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Improvement of the photovoltaic properties of polythiophene-based cells

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Abstract

The photovoltaic properties of organic cells based on a polythiophene film have been studied. An external power efficiency of $10^{-4}\%$ has been obtained in the pristine polymer diode. In order to improve this result, three complementary routes have been investigated. Optical sensitization of the polythiophene with a dye of the indane group leads to a 75 increase in power efficiency. A hybrid molecular/polymeric p–n type junction instead of the original Schottky type provides a 0.15% efficiency. Molecular rectification in oriented polymers incorporating diode-like chromophores increases the PV efficiency by a factor of 40. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Organic semiconductor; Polymer; Spectral sensitization; Molecular diode; Photovoltaic cell

1. Introduction

The interest toward semiconducting organic materials has been growing for many years [1,2]. One reason is the possibility to fabricate inexpensive and simple optoelectronic devices such as transistors, light-emitting diodes or photovoltaic cells. A large variety of organic compounds, molecules or polymers, allows the fabrication of cells with different geometries like single-layer or multilayers configurations. Several techniques, such as vacuum sublimation, Langmuir–Blodgett molecular arrangement or spin-coating deposition, are available to achieve such devices.

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In this field of investigation, we focused our efforts on easy-processable organic photovoltaic systems based on a spin-coated polythiophene film. We first present studies performed on pure polythiophene Schottky-type cells. Optical and electrical characterizations show that the efficiency of these devices is limited by the narrow absorption spectrum in the visible range and the quality of the rectifying junction.

From these first results, different routes were investigated in order to improve the efficiency of our devices. We report the effect of an extension of the absorption spectrum of the photosensitive layer by adding a dye which is absorbed in the visible region. The results obtained with this p-type doped polymeric layer associated with an n-type molecular layer are also presented. The study of this p–n type photovoltaic cell confirms the importance of the quality of the junction on the power efficiency. We also present an original concept: orientation induced molecular rectification. The principle is based on the orientation of polar diode-like molecules contained inside a polymeric binder. The oriented molecules induce a rectification effect which behaves as a distributed homojunction within a single polymeric thin film. An increase in PV efficiency by a factor of 40 is demonstrated following such orientation induced molecular rectification. The internal field created by orientation is characterized by solid electric field induced second harmonic generation (SEFISHG).

2. Experimental section

In order to measure the effect of a dye on PV efficiency, we have first prepared two different kinds of Schottky-type photovoltaic cells. All the tested devices are realized on top of standard indium tin oxide (ITO)-coated glass slides. In the pristine cell, the polymer film is obtained from spin-coating of a solution containing poly(3-butylthiophene) P3BT dissolved in chloroform. The spin-coating of this organic film or of other kinds of organic layers is realized in air. Chemical structure of P3BT and of the organic compounds we have used are given Fig. 1.

For the second type of cells, a dye is added to the solution. As a dye we use a molecule which belongs to the indane group: 1,3-bis(dicyanomethylidene)-2-(4-dibutylaminobenzylidene) indane [3] that we refer to as PR3072. The dye is simply added to the solution of chloroform containing the polymer and not grafted to it. Nevertheless, the alkyl chains make PR3072 very soluble even at a relatively high concentration. The spin-coated solution contains 16 g/l of P3BT and 16 g/l of PR3072 in chloroform. No aggregation or segregation has been observed in the films. To complete the cells, metallic electrodes are vacuum vapor deposited onto the organic film to form the top electrode. The mask allows to prepare two cells on the same substrate as shown in Fig. 2(a). Active surface of the device corresponds to the upper circle and is 28 mm².

We have also prepared p–n type photovoltaic cells. The geometry of such a device is represented in Fig. 2(c). A layer of perylene derivative, called MPP, was first deposited by vacuum sublimation onto the ITO. As the MPP is not soluble in chloroform, a film of PR3072-containing polythiophene could be spin-coated onto the MPP. The layer of doped P3BT is p-type, the film of MPP is known to be n-type [4,5].

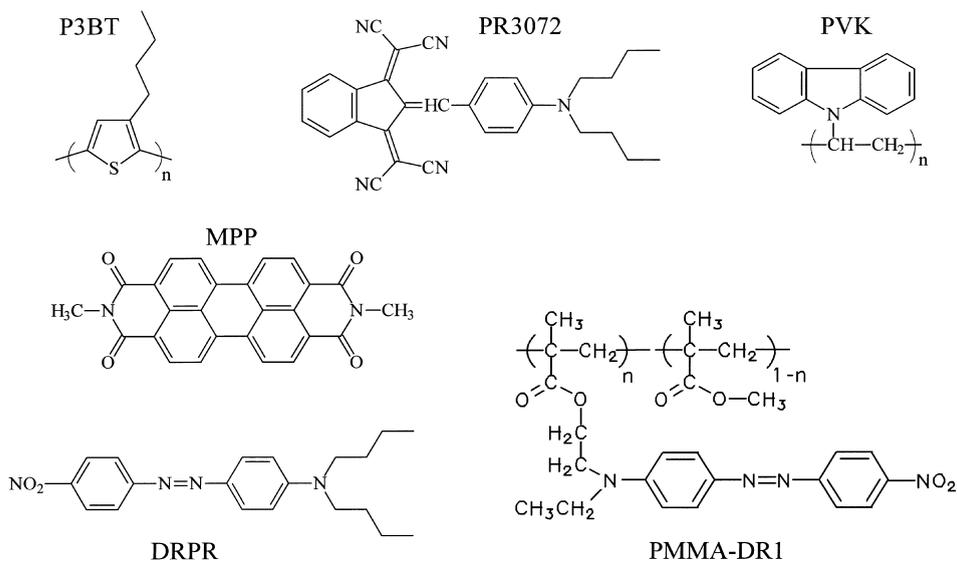


Fig. 1. Chemical structures of organic compounds.

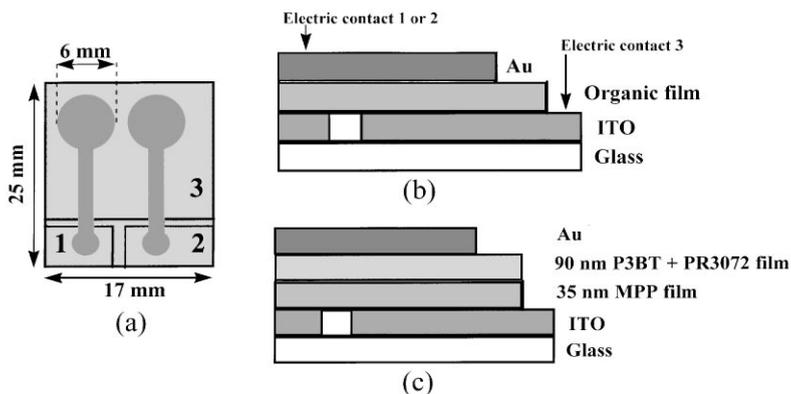


Fig. 2. (a) Top and side-view of (b) Schottky type and (c) p-n type photovoltaic cells.

The influence of oriented molecules in a polymer film on PV efficiency has been first investigated with Schottky-type cell based on a film of polyvinylcarbazole (PVK) doped with 4-(di-*n*-butylamino)-4'-nitroazobenzene (DRPR) and PR3072. Polar molecules of DRPR were oriented by applying a DC-field at a temperature close to the glass transition temperature of the blend, that is 45°C. The orientation was frozen by cooling the film down to room temperature while the electric field was maintained. We have then performed orientation of Disperse Red 1 on a single layer of a blend of PR3072 (33 wt%), P3BT (33 wt%), and a copolymer of polymethylmethacrylate and

Disperse Red 1 (PMMA-DR1) with 50%-molar chromophore concentration (34 wt%). The film was sandwiched between the ITO and Al electrodes.

Absorption spectra were plotted with a UV-Visible spectrophotometer (Perkin Elmer). The dark and light current–voltage (J – V) characteristics of the cells were recorded using an HP 4155A SC parameter analyzer. ITO was the electric reference. The voltage was applied to the other electrode. The light source was an Osram Halogen Xenophot 150 W lamp coupled with an array of optical fibers. Photovoltaic parameters, such as the open circuit voltage V_{oc} , the short-circuit current J_{sc} can be extracted. From this curve we also determine J_{max} and V_{max} which correspond to the current density and voltage, respectively, for the maximum power output $P_{max} = S \times J_{max} \times V_{max}$ where S is the illuminated surface. The fill factor FF is the ratio $(J_{max} \times V_{max}) / (J_{sc} \times V_{oc})$. The efficiency η corresponds to the external photoconversion efficiency, that is $P_{max} / S \times P_{opt}$, where P_{opt} is the incident light flux in $W\ cm^{-2}$.

The monochromatic beam for action spectrum measurements came from a Cary spectrophotometer. A mobile mirror successively sent the light on a silicium photodiode to evaluate the incident intensity and on the photovoltaic device. The photocurrent was measured by a lock-in amplifier 7220 EG&G. We then deduced the number of collected electrons per incident photons (IPCE) at different wavelengths given by

$$IPCE = \frac{1240}{\lambda} \times \frac{J_{sc}(\lambda)}{P_{opt}(\lambda)},$$

where λ , $J_{sc}(\lambda)$ and $P_{opt}(\lambda)$ denote the wavelength in nm, the wavelength dependence of J_{sc} in $A\ cm^{-2}$ and incident light flux in $W\ cm^{-2}$, respectively. The value of the spectral response is slightly under-estimated because the incident monochromatic beam does not cover the entire active zone of the electrode.

The storage of an internal electric field in organic film is evaluated by the solid electric field induced second harmonic generation (SEFISHG) technique. Through this method we determine the electric field in a direct way unlike relative measurements such as field-assisted fluorescence quenching or charge generation. For that, we carry out voltage-dependent SHG measurements. Intensity of the electric field-induced second harmonic generation (EFISHG) signal is given by Eq. (1)

$$I_{2\omega} \propto |\chi^{(2)}_{(-2\omega; \omega, \omega)} + \chi^{(3)}_{(-2\omega; \omega, \omega, 0)} E|^2, \quad (1)$$

where $\chi^{(2)}_{(-2\omega; \omega, \omega)}$ is the second-order susceptibility; $\chi^{(3)}_{(-2\omega; \omega, \omega, 0)}$ the third-order susceptibility and E the effective electric field applied inside the material.

Initially, the structure is centrosymmetric (isotropic distribution of the polar molecules). So, $\chi^{(2)} \equiv 0$ and $I_{2\omega}$ is proportional to the square of the effective field seen by the organic film, that is to say the electric DC-applied field $E_{applied}$ plus the electron work function difference between the two electrode materials E_{ddp} :

$$I_{2\omega} \propto |\chi^{(3)}_{(-2\omega; \omega, \omega, 0)} (E_{applied} + E_{ddp})|^2 \quad (2)$$

Therefore, the minimum of the initial SHG-voltage curve permits to determine the work function difference E_{ddp} . This method provides an in situ measurement of the

electron work function difference between the two electrode materials. This is quite interesting as work functions which are currently measured in vacuum or in an electrolyte solution are strongly affected by interfacial layers (as pollution films) and by the dielectric constant of the polymer. From this first SEFISHG characterization we can calculate the value of $\chi^{(3)}$. Following the polar orientation of dipolar molecules, it results an internal field E_{int} . The SHG intensity thus writes:

$$I_{2\omega} \propto |\chi_{(-2\omega; \omega, \omega)}^{(2)} + \chi_{(-2\omega; \omega, \omega, 0)}^{(3)}(E_{\text{applied}} + E_{\text{int}} + E_{\text{ddp}})|^2. \quad (3)$$

Eq. (3) cannot be solved directly as there are too many parameters to be determined simultaneously. The problem can be solved for each value of the orientation field by using an exact calculation of the SHG intensity, taking into account all the organic film and experiment parameters [6]. In this way, this newly employed method permits to determine the value of the internal field stored inside the structure.

3. Results and discussion

3.1. Photovoltaic properties of Schottky and *p-n* cells

Typical current–voltage (*J–V*) curves for the three kinds of cells are shown in Fig. 3. In order to picture all the curves on the same graph, current densities have been rescaled.

The characteristics (a) and (b) have been obtained with an irradiance of 50 mW cm^{-2} through the ITO side. Curves (a) and (b) corresponds to the response of cells based on a P3BT film (100 nm) and a P3BT + PR3072 film (220 nm), respectively. The characteristic (c) has been measured with an ITO/MPP (35 nm)/P3BT + PR3072 (90 nm)/Au device under 56 mW cm^{-2} illumination. The emission spectrum of the

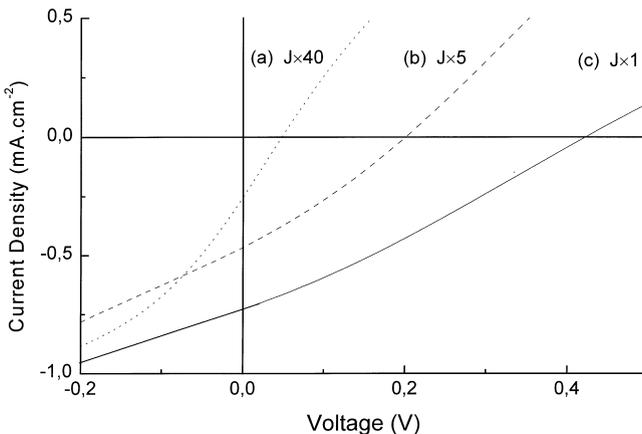


Fig. 3. *J–V* curves of (a) ITP/P3BT 100 nm/Au, (b) ITO/P3BT + PR3072 220 nm/Au, (c) ITO/MPP 35 nm/P3BT + PR3072 90 nm/Au. Incident light flux are 50 mW cm^{-2} for (a) and (b), and 56 mW cm^{-2} for (c).

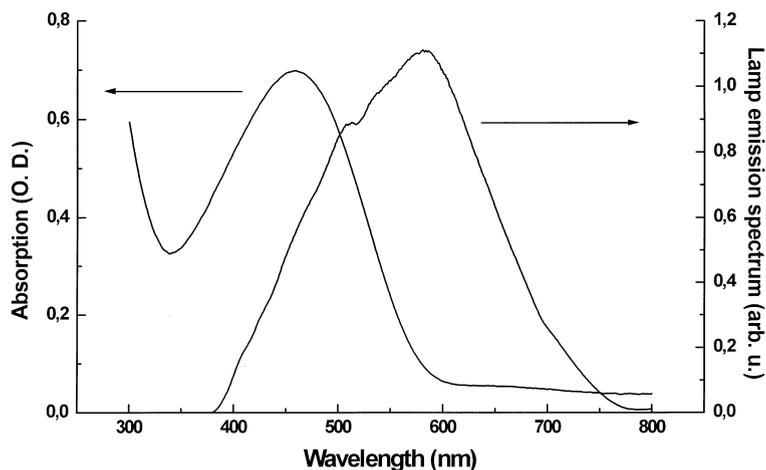


Fig. 4. Absorption spectrum of a 100 nm thick film of P3BT on ITO and Emission spectrum of the lamp used to irradiate photovoltaic devices.

lamp is represented in Fig. 4. Photovoltaic parameters were evaluated by analyzing these characteristics. In the case of a pure P3BT layer, the power efficiency η is about $1.6 \times 10^{-4}\%$. This low efficiency is partly due to the fact that the open-circuit voltage equal to 48 mV is low compared to the theoretical upper limit which is the difference between the work functions of the two electrodes. The limit is estimated to be 0.2 V for an ITO/Au system. Additionally, as shown in Fig. 4, its absorption spectrum does not match the emission spectrum of the lamp. Then, even if the polythiophene is known to exhibit a photovoltaic effect [7], a large quantity of light does not take part in the generation of the photocurrent.

Greater performances are obtained when the molecule PR3072 is added to the polythiophene. The open-circuit voltage is about 0.2 V that is close to the limit we mentioned above. The short-circuit current is 15 times higher than that in the cell containing only P3BT. The fill factor slightly increases from 0.25 to 0.29. In the same conditions of measurement as for the pristine cell, the power efficiency is multiplied by 75 and reaches $1.1 \times 10^{-2}\%$. It clearly appears that the PR3072 takes part in the photovoltaic effect. As shown in Fig. 5 the absorption spectrum of the organic film has been extended to both sides of the absorption peak of the P3BT. A better absorption can contribute to improve the photovoltaic performance if the incident photons are actually converted to charge carriers. The fact that no significant fluorescence has been detected is another positive point. It indicates that excited charges do not immediately recombine and convert incident light energy back into photons. Moreover the role of the dye is confirmed by plotting the action spectrum of the cell (Fig. 5).

First, we know from Fig. 4 that polythiophene alone does not absorb around 650 nm. Thus the peak of current at this wavelength is an evidence that PR3072 is a charge photogenerator. It would have been interesting to test the PV properties of

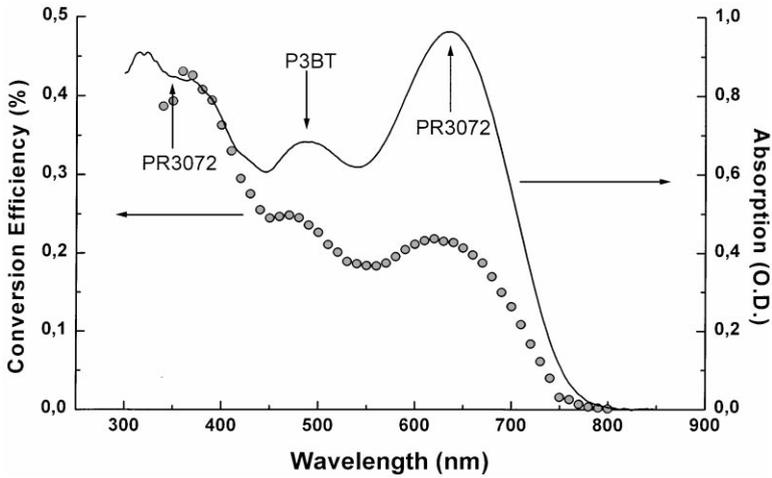


Fig. 5. Absorption spectrum of a P3BT (50 wt%) + PR3072 (50 wt%) 200 nm thick film and Spectral response of an ITO/P3BT 50 wt% + PR3072 50 wt%/Au cell.

a film of pure PR3072. But up to now we were not able to make a film by the vacuum sublimation method: the molecule degrades during evaporation. It is also not possible to prepare a spin-coated film without a polymer binder. Experiments of characterization of the conduction type of the molecule in a neutral polymer matrix instead of the polythiophene are underway. Second, as we illuminate through the ITO side and as the variations of the IPCE follow those of the absorption spectrum, we can also deduce from this graph that the active zone is located at the interface between the ITO and the organic layer. However, morphology of the ITO layer, and particularly its roughness, is not easy to control. Existence of non uniformly distributed peaks on the surface can lead to shorts or to an inhomogeneous ITO electrode which can affect the efficiency of the photovoltaic device. The p–n type configuration aims at minimizing the role of the contact between ITO and the polymeric film. As a matter of fact, ITO and MPP on the one hand, Au and PR3072-containing P3BT on the other hand, form ohmic contacts. The active zone for the charge generation is located at the interface between MPP and P3BT + PR3072. From the $J-V$ curve, we extract a V_{oc} equal to 0.43 V which overcomes the limit value inherent to the Schottky cells. The gain is much greater if we consider the current density: $J_{sc} = 0.78 \text{ mA cm}^{-2}$. The fill factor is constant at 0.29. The power efficiency $\eta = 0.12\%$ under 56 mW cm^{-2} illumination. For different light intensities, between 0.2 and 200 mW cm^{-2} , we measure a conversion efficiency equal to $0.15 \pm 0.03\%$. The independence of the efficiency on light intensities results from the fact that the photocurrent does not saturate even at high intensities. The short-circuit current density is proportional to the incident light flux as represented in Fig. 6. In this figure we have also plotted the variation of V_{oc} . It is well fitted with the usual expression $V_{oc} = (nkt/q)\log(a \times P_{opt} + 1)$ [8]. P_{opt} is the incident flux in W cm^{-2} , a is a constant, T the temperature in Kelvin, k the Boltzman constant, q the electrical charge, and n the ideality factor. In our case, we find an

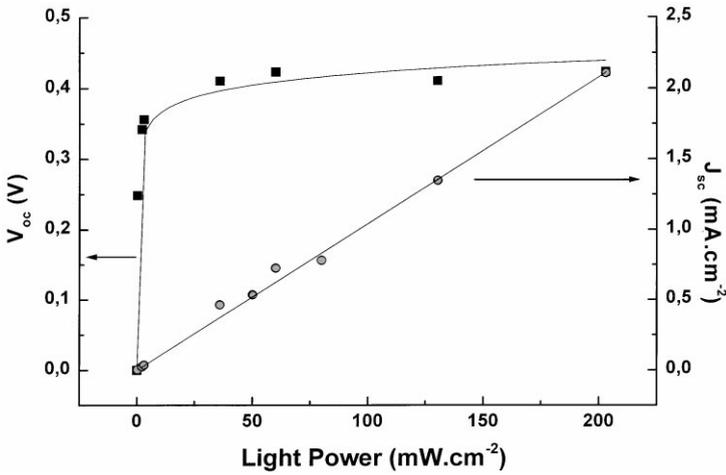


Fig. 6. Variations of V_{oc} (squares) and J_{sc} (circles) in the p-n type cell as a function of incident light flux.

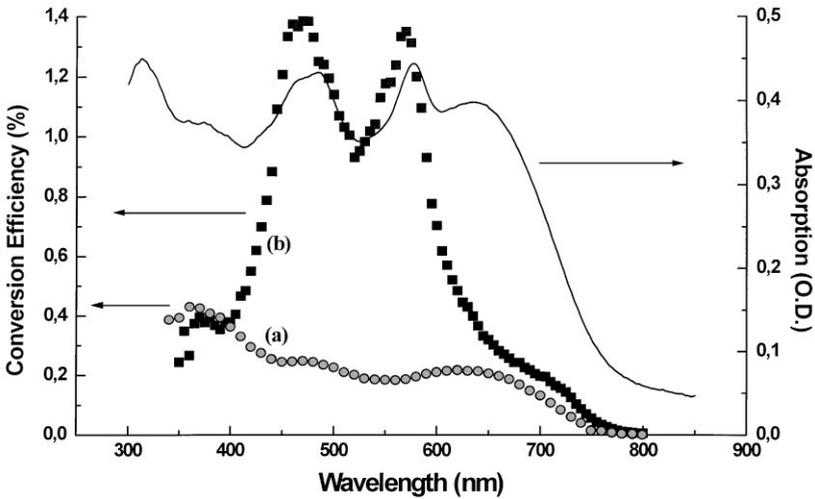


Fig. 7. Spectral response of: (a) a Schottky type cell and (b) a p-n type cell. The absorption spectrum is obtained with an ITO/MPP 35 nm/P3BT + PR3072 90 nm structure.

ideality factor equal to 2.1. The fact that n is greater than unity is generally interpreted as the presence of defects at the interface between the p- and n-type layers, which facilitates electron-hole recombination. This phenomenon does not affect the conversion efficiency which is constant in the range of illuminations used for these experiments.

Increase of the conversion efficiency of the p-n type photovoltaic cell compared to that of the Schottky one is also evidenced by plotting the action spectrum in Fig. 7. On

this graph, we have also reported the absorption spectrum of an MPP/P3BT + PR3072 bilayer structure and the action spectrum of the ITO/P3BT + PR3072/Au cell. The action spectrum of the p–n type cell closely matches the absorption spectrum of the MPP/P3BT + PR3072 layers. On the edges of curve (b) we recognize the shape of the signal due to the polymeric film represented by curve (a). Maxima of the signal around 480 and 575 nm correspond to the peaks of absorption of the MPP, revealing the significant role of the MPP layer in the photogeneration. If we compare the signals of the two curves, we can estimate that 65% is due to MPP and 35% to P3BT + PR3072. The fact that we irradiate through the ITO side, that is first through the MPP layer, and that, for the same thickness, the concentration of MPP near the active region is larger than that of PR3072 and P3BT, may explain the signal difference.

3.2. Orientation-induced molecular rectification in polymer films

We first use an ITO/PVK + DRPR + PR3072/Al device to illustrate the effect of orientation of polar molecules like DRPR on the electric properties of the film. The orientation of DRPR molecules by poling is controlled by the measurement of the intensity of the second harmonic signal $I_{2\omega}$. Fig. 8 shows SHG–voltage characteristics for different conditions of orientation. In all cases, $I_{2\omega}$ varies as E^2 in agreement with Eq. (1). The initial characteristic corresponds to the non-oriented film. In this film, molecules of DRPR are isotropically distributed. Then $\chi^{(2)} = 0$ and the variations of $I_{2\omega}$ are given by Eq. (2).

From the parabolic fit of the curve we determine a $\chi^{(3)}$ equal to 5.9 (arb.u.). At the minimum of $I_{2\omega}$, E_{ddp} is equal to E_{applied} , which permits to evaluate the electron work function difference between the two electrode materials. For the ITO/PVK + DRPR + PR3072/Al we measure a difference of potential between ITO and Al of

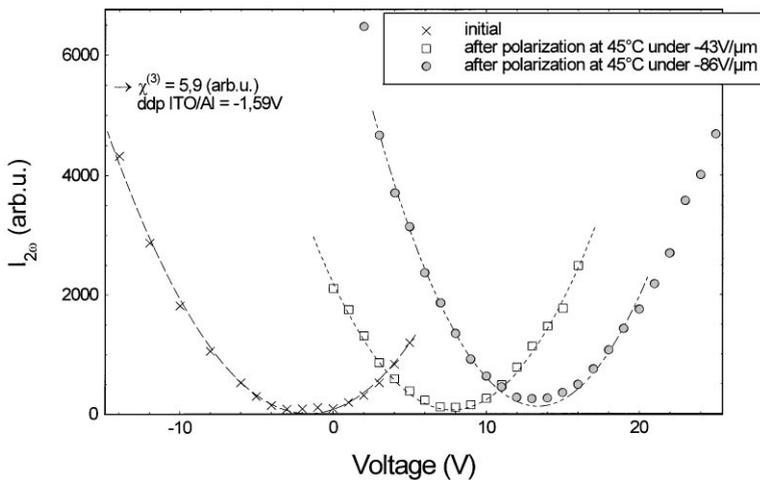


Fig. 8. SHG–voltage dependence characteristics of the ITO/PVK-doped film/Al device, before and after orientation using different voltages.

Table 1

Photovoltaic properties of the ITO/PVK-doped film/Al device, before and after orientation using different voltages

Orientation field (V/ μm)	J_{sc} (nA/cm ²)	V_{oc} (mV)	FF	η (%)
0	24.2	– 510	0.21	9.0×10^{-6}
– 43	38.5	– 800	0.29	3.0×10^{-5}
– 86	65.4	– 930	0.34	6.8×10^{-5}

– 1.59 V. The variations of $I_{2\omega}$ are plotted after applying electric fields of – 43 V/ μm and – 86 V/ μm in Fig. 8. The voltage at which minimum SEFISHG is achieved increases with increasing the polarization voltage, revealing higher internal fields stored inside the polymer film. In a previous work [9], it has been proved that the displacement of the minimum of the signal was really due to the orientation and not to an interfacial effect occurring between polymer and electrodes or to a charge trapping phenomenon. The influence of molecular orientation on the photovoltaic parameters is evidenced by recording current density–voltage characteristics under a 30 mW cm^{–2} white illumination at the initial state and after each poling condition. We only considered the first characteristic to minimize disorientation effects of DRPR molecules following white illumination. Measured photovoltaic parameters are summarized in Table 1.

We get an increase of about one order of magnitude of the power efficiency between non-oriented and oriented cells. It results from the molecular rectification effect which implies the storage of an internal electric field in the film. In this configuration, polar organization of molecular diodes is equivalent to the build up of a p–n type homojunction within the single-polymer film. Excitons must be separated more easily and, as it has been experimentally proved for another system, the mobility of charges is improved [9]. Determination of the charges drift is underway for the cells we present in this paper. Results evidence that molecular rectification induced in an oriented amorphous polymer bearing polar chromophores improves the photovoltaic efficiency of the polymeric semiconductor devices. The conversion efficiency obtained with cells based on a PVK matrix is relatively low. We have applied this orientation technique to a film of polythiophene doped with PR3072 to improve photogeneration as in the case of Fig. 5 and DRPR molecules to induce orientation. The complete photovoltaic cell had the following structure: ITO/P3BT + PR3072 + DRPR/Al. Unfortunately a high current flows through the device during DC-field molecular orientation at T_g . In such condition, no electric field is effective inside the organic film and thus molecules cannot orient themselves. Another technique called photo-assisted orientation has been employed. This method is based on the fact that resonant illumination of azo-dye molecules such as DRPR leads to a photo-induced mobility of the molecules inside the polymeric matrix [10]. The origin of the effect comes from conformation changes of the molecules following excitation by light. Such process enables DC-field poling at ambient temperature. We have performed photo-assisted poling experiment on an organic film consisting of a blend of P3BT (34 wt%),

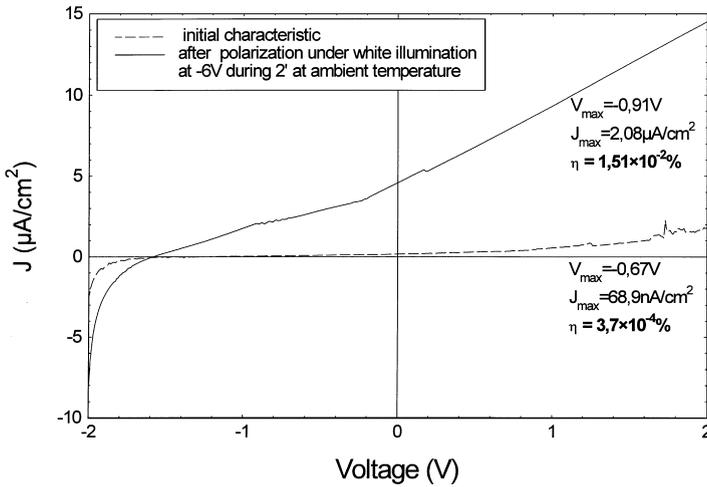


Fig. 9. Current density–voltage characteristics under 12.5 mW cm^{-2} red illumination of the ITO/P3BT (33 wt%) + copo(MMA-DR1) (33 wt%) + PR3072 (33 wt%)/Al device, through ITO, before and after polarization 2 at -6 V under white illumination. The polymer film is 240 nm thick.

PMMA-DRI (33 wt%) and PR3072 (33 wt%). The film was sandwiched between ITO and Al electrodes. Excitation was performed using white light illumination. Dye orientation following this procedure was confirmed by SHG measurements.

Fig. 9 shows the effect resulting from the photo-assisted orientation on the current density–voltage. Power efficiency is multiplied by a factor of 40. As a matter of fact, PV characteristics of cells containing DR1 must be done with an illumination beyond 600 nm (outside of the absorption band of DR1), in order to prevent any photoinduced disorientation of DR1 molecules during the I/V characteristics measurement under illumination. So, further improvement of the device should be achieved using polar dyes which do not get absorbed in the visible region.

4. Conclusion

Our results confirm the influence of the light absorption and of the quality of the junction on the power conversion efficiency. By simply adding a dye absorbing in the visible range, thus extending the absorption spectrum of the organic film, we gain two orders of magnitude with respect to the efficiency measured for a Schottky type cell based on a pure polythiophene film. We have also demonstrated the advantage of a molecular-oriented structure in the film. Next step will be the optimization of this new concept. We are now investigating new polymers and new push–pull molecules in order to store a larger electric field and to insure an efficient bipolar transport. This strategy should permit the achievement of efficient polymer photo-voltaic cells.

Acknowledgements

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