill factor of 0.89 [29]. The overall solar energy conversion efficiency is the maximum extracted power compared to the incident solar power.

Firstly we prepared the cells where the donor was the copolymer rr-P(T6Br-co-T6TPP) using in one case PEDOT:PSS and in the other PEDOT:ClO₄. The typical parameters are shown in Table 1 and Table 2.

The prepared devices showed the structure: ITO/PEDOT (PSS or ClO₄)/P3HT (or rr-P(T6Br-co-T6TPP)):PCBM/Al. The cells were not optimized for their photovoltaic performances (as evidenced by the obtained low values of J_{SC} and FF) since the measurements aimed to compare the photoelectric effects on a standard platform, while favouring the data reproducibility rather than the overall efficiency.

The fabrication reproducibility of the BHJ cells was verified preparing three identical cells for each of the two kinds of cells, i.e. those based on PEDOT:PSS and P3HT or rr-P(T6Br-co-T6TPP) as electron donors in the photoactive layer or those based on PEDOT:ClO₄ and the same donors.

The efficiencies and the main characteristic parameters of the cells containing PEDOT:PSS as hole hole-transport layer are shown in Table 1, while in Table 2 are reported the values obtained testing the cells containing PEDOT:ClO₄.

Looking at the individual efficiencies we can say that the reproducibility of the cells construction was very good (% CV ~ 2).

Blend	J_{SC} ($10^{-3}A\ cm^{-2}$)	V_{OC} (V)	FF (%)	PCE (%)	RMS (nm)	Diameter (nm)
rr-P(T6Br-co-T6TPP):PCBM	1.24 ± 0.07	0.55 ± 0.01	29.08 ± 0.02	0.201 ± 0.005	8.90	17
P3HT:PCBM	4.80 ± 0.05	0.57 ± 0.01	31.00 ± 0.05	0.86 ± 0.01	9.68	18

Table 1– Characteristic parameters of the tested solar cells fabricated with PEDOT:PSS and the two different blends.

Blend	J_{SC} ($10^{-3}A\ cm^{-2}$)	V_{OC} (V)	FF (%)	PCE (%)	RMS (nm)	Diameter (nm)
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rr-P(T6Br-co-T6TPP):PCBM	1.01 ± 0.02	0.52 ± 0.01	28.91 ± 0.06	0.150 ± 0.002	9.15	17
P3HT:PCBM	5.90 ± 0.01	0.60 ± 0.01	30.00 ± 0.04	1.06 ± 0.01	5.08	12

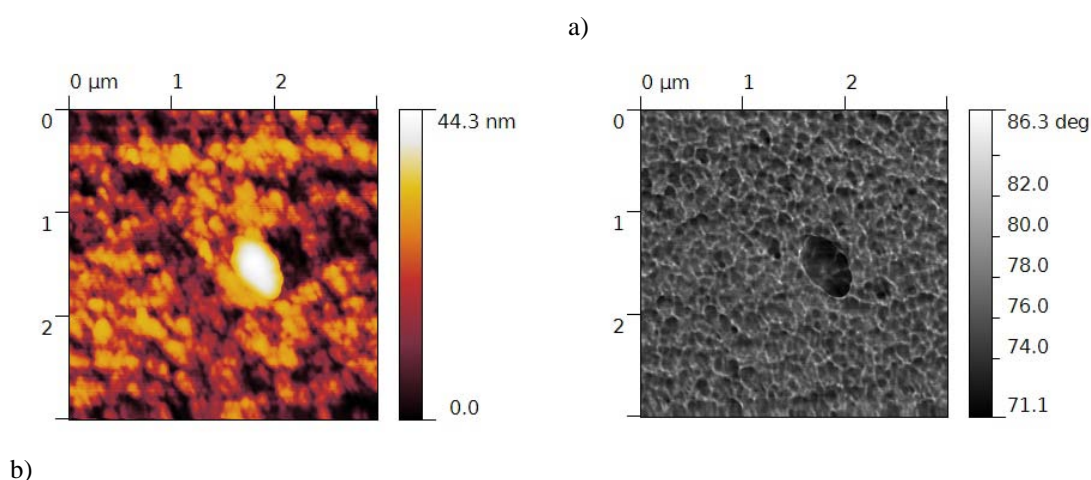
Table 2 - Characteristic parameters of the tested solar cells fabricated with PEDOT:ClO₄ and the two different blends.

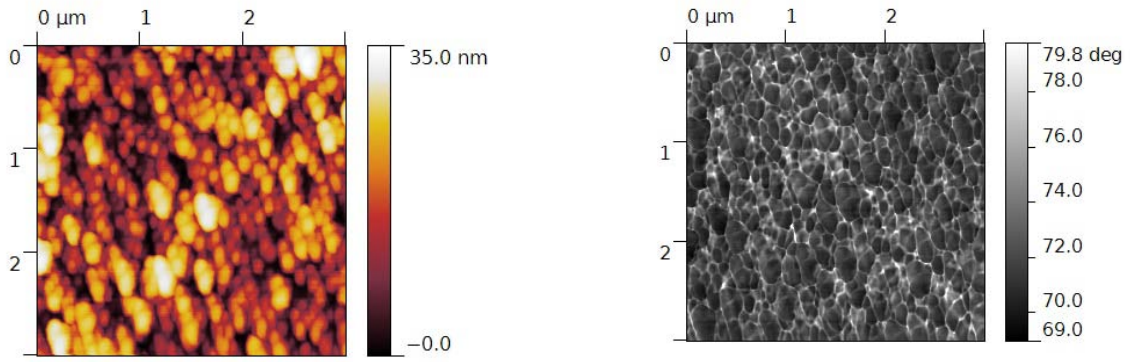
The average efficiency of the cells prepared using PEDOT:PSS as a buffer layer was attested to 0.20% when the photoactive polymer was rr-P(T6Br-co-T6TPP) and 0.86% when P3HT was used. When PEDOT:PSS was substituted by PEDOT:ClO₄, the PCE of the cells made with the copolymer lowered to 0.15% whilst those made with P3HT reached a mean efficiency of 1.06%.

Using the regioregular copolymer P(T6Br-co-T6TPP):PCBM blend instead of the commonly employed P3HT:PCBM system, the lower efficiency can be attributed to a loss of the lamellar stacking in the solid state packing due to the steric hindrance of the porphyrin moiety. Therefore, even if more excitons can be produced by inserting thiophene units bearing a chromophore which widens the absorption spectrum, steric factors significantly affect the arrangement of the polymer chains in the donor domains, maybe preventing the interpenetration of the side groups of adjacent polymer chains. The decrease of organization in donor domains results in a worse charge transport (as evidenced by the low J_{SC} values measured) which overcomes the expected improved cell performance related to its optical absorption characteristics.

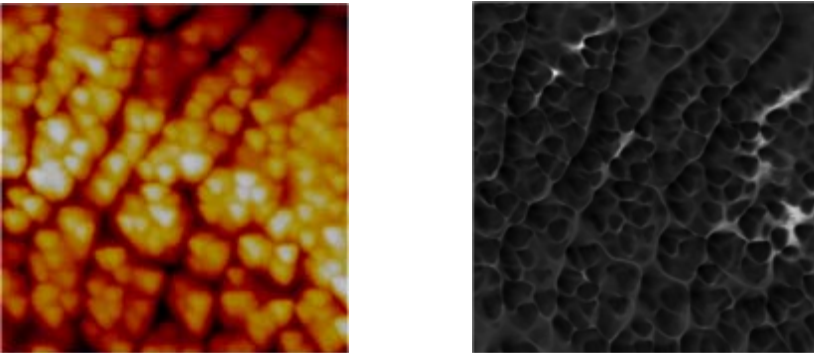
Comparing the efficiencies obtained for the BHJ cells fabricated either with PEDOT:PSS or PEDOT:ClO₄ we can state that the values are almost the same even if higher PCEs result when the donor is the P3HT using PEDOT:ClO₄ (20%) whereas when the donor is the copolymer, higher PCEs are obtained using PEDOT:PSS. These differences are hardly explainable but support the point of view that PEDOT electrochemical synthesis can be used as a valid alternative to PEDOT:PSS coating.

3.6 AFM morphological characterizations

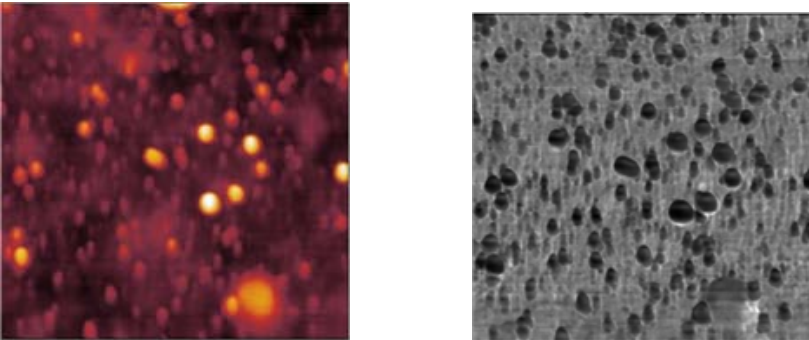




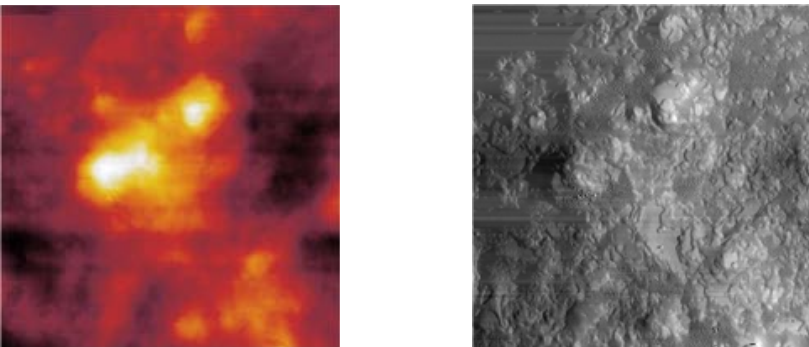
c)



d)



e)



f)

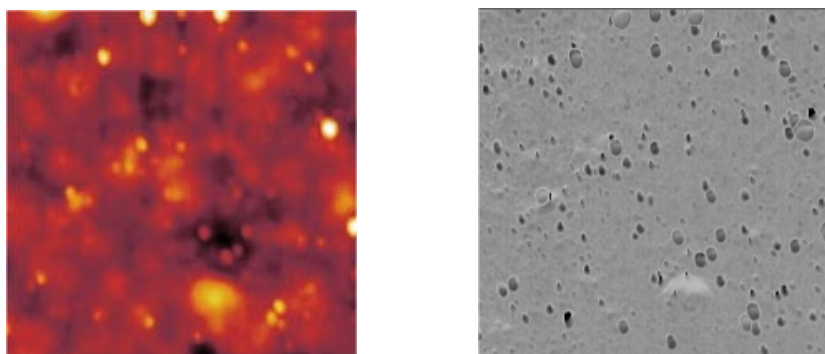


Figure 5 - AFM images of the prepared blends (left: height modulated images; right: phase modulated images) a) PEDOT:PSS, b) PEDOT:ClO₄, c) rr-P(T6Br-co-T6TPP):PCBM with PEDOT:PSS, d) P3HT:PCBM with PEDOT:PSS, e) rr-P(T6Br-co-T6TPP):PCBM with PEDOT:ClO₄, f) P3HT:PCBM with PEDOT:ClO₄. The image area size is 3 μm × 3 μm.

Figure 5 shows Atomic Force Microscopy (AFM) surface topographies of PEDOT:PSS, PEDOT:ClO₄ and photoactive layers.

The PEDOT:PSS layer displays a root mean square (RMS) roughness of 3.92 nm and the morphology of the domains is cauliflower-like. In the height modulated image the boundaries between the different particles are not well defined because PEDOT:PSS is a gel where the external polymeric chains interact so leading to grains merging. The phase modulated image highlights better the particles of PEDOT:PSS that are composed by two different parts. The inner ones are black and are composed by PEDOT:PSS. The outer parts are grey and consist essentially of PSS that is added in excess to the commercial formulation to generate a negative charge on the particles in order to increase their stability[30]. The separation between the two polymers is not very sharp probably because PEDOT concentration decreases at the particles boundaries..

The PEDOT:ClO₄ shows a RMS roughness of 4.53 nm with an ellipsoidal morphology of the particles. The shape of the domains is very well defined both in the height and in the phase modulated images. Probably, in this material the formation of crystalline domains is preferred, due to the smaller size of ClO₄⁻ anions, and so the boundaries of the different grains appear very clear-cut. The preferential formation of crystalline domains has been reported for PEDOT:Tos (tosylate) [31].

Tables 1 and 2 report also the RMS roughness of the photoactive films together with the average diameter size of the grains. At first glance, the blends deposited on the commercial PEDOT:PSS layer show a less homogeneous morphology, with a coarse structure and with aggregates having a larger average domain size. This is particularly true for rr-P(T6Br-co-T6TPP):PCBM sample, in which the cauliflower-like domains, typical of PEDOT-PSS chains, are still visible, even if surrounded by the copolymer chains. P3HT also shows an irregular surface, with a lot of dots ascribable to the nanoaggregates of PCBM. Passing from commercial to electrosynthesized PEDOT, we can observe small difference in the copolymer sample, but a very different behaviour of the conventionally adopted P3HT. In fact, this time the photoactive blend shows very small aggregates with the lowest roughness, as evidenced by the RMS value. Using LiClO₄ it is possible to obtain a compact structure with clusters of small dimension due to the easily insertion of Li⁺ inside the polymer matrix during the electrosynthesis, which can occupy all the empty spaces in the polymer chains. The high interfacial area of the electron-acceptor domains in the electron-donor matrix as well as their uniform distribution can effectively lead to a better control of the separation of the components of the photoactive blend, giving a positive effect on the conversion efficiency.

In view of these foregoing, we can conclude that the PEDOT layer is not only a “buffer layer” (from an electrochemical point of view) but its morphology is able to drive that of the further layers deposited on it. The electrochemically

deposited PEDOT has then beneficial effects on the morphology of the P3HT sample only, since in the case of rr-P(T6Br-co-T6TPP) polymer its lower solubility and high tendency to self-aggregate probably prevent an uniform separation of the active blend components on a nanoscale domain to be achieved. This behaviour still remains unclear, since the final morphology of the active layer is influenced by many factors acting simultaneously, such as the solubility of the components in the filming solvent, the affinity between the filming solvent and the underlying PEDOT layer and the affinity among the electron-acceptor molecules, the electron-donor polymer and the buffer layer components.

4. Conclusions

In this work bulk heterojunction solar cells were fabricated employing different PEDOT buffer: one deposited by electrochemical synthesis and the other by casting a commercial polymer. Electrochemical deposition of the layer is quite a delicate process, but may offer some advantages like the use of low monomer concentrations, short times for the synthesis and good control of the film thickness. Two different donor materials were studied, i.e. P3HT and a copolymer containing a porphyrin moiety on a thiophene monomer, *ad hoc* synthesized to widen the absorption visible spectrum.

The cells composed by PEDOT:PSS and rr-P(T6Br-co-T6TPP):PCBM showed a power conversion efficiency of ~0.20% while the devices composed by PEDOT:ClO₄ and the same blend showed an efficiency of about 0.15%. The efficiencies are affected by the porphyrin hindrance which does not allow for the formation of crystalline nanodomains, thus preventing the chains solid state packing. The efficiencies of the devices fabricated with PEDOT:ClO₄ instead of PEDOT:PSS resulted enhanced when P3HT was employed as blend donor material.

Electrochemically synthesized PEDOT can represent a possible alternative to PEDOT:PSS casting and the film properties could be improved by acting on the synthesis parameters. Further studies could involve the electrosynthesis of the photoactive layer as well, by choosing properly the monomers and optimizing the electrochemical co-deposition parameters.

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