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Alkyl Thiophene Vinylene Electropolimerization in C$_8$mimPF$_6$, Potential Use in Solar Cells

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Abstract

We report the electrosynthesis of a novel semiconductor polymer based on alkyl vinylthiophene derivative in the presence of an ionic liquid (IL). The polymerization was performed under galvanostatic conditions and the polymer was studied as potential donor component of a multilayer heterojunction organic solar cell (OSC). The monomer used was (E)-1,2-di-(3-octyl-2-thienyl) vinylene (OTV) and the IL used for the electropolymerization was 1-octyl-3-methylimidazole hexafluorophosphate C$_8$mimPF$_6$. Optical properties, stability and morphology of the polymer were analyzed using FT-IR, UV-vis, Raman and XPS spectroscopy. Voltammetry analysis and scanning electron microscopy (SEM-EDX) were also performed on the polymer. The OSC assembled with the polymer of OTV was used as electro donor and C$_{60}$ as acceptor. Molybdenum trioxide (MoO$_3$) and bathocuproine (BCP) were used as buffer layer between anode and cathode respectively. I-V curves, in the dark and under AM 1.5 solar simulator were performed to measure its efficiency.

Keywords

Conducting Polymer, Vinylene Thiophene, Ionic Liquids, Organic Solar Cells

1. Introduction

The excellent combination between the conductive properties of a metal added to the many advantages of plastics such as chemical inertness, processability, low cost and low density doped polymers give important applications in optoelectronic devices [1] including Field Effect Transistors (FET) [2], Organic Thin

Film Transistos (OTFT) [3], Organic Light Emitting Diodes (OLED) [4] [5] and Organic Solar Cells (OCS) [6].

The high global demands for energy supply as a result of population growth and industrialization coupled with the imminent depletion of fossil fuel reserves have caused severe damage to the ecosystem. This situation has led to a growing interest in promoting the use of renewable energy sources, environmentally benign alternatives, which allow a sustainable, decentralized and affordable energy supply, thus protecting the environment. The abundance of sunlight and high radiation in vast sectors of the planet can be used to produce electricity through photovoltaic systems, the best way to obtain clean energy in favor of a modern society highly dependent on electricity. In this area, the important technological advance has allowed the development of three types of photovoltaic cells: crystalline silicon [7], organic solar cells (OSC) [8] and dye sensitized solar cells (DSSC) [9]. These two latest technologies are being considered as the most promising candidates for next generation solar cells because of their low cost, light weight, flexibility and mass production feasibility.

Within the vast range of existing monomer units to polymerize, this work has addressed the study with structures derived from vinylene thiophene. Its structure consists of a vinyl bond between thiophene rings, which can reduce the aromatic character of the ring, with a consequent increase in the delocalization of π electrons and the decrease in the rotational disorder between aromatic rings [10]. In short, vinylene thiophene structures provide the following structural characteristics: planarity, capacity charge delocalization by the presence of five conjugated double bonds and stability, fundamental in obtaining electroactive polymer. The incorporation of alkyl type groups in the β position of the thiophene ring was to improve the degree of solubility of polymers in organic solvents (THF, $CHCl_3$, CH_2Cl_2, CH_3OH) [11].

In the mid-1970s, an alternative to replace volatile organic compounds (VOCs) was discovered to perform chemical synthesis and to develop environmentally friendly processes, ionic liquids (ILs). ILs are organic salts which are constituted of a cation and an anion, unlike the common salts have a low tendency to crystallize due to the asymmetric and voluminous structure of the cation [12], e.g. 1-alkyl-3-methylimidazolium, N-Alkylpyridinium and tetraalkylammonium. The Plechkova and Seddon [13], researchers have estimated 10^6 possible combinations of ILs, by the use of the cations and anions became known so far. Among the many advantages of ILs include its intrinsic properties such as low toxicity, non-flammability, high ionic conductivity, high thermal and chemical stability, and ability to dissolve the organic and inorganic compounds in a wide temperature range near room temperature [14] [15]. Use of ILs in the production of conducting polymers has been studied in aromatic systems such as polypyrrole [16], polythiophene [17], vinyl benzotriazole [18] and in systems such as methylmethacrylate [19].

Related vinyl polymerization studies of monomer units in ILs, have shown that occur via radical cation, yielding electroactive polymer material with high

conductivity [20]. It is known that the chemical environment during the redox process affects conductivity, morphology, degree and rate of polymerization. In this regard, Woecht *et al.* [21] reported that ILs strongly influences the propagation rate coefficient depending on the type of monomer and IL used; suggesting that the origin of this phenomenon probably lies in the polarity of the IL.

We report here the electropolymerization of (E)-1,2-di-(3-octyl-2-thienyl) vinylene (OTV) in the IL 1-octyl-3-methylimidazole hexafluorophosphate C_8mim-PF_6.

2. Methods

2.1. Synthesis of Ionic Liquid

The IL C_8mimPF$_6$ was synthesized in one step without the use of solvents, according to the procedure described by Fang *et al.* [22], which comprises reacting equimolar amounts of 1-methylimidazole (99%), 1-bromooctane (99%) and potassium hexafluorophosphate salt, KPF$_6$ (98%); all reactive were purchased from Aldrich.

2.2. Synthesis of Monomer Unit (E)-1,2-di-(3-Octyl-2-Thienyl) Vinylene (OTV)

The monomer was synthesized as described by Martinez *et al.* [23]. First, was synthesized the Grignard reagent, octyl magnesium bromide (**Figure 1(a)**), a new C-C bond was then generated by Kumada coupling between the octyl group and the thiophene ring through the catalyst NiCl$_2$ (dppp) (**Figure 1(b)**). Next, formylation, also known as Vilsmeier reaction, was formed in situ from DMF and POCl$_3$ (**Figure 1(c)**). Finally, (E)-1,2-di-(3-octyl-2-thienyl) vinylene (OTV) was performed by the McMurry reaction using the Mukaiyama reagent (TiCl$_4$/Zn in THF) [24] [25] [26] (**Figure 1**).
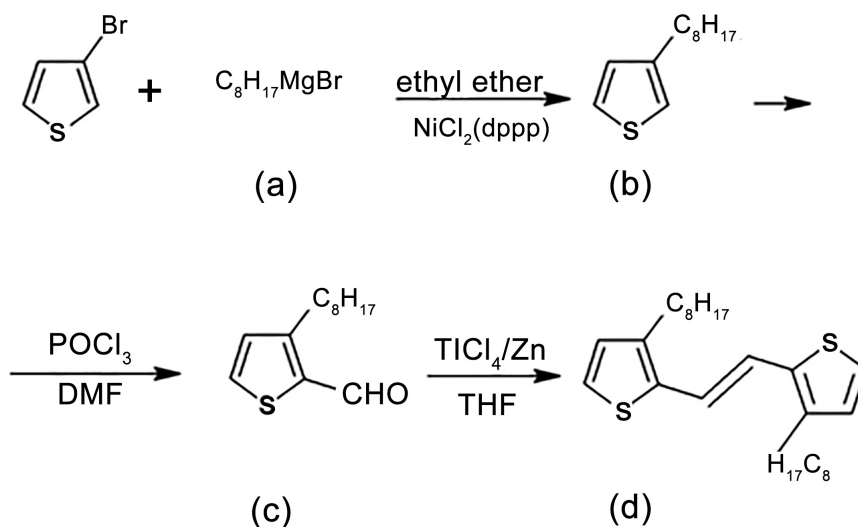

Figure 1. Synthesis of (E)-1,2-di-(3-octyl-2-thienyl) vinylene (a) octyl magnesium bromide, (b) 3-octylthiophene, (c) 2-fomil-3-octylthiophene) and (d) (E)-1,2-di-(3-octyl-2-thienyl) vinylene.

2.3. Electropolimerization of OTV in IL

The polymer (POTV) was obtained by galvanostatic electrodeposition technique on three types of anode: Pt, ITO glass and PET with a work surface of 2 cm^2; before using the electrodes, they were washed with H_2O and then with acetone in ultrasonic bath. As counter electrode a graphite bar or Pt sheet was used. The electrochemical cell has two compartments separated by a glass frit, allowing both electrodes in a parallel arranging in each compartment. The polymerization was conducted at a current density of 2 mA/cm^2 and at temperature of 30°C, under nitrogen inert atmosphere. The IL is dried under vacuum at 75°C prior to use. POTV was obtained from 0.4 mmol mixture IL/CH_2Cl_2 = 5/2 mL. The polymer was thoroughly washed with methanol, and then dried in vacuum oven at 70°C for 6h.

2.4. Organic Solar Cell Construction

The cell is based on superposed multilayer structured on ITO-glass according to the following layer order: ITO/MoO_3/POTV/C_{60}/BCP/Al/Se (BCP: bathocuproine). Two types of cells were made, depending on the deposition techniques: spin coating and vacuum evaporation. By the technique of spin coating a polymer solution of 10 mg/mL was used. 50 uL of solution is deposited on the substrate (glass ITO/MoO_3) at a speed of 1500 rpm for 30 seconds. The other components were deposited under vacuum at 10^{-4} Pa, the thin film deposition rate and thickness were estimated in situ on a quartz monitor: MoO_3 (2 nm), POTV (Deposited by stin coating), C_{60} (40 nm), BCP (5 nm), Al (3.4 nm) and Se (10 nm). By the technique of vacuum deposition, in a vacuum chamber at 10^{-4} Pa was placed the ITO-glass substrate and then was deposited the following components, layer by layer: MoO_3 (2 nm), POTV (10/20 nm), C_{60} (40 nm), BCP (5 nm), Al (3.4 nm) and Se (10 nm). The use of buffer layer (MoO_3, BCP) is very important in these devices, because this layer produces good work function adjustment, surface defects passivation, and ITO surface smoothing [27]. The devices were measured under conditions of darkness and light (AM 1.5 solar simulator of 100 mW/cm^2) through the ITO glass. I-V graphs were obtained which were performed at room temperature without an inert atmosphere.

2.5. Characterization Methods

NMR, IR and UV-Vis. confirmed precursor and monomer purities and structures. The ILs were characterized by NMR, IR, cyclic voltammetry and refractive index. The POTV was analyzed using mass spectroscopy, UV-vis, IR, XPS, Raman, morphological analysis SEM-EDX and differential pulse voltammetry (DPV).

3. Results and Discussion

3.1. Electrochemical Polymerization

Obtaining polymers using as solvent ILs was feasible without the need to add support electrolyte to the process. However, even having a structural similarity

between the monomer unit and the cation of IL, *i.e.* both have a planar aromatic structure and side alkyl chain it was not possible to solubilize the monomer in pure IL. This situation may be associated with a faint solvation by the IL, due to the strong interactions between cation-anion of IL, being at a disadvantage the interactions cation-solute and anion-solute. Therefore CH_2Cl_2 was used only in the necessary amount to solubilize the monomer unit in the required volume of IL. In turn, this process reduces slightly the viscosity of IL.

While the electropolymerization was a quick process that after the first few seconds of was started the current path, the coating was observed at the anode, the polymers obtained on anode of ITO glass and ITO-PET had poor adhesion on the electrodes. Rather important part diffused into the solution and avoided the formation of homogeneous polymeric films on the anode surface, appearing as islands. The Table 1 summarizes the experimental conditions of the electro-polymerization.

3.2. Spectroscopic Analice of POTV: Uv-vis, FTIR, Raman and XPS

The peaks absorption of UV-vis (Figure 2) was associated with the transitions of the aromatic rings $\pi - \pi^\star$. It was observed that there are no significant variations in the displacement of the bands by the use either platinum electrodes or ITO glass; the maximum peaks only differ in 7 nm.

Figure 3 shows the FTIR spectrum for POTV, which were measured through the attenuated total reflection (ATR). The blue spectrum corresponds to the polymer obtained on the electrode ITO-PET, while green spectrum corresponds to POTV obtained on Pt. The absorption bands in the range of 2900 - 2800 cm^{-1} are assigned to C-H stretching of alkyl chain (octyl group). To The 1557 cm^{-1} stretching vibration is assigned to C = C. The vibrations of the ring corresponding to C-C and C-H appear to 1268 and 1129 cm^{-1}, respectively. P-F vibration binding of the counterion appears in 828 cm^{-1}. Finally, C-H deformation (out of plane) corresponds to the thiophene ring in the 2,5-disubstituted α-α' [17] link to 709 cm^{-1}.

In the resonance Raman spectrum (Figure 4) 1601 cm^{-1} signal was assigned to the vinyl bond stretch between C = C. The signals at 1542 and 1421 cm^{-1} corresponds to the asymmetrical and symmetrical stretching of the C = C of the thiophene ring, respectively. Finally, vinyl bond C-H deformation was observed at 1298 cm^{-1} and C-C stretching at 1196 cm^{-1}.

Table 1. Conditions of electropolimerization of OTV in C_8mimPF_6.

Pair anode/cathode	IL	Time reaction (h)	Yield of POTV (%)
Pt/Grafitte	C_8mimPF_6	3	11.6
ITO-PET/Graphite	C_8mimPF_6	2	<5[a]
ITOglass/Graphite	C_8mimPF_6	2	<5
Pt/Pt	C_8mimPF_6	4	22

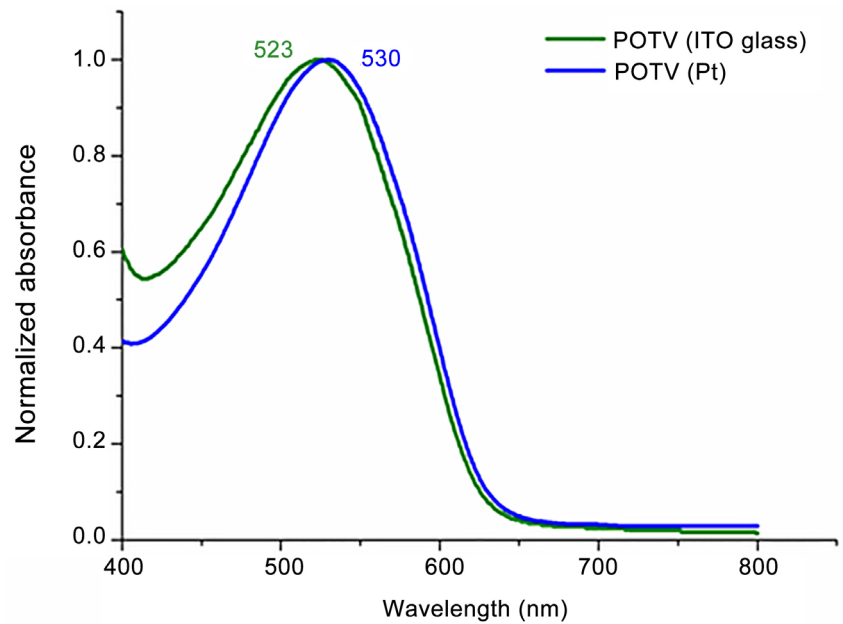a. 4 electrodes of ITO-PET were submerged c/1h.

Figure 2. Absorption spectrum of POTV on Pt electrode and ITO glass doped with PF6 measured in CHCl$_3$ at room temperature.
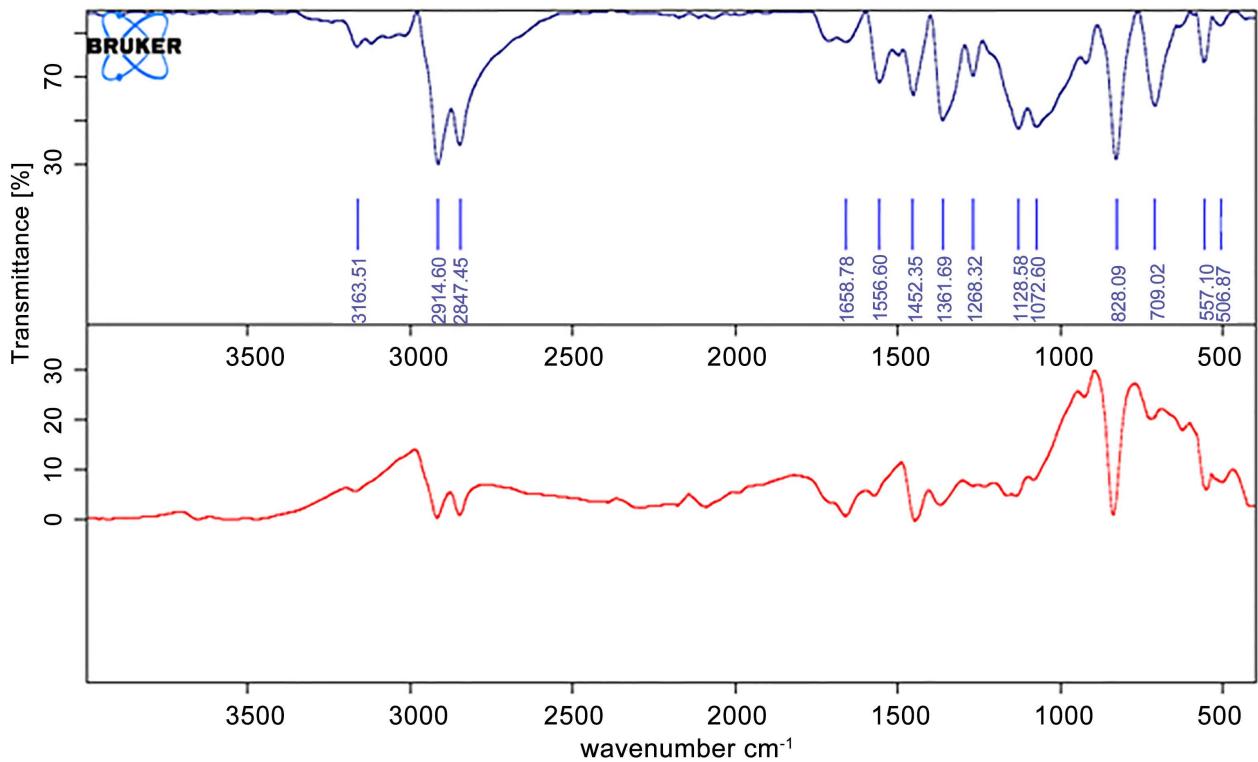

Figure 3. Infrared spectra of the polymers. Blue: POTV on ITO-PET; Red: POTV on Pt.

In the XPS spectrum, **Figure 5**, the elements present in the sample were: C1s, S2p, F1s, O1s y P2p [28]. The prominent mark was assigned to F1s located at 686.3 eV. This signal together with signal P2p clearly confirm the incorporation of the dopant anion and the polymer matrix [29].
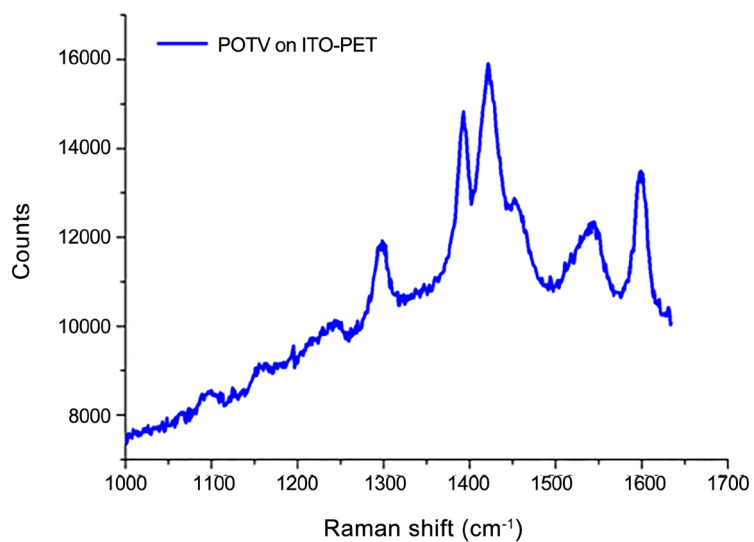
Figure 4. RAMAN spectrum of POTV on ITO-PET.
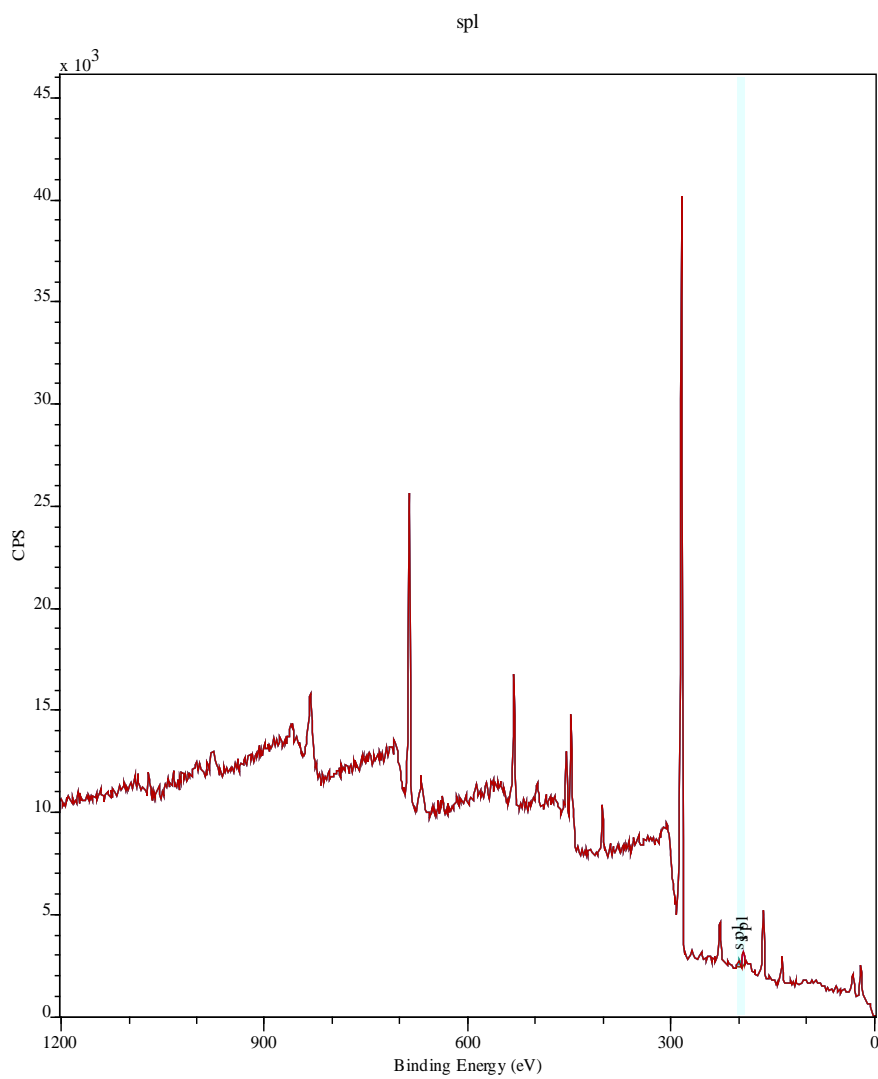
Figure 5. RAMAN spectrum of POTV on ITO-PET.

3.3. Morphological Analysis

The morphology of the different polymers was determined by SEM (Figure 6). The image for POTV on ITO-PET (picture on the left of Figure 6) shows a nodular morphology, whose nuclei have the appearance of a cauliflower, coincident with those reported in literature [30] [31]. A similar situation was observed for POTV on Pt (picture on the right of Figure 6), in whose morphology it is possible to appreciate granular and coral-like growths. These small differences may be associated with the nucleation and growth type of the polymer in the electropolymerization process on the different substrates. Also can be attributed to the influence of possible links in positions α, β in the POTV. Observing morphology can be deduced that the process was determined by the type of nucleation in 3D [32] [33].

From the EDX (Figure 6) the incorporation of the anion PF_6^- (part of IL) was confirmed in the polymer.

3.4. Voltammetric Analysis

Differential pulse voltammetry (DPV) (Figure 7) was performed in benzonitrile using $TBAPF_6$ (0.1 M) as supporting electrolyte. A platinum wire as the counter electrode, the pseudo reference electrode Ag/AgCl and platinum as working electrode. Ferrocene was used as internal reference. From the graph were obtained the oxidation and reduction potential of the polymer. The band gap for
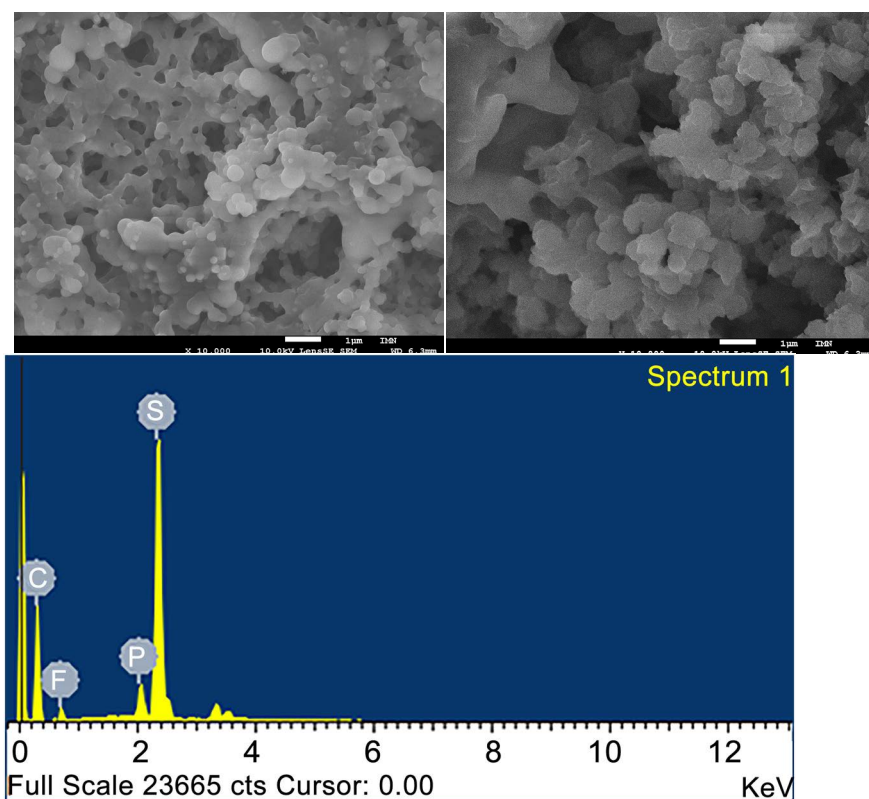

Figure 6. SEM images of POTV on ITO-PET (left) and on Pt (rigth). Graph of EDX for POTV on ITO-PET (down).
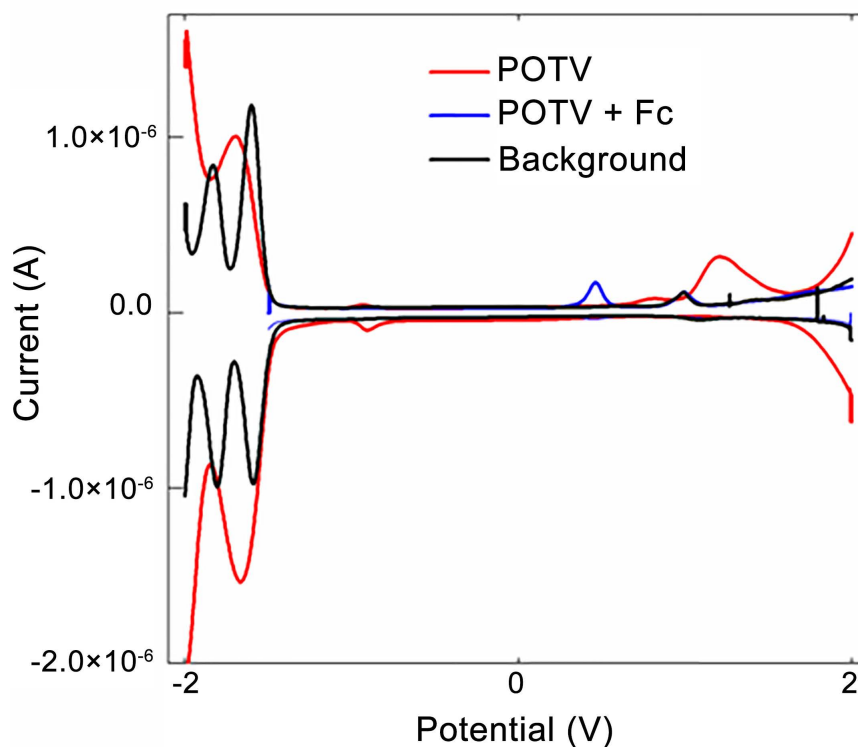

shows one of the most representative I-V graphs of each cell.

It can be observed that the best PCE values are achieved by spin-coating deposition, recording a value of $2.1 \times 10^{-3}\%$. A strong decrease of Rsh and Rs is observed in comparison to evaporation deposits, in the same way the values of Voc, Jsc and FF are better. On the other hand, evaporation leads to the breakdown of polymer chains, resulting in structures with less conjugation, a situation that is reflected in a slightly lower value of PCE of $2.9 \times 10^{-4}\%$. This contributes to an increase of the value Rs in the device which leads to a decrease in the performance of the device, and finally to a low value of the FF.
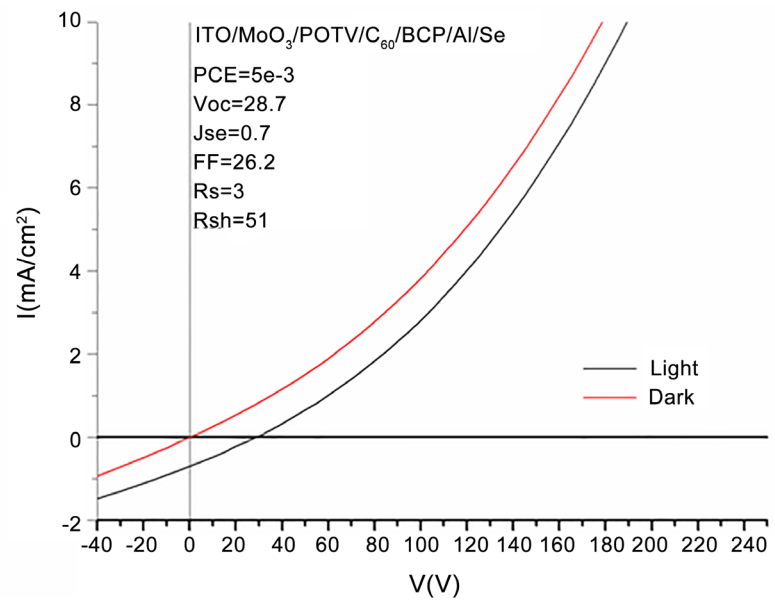
(a)
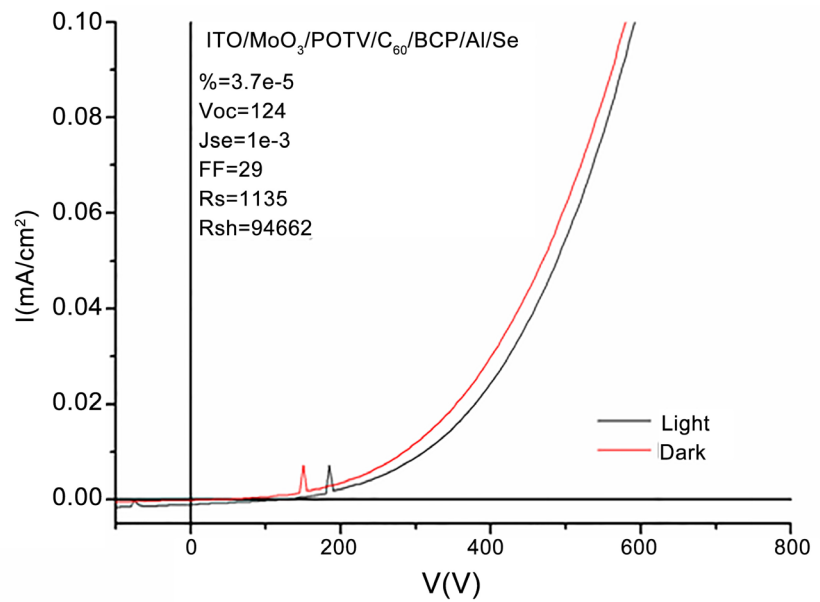
(b)

Figure 8. I-V curves for OSC with polymer deposit by (a) spin-coating and (b) evaporation.

4. Conclusion

The OTV monomer was possible to electrochemically polymerize by using an ionic liquid, C_8mimPF_6 as solvent. The polymer yields were dependant on the anode substrate and pair anode/cathode used in the electropolymerization. The ITO-glass and ITO-PET electrodes significantly reduce the electrodeposition of the monomer. Therefore, it can be said that there was a strong dependence on the nature of the anode surface and the amount and morphology of obtained polymer. From the DPV measurements, the polymer presented a good level HOMO/LUMO, however the bilayer heterojunction solar cells gave deficient energy conversion percentages $<10^{-3}$, independent of the method by which the polymeric material was deposited, it would be possible to estimate other types of assembly between different substrates which could improve the efficiencies of OCS. Bulk heterojunction for instance, increases the contact surface between the donor and acceptor to interlockable networks. It might also be considered the use of different buffer layers.

Acknowledgements

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