

Numerical Modeling of Organic Solar Cell with Heterojunction Obtained from New II Conjugated Oligomers with Holes Transporter Type

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Abstract--The photovoltaic cells based on the organic semiconductors are the subject of research moved by the possibility of carrying out solar cells of great surface, flexible devices, light and cheap, while benefiting from the great processability of organic materials. Faced with the environmental constraints and with the exhaustion of the resources of fossil energy, the strong renewed interest for organic conversion statement is mainly due to the great effectiveness conversion improvement of accomplished organic solar cells these last ten years

In this article we present a simulation of heterojunction organic solar cell containing new conjugated donor derived from oligothiophene with the perylene derivative (D5P). This study uses a method of calculation of the photocurrent delivered by the cell from the equations of continuities and currents by analogy to the phenomena of charges transport according to the model of a heterojunction n/p.

The principal photovoltaic parameters of this structure are calculated by the simulation of equation I(V), under illumination AM_{1.5}.

The optimization of donor layer thickness shows clearly that the best results are obtained with the finest structures, the conversion efficiency increases from 0.82% to 1.19%.

Key words: organic solar cell, derivative of Oligothiophene, photocurrent, equation of continuity.

Nomenclature

$D_n = \frac{\mu_n KT}{q}$	Diffusion constant of electrons.
$D_p = \frac{\mu_p KT}{q}$	Diffusion constant of holes.
μ_n	Mobility of electrons.
μ_p	Mobility of holes.
$\Delta n = n - n_e$	Density of excitons generated (electrons), n_e : density in balance.
τ_n	Life time of minority carriers of n layer (electrons).

$\Delta p = p - p_e$	Density of generated holes, p_e : density in balance.
τ_p	Lifespan of minority carriers of n layer (holes).
G_n	Rate of electrons generation.
G_p	Rate of holes generation.
$\Phi_i(\lambda)$	Flux of incidents photons by cm ⁻² by s ⁻¹ by unit of wavelength.
R	Reflexion coefficient.
α_1	Absorption coefficient in derived from oligothiophene layer.
x_b	Thickness of the D5P layer.
L_p	Diffusion length of holes.
S_n	Speed of recombination of the electrons on the surface.
α_2	Absorption coefficient in D5P.
S_p	Speed of recombination of the holes to the back contact.
L_n	Diffusion length of the electrons
I	Current
I _{sc}	Short-circuit current
J	Current density
V	Tension
V _{oc}	Open circuit tension.
FF	Fill factor.
η	Conversion efficiency.
μ_n	Mobility of electrons.
μ_p	Mobility of holes.
$\Delta n = n - n_e$	Density of excitons generated (electrons), n_e : density in balance.
μ_n	Mobility of electrons.
μ_p	Mobility of holes.

I. INTRODUCTION

Taking into account the weak performances of the organic solar cells studied during the twenty last years courses, majority of work on this topic concerned with the fundamental problems posed by the operation of the cells, of the problems involved in the fact that the chemical

structure of the materials which make it up was not optimized for photovoltaic conversion (bad coverage of the solar spectrum, photostability and reduced lifespan). The real prospect now is to lead to usable cells within the framework of targeted applications, implies necessarily the development of new organic semiconductors specifically designed for photovoltaic conversion. From this point of view the simpler structure of the cells in thin layers (heterojunction) seems adapted better to the evaluation of new organic semiconductors and an attempt to connect the performances of the cells to the chemical structure of the organic semiconductors.

We propose in this investigation, contrary to the literature where the results are only experimental, a method of simulation based on the resolution of the equations of currents (continuities) for an organic solar heterostructure of oligomere/small molecule type based on a new π -conjugated system in which three chains of linear oligothiophenes (nT) are connected to a central, plane and rigid heart of trithienobenzene, by using the D5P like acceptor and electrons transport layer.

II. DESCRIPTION AND MECHANISMS OF GENERATION IN THE ORGANIC SOLAR CELLS

A. Mechanisms of Conversion

The currently allowed photovoltaic process is the absorption of a photon by the active organic layer which generates an exciton (instead of the free carriers in the inorganic case) which diffuses through the material [1]. The processes of conversion can be schematically summarized in 4 stages [2-6]:

- The absorption of a photon leading to the formation of an excited state of organic material with the creation of pair electron-hole located in strong interaction (exciton).
- Diffusion of the exciton until a site of dissociation.
- The dissociation of the exciton and the creation of free charge carriers.
- The transport of the charges (holes and electrons) in each organic material and collection of the loads to the electrodes.

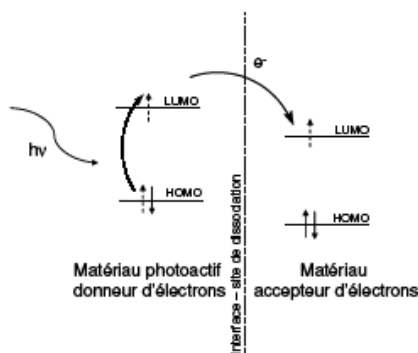


Fig. 1 : Diagram of creation and dissociation of the exciton.

The absorption of photons by an organic material, leads this material to the excited state, it creates for itself pairs electron-holes located in strong interaction, of coulomb nature, usually called excitons. These excitons diffuse then towards the interface between transporter material of holes and transporter material of electrons. The dissociation of excitons at the interface between two materials is assured if the life time of the excitation is sufficient so that the exciton meets an internal field. Once the charges got separated, those must be moved towards

the corresponding electrode. By using asymmetrical electrodes thus allowing to collect the holes with an electrode with low work function and the electrons with another electrode with high work function.

B. Description of The Organic Solar Cells

The materials used in the active layer of the organic photovoltaic cells can be polymers, oligomers, small molecules... They all must however have a π -conjugated system, making it possible to absorb in the visible one and to create charges, then making it possible to transport them. In addition, these materials must be able to be easily implemented by wet process (deposit of a solution on a substrate) or by vacuum evaporation.

Among the materials acceptors of electrons we find derivatives of perylene (perylene-3,4,9,10-bis(dicarboximide) (PDI), perylene-3,4,9,10-tétracarboxylic-3,4,9,10 dianhydride (PTCDA)) or C60 (Buckminsterfullerene), the PCBM (1-[3-(methoxycarbonyl)propyl]-1-phenyl- [6,6]C61)[7, 8]. For the materials donors of electrons, we find the oligothiophenes, phthalocyanines. Polymers are also largely used like the derivatives of p - phenylenevinylene (poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene] MDMO-PPV)[9], of the polyfluorene (poly(9,9'-dioctylfluorene-co-bithiophene), F8T2) and of polythiophene (poly(3-hexylthiophene), P3HT)[10].

The mixture of these two types of materials, donors and acceptors, led to two principal technologies for the organic photovoltaic cells. They differ by morphology from the active layer: this one can be either in the form of double-layered or in the form of interpenetrated networks.

1). Cells of the double-layered heterojunction type

The first organic photovoltaic cells realized are composed of two layers of two materials, one donor and the other acceptor, as the fig. 2 shows it, forming a junction p-n then. The separation of the charges is achieved at the interface between the two layers.

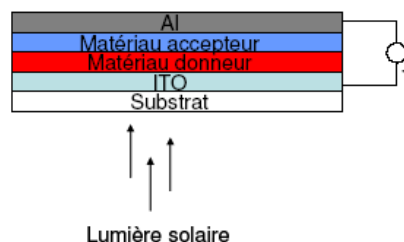


Fig. 2: Diagram of an organic photovoltaic cell in double-layered form.

The organic photovoltaic cells of double-layered type evaporated were studied since nearly three decades [11]. In 1986, C W Tang[12] obtains conversion efficiencies of 0,95% (AM2, 75 mA/cm²) with double-layered of CuPc/PV (perylene-3,4,9,10-tétracarboxyl-bis-benzimidazole) between an electrode of ITO and a silver electrode. M. Hiramoto in 1990 takes again the cell of Tang with a cell ITO/Me-PTCDI/H₂Pc/Au [13], the conversion efficiency is 0.56% (AM2 76 mw/cm²). D. Meissner since 1991 [14] works on these cells of the Tang type containing phthalocyanines and perylenes. In 2000 Meissner proposes the insertion of a Co-evaporated layer of fullerene and zinc phthalocyanine (1:1) between the two layers of the traditional structure (ITO/ZnPc/Perylene/Or). The conversion efficiency of the cell increases to a significant degree up to 1% under AM1.5 [15-17]. The

barrier of the 1% was recently exceeded by S.R. Forrest on a CuPc/C60 structure with the modified electrodes, reaching 3.6% of effectiveness of conversion under 150 mW/cm² AM_{1.5} for a very weak surface of cells of 1 mm² [18].

2). Cells of the bulk heterojunction type

Another technology was developed since 1992 by Sariciftci and al[19] with a structure of the active layer in networks interpenetrated with of MEH-PPV (poly[2-methoxy, 5-(2'-ethylhexyloxy) - p - phenylenevinylene] and of C60 or PCBM[20]. This technology leads then to conversion efficiencies of 2,5 % into 2001 (AM_{1.5}, 80 Mw/cm²)[21]. The best results are obtained today with a mixture P3HT/PCBM[22] giving of the efficiencies from 4,4 to 5 %[23, 24] (AM_{1.5}, 100 mW/cm²) or of 5,2 %[25] (AM_{1.5}, 80 mW/cm²).

III. SIMULATION OF THE CELL WITH HETEROJUNCTION D/A (NEW STAR SHAPED OLIGOTHIOPHENE (OT)/DERIVATIVE OF PERYLENE (D5P))

We chose a structure of donor-acceptor heterojunction type using the new conjugated derivative star shaped oligothiophene acting as donor (type p) and the perylene derivative (dipentil perylene (D5P)) like acceptor (type n).

The cell is consisted of the structure with following D-A heterojunction[26]:

ITO / PEDOT (30nm) / D (20nm) / A (20nm) / LiF (0.6nm) / Al (80nm).

We are interested here in a solar cell of oligomere/small molecule type based on a new π-conjugated system in which three chains of linear oligothiophenes (nT) are connected to a central, plane and rigid heart of trithienobenzene, by using the D5P like acceptor and layer of transport of electrons, with the chemical formulas as well as the absorption spectra of the two compound are given by (fig. 3), (fig. 4) successively [26]. The two electrodes are made up of ITO and of Al. Illumination is carried out ITO side which transmits nearly 80% of the light, the ITO is generally used as anode, it is covered with a layer of PEDOT:PSS (poly(ethylenedioxythiophene): poly(styrene sulphonate)). The back electrode consists of Al, the evaporation of the aluminium electrode is preceded by the deposit of a fine layer of lithium fluoride (LiF) between organic material and aluminium.

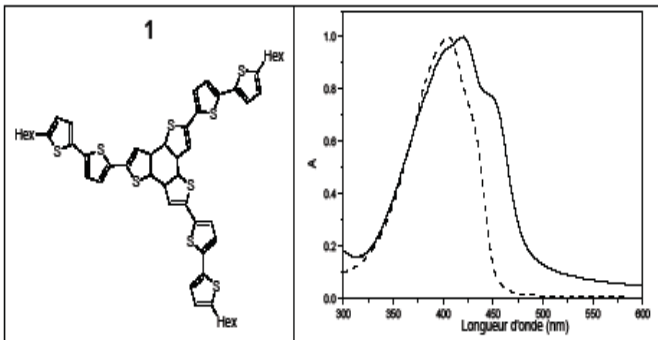


Fig. 3:chemical formula; absorption spectrum of the donor derivative of oligothiophene with structure in star (OT) in film (solid) and solution (dash)[26].

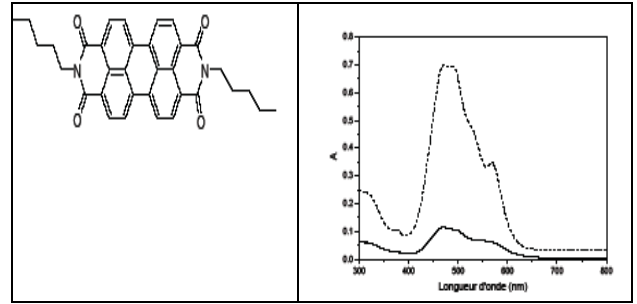


Fig. 4: Chemical formula; absorption spectrum of the acceptor derivative of perylene (D5P) [26].

A. Calculation of current for the cell derivative of oligothiophene (OT)/D5P

The absorption for our structure is carried out in the two layers. In this configuration only the excitons generated in the vicinity of the interface are effective for the generation of the photocurrent, this photocurrent is the sum of the current generated on the level of donor and the current in the acceptor.

For the simulation of the photocurrent of the cell we use the geometry of (Fig. 5) according to the model of D. Meissner [27].

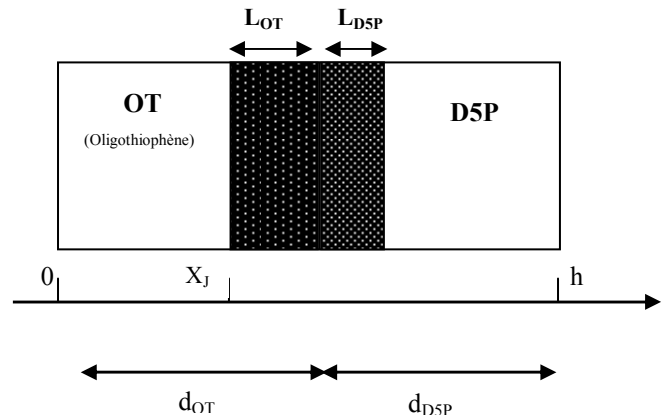


Fig. 5 : Geometrical model of the derivative of oligothiophene (OT)/D5P structure [27].

Where d_{OT}, d_{D5P} are the dimensions of layers oligothiophene (OT) and D5P respectively and L_{OT}, L_{D5P} the diffusion lengths. For calculation we take L_{OT}=12 nm and L_{D5P}=1 nm.

The numerical resolution of the equations of continuities and the currents, by the iterative method allowed to determine the distribution of excitons along the cell and to deduce the equation which characterizes the current for each point of the cell.

- Equations of continuities:

$$\frac{\partial n}{\partial t} = G_n - \frac{\Delta n}{\tau_n} + \frac{1}{q} \text{div}(J_n) \tag{1}$$

$$\frac{\partial p}{\partial t} = G_p - \frac{\Delta p}{\tau_p} - \frac{1}{q} \text{div}(J_p) \tag{2}$$

- Equations of currents:

$$J_n = q\mu_n nE + \mu_n KT \frac{\partial n}{\partial x} \tag{3}$$

$$J_p = q\mu_p pE - \mu_p KT \frac{\partial p}{\partial x} \tag{4}$$

1). Calculation of the current in the derivative of oligothiophene (OT) layer (p)

This layer presents the donor; it gives us a photoelectron (In) expressed by the equation (7).

- Boundary conditions:

$$S_n \Delta_n = D_n \left. \frac{\partial \Delta n}{\partial x} \right|_{x=0} \quad (5)$$

$$\Delta n \Big|_{x=x_j} = 0 \quad (6)$$

$$J_n = \frac{q \alpha L_n \Phi_i (1-R)}{(\alpha^2 L_n^2 - 1)} \left[\frac{\left(\frac{S_n L_n}{D_n} + \alpha L_n \right) \exp(-\alpha x_j) \left(\frac{S_n L_n}{D_n} \cosh\left(\frac{x_j}{L_n}\right) + \sinh\left(\frac{x_j}{L_n}\right) \right)}{\frac{S_n L_n}{D_n} \sinh\left(\frac{x_j}{L_n}\right) + \cosh\left(\frac{x_j}{L_n}\right)} \right] \quad (7)$$

$$L_n = L_{OT} \quad (8)$$

2). Calculation of the current in derivative of perylene(D5P) layer (n)

This layer gives us a photohole (Ip).

- Boundary conditions:

$$S_p \Delta_p = D_p \left. \frac{\partial \Delta p}{\partial x} \right|_{x=h} \quad (9)$$

$$h = d_{OT} + d_{D5P}$$

$$\Delta p \Big|_{x=x_j + L_{OT} + L_{D5P}} = 0 \quad (10)$$

$$J_p = \frac{q \Phi_i (1-R) \exp(-\alpha_1 (x_j + L_{OT})) \exp(-\alpha_2 L_{D5P}) \alpha_2 L_p}{(\alpha_2^2 L_p^2 - 1)}$$

$$\left[\frac{S_p L_p}{D_p} \left(\cosh\left(\frac{x_b}{L_p}\right) - \exp(-\alpha_2 x_b) \right) + \sinh\left(\frac{x_b}{L_p}\right) + \alpha_2 L_p \exp(-\alpha_2 x_b) \right] \quad (11)$$

$$\frac{S_p L_p}{D_p} \sinh\left(\frac{x_b}{L_p}\right) + \cosh\left(\frac{x_b}{L_p}\right) \quad (12)$$

$$L_p = L_{D5P} \quad (13)$$

3). The current in the active area (Ig)

The excitons generated in the active region (in the vicinity of the interface) are effective on the level of dissociation (production of the carriers), therefore, the photocurrent in this zone is:

$$J_g = q \Phi_i (1-R) \exp(-\alpha_1 x_j) \left[(1 - \exp(-\alpha_1 L_{OT})) + \exp(-\alpha_1 L_{OT}) (1 - \exp(-\alpha_2 L_{D5P})) \right] \quad (14)$$

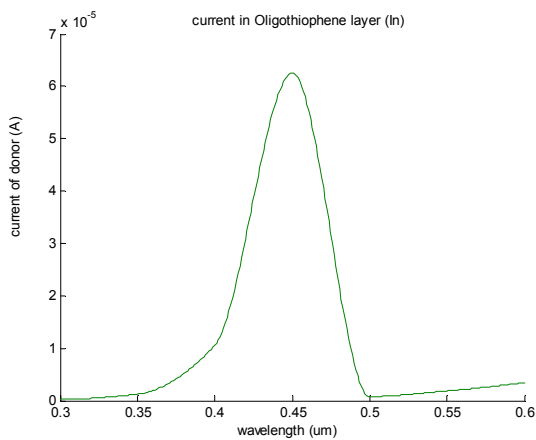


Fig. 6: Variation of the current of derivative of oligothiophene layer according to the wavelength.

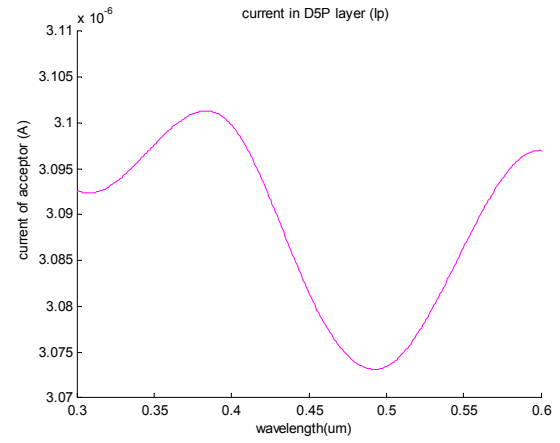


Fig. 7: Variation of the current of D5P layer according to the wavelength.

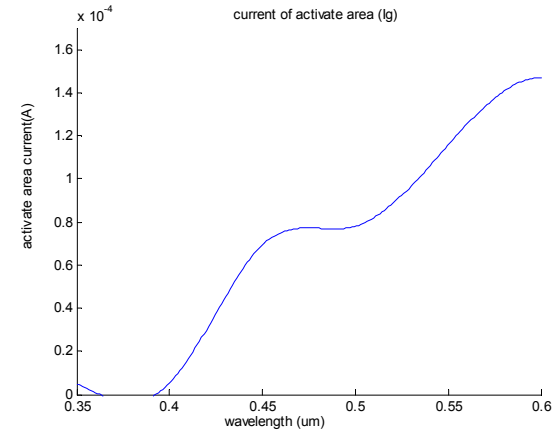


Fig. 8: Variation of the current of active area according to the wavelength.

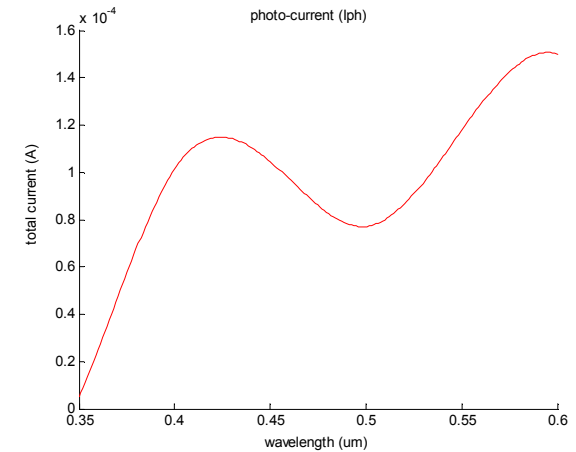


Fig. 9: Variation of the total current according to the wavelength.

The (Fig. 9) shows interesting values of the total photocurrent, it depend on the current of the active layer as well as donor. The photocurrent of the active area (Fig. 8) is considerable compared to the photocurrents of the oligothiophene layers and D5P (Fig. 6) and (Fig. 7). The total current of the cell shows a growth value with a peak of 0,11 mA at 425 nm corresponding to a maximum absorption of the donor (interval of 400 nm at 500 nm) and a maximum of 0,15 mA at 559 nm where the active layer reaches the value max of 0,148 mA. These results affirm to us that the principal generation of the photocurrent is localised in the active area, so the excitons generated in the active area (in the vicinity of the interface) are effective on the level of dissociation (production of photocurrent).

B. I(V) characteristic

The equivalent electric circuit is given by (Fig. 10), according to [27], where $R_s = R_{Al} + R_{D5P} + R_{OT} + R_{ITO}$.

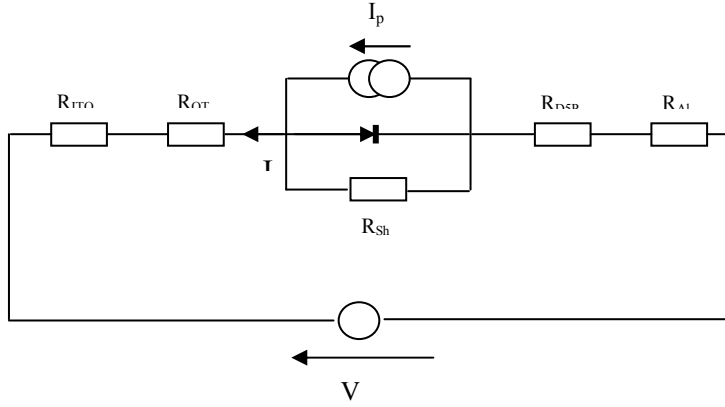


Fig. 10 : Electric circuit of Oligothiophene/D5P cell [27].

According to this equivalent circuit, we deduced the equation characteristic $I(V)$ of the cell:

$$I(V) = I_{ph} - I_s \left[\exp \left(\frac{V + R_s I}{U_T} \right) - 1 \right] - \frac{V + R_s I}{R_{sh}} \quad (15)$$

The (Fig. 11) represent $I(V)$ characteristic, the conversion efficiency and the fill factor is given in (Table. 1) under $AM_{1.5}$ (77 mW/cm^2).

Table 1: Performances of the double-layer structure Oligothiophene/D5P.

$I_{sc}(\text{mA/cm}^2)$	$V_{co}(\text{mV})$	$\eta(\%)$	FF(%)
1.6	547	0.82	72.54

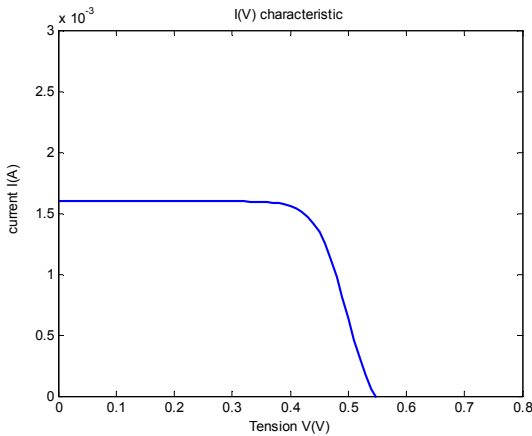


Fig.11: $I(V)$ characteristic for the Oligothiophene/D5P structure.

C). Optimization of donor thickness

In order to optimize the performances of the cell based on the derivative of oligothiophene, we analyzed the thickness effect of the donor layer; the thickness of the acceptor layer remains constant and equal to 20 nm. (Fig. 13) shows the characteristics $I(V)$ of the cell for the three thicknesses $d_{OT} = 15, 20$ and 40 nm . In these cases, the cell delivers maxima of $I_{sc} = 2.3 \text{ mA/cm}^2$, $V_{oc} = 556 \text{ mV}$, a factor of form FF larger than 0.7 and conversion efficiency arrived at 1.19%.

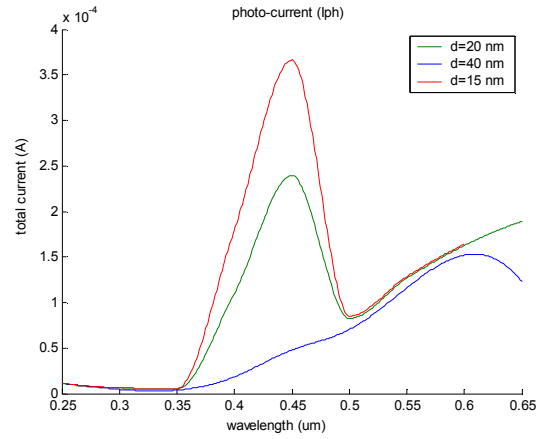


Fig.12: Effect of the donor layer thickness (d_{OT}) on the total current.

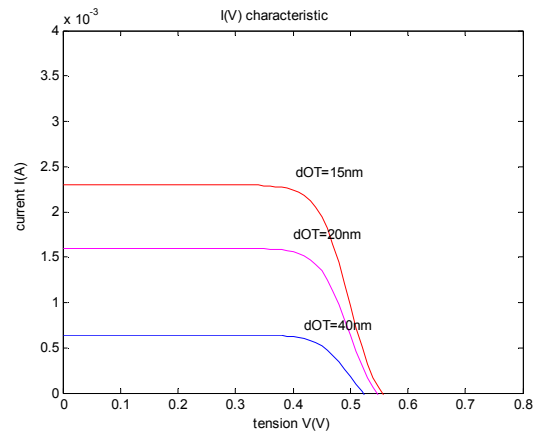


Fig. 13: Variation of characteristic $I(V)$ according to the thickness d_{OT} .

The Table.2 summarizes the results obtained for the various thicknesses.

Table.2: Characteristics of the cell according to the thickness of donor.

Donor thickness (d_{OT})(nm)	$I_{sc}(\text{mA/cm}^2)$	$V_{co}(\text{mV})$	$\eta(\%)$	FF(%)
40	0.64	523	0.33	74.85
20	1.6	547	0.82	72.54
15	2.3	556	1.19	71.50

The obtained results on the cell for different thicknesses are consistent with the photocurrents (Fig. 12) and show that the greatest effectiveness is obtained for thicknesses $d_{OT} \leq 20 \text{ nm}$. These characteristics place this cell among most effective obtained from π -conjugated oligomers with holes transporter type.

IV. CONCLUSION

Up to now the results obtained for organic solar cells either experimental or based on statistical statements starting from the spectral answers of the cells. We worked out a numerical model based on the resolution of the equations of continuities who gave the results in good agreement with literature and which allowed, moreover a better control of the performances of the organic cells, for their improvement. With the obtained results, we can consider the cells of the heterojunction type based on these new donors resulting from oligothiophenes among most effective obtained from oligo- and polythiophenes

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