Chemical Sensitization for Electric Properties Improvement of PBDB-T-SF Polymer for Solar Cells Application

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Abstract. This paper reports the effect of ferric chloride (FeCl₃) sensitization on poly[(2,6-(4,8 bis -(5(2ethylhexylthio)4fluorothiophen2yl)benzo[1,2b:4,5b']dithiophene))-alt-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'c:4',5'c']dithiophene4,8 dione)] (known as PBDB-T-SF) in thin films (93 nm thickness), spin coated onto glass and ITO substrates. The optical properties do not undergo significant changes after FeCl₃ immersion. Instead, FeCl₃ sensitization leads to a dramatic decrease in resistivity of seven orders of magnitude comparing to the pristine thin films. This change is not stable over time, depending on FeCl₃ solution concentration and polymer thin-film thickness, but remains remarkable after a new immersion.

1. Introduction
Organic solar cells have recently become of great interest for both scientific research (academia) and industry owing to their multiple advantages. In this context, organic polymer materials have gained significant attention for photovoltaic applications, considering their attractive characteristics: conductive properties, lightweight, corrosion resistance [1–4], mechanical flexibility, etc., properties that are absent in most inorganic semiconductors [3, 5, 6]. In view of envisaged applications, both optical and electric properties of polymer materials are of great importance, but they are strictly related to the structural and morphological characteristics, varying with the size range of investigations. In the case of charge carrier transport through the polymer bulk material, from global point of view, the interconnections between polymeric chain domains are important for charge passage on the way to the electrodes, while, from local point of view, the links between the chains have to be taken into account, as much as the π-conjugation along the chains [1, 7, 8].

There are many ways to change the physical properties of polymer materials by adding a small amount of a different chemical element, through several techniques and methods; this will produce a disruption of crystal structure of the polymer, affecting, in this way, all its physico-chemical properties [9]. One method is polymer synthesis via fluorination, representing the insertion of fluorine atoms into the polymeric backbones. This is the reason of studying poly[(2,6-(4,8-bis(5-(2-ethylhexylthio)-4-fluorothiophen-2yl)benzo[1,2b:4,5b']dithiophene))-alt-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2ethylhexyl)benzo[1',2'c:4',5'c'] dithiophene 4,8 dione)], known as PBDB-T-SF or PCE13 [10–13], which contains two fluorine atoms. Being the most electronegative chemical element, fluorine brings many benefits to the host material. It avoids the steric hindrance of molecules, while it is down shifting the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels...
Besides, it improves the interactions between the molecules and between the polymeric chains, enabling the charge carrier transport, also facilitating exciton (electron-hole pair) separation by reducing the Coulomb potential [5, 9–11, 18, 19].

A second method, applied to enhance electric properties of this fluorinated polymer, is ferric chloride (FeCl$_3$) sensitization. The FeCl$_3$ is a cheap chemical agent, behaving as a $p$-type material and its molecules are capable of moving freely between polymer molecules, being assimilated by the polymer matrix [20, 21]. Because of its nature, depending on the involved amount, FeCl$_3$ is able to favour free electrons transport, improving the electric conductivity, or it can become an obstacle or a trap (if it is in excess) for charge carrier transport, but without damaging the polymer structure [20]. The temporal stability of the effect of ferric chloride on the polymer can be also lighter or stronger, depending on the thin-film thickness [21].

The present paper investigates the effect of FeCl$_3$ sensitization on the optical and electric properties of PBDB-T-SF thin films.

2. Materials and methods

The samples have been prepared using PBDB-T-SF (Figure 1), having an average molecular weight of 50,100, purchased from Ossila. The polymer solution in chlorobenzene (16 g·L$^{-1}$) was deposited by spin coating (600 – 800 rpm) as thin films (Figure 2) onto glass substrates and indium tin oxide (ITO) coated substrates (15 Ω/□), purchased from Kintec. After drying for 1 h at 100 °C, samples were submerged for 1 h in a FeCl$_3$ solution in nitromethane (5 g·L$^{-1}$).

The thickness of the as-prepared films was measured with a Veeco Dektak 6M Stylus Profilometer. The optical properties have been measured at room temperature; for the spectral range of 250 – 1100 nm, a two-beam spectrophotometer UV/VIS S9000 was used for absorption spectra recording, while determination of the refractive index, extinction coefficient and dielectric constant was performed with an UVVISEL ellipsometer (Horiba Jobin Yvon).

![Figure 1. Molecular structure of PBDB-T-SF.](image)

![Figure 2. Thin-film patterns: A. polymer deposited on glass substrate; B. polymer deposited on ITO coated glass substrate; C. polymer sample immersed in FeCl$_3$ solution.](image)
The electric properties were measured using a two-point technique during several successive cooling and heating cycles in temperature range of 30 – 90°C, under dark and white light illumination conditions.

3. Results and discussions
The thickness of as-prepared PBDB-T-SF thin films was about 93 nm, value which is increasing with almost 20 nm after first immersion in FeCl₃ solution. For the second immersion, this amount is decreasing to 15 nm, after which it remains constant (Figure 3). Therefore, it may exist a limit of the adherence tendency of FeCl₃ solution to PBDB-T-SF thin-film surface, fact which has been confirmed by the electric behaviour of samples.

![Figure 3. Thickness values for the FeCl₃ sensitized PBDB-T-SF thin film: 0 – no immersion; 1 – 1st immersion; 2 – 2nd immersion; 3 – 3rd immersion.](image)

The absorption spectrum of PBDB-T-SF exhibits (Figure 4) two absorption peaks located at 576 nm and at 621 nm, notifying strong π–π intermolecular interactions [10].

An important decrease in the absorption spectrum intensity of FeCl₃ sensitized polymer thin film is emphasized mostly in the visible wavelength range, because of the presence of FeCl₃, which is slightly assimilated by polymer chains. Besides, an enhanced absorption in the Near Infrared (NIR) domain can be noticed.

Moreover, it has to be taken into account that the absorption spectrum of as-prepared FeCl₃ layer displays low intensity bands. A chemical change that may occur in polymer matrix due to action of ferric chloride is anticipating, also responsible for the colour change, from light blue to dark blue.

The refractive index of pristine thin film, at 650 nm, was found to be \( n_{\text{max}_{\text{PBDB-T-SF}}} = 2.99 \) (Figure 5). After immersion, only some changes in the magnitude of the refractive index can be emphasized, but no significant changes in its behaviour: \( n_{\text{max}_{\text{FeCl₃}}} \) remains constant, the initial maximum refractive index shows a decrease to \( n_{\text{max}_{\text{PBDB-T-SF:FeCl₃}}} = 2.47 \), maintaining its wavelength position at 650 nm; at the same time, a second peak, located at 930 nm, occurs, \( n_{\text{2max}_{\text{PBDB-T-SF:FeCl₃}}} = 2.05 \). Figure 6 illustrates the spectral dependence of the extinction coefficient, the features of which are similar to those of the absorption spectrum.
Figure 4. Absorption spectra of polymer thin film (continued line), FeCl$_3$ film (dotted line) and FeCl$_3$ sensitized polymer thin film (dashed dotted line).

Figure 5. Pseudo-refractive index for polymer thin film (continued line), FeCl$_3$ film (dotted line), FeCl$_3$ sensitized polymer thin film (dashed dotted line).
Figure 6. Pseudo-extinction coefficient for polymer thin film (continued line), FeCl₃ film (dotted line), FeCl₃ sensitized polymer thin film (dashed dotted line).

The effects of the FeCl₃ sensitization on polymer thin film describe a strong decrease in terms of electric resistivity, of six orders of magnitude (Figure 7), after the first immersion. It defines an unstable behaviour: after 24 hours, its resistivity increases by about three orders of magnitude, while after 48 hours, it returns to the initial resistivity of as-prepared polymer thin film. After 6 days, a new immersion proceeds and similar effects were registered, but their amplitude was less with respect to the first immersion: only three orders of magnitude decrease and a recovery time of 24 h have been noticed.

Figure 7. Time dependent resistivity with respect to FeCl₃ sensitization.

Concerning the temperature effect on resistivity (Figure 8), an expected behaviour is emphasized, consisting in a decrease in resistivity with increasing temperature [22].
Figure 8. Temperature dependence of FeCl₃ sensitized PBDB-T-SF thin films under dark condition measurements.

Figure 9. Temperature dependence of resistivity during several heating and cooling cycles under dark and illumination conditions (for as-prepared polymer thin film – top left graph; for FeCl₃ sensitized polymer thin film – top right graph; for after 24 h of FeCl₃ sensitization – bottom left graph; for a second immersion in FeCl₃ of polymer thin film – bottom right graph).
Comparing to the as-prepared thin-film resistivity, the sensitized thin films exhibit a slight decrease. This fact is presented in detail in Figure 9, during several heating and cooling cycles under dark and light conditions. In Figure 9, the top left graph describes as-prepared thin film, from which it can be easily inferred the effect of illumination-a resistivity decrease. This statement is not confirmed in the case of sensitized films, in which the presence of light increases the resistivity; this fact needs further investigations, in order to be fully understood.

4. Conclusion and perspectives

In conclusion, this paper presents a solution for enhancement of electric conductivity of polymer thin films used in solar cells, by ferric chloride (FeCl$_3$) sensitization. The PBDB-T-SF thin films (93 nm thick) exhibit a good absorption in visible range, which is slightly decreased after FeCl$_3$ sensitization. From ellipsometric measurements of refractive index and extinction coefficient, the mentioned behaviour is confirmed. Besides, the electric resistivity decreases dramatically after first immersion, from $>10^3$ Ω·cm (pristine thin films) to $10^{-3}$ Ω·cm, effect which lasts one day, with a slow recovery. Instead, the resistivity variation with temperature for sensitized films is slower comparing with that of pristine films, while the effect of light is different, an increased resistivity.

5. References

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