

Photovoltaic properties of Schottky and $p-n$ type solar cells based on polythiophene

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The electrical and photovoltaic properties of organic Schottky and $p-n$ type cells have been studied. Schottky devices are based on a spin-coated film of poly(3-butylthiophene) blend with the dye 1,3-bis-(dicyanomethylidene)-2-(4-dibutylaminobenzylidene)indane which is sandwiched between indium tin oxide (ITO) and gold electrodes. A depletion zone of 9.5 nm thick has been determined on a 220-nm-thick film. The conversion efficiency is equal to 0.01% under 100 mW cm⁻² white light illumination. Effects of dye loading, film thickness, and light intensity are described. A model based on simple assumptions is used to fit the photoaction spectra. By evaporation under vacuum of a layer of N,N' -dimethyl-3,4,9,10-perylenetetracarboxylic diimide between the ITO and the polymer film, we have fabricated hybrid polymer-molecular $p-n$ type photovoltaic cells. The role of this molecule in the photogeneration has been studied. A constant power conversion efficiency of 0.15% has been measured under white light illumination between 0.2 and 200 mW cm⁻². © 2001 American Institute of Physics. [DOI: 10.1063/1.1378064]

I. INTRODUCTION

Much work has been devoted to the fabrication and study of photovoltaic cells based on evaporated molecules¹⁻⁴ or polymer spin-coated films.^{5,6} In the latest category, poly(p -phenylene vinylene) and its derivatives,⁷⁻¹⁰ and polyalkylthiophenes and their derivatives¹¹⁻¹⁵ are largely used. Limits in energy conversion of such photovoltaic cells are mainly due to poor photogenerated exciton separation and low mobility of holes and electrons in the polymer film. In order to improve the dissociation of excitons and the charge transport to the electrodes, polyalkylthiophenes have been associated to electron acceptors like buckminsterfullerenes (C₆₀).^{16,17} This donor-acceptor network leads to an extremely rapid electron transfer from the polymer to the C₆₀ with a very low back transfer¹⁶ that induces a higher dissociation rate from the quenching of the polythiophene photoluminescence.

In this article we report results obtained by mixing the poly(3-butylthiophene) (P3BT) with the 1,3-bis-(dicyanomethylidene)-2-(4-dibutylaminobenzylidene)indane dye (PR3072). This molecule was chosen since it is an acceptor, due to the four cyanine groups, and further it absorbs light in the 300 nm region and between 550 and 700 nm. PR3072 can then play the acceptor role of the C₆₀ with an absorption spectrum which is complementary to that of P3BT in the visible range. PR3072/P3BT blends were deposited in thin layers from spin-on coating and were used in sandwiched structures between gold and indium tin oxide (ITO) electrodes.

Since the physical and electrical properties of ITO are not easy to control, we have added an evaporated molecular

film between the ITO and the polymer film in order to shift the rectifying contact. As such, the influence of the ITO properties is minimized. The photovoltaic response of such a hybrid polymer-molecular $p-n$ type photovoltaic cell is presented.

II. EXPERIMENT

P3BT has been synthesized from an organometallic coupling on a dihalogenated monomer.¹⁸ PR3072 was prepared as described by Bello *et al.*¹⁹ The N,N' -dimethyl-3,4,9,10-perylenetetracarboxylic diimide (MPP) was provided by the IEV group of Forschungszentrum from Jülich. Chemical structures of these organic compounds are given in Fig. 1.

Preparation of the polymer films and characterization of the cells are performed in air. For the fabrication of the photovoltaic cells, we have used as substrates ITO on glass. To facilitate the electrical contact, Cr-Au dots are evaporated on the ITO substrate. P3BT-based films are prepared by spin coating a blend of P3BT and PR3072 in chloroform solution on cleaned ITO. Due to the alkyl chains, P3BT and PR3072 are compatible in the solution as well as in the solid state. No segregation was observed, even at high concentrations of PR3072. In the case of hybrid $p-n$ type photovoltaic cells, MPP layers are deposited by vacuum evaporation. Then, a top electrode gold electrode is evaporated in vacuum. Geometries of the Schottky and $p-n$ type cells are shown in Fig. 2. The illuminated sample surface corresponds to the upper disk and has a 0.28 cm² surface. Organic film thickness is determined using a Dektak³ST surface profiler. Absorption spectra are performed using a Perkin Elmer Lambda 19 UV-visible (VIS) spectrophotometer. Fluorescence spectra are obtained by using a F4500 Hitachi spectrofluorimeter. Current density-voltage ($J-V$) characteristics are plotted with a

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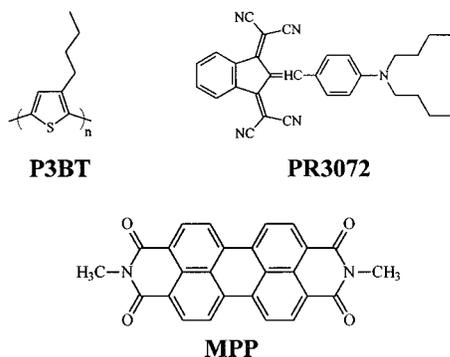


FIG. 1. Chemical structures of P3BT, PR3072, and MPP.

HP1455A semiconductor parameter analyzer. The current is recorded while voltage cycles are applied to the gold electrode in order to get stable signals and to observe any possible hysteresis. The light source is a 150 W Osram Xenophot halogen lamp connected to an optical fiber. Light intensities are measured using a Scientech 362 powermeter.

Action spectra are measured by illuminating the photovoltaic cells using a monochromatic beam issued from a Cary 14 UV/VIS spectrometer. Light energy is probed by a Hamamatsu S2281 photodiode. The induced current is measured using a 7220 EG&G lock-in amplifier.

External power conversion efficiency η is calculated according to

$$\eta = (J_{\max} V_{\max}) / G, \quad (1)$$

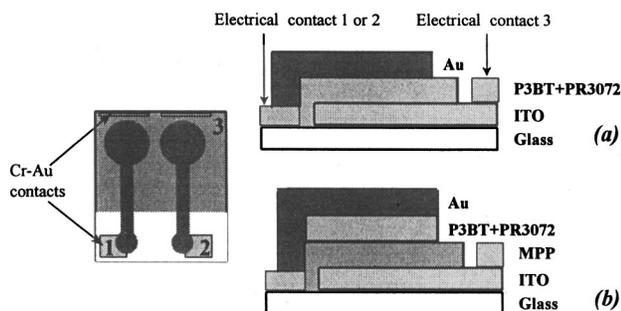
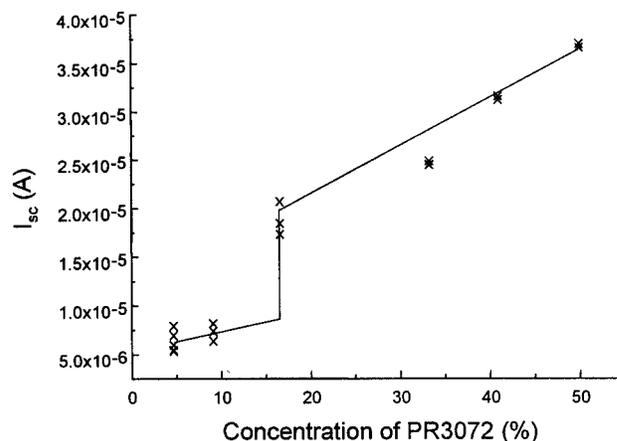
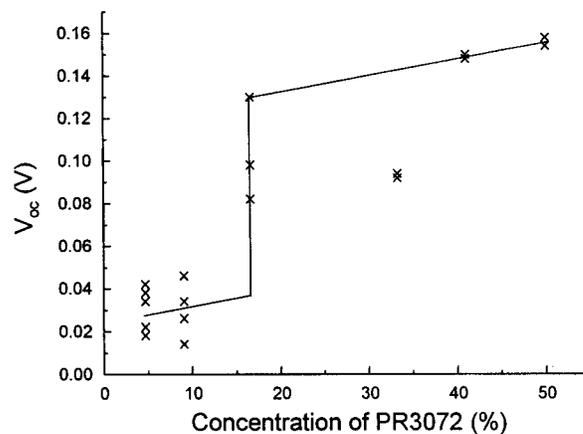
where J_{\max} (A cm^{-2}) is the maximum current density, V_{\max} (V) is the maximum voltage delivered by the photovoltaic cell, and G (W cm^{-2}) is the total incident illumination intensity. The efficiency of collected carriers per incident photons (IPCE) is given by the following expression:

$$\text{IPCE} = 1.24 J_{\text{sc}} / (G \lambda), \quad (2)$$

where J_{sc} (A cm^{-2}) is the short-circuit current density and λ (μm) is the wavelength.

III. SCHOTTKY TYPE ORGANIC PHOTOVOLTAIC CELLS

An ideal Schottky contact is defined from its depletion zone which is the volume inside the semiconductor where the built-in electrical field is present. Poly(3-butylthiophene)

FIG. 2. Schematic views of (a) Schottky and (b) hybrid p - n type photovoltaic cells.FIG. 3. Dependence of V_{oc} and I_{sc} with the percentage of PR3072 in P3BT films.

is a p -type material. It forms a Schottky barrier with the electrode which has the lowest work function, thus ITO in our case. The photovoltaic effect therefore occurs in the depletion zone of this junction since an electrical field exists and enables the electron-hole pair separation. The depletion zone is characterized by its width W .

A. Effects of the dye PR3072

The I - V characteristics of ITO/P3BT+PR3072/Au cells have been plotted under 100 mW cm^{-2} white light illumination. Cells are based on films containing P3BT and PR3072 in the range of 5 and 50 wt %. Thickness of the films is $145 \text{ nm} \pm 5 \text{ nm}$. Variations of the short-circuit current I_{sc} and the open-circuit voltage V_{oc} are given in Fig. 3. With dye concentration, I_{sc} increases from 5 to $35 \mu\text{A}$ and V_{oc} from 30 to 160 mV. Variations are not linear and a sharp increase of I_{sc} and V_{oc} occurs around 16 wt % of PR3072.

Figure 4 shows the best photovoltaic characteristic obtained with this type of cell. It corresponds to cells containing 50 wt % of dye in the film. Under white illumination of 50 mW cm^{-2} , we measure a J_{sc} of $92 \mu\text{A cm}^{-2}$, a V_{oc} of 210 mV, and a fill factor FF equal to 0.29. Efficiency η is superior to 0.01%. This last result has to be compared to the external power conversion efficiency η of an ITO/P3BT/Au cell which does not exceed $1.6\% \times 10^{-4}\%$ under comparable white light illumination. This way, we then demonstrate that a factor of 60 improvement can be obtained by adding

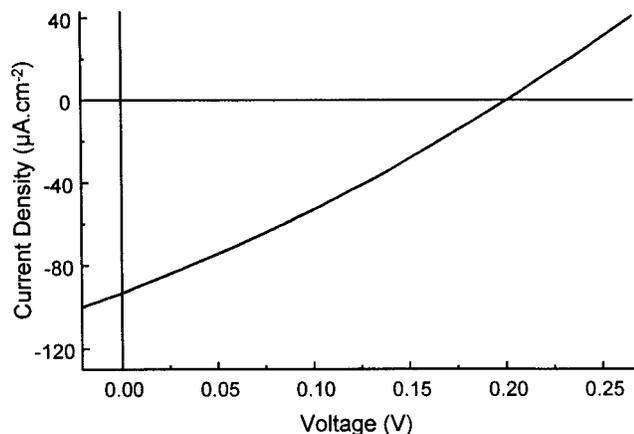


FIG. 4. $J-V$ characteristic of an ITO/P3BT (50 wt %)+PR3072 (50 wt %)/Au cell under incident white light illumination at 50 mW cm^{-2} .

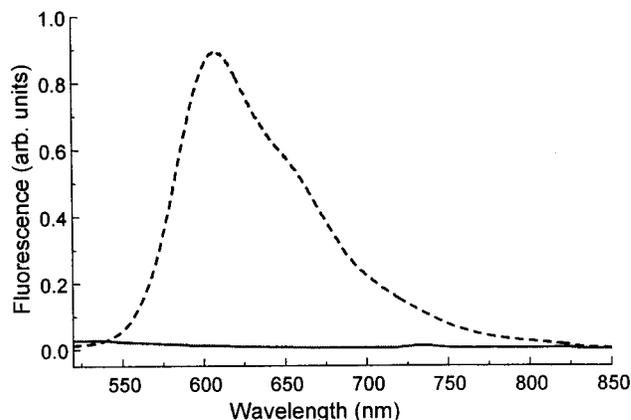


FIG. 6. Fluorescence spectra of a pure P3BT film (dash line) and of a P3BT film with 5 wt % of PR3072 (solid line).

PR3072 dye in a Schottky type polythiophene-based photovoltaic cell. We will now focus on the PR3072 dye effect in the photogeneration phenomenon.

As shown in Fig. 5, the absorption spectrum of the PR3072 complements that of the P3BT in the visible range, and particularly between 500 and 700 nm. The absorption spectrum of the blend P3BT and PR3072 is broader and the number of photons absorbed in the visible range is then higher than in a pure P3BT film. Moreover, the fluorescence spectrum of a solution of PR3072 in chloroform excited at $\lambda=490 \text{ nm}$ is completely flat. It reveals that the incident energy absorbed by the dye is not giving rise to fluorescence. Result of the absorption is then a photocurrent generation. In the action spectra represented in Fig. 5, obtained by illumination through ITO, a current maximum appears at 630 nm. At this wavelength, the P3BT does not absorb. The signal we observe is therefore only due to the PR3072. It implies that the PR3072 molecule really takes part in the photogeneration process.

Another aspect is the fluorescence quenching of the P3BT when it is mixed with PR3072 (see Fig. 6). A pure P3BT film exhibits a maximum of fluorescence at 607 nm when illuminated with a 490 nm beam. However, no fluorescence is observed in a P3BT film containing 5 wt % of PR3072. The dye enables the separation of charges photoge-

nerated by the P3BT before radiative recombination. This point is confirmed by the energy-level diagram given in Fig. 7. Energy levels have been determined by voltamperometry measurements combined with absorption spectra of a PR3072 solution and a P3BT solution. Due to the position of the lowest unoccupied molecular orbital of the PR3072 compared to that of the P3BT, the photogenerated electron in P3BT is transferred from the P3BT to the PR3072, therefore cannot recombine with the hole in the highest occupied molecular orbital level of the P3BT.

The role of the dye in the fluorescence quenching does not totally explain the higher efficiency measured, since the improvement of V_{oc} and I_{sc} occurs at around 16 wt % of PR3072. We have to consider the transport of the electric charges in the film. To induce a current, holes and electrons must be collected at the gold and ITO electrodes, respectively. Holes are transported through the film by the P3BT which is a *p*-type polymer. Then, electrons must be transported by the dye PR3072. This property of electronic conduction of an indane molecule has been evidenced by time of flight measurements on a film obtained by vacuum-evaporation of 2-methyl-2-pentyl-1,3-bis(dicyanomethylidene)indane.²⁰ In this structure, molecules are close to each other thus the transport is facilitated. In our photovoltaic cells, molecules are in a polymer matrix. Conduction of elec-

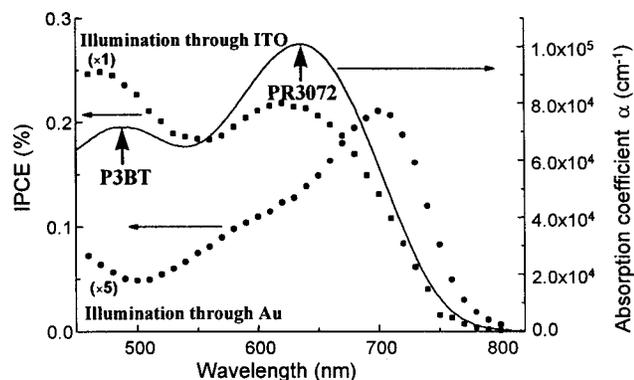


FIG. 5. Photovoltaic action spectra of an ITO/P3BT (50 wt %)+PR3072 (50 wt %)/Au cell.

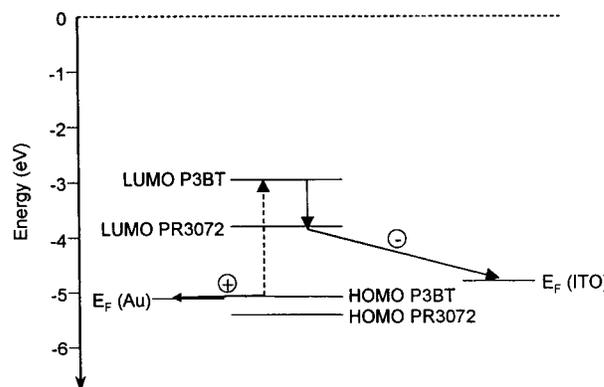


FIG. 7. Energy level diagram of an ITO/P3BT+PR3072/Au photovoltaic cell and schematic description of charges transfer after the excitation of P3BT.

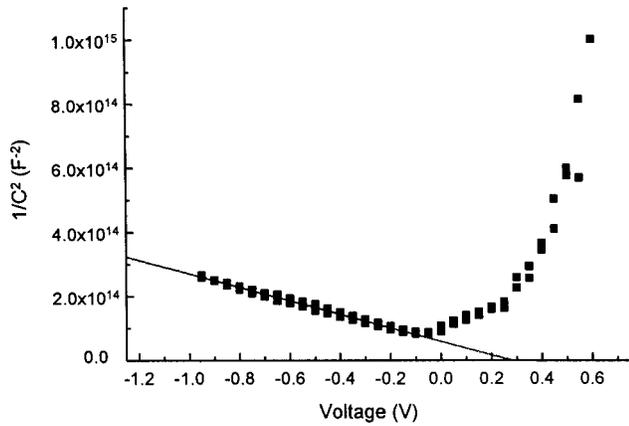


FIG. 8. Plot of $1/C^2$ against dc voltage applied to the gold electrode of an ITO/P3BT (50 wt %)+PR3072 (50 wt %)/Au cell. Film is 220 nm thick. The ac voltage is 1.1 V at a frequency of 6 Hz.

trons is then possible only if there exist percolated paths of PR3072 between the region of photogeneration and the ITO electrode. Scher and Zallen showed that a macroscopic conductivity appears in a three-dimensional system when 15 vol% of conducting particles are added to an insulating polymer.²¹ By analogy, P3BT can be considered as an insulating matrix for the electrons and molecules of PR3072 as electron conductors. Van der Waals volumes of a P3BT monomer and a PR3072 molecule are of 0.143 and 0.476 nm³, respectively. Molar masses are of 138 g for P3BT and 457 g for PR3072. From these data, we find that a mass percentage of 16 wt% corresponds to a volumic percentage of 16 vol%. This value is in a good agreement with the volume percentage of 15 vol% mentioned in the literature and confirms the participation of the PR3072 in the conduction of photogenerated electrons.

B. Width of the depletion zone

Experimentally, the width of the depletion zone W is determined from the plot of $1/C^2$ as a function of the applied voltage in the dark, where C is the Schottky depletion zone capacitance.^{22,23} This plot is given in Fig. 8. The dc voltage is applied to the gold electrode in the following successive steps: 0 V \rightarrow +0.6 V \rightarrow 0 V \rightarrow -1.2 V \rightarrow 0 V. The value of the ac voltage used for the measurement is 1.1 V at 6 Hz. No hysteresis is observed between the up and down parts of the curve. In the blocking conditions (i.e., negative voltage at the gold electrode), $1/C^2$ varies linearly with V , which is typical of a Schottky type depletion zone. The depletion zone is located between the ITO and the polymer film. This part of the curve can be fitted with the following expression:

$$1/C^2 = 5.90 \times 10^{12} - 2.11 \times 10^{13} V. \quad (3)$$

The width of the depletion zone can be written as

$$W = \kappa \epsilon_0 / C, \quad (4)$$

where κ is the dielectric constant of the film and ϵ_0 is the permittivity of vacuum.

Taking $\kappa=4$ and using the value of C measured at $V=0$ in the equation $1/C^2=f(V)$, the barrier width W at zero

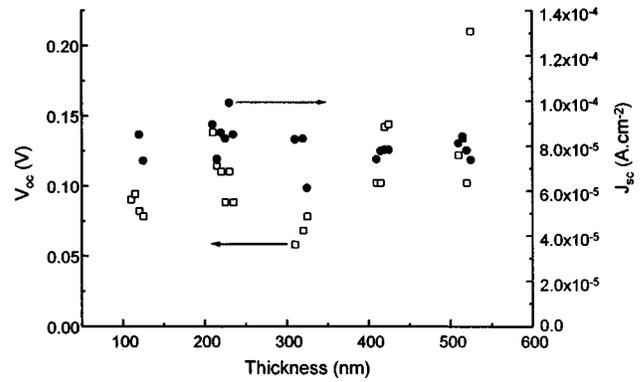


FIG. 9. Dependence of V_{oc} and J_{sc} with the thickness of the (P3BT + PR3072) film. Intensity of the total incident white light illumination is of 50 mW cm⁻².

bias is of 9.5 nm. The interception of the slope with the base line gives a potential barrier V_b of 0.28 V. Also using the general expression: $1/C^2 = 2(V_b + V)/(e\kappa\epsilon_0N)$, where e is the electronic charge and N is the total charge, N can be estimated at 1.36×10^{18} cm⁻³ at zero bias.

C. Photovoltaic action spectra

The study of the photovoltaic action spectra measured on an ITO/P3BT+PR3072/Au cell with a 220-nm-thick film

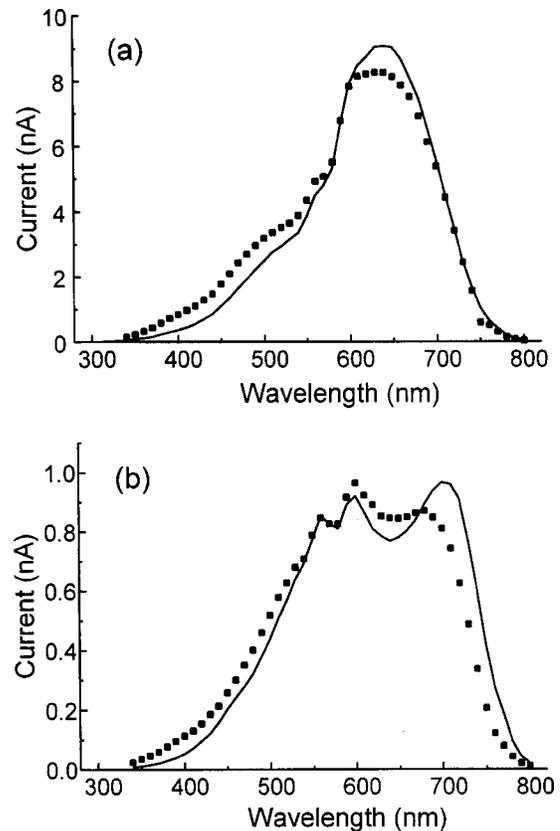


FIG. 10. Dependence of the photocurrent with the wavelength of an ITO/P3BT (50 wt %)+PR3072 (50 wt %)/Au cell illuminated through the ITO (a) and through the gold electrode (b). Solid lines have been obtained from the Eqs. (7) and (8), respectively for (a) and (b), with $d=220$ nm, $W=9.5$ nm, and $\phi=0.3$.

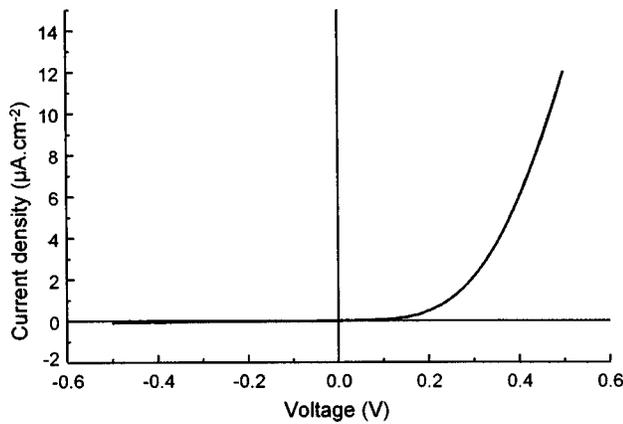


FIG. 11. J - V characteristic in the dark of an ITO/MPP (35 nm)/P3BT + PR3072 (90 nm)/Au cell.

and containing 50 wt% of PR3072 (see Fig. 5) provides several informations about the photovoltaic device characteristics. The response of the photovoltaic cell matches the absorption spectrum when the device is illuminated through the transparent ITO electrode. This indicates that the zone of photogeneration is located at the interface between the ITO and the polymer film. The IPCE is around 0.2% between 450 and 700 nm. On the opposite, when illumination is performed through the gold electrode, the IPCE varies reversely with respect to the absorption spectrum. This confirms that the active zone is located on the other side than the interface between gold and the polymer film. Indeed, the more the film absorbs, the smaller is the number of photons reaching the depletion zone. The number of generated charges decreases and variations of the measured signal will be opposite to that of the absorption spectrum. The depletion zone is spatially limited and its width has been estimated at 9.5 nm, thus is small compared to the film thickness. Nevertheless, as shown in Fig. 9, the photocurrent does not decrease in thicker films. Since the extension of the depletion zone does not change with the film thickness, the number of photogenerated charges must be quite constant whatever the thickness. The stability of J_{sc} indicates that the same quantity of charges is collected at the electrodes. Electron and hole transport is not a function of the film thickness in the range we investigated. This also implies that the trapping probability of the photo-generated charges in the bulk of the polymer film remains low.

From the value of W , we have fitted the variations of the current probed as a function of the excitation wavelength (see Fig. 10). The model we used is based on the simple following expression:

$$I = n_c e, \tag{5}$$

where I is the current, n_c is the number of collected charges per unit of time, and e is the electron charge. n_c is equal to the product of the number of photons absorbed in the depletion zone with the collection efficiency ϕ . For one wavelength, if we illuminate through the ITO, n_c can be written as follows:

$$n_c = \phi n_{inc} T_{ITO} [1 - \exp(-\alpha W)], \tag{6}$$

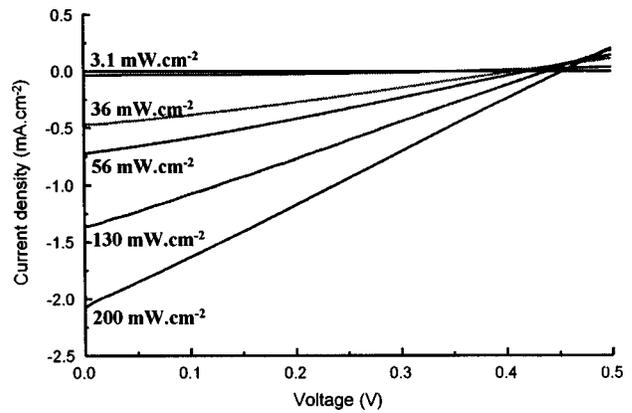


FIG. 12. J - V characteristics of an ITO/MPP (35 nm)/P3BT + PR3072 (90 nm)/Au cell under various white light illuminations.

where n_{inc} is the number of incident photons per unity of time and T_{ITO} the transmission coefficient of the substrate (glass+ITO). The last term corresponds to the quantity of light absorbed in the depletion zone. Finally, we obtain

$$I = \phi n_{inc} T_{ITO} [1 - \exp(-\alpha W)] e. \tag{7}$$

Using a monochromatic excitation beam through the gold electrode, the collected current is thus given by

$$I = \phi n_{inc} T_{Au} \exp[-\alpha(d-W)] [1 - \exp(-\alpha W)] e, \tag{8}$$

where T_{Au} is the transmission coefficient of the gold electrode whether $\{\exp[-\alpha(d-W)]\}$ represents that of the thickness of the film before the depletion zone. d is the total thickness of the film, i.e., 220 nm. Data concerning transmission coefficients have been determined by plotting separately the absorption spectra of the film and of the electrodes.

The theoretical curves, plotted from Eqs. (7) and (8), with $W=9.5$ nm, $d=220$ nm, and the fitting parameter $\phi=0.03$, are represented as straight lines on Fig. 10. Despite the simplicity of the model in which ϕ is the only parameter, there is good agreement between calculations and measurements. Magnitudes are respected and the model is able to describe the current variations. The collection efficiency ϕ is equal to 3% whatever the direction of the illumination, which is expected since the cell characteristics are not supposed to vary with this parameter.

In this model, no consideration of the contribution of excitons generated within a diffusion length of the depletion zone were taken. This means that the value of ϕ is a bit surestimated. In order to obtain a correct description, our model should be modified and may include the exciton diffusion length which is reported to be about 5–7 nm.^{24–26}

Despite the improvement of the performance of our photovoltaic cells due to the PR3072 molecule, the open-circuit voltage V_{oc} remains low. A value of 0.2 V was measured on our best devices but a more common value of 0.15 V was obtained, thus lower than the theoretical value defined as the difference between the work functions of the electrodes, i.e., 0.3 V for an ITO/Au couple. We have also observed that the morphology as well as the electrical properties of the ITO can change from one batch to another, with a strong influence on the cell efficiency. In order to avoid this difficulty,

TABLE I. Comparison of current densities of Schottky and $p-n$ cells at -0.4 and 0.4 V from $J-V$ characteristics plotted in the dark.

	Current density at -0.4 V (A)	Current density at $+0.4$ V (A)	Ratio $ J_{+0.4\text{ V}}/J_{-0.4\text{ V}} $
Schottky type cell: ITO/P3BT+PR3072/Au	-1.1×10^{-4}	1.1×10^{-4}	1
$p-n$ type cell: ITO/MPP/P3BT+PR3072/Au	-5.7×10^{-8}	6.1×10^{-6}	106

the cell geometry was modified. In the $p-n$ type cells fabricated here, the photogeneration zone is no longer located at the interface between the ITO and the polymer film. Efficiencies measured on such $p-n$ type cells are presented in the following section.

IV. $p-n$ TYPE ORGANIC PHOTOVOLTAIC CELLS

In the ITO/MPP/P3BT (50 wt %)+PR3072 (50 wt %)/Au photovoltaic cell, contacts between metals and organic layers are ohmic. The photogeneration zone is located at the junction between the MPP and the polymer. The influence of the ITO on the performance of the cell is then minimized. The induced improvements are clearly evidenced from the dark current measurements. $J-V$ characteristics in the dark and under various intensity of white light illumination are plotted in Figs. 11 and 12.

In Table I, rectifying ratios are compared for Schottky type and $p-n$ type cells. Although the Schottky type cell exhibits the same current values at $+0.4$ and -0.4 V, the $p-n$ type cell presents a strong rectifying characteristic with a ratio of 106. This is mainly due to a lower saturated reverse current which is 300 times lower in the $p-n$ type cell and the ideality factor n which is below 1.5. Figure 12 shows that under white light illumination, the fill factor FF decreases from 0.4 for 3 mW cm^{-2} to 0.25 for 200 mW cm^{-2} . The external power conversion efficiency is reproducible, constant and equal to 0.15% between 0.2 and 200 mW cm^{-2} . Variations of V_{oc} as a function of J_{sc} and that of J_{sc} with the

intensity of light illumination G are represented in Figs. 13 and 14. Experimental curves have been fitted using the following expression:

$$V_{oc} = (nkT/e) \ln[(J_{sc}/J_s) + 1], \quad (9)$$

where k is the Boltzmann constant, T is the temperature, and J_s is the saturated reverse current. n is called the ideality factor and is equal to 1 for an ideal cell. We have

$$J_{sc} \propto (G)^b, \quad (10)$$

where G is the intensity of the total incident illumination and b is a constant.

A best fit for b , n , and J_s for $p-n$ type and Schottky-type photovoltaic cells is given in Table II. It has to be noticed that in both cases the short-circuit current is proportional to the intensity of incident illumination. We do not observe any saturation effect even at light intensities, as high as 200 mW cm^{-2} . This results in a constant power conversion efficiency, typically of 0.15% for the $p-n$ type cell, which is thus 15 times greater than that measured for the best Schottky-type cells.

In Fig. 15 are reported the action spectra of Schottky and $p-n$ cells obtained by illumination through ITO as well as the absorption spectrum of a 90-nm-thick layer of P3BT (50 wt %)+PR3072 (50 wt %) deposited on a 35 nm layer of MPP. Improvement of the efficiency is mainly due to the contribution of the MPP layer to the photogeneration. As shown by the action spectra in Fig. 15, maxima in the photocurrent correspond to those of MPP absorption.

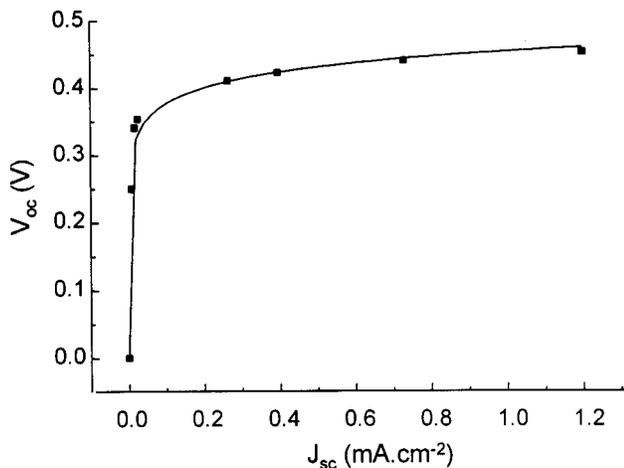


FIG. 13. Plot of V_{oc} with J_{sc} for a $p-n$ photovoltaic cell. The solid line is obtained from Eq. (9).

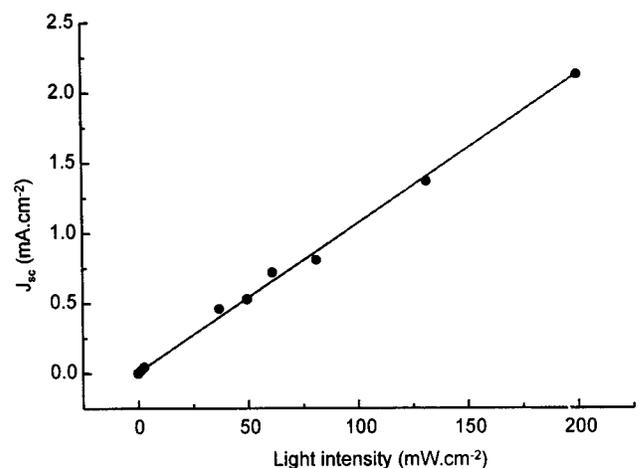


FIG. 14. Plot of J_{sc} with the intensity of illumination G . Experimental plots have been fitted by the Eq. (10).

TABLE II. Parameters b , n , and J_s for Schottky and p - n type cells.

	b	n	J_s (A)
Schottky type cell: ITO/P3BT+PR3072/Au	0.94 ± 0.04	2.2 ± 0.2	$6.1 \times 10^{-7} \pm 0.3 \times 10^{-7}$
p - n type cell: ITO/MPP/P3BT+PR3072/Au	0.91 ± 0.02	1.45 ± 0.03	$1.8 \times 10^{-9} \pm 0.1 \times 10^{-10}$

Concerning the aging of the cell, we have noticed a bleaching of the film when the cell is illuminated using a typical intensity of 100 mW cm^{-2} during a couple of hours. Comparison of the absorption spectra before and after illumination shows that it corresponds to a degradation of the PR3072 molecule. However, the MPP and P3BT absorptions remain constant. In fact, the P3BT is protected by the MPP layer, which absorbs in the same region. In the absence of MPP, a degradation of the P3BT is also observed. From the optical density of a 35-nm-thick MPP layer and an incident light intensity of 100 mW cm^{-2} , we can estimate that the bleaching begins at a light intensity above 60 mW cm^{-2} .

This degradation for both PR3072 and P3BT is only due to the light and not to other conditions of characterization. Indeed, regular J - V characteristics of a cell left in air between two measurements have shown that its power conversion efficiency, from 0.13% under 100 mW cm^{-2} at the beginning of the study, remained stable over 6 months.

V. CONCLUSION

A study was conducted where different blends of poly(3-butylthiophene) were used for fabrication of Schottky and p - n type photovoltaic cells. It appeared that the original conversion efficiency could be improved by a factor of 60 to reach 0.1% when optimum dye contents are used. The improvement is drastic only if the dye loading exceeds 16 vol%. Beyond this point, there exists a percolated path of PR3072 molecules that are able to transport electrons to the ITO. Better results have been obtained on p - n type cells. In this configuration, the active zone is not located at the interface between the polymer film and the ITO but at the contact between the polymer film and the MPP layer. Power conver-

sion efficiencies of 0.15% have been obtained under a wide range of white light intensities from 0.2 to 200 mW cm^{-2} . In order to obtain prolonged high intensity illumination, more stable dyes with respect to PR3072 are tested in order to prevent the bleaching of the film and to allow a constant power efficiency during long time uses.

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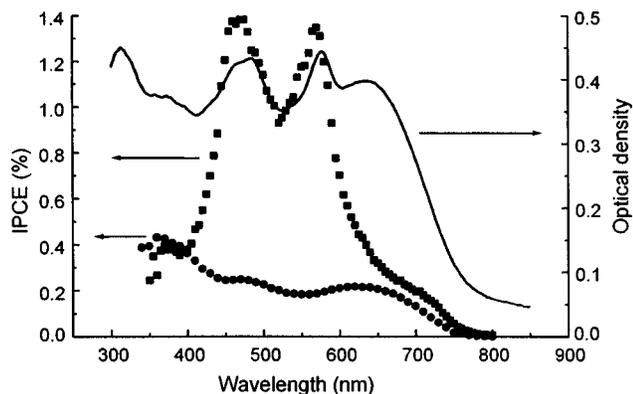


FIG. 15. Photovoltaic action spectra of Schottky (full circles) and p - n cells (full squares) obtained from illumination through ITO. The absorption spectrum of a MPP (35 nm)/P3BT(50 wt %)+PR3072 (50 wt %) (90 nm) bilayer structure is represented using the solid line.

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