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Optimization of the properties of bulk heterojunctions obtained by coevaporation of Zn-phthalocyanine/perylene

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Abstract

Zn-phthalocyanine (ZnPc)–perylene tetracarboxylic dianhydride (PTCDA) "bulk heterojunctions" has been obtained by vacuum evaporation from a single heated source. The composition, in weight, of the initial powder was 0, 10, 25, 50, 100% of PTCDA. The deposited films have been characterized by infrared, visible and near UV absorption, scanning electron microscopy and X-ray photoelectron spectroscopy (XPS). "Diodes bulk heterojunctions" ITO/ZnPc:PTCDA/Al and ITO/PEDOT:PSS/ZnPc:PTCDA/Al have been also realized and studied by I–V characteristic measurements in the dark and under illumination (ITO: indium tin oxide; PEDOT:PSS: poly(3,4-ethylene dioxythiophene) oxidized (doped) with poly(4-styrenesulfonate)). It is shown, in the case of pure ZnPc or PTCDA thin films that the properties of the initial molecules are preserved, during the deposition process.

The introduction of PTCDA in the ZnPc induces a best covering of the visible spectrum. It is shown that the films with the optimum PTCDA concentration in ZnPc (25% weight) for the expansion of light absorption spectrum give the best results in solar cells.

The formation of a blend PTCDA:ZnPc was found to improve the photovoltaic performances of the solar cell. This improvement is attributed to the expansion of light absorption spectrum and to charge separation by the bulk heterojunctions. Moreover, the presence of a thin PEDOT:PSS film at the interface ITO/ZnPC:PTCDA allows one to achieve a significant solar cell efficiency of nearly 0.2%.

Keywords: Bulk heterojunctions; ZnPc; PTCDA; Plastic solar cells

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1. Introduction

Recently the new concept of "bulk heterojunctions" has been introduced to describe organic photovoltaic devices [1,2]. These bulk heterojunctions consist of organic electron donor and acceptor blends. Such blends allow some efficiency in the fundamental process necessary to achieve significant solar cell efficiency. These fundamental steps are absorption of light, creation and separation of carriers at the donor/acceptor interfaces and transport of the carriers through the bulk of

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the device from the creation site to the appropriate collecting electrodes.

The first difficulty is to use organic material, whose absorption spectrum corresponds more or less to the solar spectrum. The absorption of light induces the creation of exciton rather than free charge. The second objective is the separation of the created exciton. Such separation takes place at donor–acceptor interfaces. Since the created electron–hole pairs have very short free carrier length (≅10 nm), these interfaces should be distributed in the whole bulk of the sample to optimize the separation efficiency. Moreover, after separation the holes and electrons should not recombine before being swept out of the device to the external circuit. Therefore, phase separated paths should be present in the films, where the free charges are transported through the device. This is induced by electrodes that have different work functions, thus providing a built-in electric field over the active layer.

In the present work, bulk heterojunctions have been achieved by coevaporation of organic donor and acceptor.

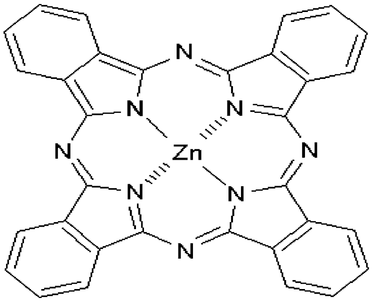
The electron donor used is zinc phthalocyanine and the electron acceptor is a perylene.

Phthalocyanines are among the promising materials for organic solar cells since they are stable and they exhibit high photoconductivity. PTCDA are electron acceptors with high photostable, broad visible light absorption. Moreover, they can be easily sublimated, which allows bulk heterojunction fabrication by a simple method using conventional vacuum deposition equipment.

We have first optimized the blend proportions in the light of absorbance spectrum and then the first solar cells have been tested.

2. Experimental

2.1. Cells fabrication

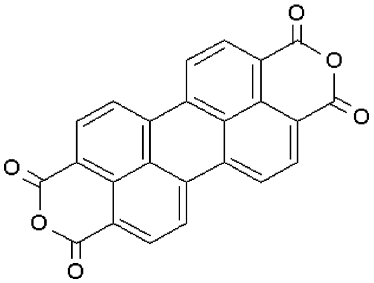


Scheme 1. Zinc phthalocyanine (ZnPc).

Zinc phthalocyanine (ZnPc) (Scheme 1), is a blue pigment, while the PTCDA used, the perylene-3,4,9,10-tetracarboxylicdianhydride (PTCDA) ($C_{24}O_6H_8$) (Scheme 2) is a red pigment. The organic blend (ZnPc/PTCDA) was deposited by sublimation on a transparent conductive oxide (TCO) coated glass.

The TCO used was commercial indium tin oxide (ITO) (provided by Solems). The whole glass substrates were covered, therefore some ITO must be removed to obtain the under electrode. After masking a broad line of 4 mm, the ITO was etched by using Zn + HCl as etchant [3].

Then the substrates were cleaned by using the H_2O_2 treatment following a process described by Osada and colleagues [4], which corresponds to the first solution (SC1) of the RCA process first described by Kern and Puotinen [5]. The substrates were treated with an 80 °C $H_2O–H_2O_2$ (30%)–NH_4OH (25%) solution (5:1:1 vol parts) for 20 min, followed by rinsing with boiling distilled H_2O for 5 min. The use of boiling water was proven to be helpful to obtain impurity free surfaces.



Scheme 2. Perylene-3,4,9,10-tetracarboxylicdianhydride (PTCDA).

The deposition apparatus was equipped with a Pyrex glass chamber designed in the laboratory. During deposition the substrate holder was cooled by melting ice. The thickness of the organic layers was measured in situ by an HF quartz monitor. The thickness was checked by cross-section visualization by using a scanning electron microscope (SEM). All the depositions were done in a vacuum of 10^{-3} Pa.

The evaporation cell temperatures during the depositions were measured by copper–constantan thermocouple introduced into the Pyrex cell. The deposition rate, v, was $v \cong 0.5\ \mathrm{nm\,s^{-1}}$ using a cell temperature of 350 °C.

It has been shown that the sublimation temperatures of the organic compounds used in the present work are very similar. Different powder "mixtures" were used from 10 weight % of PTCDA to 50 weight % of PTCDA. The film thickness varies from 80 nm to 120 nm.

In the case of ITO/PEDOT:PSS/ZnPc:PTCDA/Al structures the PEDOT:PSS has been spin coated onto the ITO and heated at 120 °C for 2 h before introduction of the substrate in the vacuum chamber. PEDOT:PSS (BAYER) was spin coated because it was in aqueous dispersion with H_2O as pristine solvent.

Finally, Al upper contacts were deposited onto the organic layer by vacuum evaporation at low pressure close to 10^{-4} Pa. A mask was used to determine a well defined shape for the Al electrode, which gives an active area of 2 mm^2.

2.2. Characterization techniques

To study the properties of the different blends, the films were characterized by infrared absorption measurements (I-R and visible), scanning electron microscopy measurements (SEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction and current voltage (I–V) characteristics in the dark and under illumination.

Infrared spectra were obtained with an FTIR spectrometer. Absorption band positions are given in wave numbers (cm^{-1}).

The observations of the morphology of the surface and of the cross-section of the films were performed by using a JEOL 6400F field effect scanning electron microscope (SEM) to compare the surface topography of the different blends and to check their cross-sections. The accelerating voltage used was 7000 V.

Electron spectroscopy for chemical analysis (ESCA) measurements were conducted with a Leybold spectrometer at the University of Nantes, CNRS. The ESCA was used for XPS measurements. The X-ray source was a magnesium cathode (1253.6 eV), operating at 10 kV and 10 mA. The energy resolution was 1 eV at a pass energy of 50 eV. High resolution scans with a good signal/noise ratio were obtained in the C1s, N1s, O1s, Zn3d regions of the spectrum. The quantitative studies were based on the determination of the C1s, N1s, O1s, Zn2p$_{3/2}$ peak areas with, respectively, 0.2, 0.36, 0.61, 7.2 as sensitivity factors; the sensibility factors are given by the manufacturer.

In order to investigate the crystalline structure of the films, they were analyzed using an automated step-scanned Siemens diffractometer with CuKα radiation source ($\lambda = 0.15406$ nm).

For I–V measurements, the ITO/blend/Al sandwich structures were used. The I–V curves of the cells were measured in room air, using a Lambda power supply as source voltage and Keithley apparatus. The curves were measured in the dark and under AM1.5 illumination using an Oriel solar simulator equipped with filters ($P = 100\ \mathrm{mW/cm^2}$).

3. Experimental results

As told before the organic blend was obtained by simultaneous deposition of ZnPc and PTCDA. The different fraction of PTCDA used were: 0, 10, 25, 50, 100 wt.% of PTCDA in ZnPc. The pure ZnPc and PTCDA thin films were used as references.

The infra red spectra of ZnPc and PTCDA thin films (Fig. 1) are similar to those of corresponding powder, which confirms that these organic molecules are not destroyed by the deposition process.

The I-R spectrum of different blend compositions is also reported in Fig. 1. The more intensive absorption peak of ZnPc is situated at 725 cm^{-1},

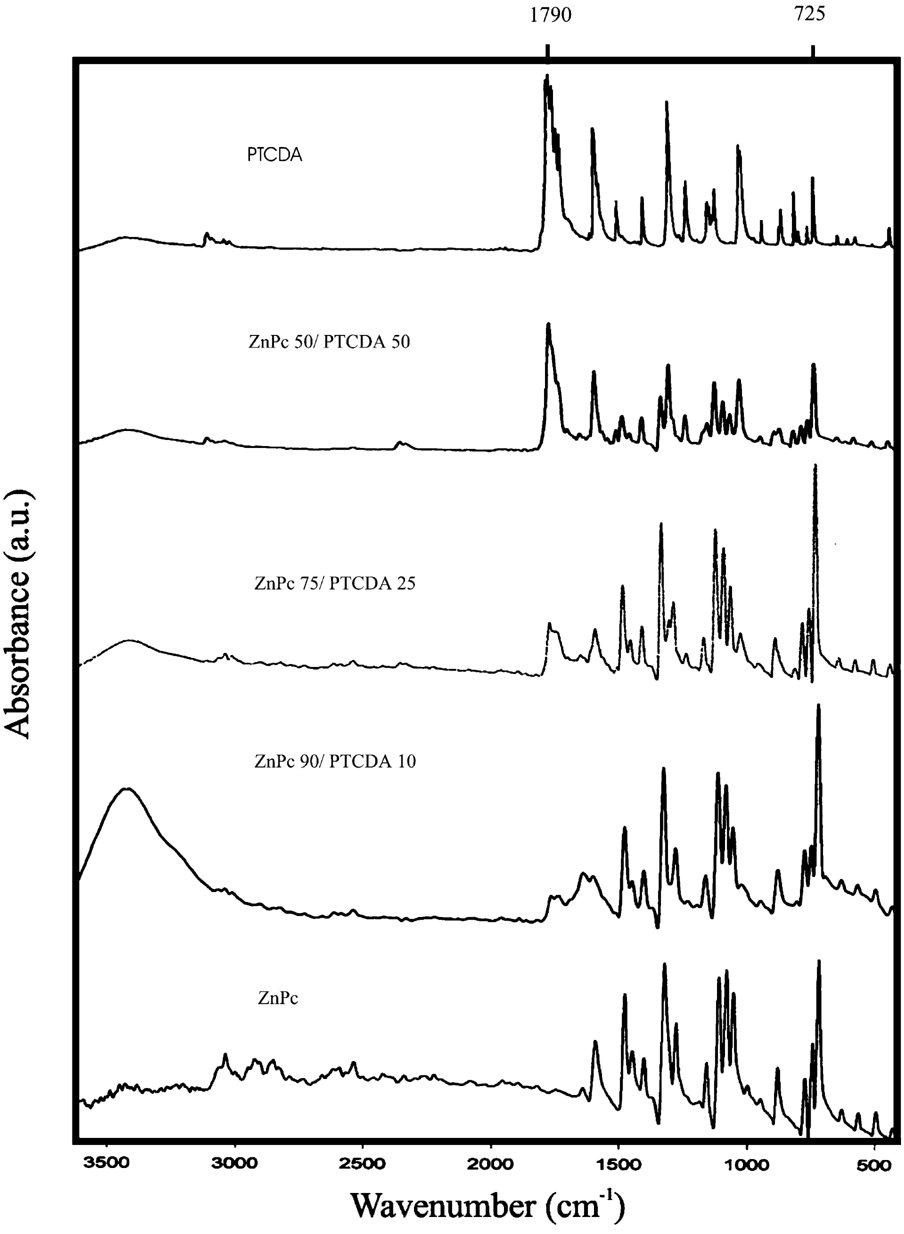


Fig. 1. The I-R spectra of blend of ZnPc/PTCDA: 100/0, 90/10, 75/25, 50/50, 0/100.

this absorption band is attributed to the C—H wagging vibrations modes [6]. In the case of PTCDA, the C=O stretching band is clearly visible at 1790 cm^{-1}. It is also the easiest to discriminate from the others. The intensity ratio of these two absorption peaks can be used to follow qualitatively the variation of the film composition. It can be clearly seen in Fig. 1 that the experimental result follows qualitatively the expected variation.

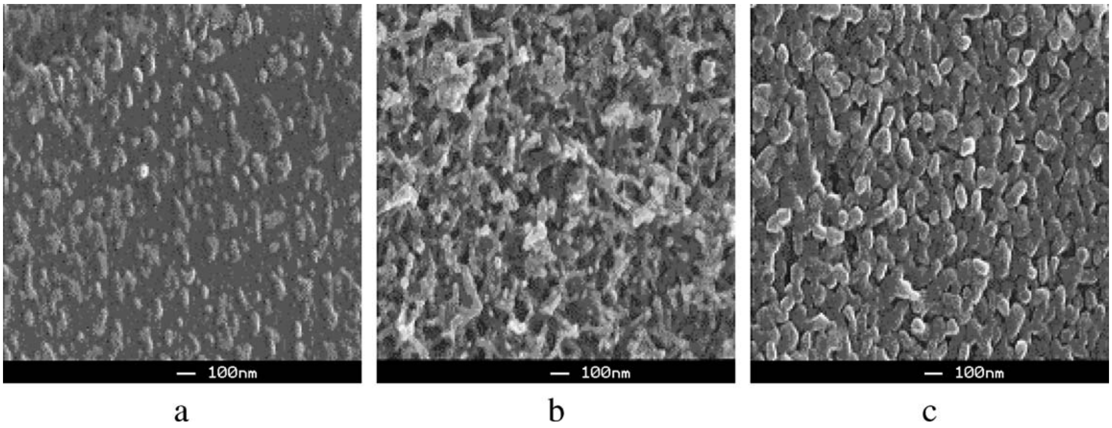


Fig. 2. SEM images of ZnPc thin film (3a), PTCDA thin film (3b), blend of ZnPc and PTCDA 50/50 (3c).

SEM observation allows one to follow the evolution of the surface morphology of the films with the composition of the blends (Fig. 2). The pure ZnPc films appear quite smooth with small heaps randomly distributed in a homogeneous matrix (Fig. 2a). The pure PTCDA films are quite porous and formed of small fibrilar structures randomly oriented (Fig. 2b). In the case of blend, the film morphology is quite different from both kinds of films. The blends are composed of grains more or less fibrilar and broader than the fibrils of pure PTCDA films (Fig. 2c). Such evolution of the film morphology confirms that there is a good homogeneity of the mixture of the organic compound involved in the blend.

The visualization of a cross-section of a structure glass/ITO/organic blend shows that the adherence between the ITO electrode and the organic film is very good without any visible porosity (Fig. 3). The thickness of the films can be directly measured. In the present case it is 110 nm. Such thickness has been used to achieve the first solar cells.

Typical XPS spectra are presented in Figs. 4, 5 and 6. In Figs. 4 and 5 are given the reference spectra of pure ZnPc and PTCDA thin films, respectively, while Fig. 6 gives the typical spectra of a ZnPc/PTCDA blend. The decomposition of these spectra is illustrated in Table 1.

As expected, in the case of ZnPc, one contribution is detected for the N1s peak at 399 eV, which corresponds to the value expected for nitrogen in phthalocyonine, since it has been shown that the component N1s at 398.9–399.2 eV should be assigned to nitrogen atoms chelated with zinc atom [7].

The C1s peak can be decomposed into four components which are assigned [8] to C–H group at 285 eV, a mixture of carbon bonded to nitrogen and C–OH group around 286 eV, a contribution of C=O around 286.5 eV and $\pi-\pi^*$ shake-up satellite around 289.8 eV.

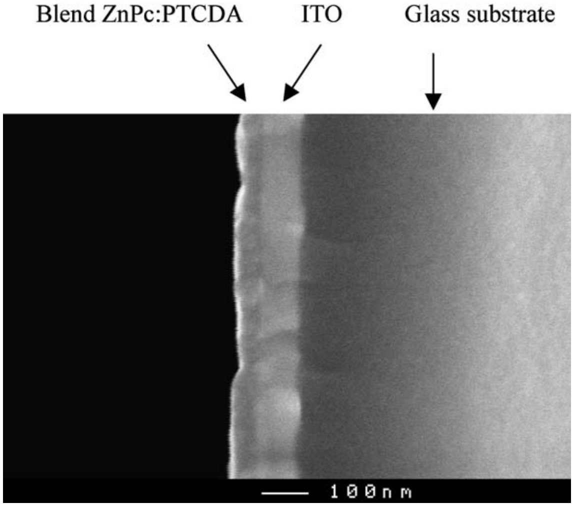


Fig. 3. Cross-section of a glass/ITO/blend structure.

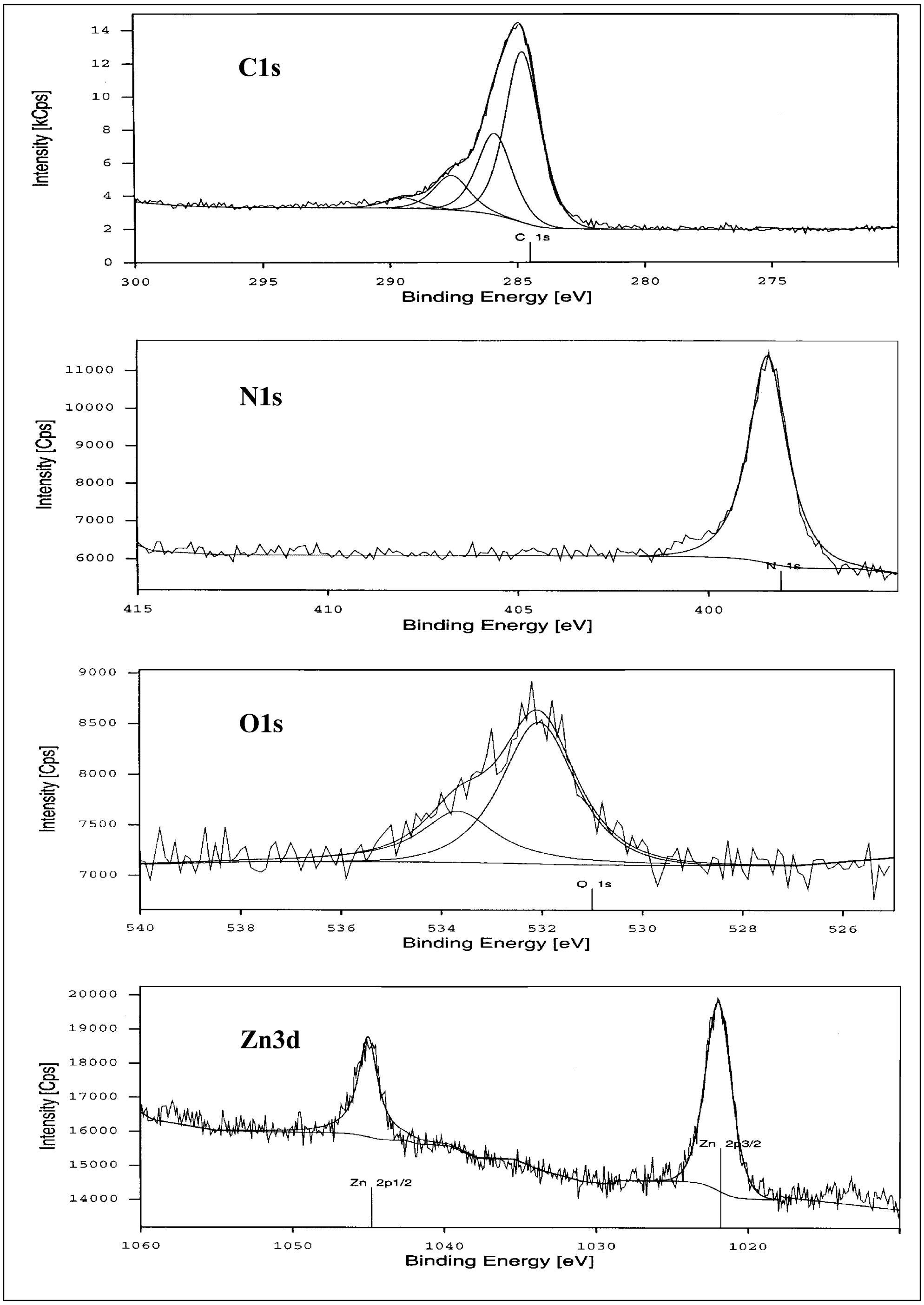


Fig. 4. X-ray photoelectron spectroscopy (XPS) of ZnPc: C1s (a), Zn2p$_{3/2}$ (b), N1s (c), O1s (d).

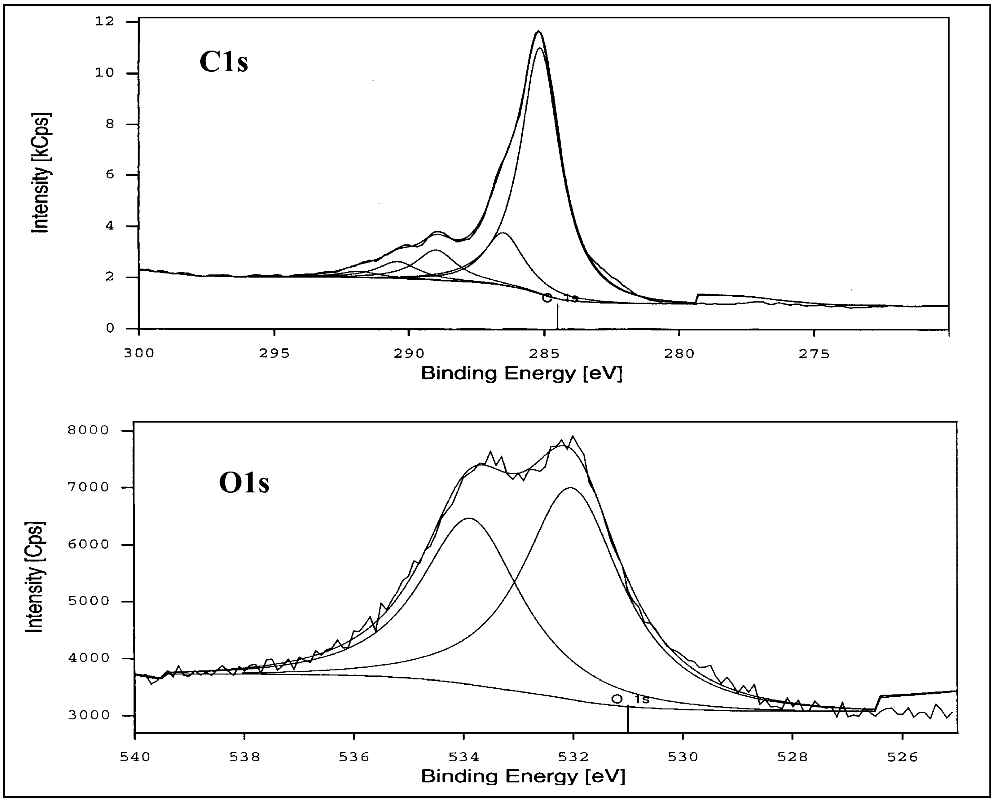


Fig. 5. X-ray photoelectron spectroscopy (XPS) of PTCDA: C1s (a), O1s (b).

In correlation with C1s decomposition, the O1s peak can be decomposed into two components at 532.2–532.5 eV and 533.6–533.9 eV, which are assigned to C=O and C–O–H groups, respectively. The formation of such carbon–oxygen functionalities may be due to a surface contamination. This surface contamination is related to the fact that the sample, after deposition, is transferred to the XPS analysis chamber via room air. When the surface of the films is etched by argon ions this surface contamination disappears, however, we have not presented these spectra because the etching destroys, at least partly, the C–N bonds of ZnPc.

The $Zn2p_{3/2}$ peak is situated at about 1022.5 eV. Such a result cannot be very effective in revealing details of the films since the chemical shift of the $Zn2p_{3/2}$ by different chemical states is very small [8]. Its chemical shift is too small to reveal in what state the zinc atom in the film is present.

In the case of PTCDA (Fig. 5) the main contribution of the C1s peak, which is situated at 285 eV, can be assigned to C–C bonds associated with the PTCDA core of the molecule, i.e., C atoms that are only bonded to other C atoms and which are neither directly nor secondarily bonded to oxygen. The contribution at 289 eV arises from C atoms of the carbonyl group. The contribution situated at 286.5 eV can be attributed to these carbons bonded to carbonyl function. The binding energy of these secondary carbons can be clearly discriminated from C of the carbonyl group and from the carbon of the PTCDA core of molecule [8]. The fourth broad contribution at 290.6 eV is assigned to a shake-up feature associated with the carbonyl groups [9,10].

The corresponding O1s spectrum for the PTCDA film is dominated by two contributions. One due to the carbonyl O atoms at 532.2 eV, the other arising from anhydride O atoms at 534 eV.

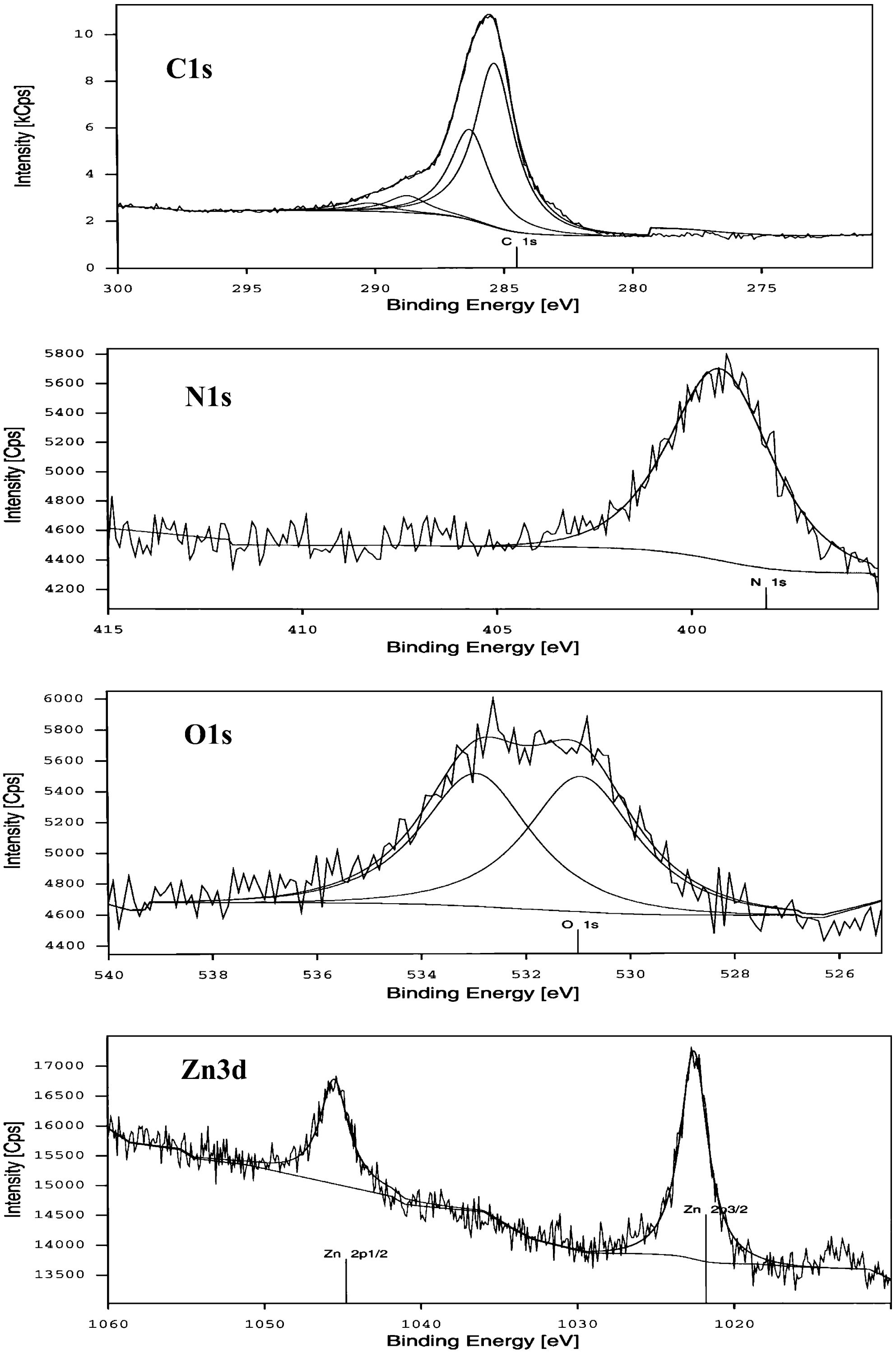


Fig. 6. X-ray photoelectron spectroscopy (XPS) of ZnPc/PTCDA 75/25: C1s (a), Zn2p$_{3/2}$ (b), N1s (c), O1s (d).

Table 1
XPS analysis after decomposition of the peaks

	Bending energy (eV) of the different components								
	C1s				O1s		N1s		$Zn2p_{3/2}$
ZnPc	285	286	286.5	289.8	532.5	533.6	399	400.5	1022.5
PTCDA	285	286.5	289	290.5	532.2	534			
ZnPc/PTCDA	285	286.4	289	289.19	530.65	533.43	398.79		1022.5

It is clear that the intensity ratio of the two oxygen peaks (C=O/C–OH) is not 2/1 as theoretically expected for PTCDA. This has been observed previously in such films and it has been attributed to a shake-up feature from the C=O peak, which contributes to the C–O peak and increases its relative intensity [11], of course there is no N1s contribution in pure PTCDA.

In the case of the blend the typical contributions from each organic molecule present are simultaneously visible (Fig. 6), which corroborates the homogeneity of the blend (Table 1). Moreover, it should be noted that there is no appreciable variations in the binding energies of the different contributions. However, it should be noted that the full width at half maximum (FWHM) of the N1s peak is only 1.3 eV in the case of pure ZnPc, while it is 3 eV in the case of the blend, indicating some interaction between ZnPc and PTCDA in the blend.

X-ray diffraction study (Fig. 7) shows that the deposited films are amorphous. For comparison, XRD diagrams of the reference powder are also presented. It can be concluded that there is not any crystalline precipitation of one of the components in the films.

These observations implied that most of molecules did not crystallize owing to the interactions between ZnPc and PTCDA molecules in the blend films.

Knowing that, ZnPc thin films are blue, while PTCDA thin films are red, the colour of the blend film follows the composition of the initial powder mixture.

The optical density of ZnPc is presented in Fig. 8a. The spectrum shows the typical three absorption peaks related to the π–π^* transition at 350 (partly masked by the glass substrate), 615 and 650 nm [7]. In the case of PTCDA, two main peaks are clearly visible at 500 nm and 535 nm (Fig. 8a). It can be seen that the absorbance spectrum of the blends consists of the sum of those of ZnPc and PTCDA spectra. Fig. 8a indicates that the introduction of PTCDA in ZnPc expands the light absorption spectrum of the films in the 400 nm–600 nm region, which contributes to an enhancement in the photo carrier generation. Therefore, it can be seen in Fig. 8b that the optimum PTCDA weight concentration is around 25%. For such composition, the absorbance spectrum of the blend corresponds more or less to the solar spectrum. Such an absorbance spectrum improves creation of excitons, which should improve the solar cell performance. However, after creation the exciton should be separated and then collected at the electrodes, which necessitates, as shown above, bulk heterojunction and phase separated way. Therefore, in a first attempt, we have tested the blend exhibiting good absorbance spectrum in solar cell devices. The ZnPc:PTCDA blend has been used and the results obtained have been compared to those obtained with pure ZnPc films.

After deposition of the aluminium upper electrode, contacts have been obtained using copper wire stuck to the electrodes by silver paste. The I–V characteristics of the organic cells have been measured, in room air, in the dark and under illumination using a solar simulator using AM1.5 conditions. Typical results are shown in Figs. 9 and 10. It can be seen that the structures exhibit a diode behaviour and, under illumination, a photovoltaic effect is clearly visible. The I–V characteristics of pure ZnPc are plotted in Fig. 9. The current density is $I_{sc} = 0.07\ \mathrm{mA/cm^2}$ as short circuit current density, with $V_{oc} = 0.42$ V as open

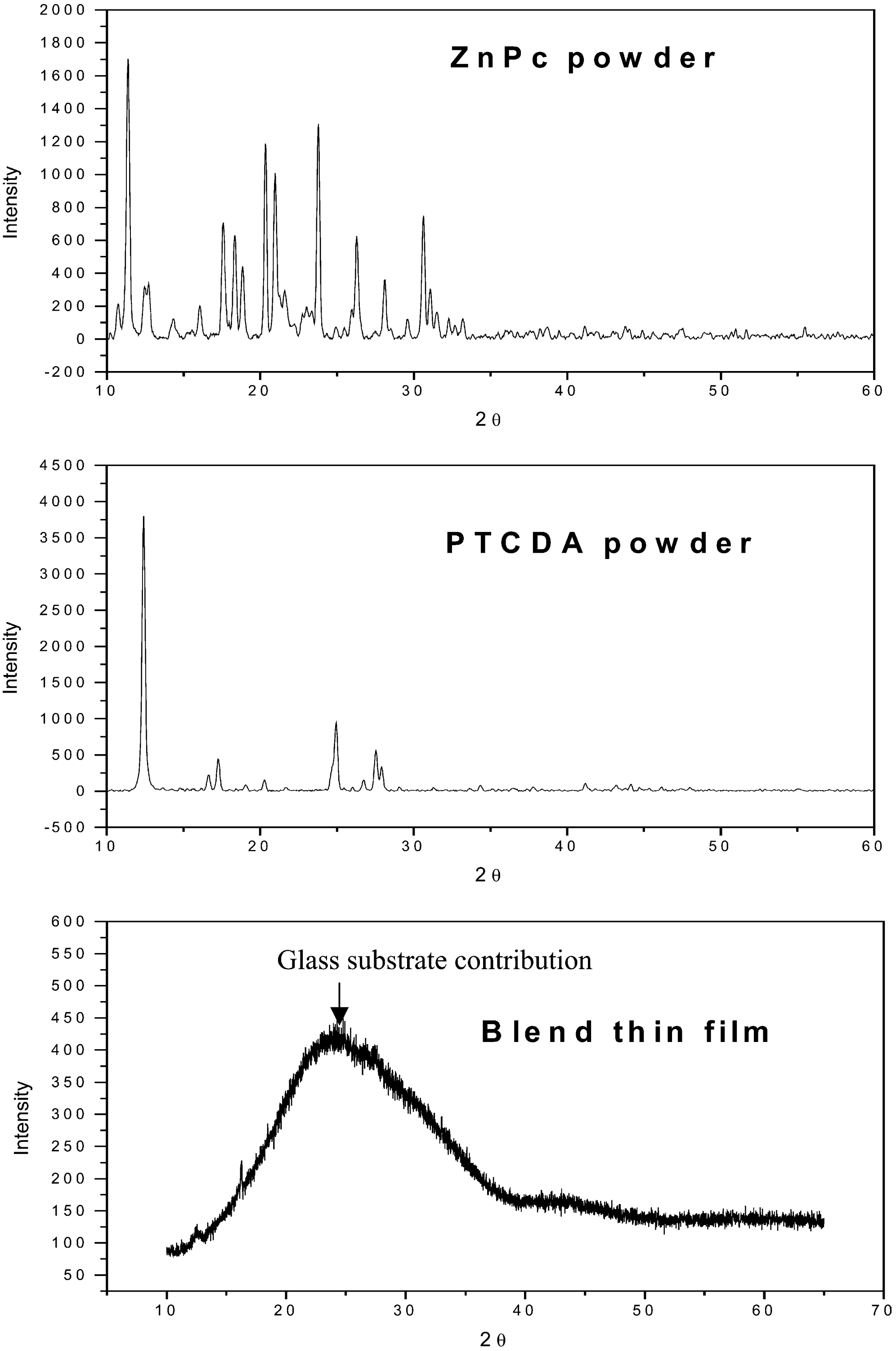


Fig. 7. X-ray diffraction diagram of ZnPc powder, PTCDA powder and ZnPc/PTCDA 75/25 tin film.

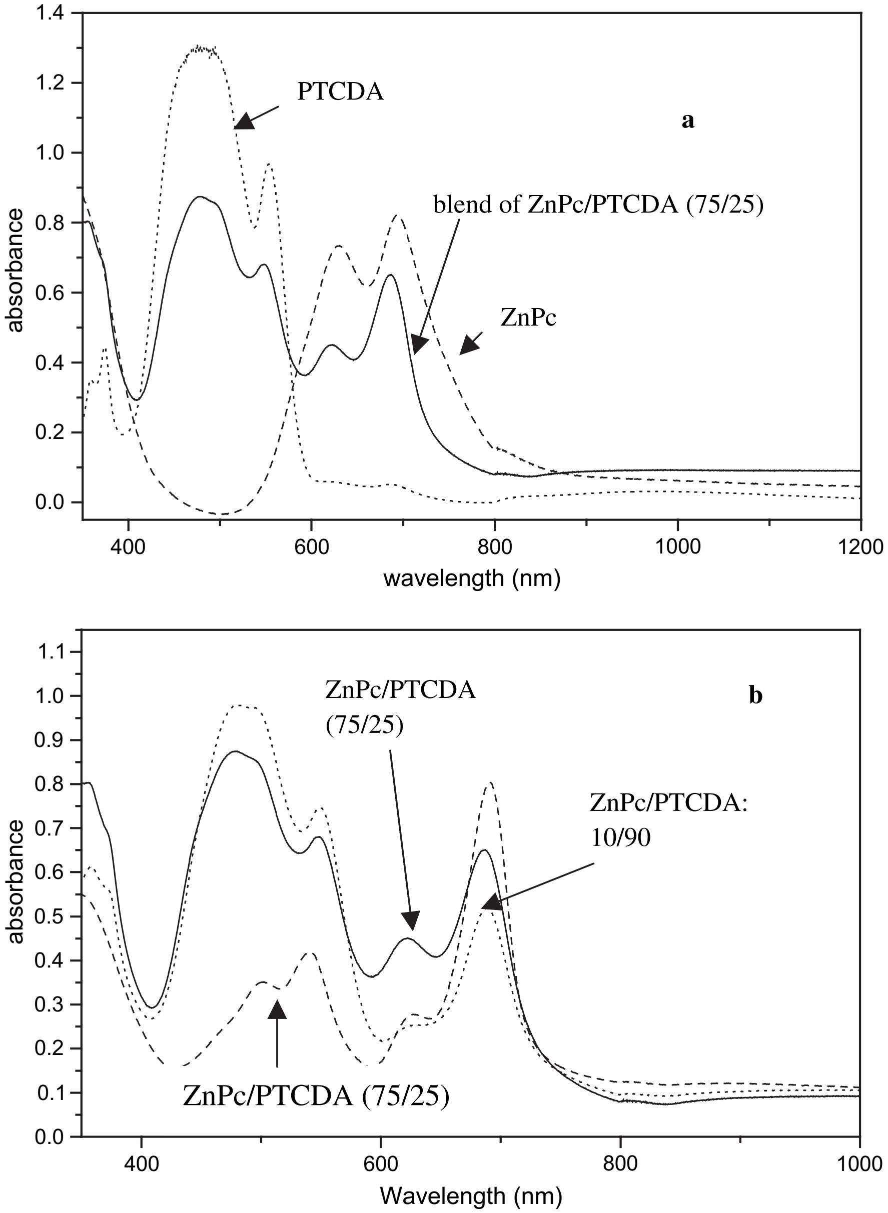


Fig. 8. (a) The absorbance spectra of: PTCDA pure film (dotted line), ZnPc pure film (dashed line), blend of ZnPc/PTCDA 75/25. (b) The absorbance spectra of three blend of ZnPc/PTCDA: 10/90 (dotted line), 75/25 (solid line), 50/50 (dashed line).

circuit voltage and FF = 0.21 as fill factor, the corresponding efficiency can be estimated to be 0.006%.

In the case of ITO/ZnPc:PTCDA/Al (Fig. 10), the blend used corresponds to 25 weight % of PTCDA, the best efficiency achieved is $\eta = 0.09\%$ with $I_{sc} = 0.64\ \mathrm{mA/cm^2}$, $V_{oc} = 0.4\ \mathrm{V}$ and FF = 0.35. The improvement of the solar cell performance by PTCDA doping of the ZnPc can be attributed to the expansion of the light absorption spectrum but also to the presence of bulk heterojunctions.

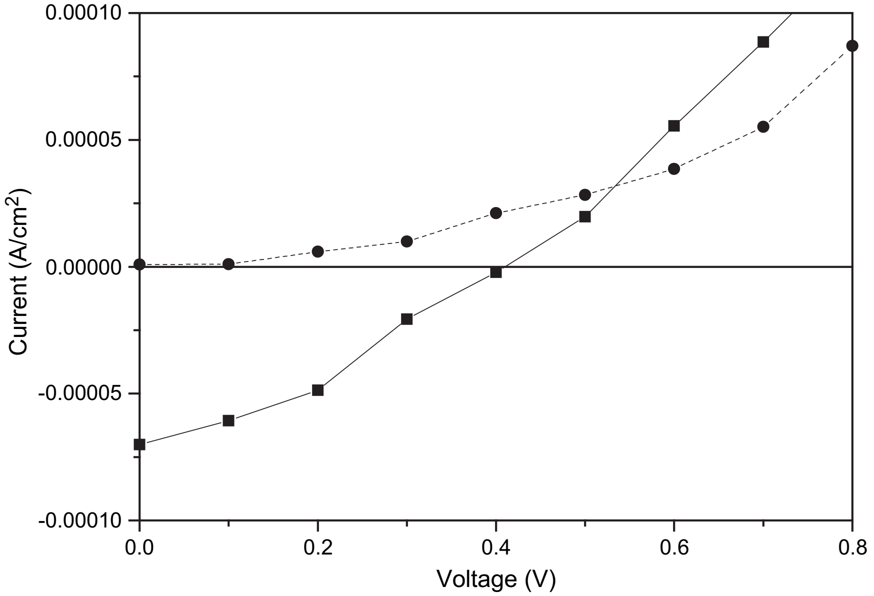


Fig. 9. *I–V* characteristics of an ITO/ZnPc/Al structure.

In order to check the influence of the absorption spectrum of the blend on the solar cell performance, some cells have been grown with a blend containing 50 at.% of PTCDA. In the case of the blend with 50 weight % of PTCDA the best efficiency achieved is $\eta = 0.05\%$ with $I_{sc} = 0.4\,\mathrm{mA/cm^2}$ as short circuit current density, $V_{oc} = 0.63\,\mathrm{V}$ as open circuit voltage and $\mathrm{FF} = 0.22$ as fill factor. The contribution of the expansion of the light absorption spectrum is clearly demonstrated by the good correlation between the optimum efficiency and the absorption spectrum of

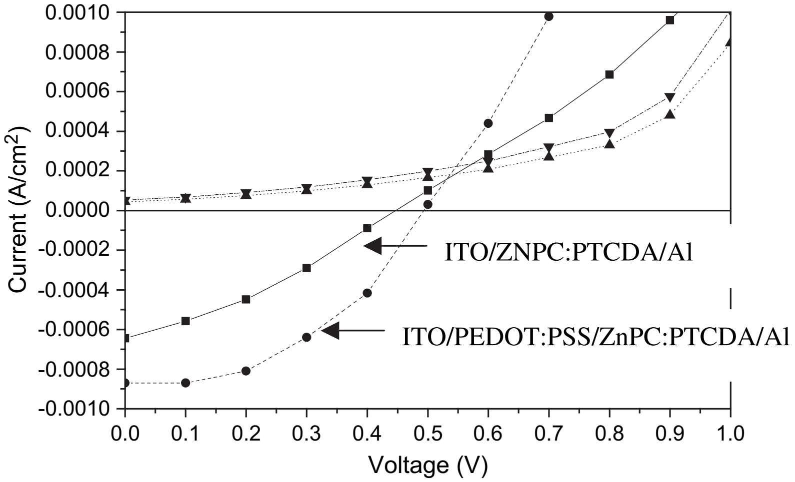


Fig. 10. *I–V* characteristics of: ITO/ZnPc:PTCDA/Al in the dark (▲), under illumination (■) and ITO/PEDOT:PSS/ZnPc:PTCDA/Al in the dark (▼), under illumination (●).

the blend. The best cells use the blend which exhibits the best coverage of the solar light spectrum.

After photon absorption and exciton creation, the exciton should be dissociated at a large donor/acceptor interface area. This large interface area is created by the blend structure.

After photon absorption and exciton creation carriers are separated at a p/n junction situated in the bulk and then they should be collected by the electrodes. This necessitates homogeneous pathways along the section of the structure. In fact, by varying the PTCDA concentration we have shown that we modify the morphology of the films. For heavy concentration of PTCDA some change in morphology can disrupt the homogeneous pathways, which may decrease the carrier mobility and therefore the efficiency. As shown above, this efficiency can be increased by varying the PTCDA weight concentration in the blend. It has been shown elsewhere [12] that, in the case of CuPc the maximal photovoltaic performance was achieved in the cell with 9.1% perylene doping.

Also electrode interface properties have significant influence on cell performances. ITO is well known to exhibit a rough surface, which can induce some current leakage effect, the organic absorber film being quite thin. By introduction at the interface ITO/ZnPc:PTCDA of a PEDOT:PSS film deposited by spin coating, the surface of the ITO film can be smoothed. The PEDOT:PSS blend has a conductivity (10 S/cm) which follows a metallic behaviour. Therefore, it can decrease the losses related to current leakage effect since it smooths the electrode surface. Moreover, it appears that PEDOT:PSS improve the band structure adaptation, which improves the efficiency of carrier extraction from the organic film. Fig. 10 shows that the presence of the PEDOT:PSS interface layer improves significantly the solar cell performances, an efficiency of $\eta = 0.2\%$ has been achieved with $I_{sc} = 0.87\ \mathrm{mA/cm^2}$, $V_{oc} = 0.50\ \mathrm{V}$ and FF = 0.45.

4. Conclusion

PTCDA and ZnPc have been deposited by evaporation under vacuum. The properties of these films are more or less preserved during the heating of the sample needed for evaporation. Blend formation by PTCDA's introduction in ZnPc was found to improve the absorption characteristics of ZnPc. The correlation between the absorption of the blend and the visible spectrum is improved. This improvement has been attributed to the expansion of light absorption spectrum. The optimum PTCDA doping concentration in ZnPc for the expansion of light absorption spectrum has been shown to be 25 weight % of PTCDA. Among the blend used in the present work this concentration is also optimum for the solar cells. It is shown that the formation of a blend ZnPc:PTCDA increases the photovoltaic performances by comparison with ZnPc. This improvement can be attributed to the broadening of the absorption spectrum of the blend and to the "bulk heterojunction" effect. Also, the use of PEDOT:PSS at the ITO/blend interface improves the cells efficiency.

Some improvements of the device remain necessary to improve the fill factor. Some very thin LiF layers at the interface blend/Al will be tested in the near future. Some heating treatments are also under study.

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