

Optical diagnostic of photovoltaic events in plastic solar cells

J.-M. NUNZI

ERT Cellules Solaires Photo Voltaïques Plastiques
Laboratoire POMA, UMR-CNRS 6136
jean-michel.nunzi@univ-angers.fr

Plastic photovoltaic solar cells represent a very attractive technology for the development of low cost renewable energy resources. Recent progress achieved using organic mono-crystal, multilayered thin film and interpenetrated network technologies permit to expect a very fast increase in the conversion yield of organic solar cells in order to make them a competitive alternative to the various forms of silicon cells. Such progress requires a specific diagnostic of the peculiar physics of amorphous organic semiconductors and devices.

We first give a review of the essential features of plastic photovoltaic solar cells. We then review the principles, uses and applications of the specific optical characterization tools that we implemented for the diagnostic of plastic solar cells: time of flight in different geometries, pump-probe spectroscopy, second harmonic generation and various ways of studying and interpreting the current-voltage characteristics of the cells.

1. Introduction

Recent progress achieved using organic mono-crystal, multilayered thin film and interpenetrated network technologies permit to expect a very fast increase in the conversion yield of organic solar cells. This will possibly make them a competitive alternative to the various forms of silicon cells. Indeed, the passed two years have seen a significant jump in the conversion yield of organic photovoltaic (PV) solar cells, passing from a 1% yield achieved 15 years ago [1], to a 5% yield achieved one year ago [2]. This opens the perspective to see very soon, on a typical 5 years time-scale, organic PV cell with solar efficiencies in excess of 10%. The long term objective of such very active research is to reduce the cost of PV modules. In this conference, we discuss some of the key technical aspects of the problem.

There is no short term ambition to replace silicon, nor thin film technologies (a-silicon, CIS or photosensitised cells), but to develop a long term

technology based on environmentally safe materials with almost unlimited availability. Plastic materials bear this potentiality. Such objective becomes feasible nowadays, in the same way as we face the development of efficient organic displays in the electronic industry (see [3] for a review). Those displays were developed after a 10-years laboratory research effort because they offer a low cost “easy” technology and a technically attractive alternative to liquid crystal displays. In this review, we use the organic light emitting diode (OLED) technology [4] to draw the research guidelines in organic PV cells. OLED literature will be taken as a reference all along this chapter.

Progress in organic PV cells require a clear understanding of the peculiar physics of amorphous organic semiconductors and devices [5]. In this conference, we first give an electrical description of organic solar cells: from the organic material to the device. A critical analysis of the physical processes leading to the photovoltaic effect in organic materials permits to size the maximal and minimal yields achievable using different device structures. This permits also to size the main physical parameters permitting the achievement of a 10% solar energy conversion in trial devices. We then describe some materials and device structures which are pertinent in view of such objective. We finally present the optical diagnostics which permit to investigate specifically the plastic solar cells.

2. Organic semiconductors

2.1. Charge transport and mobility

Transport and mobility in organic materials require a knowledge of the charged species. A review of transport properties is given by Schott [6]. Energy levels of the charges are usually determined by cyclic voltametry as concerns materials in solution. They can be characterized by XPS or UPS (X-ray and UV photo-electron spectroscopies) as concerns solid materials. In small molecules, charged species are localized spatially, they are simply the cation (positive) and anion (negative) radicals. In polymers, the electron-phonon coupling leads to the so-called polarons which are charges dressed by a reorganization of the lattice [7]. Polarons may be regarded as defects in conjugated polymer chains. Such defect stabilises the charge which is thus self-trapped as a consequence of lattice deformation. So in the vast majority of organic semiconductors, transport bears all characteristics of a hopping process in which the charge (cation or anion) propagates via side to side oxidation-reduction reactions (Fig. 1a). One must distinguish between intra-molecular charge transport along a conjugated polymer chain and intermolecular charge transport between adjacent molecules or polymer chains

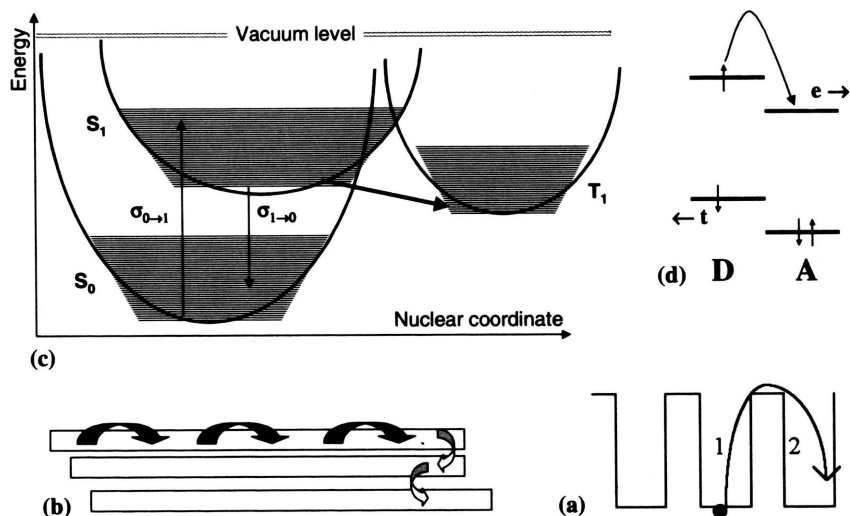


FIGURE 1. Photophysics of organic semiconducting materials: hopping process between molecules 1 and 2 (a), intra- (full arrows) and intermolecular (broken arrows) charge-transport (b), absorption ($S_0 \rightarrow S_1$), luminescence ($S_1 \rightarrow S_0$) and inter-system crossing ($S_1 \rightarrow T_1$) (c), charge separation of an exciton into a free electron (e) – hole (h) pair at a donor (D) – acceptor (A) junction (d).

(Fig. 1b). The former which is specific to conjugated polymers is the most efficient. Charge mobility in organics is field dependent, especially in the low mobility materials in which it usually follows phenomenologically the Poole-Frenkel law: $\mu \propto \exp(\sqrt{E})$ [8]. Mobility can be experimentally determined by photo-current transients (time of flight) [9], field effect transistor saturation currents [10], space charge limited currents [11] or impedance spectroscopy [12]. Mobilities in organic semiconductors are usually rather small: from $10^{-2} \text{ cm}^2/\text{Vs}$ in well ordered conjugated polymers (liquid crystalline polyfluorene)[13], down to $10^{-8} \text{ cm}^2/\text{Vs}$ in guest-host polymer systems (dye doped poly-vinylcarbazole – PVK, for instance) [14]. Electron and hole mobilities differ by orders of magnitude in a single material; in small molecules such as the widely studied tris (8-hydroxyquinolinolato) aluminium – [9], as well as in conjugated polymers such as the famous poly-paraphenylvinylene – PPV [12]. The lowest mobilities are usually dispersive, which is the result of a distribution of mobilities [15]. Mobility can increase by up to two decades upon applied voltage, being eventually very large above $1 \text{ MV}/\text{cm}$ in conjugated polymers [16]. Mobility is increased by orders of magnitude when the molecular packing is improved. This is achieved by molecular ordering.

Single crystals have the best performances [17], electron mobility in fullerene C_{60} single crystals is $2.1\text{cm}^2/\text{Vs}$ [18], but it is reduced by at least 3 orders of magnitude by imperfect purification and uncontrolled crystallization [18], as well as by oxygen traps [19]. With this in mind, mobility in photovoltaic materials can be improved using liquid crystals made from molecules (columnar LCs [20]) or polymers (nematic LCs [13]). Mobility is also increased by orders of magnitude, up to $0.1\text{cm}^2/\text{Vs}$, between a random polymer (poly 3 alkylthiophene – P3AT) and its regioregular analogue [21,22], the last one leading to supraconductivity at low temperature in a field-effect device [23]. Charge transport is also improved by purification or deposition conditions; for instance, mobility becomes non-dispersive in Alq_3 upon purification (oxygen induces traps) [24] and it becomes non-dispersive in soluble PPV derivatives upon selection of the solvent used for deposition [25]. Mobility is usually low and dispersive in randomly distributed polar molecules, but it is increased significantly when the dipoles are organized [26]. A record non dispersive electron mobility of up to $2.10^{-4}\text{cm}^2/\text{Vs}$ was recently achieved in an air stable amorphous glassy molecular material [27]. Another record non dispersive hole mobility of $10^{-2}\text{cm}^2/\text{Vs}$ was also achieved in an amorphous glassy molecular material [27]. Important is that mobility always drops by at least 2 orders of magnitude with impurities or defects (traps).

2.2. Light absorption and exciton diffusion

Light absorption by organic materials can also be rationalized using photophysics concepts [29]. Time resolved analysis of all the different events following absorption of light can usually be achieved through pump-probe spectroscopy of flash photolysis. It is from the optically excited state that the neutral excitation (exciton) can give rise to a free charge pair (Fig. 1d). Absorption and photoluminescence usually involve the same energy levels: the fundamental S_0 and first excited S_1 singlet states (Fig. 1c). Upon light absorption, molecules are excited from the fundamental to the excited state with a cross section $\sigma_{0\rightarrow 1}$. Singlet-singlet transitions are very efficient ones, equivalent to the direct transitions in semiconductor crystals, leading to singlet excitons with a rather short lifetime (nanoseconds). The absorption spectrum extends inside the visible and near-infrared ranges. The exciton energy can then decay to the ground state radiatively, with a cross-section $\sigma_{1\rightarrow 0}$ which is almost the same as $\sigma_{0\rightarrow 1}$ (dipole coupling with the electromagnetic field): typically 10^{-16}cm^2 in organic dyes and pigments. This is the usual luminescence which is a loss mechanism in photovoltaic cells. The exciton energy can also decay down to the ground state through vibrations (phonon emission in extended states). Speed of this decay is almost proportional to

$N!$ where N is the number of vibration quanta ν_{vib} (stepladders in Fig. 1c) needed to decay down to the lower electronic state: $N \approx (\lambda_{\text{max}} \nu_{\text{vib}})^{-1}$. Another exciton decay channel is through inter system crossing (ISC) to the lower triplet state T_1 (Fig. 1c). ISC efficiency is driven by spin-orbit coupling inside the molecule. The largest permitted orbital moments permit the most efficient ISC. ISC is reduced in planar linear chromophores. Energy in triplet states is carried by triplet excitons. Triplet excitons have a greatly increased lifetime (microseconds), because radiative decay to the ground state is forbidden. It is equivalent to indirect transitions in crystals. Triplet excitons can diffuse over large distances, up to 100 nm if no trapping occurs, although singlet excitons would not diffuse more than 10 nm by radiative energy transfer. Finally, singlet or triplet excitons can decay into geminate pairs of charges: charge generation, which is the useful channel for the PV effect. This can also be probed by pump-probe spectroscopy. Exciton diffusion length is evaluated using the photovoltaic action spectra (Sec. 3.2).

2.3. Charge generation

Exciton dissociation into a pair of charges occurs under large electric fields which can compete with Coulomb interaction. The process is usually described by the so-called Onsager theory which gives the efficiency of photo-dissociation ϕ of the exciton as a power series of the electric field E : $\phi = \phi_0 \exp\left(-\frac{r_c}{r_0}\right) \left[1 + \frac{r_c e E}{2! k_B T} + \dots\right]$, with $r_C = e^2/4\pi\epsilon k_B T$ the critical distance below which Coulomb energy is larger than kinetic energy and r_0 the “thermalisation distance”. Exciton dissociation can be equivalently promoted by charge transfer between donor and acceptor molecules (Fig. 1d) A partner of the donor acceptor pair can simply be an impurity (O_2 for instance is an acceptor [29]). A junction at the interface with a metal or at the interface between a donor and an acceptor layer can also be a region of exciton dissociation. Such junction effect can be phenomenologically interpreted in terms of an interfacial electric field, especially if the materials are the doped layers of a p-n junction. It is clear that long exciton lifetimes will permit efficient charge generation events.

3. Physics of plastic solar cells

3.1. Photovoltaic effect

The production of electric energy from sun-light is the result of a chain process (Fig. 2). Sunlight photons are absorbed inside the device (A), carriers are then generated from exciton dissociation (G), carriers are collected by the

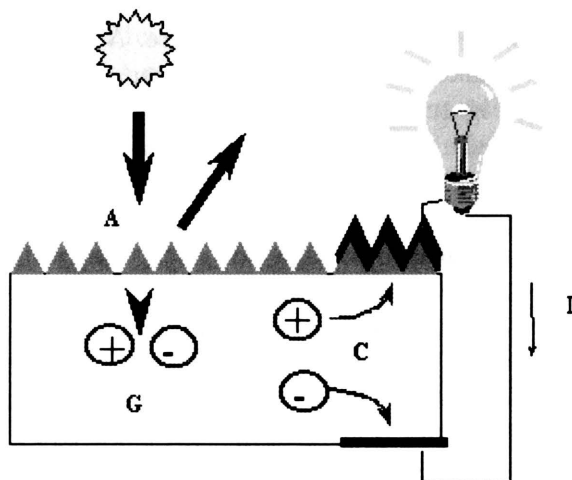


FIGURE 2. The photovoltaic process: Photon Absorption (A), Carrier Generation (G), Carrier Collection (C).

electrodes and driven into the external circuit (C). These are the productive events of the PV process [30]. A more detailed analysis permits to understand and eventually improve the different steps of the PV effect [31].

Absorption of photons: In most organic devices only a small portion of the incident light is absorbed because: The bandgap is too high. A bandgap of 1.1 eV (1100 nm) is required to absorb 77% of the solar radiation on the earth whereas the majority of semiconducting polymers have bandgaps higher than 2.0 eV (600 nm), limiting the possible absorption to about 30%. The organic layer is too thin. Low charge carrier and exciton mobilities require layer thickness on the order of 100 nm. Fortunately the absorption coefficient of organic materials is generally much higher than in silicon so that only about 100 nm are necessary to absorb between 60 and 90% if a reflective back contact is used.

Reflection: Reflection losses are probably significant but little investigated in these materials. Systematic measurements of photovoltaic materials are desired to provide knowledge of their impact on absorption losses. Anti-reflection coatings as used in inorganic devices may then prove useful once other losses such as recombination become less dominant. Surface of the devices can also be structured as in Fig. 2.

Exciton diffusion: Ideally, all photoexcited excitons should reach a dissociation site. Since such a site may be at the other end of the semiconductor, their diffusion length should be at least equal to the layer thickness

(for sufficient absorption) – otherwise they recombine and photons are wasted. Exciton diffusion ranges in polymers and pigments are usually around 10 nm.

Charge separation: Charge separation is known to occur at organic semiconductor/metal interfaces, at impurities such as oxygen or between materials with sufficiently different electron affinities (EA) and ionisation potentials (IA). In the latter, one material can then act as electron acceptor (A) while the other keeps the positive charge and is referred to as electron donor (D). If the difference in IA and EA is not sufficient, the exciton may just hop onto the material with the lower bandgap without splitting up its charges. Eventually it will recombine without contributing charges to the photocurrent.

Charge transport: The transport of charges is affected by recombination during the travel to the electrodes – particularly if the same material serves as transport medium for both electrons and holes. Also, interaction with atoms or other charges may slow down the travel speed and thereby limit the current.

Charge collection: In order to enter an electrode material with a relatively low workfunction (Al or Ca) the charges often have to overcome the potential barrier of a thin oxide layer. In addition, the metal may have formed a blocking contact with the semiconductor so that they can not immediately reach the metal.

3.2. Characteristics of organic solar cells

Drawing the current-voltage characteristics of a cell in the dark and under illumination (Fig. 3) permits to evaluate most of its photovoltaic performances as well as its electric behaviour [32].

The short circuit current I_{sc} is the one which crosses the cell at zero applied voltage, it is a function of illumination G . Charges travel under an internal potential difference typically equal to V_{oc} .

The open circuit voltage is measured when current in the cell is 0, corresponding to almost flat valence and conduction bands.

I_{max} and V_{max} values are defined in order to maximize the power $|I_{max} V_{max}|$. This one is the maximum power P_{max} delivered by the PV cell.

The fill factor FF is the ratio of the maximum power to the external short and open circuit values: $FF = \frac{P_{max}}{V_{oc} I_{sc}} = \frac{V_{max} I_{max}}{V_{oc} I_{sc}}$.

Under monochromatic lightning at a wavelength λ , the yield of electron generated per incident photon: the Internal Photon to Current Efficiency (ICPE) is defined as: $IPCE = \frac{J_{sc}}{G \lambda} \frac{hc}{e}$, with J_{sc} the short-circuit current den-

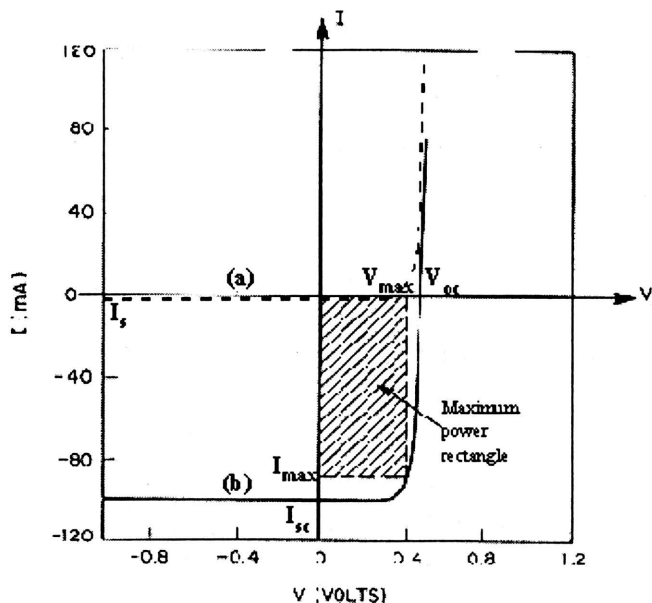


FIGURE 3. I - V characteristics of an ideal solar cell: (a) in the dark, (b) under illumination.

sity, or numerically in a very simple manner: $\text{IPCE} = 1.24 \frac{J_{sc}}{G\lambda}$, with J_{sc} in A cm^{-2} , G in W cm^{-2} and λ in μm . ICPE is the measured parameter in the photovoltaic action spectra.

The external photovoltaic yield η is defined as the ratio of the maximum electric power extracted to the illumination G times the surface S of the module: $\eta = \frac{P_{\max}}{SG}$ (it is often expressed as a percentage). Conversion yield is the key parameter as concerns cells productivity. It must be evaluated carefully [33], and not be confused with ICPE.

3.3. The power efficiency of organic solar cells

Solar cells are evaluated by their energetic conversion efficiency η (as defined above). It is essentially the product of 4 contributions: $\eta = \phi A F F V_{\max}/(h\nu)$. The fill factor can be almost close to 1 (or 0.8), provided shunt resistance is large ($R_{sh} > 25 \text{K}\Omega$) and series resistance is small ($R_s < 50 \Omega$). The ratio $eV_{\max}/(h\nu)$ between the extracted electron energy (0.5 eV) and the average energy of the absorbed photons (2 eV) reaches 1/4 in current organic PV cells. One can expect a photogeneration yield ϕ close to 1 at the active junction [34, 35, 36]. In a homogeneous layer, this would require

an exciton diffusion length close to the thickness of the diode, which is also possible in some pigments [37]. Organic colorants have an absorption in the visible range greater than $\alpha \geq 10^7 \text{ m}^{-1}$ over a 100 to 200 nm band-width. This corresponds to a 85% absorption in a 100 nm-thickness layer accounting for reflection on a metallic back electrode. Let us take a sunlight absorption $A = 1/2$. We thus get the order of magnitude of an optimised “achievable” photovoltaic conversion efficiency: $\eta \approx 10\%$. This is the necessary level for a realistic technology.

Two parameters require a particular engineering: the **exciton diffusion length** (Sec. 2.2) and the **charge mobility** (Sec. 2.1) Both are sizable.

- This is presumably the improvement of the exciton diffusion length which has recently permitted to reach a 3.6% solar efficiency with a bi-layer molecular cell [38] analogous to the original Tang cell [39]. An exciton diffusion length close to 100 nm is needed in homogeneous solar cell materials. Exciton diffusion is controlled by dipole coupling between molecules. It can be large in “pure” materials (trap free materials) made of “small” molecules exchanging energy through so-called H coupling (as opposed to the J coupling) [40], when luminescence yield vanishes. This is the usual case for small molecules in a crystalline or polycrystalline state, when molecules are stacked parallel to each other. One must notice that it can be larger than in some inorganic materials because most organic materials behave as “direct gap” semiconductors.
- It is the large mobility of charges ($1\text{-}3 \text{ cm}^2/\text{Vs}$) which may explain the exceptional solar efficiency obtained in pentacene crystals [41]. Photo-generated charges must indeed cross the solar cell fast enough, from the active junction to the counter electrode, in order for the current to be evacuated to the circuit faster than photo-generation brings charges into the device. Otherwise, a space charge field in the cell would screen the internal field of the cell and photo-generation efficiency would vanish. Under AM1 solar illumination, a 10% efficiency would correspond to a $J = 20 \text{ mA/cm}^2$ current extracted out of the cell. Space charge limited current follows the law: $J_{\text{sc}} = \frac{9}{8} \varepsilon \mu \frac{V^2}{L^3}$, in which V is the working voltage and L the organic semiconductor thickness. We get a lower limit for the mobility: $\mu \geq 2 \cdot 10^{-4} \text{ cm}^2/\text{Vs}$. This can be an electron or a hole mobility which must reach this value, or both, depending on the cell structure.

3.4. Junctions

The junction is the place where the exciton dissociates. A monolayer cell will make a Schottky junction with one of the electrodes. A bi-layer cell will

preferentially develop a p-n junction at the interface if semiconductors are doped, or a Donor-Acceptor one (Fig. 1d) if they are intrinsic (undoped). Several examples are given in [42].

A junction will result from the equalization of the chemical potential of the electron (Fermi level in inorganic semiconductors) in the two different materials [43]. The case of a Schottky cells for the contact between a metal and a p-type semiconductor is illustrated in Fig. 4. Let ϕ_m be the ionisation potential (IA) of the metal in a vacuum. The same is ϕ_s for the semiconductor (Fermi level). The nature of the contact depends on the relative height of the Fermi levels ϕ_m and ϕ_s .

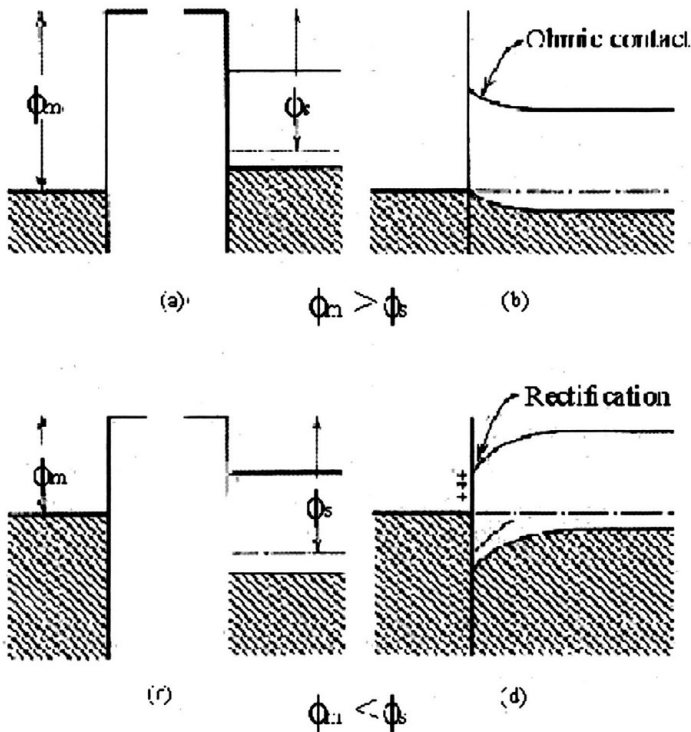


FIGURE 4. Energy levels of a metal to p-type semiconductor contact. Before and after contact for $\phi_m > \phi_s$ (a, b). Before and after contact for $\phi_m < \phi_s$ (c, d).

- If $\phi_m > \phi_s$, electrons diffuse from the semiconductor to the metal. We thus get a positive accumulation in the semiconductor. No barrier forms at the interface and the contact is ohmic.
- If $\phi_m < \phi_s$, electrons diffuse from the metal to the semiconductor (holes in the reverse direction). Diffusion stops when the space charge field

at the interface is large enough to compensate for the potential difference. Owing to the small carrier density in organic semiconductors, the so-called depletion layer extends in the semiconductor only. This is a rectifying contact: a Schottky contact.

4. Structure and technology of organic solar cells

4.1. Cell structures [5, 30, 31, 40]

In order to meet the specific requirement for an efficient photon to charge conversion, different device architectures have been developed. Figure 5 shows a typical bi-layer device (p-n diode). Charge separation occurs at the interface between the two layers. Ideally the, donor material should only be in contact with the electrode material with the higher workfunction (typically ITO) and the acceptor -material with the lower workfunction electrode (typically Al). Of course, as the height of the workfunction of ITO is between Al and Au ($Al < ITO < Au$), the structure is inverted in Fig. 5. The different architectures are:

Single layer cells which consist of only one semiconductor material and are often referred to as Schottky type devices or Schottky diodes since charge separation occurs at the rectifying (Schottky) junction with one electrode. The other electrode interface is supposed to be of ohmic nature. The structure is simple but an absorption covering the entire visible range is rare using a single type of molecule. The photoactive region is often very thin and since both positive and negative pho-

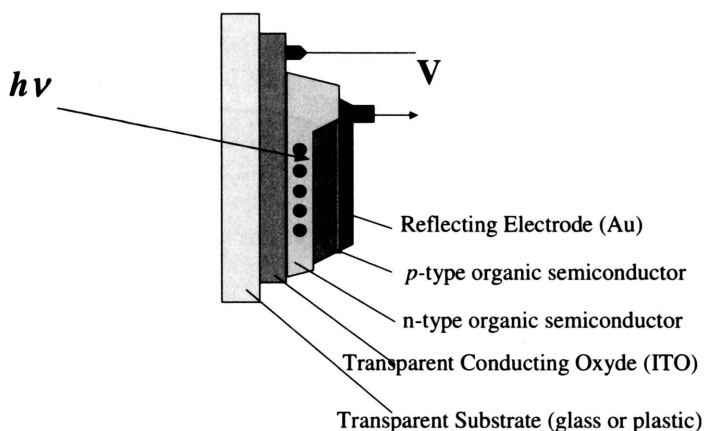


FIGURE 5. Typical structure of a bi-layer organic solar cell.

to excited charges may travel through the same material recombination losses are generally high. Such cells are currently used for screening and evaluation purposes. They are also well studied for laser diagnostics of internal photo-physics events.

Double layer cells benefit from separated charge transport layers that ensure connectivity with the correct electrode and give the separated charge carriers only little chance to recombine with its counterpart. The drawback is the small interface thickness that allows only excitons of a thin layer (exciton diffusion length + depletion layer thickness) to reach it and get dissociated.

Blend cells exhibit a large interface area if the molecular mixing occurs on a scale that allows good contact between alike molecules (charge percolation in an **interpenetrated network**) and most excitons to reach the D/A interface. This can usually only be partly achieved, so the defects of the network structure – particularly the connectivity with the correct electrode – represents a technological challenge [44].

4.2. Emerging technologies in organic solar cells

In the past years, the main difficulty to obtain large solar conversion efficiencies was related to the small exciton diffusion length of the materials used in organic PV cells [45]. In most cases, the useful interface region in a planar p-n-type solar cell is limited to almost 10% of the thickness which is necessary to absorb a significant proportion of sun light, where the built-in junction-field is large, as pictured in Fig.6 [46]. The efficiency of such diode is limited to almost 1% [47]. This difficulty was recently overcome in a CuPc/C₆₀ cell designed with improved electrodes, yielding a 3.6% ef-

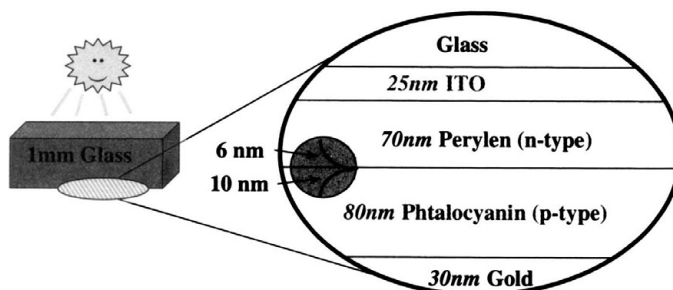


FIGURE 6. Scheme of a bi-layer p-n-type molecular PV cell showing the extension of the photoactive region in which excitons dissociate, around the junction [5].

efficiency [38]. This proves that bi-layer cells can be good candidates for an efficient energy conversion [34].

In year 2000, the Lucent group got a 4.5% efficiency with a halogen (Br or I₂) doped pentacene monocrystal (C₂₂H₁₄) [48]. Efficiency was even larger: 5%, by considering only the surface of the cell and not the crystal one. The same material deposited in a thin polycrystalline film gave a lower 2.2% efficiency. This breakthrough may result from several favourable factors:

- Pentacene behaves as direct band gap for absorption, but exciton decays rapidly to a triplet exciton which has a long lifetime.
- The crystal is dense and pure, permitting a large exciton diffusion length.
- Hole mobility in pentacene reaches 1 cm²/Vs.
- The material was doped, which permits exciton dissociation apart from contact electrodes, reducing the quenching of excitons before charge transfer.

This result opens-up the possibility to build single layer solar cells for an efficient PV conversion. However, absorption cannot cover all the solar spectrum with a single layer of an omogeneous organic material, so that a bi-layer diode remains a potentially attractive device [49]. Additionally, halogen doped crystals may be highly unstable materials, but this also can be overcome using controlled molecular doping with strong acceptor molecule [50]. Promising structures which combine some advantages of the crystalline diodes with the processability of multilayer devices are the columnar liquid crystal cells [36, 51], or any other self-organized device structure [52, 53].

In order to circumvent problems associated with the weak extension of the depletion layer in layered organic solar cells, the idea is to increase the effective surface of the junction using composite materials, in blend cells. The first successful device was built more than 10 years ago with dye-sensitised solar cells [54] (so called Grätzel cells). The concept was applied more recently with success to solid single-layer polymer solar cell. It is based on the efficient – ultrafast – charge transfer which occurs between C₆₀-derivatives as charge acceptor and semiconducting polymers as charge donor [55, 56]. Such cells exceed 3% solar efficiency. From a chemical point of view, the advantage is that materials do not have to be optimised for charge AND exciton transport, because excitons can dissociate everywhere in the mixture, they do not have to migrate owing to the close distance between donor and acceptor moieties (Fig. 7). From a topological point of view, the effective surface of the junction is significantly improved by the interpenetrated network. Difficulty lies in the fabrication of a doubly connected network made

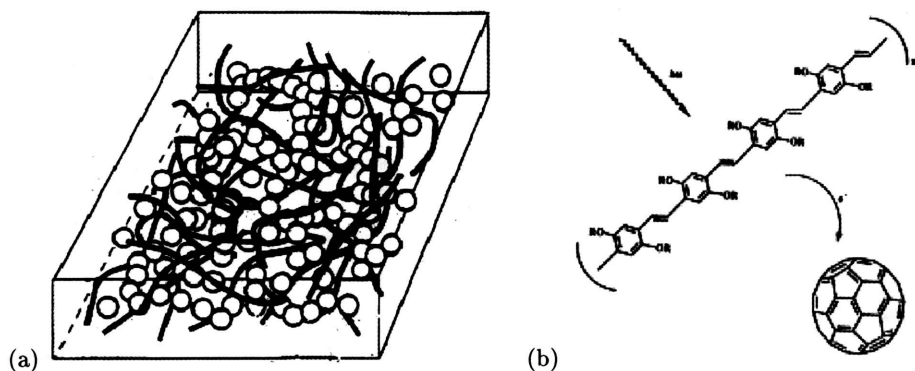


FIGURE 7. Scheme of an interpenetrating network of a donor polymer and an acceptor C_{60} -derivative (a), Detail of an ultrafast charge transfer event (b) [50].

of an electron transport material (conjugated polymer) and a hole transport material (C_{60}) [57]. A recent trial was to use small co-evaporated molecules to build a model interpenetrated network [58]. A power conversion efficiency of 2.2% was achieved in this way. There has been also attempts to link the donors and acceptors chemically, but experimental results do not yet show any significant progress in this direction [59, 60]. Another actual difficulty lies in the stability of the cells: both structural and photochemical stability [61]. There is still many room for improvement in the technology of interpenetrated networks [62]: some attempts consist in replacing C_{60} by inorganic semiconductor nano-materials (so-called hybrid cells) [63, 64], as a strategy for further improvement of stability and performance of the technology. A 1.7% solar efficiency was recently reported using a hybrid blend consisting of 7-nanometer by 60-nanometer CdSe nanorods and the conjugated polymer poly-3 (hexylthiophene) [65]. The blend was assembled from solution, yielding an external quantum efficiency of over 54%.

A new route for the improvement of organic solar cell efficiency was demonstrated by the CEA group in Saclay [66, 26]. It consists in the orientation of polar chromophores inside the volume of the cell. A polar orientation is different from an axial orientation: the former permits to tune and optimise separately absorption of light and transport of excitons and charges, as do liquid crystals; the latter permits in addition to induce an internal polarization field [67, 68]. This field improves exciton dissociation inside the cell (Sec. 2.3) as well as charge mobility [26]. An internal polarization may also help reducing the potential barriers at the electrodes, thus improving series resistance. The practical demonstration of a polar orientation was made using several blends of polymers incorporating polar chromophores [69, 70, 71].

A two orders of magnitude efficiency improvement was obtained in a blended polythiophene structure (Fig. 8). The efficiency $\eta = 0.02\%$ was still very low because the materials used were not optimised for absorption, charge generation, charge transport AND orientation. There is need to optimise both the polymer matrix and the polar chromophores in the oriented blend in order to get significant efficiencies.

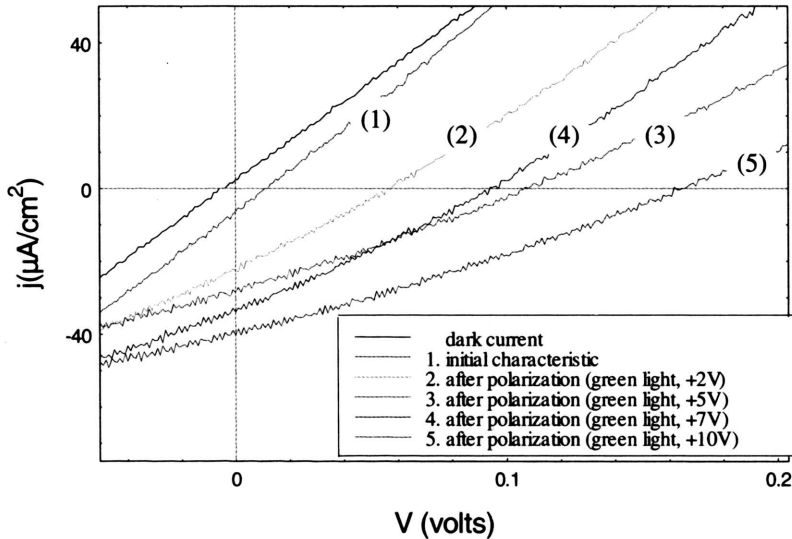


FIGURE 8. Current/Voltage characteristics in the dark and under $12 \text{ mW}/\text{cm}^2$ red light illumination through for an ITO/P3BT + poly- (MMA-DR1) + Indane Dye/Au device, before and after polarization sequences [67].

5. Conclusion

Several possibilities are open to fabricate efficient solar cells: single layers, double layers, blended or interpenetrated cells, hybrid cells, as well as molecularly organised and oriented cells. All offer a new range of interesting research in physics, in chemistry and in technology, and all offer strategies to build an efficient PV technology. Such cells will obviously make soft and possibly bendable or foldable PV modules. They will be adapted to the fabrication of solar roofs, but also sails, tents and all kind of plastic outdoor furniture or portable devices. Importantly, plastic solar cells will permit to orient future generations of photovoltaic solar cells toward an ultra-low-cost technology.

Progress in this emerging domain requires the development of specific optical diagnostic tools for in-situ studies of photovoltaic parameters and events. This particular aspect is discussed in the conference.

Acknowledgements

Thank are expressed to IMMO and POMA CNRS laboratories which contribute actively to this research in Angers: namely R. de Bettignies, J. Roncali, A. Gorgues, P. Hudhomme, E. Levillain, L. Perrin, J.M. Raimondo, I. Perepichka, J. Cousseau, M. Cariou, B. Sahraoui, S. Dabos, and S. Alem as well as to the Laboratoire des Composants Organiques of CEA-DRT-LIST in Saclay for an active collaboration.

References

1. E. GAUTIER-THIANCHE, C. SENTEN, A. LORIN, C. DENIS, P. RAIMOND, J.M. NUNZI, *J. Appl. Phys.*, Vol.83, 4236, 1998.
2. I. SEGUY (et al.), An all-columnar bilayer light-emitting diode, *Synth. Metals*, Vol.111-112, 15, 2000.
3. J. ROSTALSKI, D. MEISSNER, Monochromatic versus solar efficiencies of organic solar cells, *Sol. Energy Mat. Sol. Cells*, Vol.61, 87, 2000.
4. *Current Opinion in Solid State and Materials Science*, Vol.4, 373, 1999.
5. C.W. TANG, Two-layer organic photovoltaic cell, *Appl.Phys.Lett.*, Vol.48, 183 1986.
6. J.H. SCHÖN, CH. KLOC, B. BATLOGG, Efficient photovoltaic energy conversion in pentacene-based heterojunctions, *Appl. Phys. Lett.* Vol.77, 2473, 2000.
7. P. LE BARNY, V. DENTAN, H. FACOETTI, M. VERGNOLLE, G. VÉRIOT, B. SERVET, *C. R. Acad. Sci. Paris 1 (Série IV)*, 493, 2000.
8. J. KALINOWSKI, Electroluminescence in organics, *J. Phys. D: Appl. Phys.*, Vol.32, R179, 1999.
9. J. SIMON, J.-J. ANDRÉ, *Molecular Semiconductors: Photoelectrical Properties and Solar Cells*, Springer, 1985.
10. M. Schott, *C. R. Acad. Sci. Paris 1 (Série IV)*, 381, 2000.
11. D. EMIN, in: *Handbook of Conducting Polymers*, T.A. Skotheim (Ed.), Vol.2, Chap.26, M. Dekker, 1996.
12. W.D. GILL, in: *Photoconductivity and related phenomena*, J. Mort and D.M. Pai (Eds.), p.63, Elsevier, 1976.
13. R.G. KEPLER, P.M. BEESON, S.J. JACOBS, R.A. ANDERSON, M.B. SINCLAIR, V.S. VALENCIA, P.A. CAHILL, *Appl. Phys. Lett.*, Vol.66, 3618, 1995.
14. G. HOROWITZ, *Adv. Mater.*, Vol.10, 365, 1998.

15. P.W.M. BLOM, M.J.M. DE JONG, J.J.M. VLEGGAR, *Appl. Phys. Lett.*, Vol.68, 3308, 1996.
16. H.C.F. MARTENS, J.N. HUIBERTS, P.W.M. BLOM, *Appl. Phys. Lett.*, Vol.77, 1852, 2000.
17. M. REDDECKER, D.D.C. BRADLEY, M. INBASEKARAN, E.P. WOO, *Appl. Phys. Lett.*, Vol.74, 1400, 1999.
18. E. GAUTIER-THIANCHE, C. SENTAIN, A. LORIN, C. DENIS, P. RAIMOND, J.-M. NUNZI, *J. Appl. Phys.*, Vol.83, 4236, 1998.
19. H. SCHER, in: *Photoconductivity and Related Phenomena*, J. Mort and D.M. Pai (Eds.), Elsevier, p.63, 1976.
20. M.N. BUSSAC, L. ZUPPIROLI, *Phys. Rev.* Vol.B55, 15587, 1997.
21. J.H. SCHÖN, C. KLOC, A. DODABALAPUR, B. BATLOGG, *Science*, No.289, 599, 2000.
22. J.H. SCHÖN, C. KLOC, R.C. HADDON, B. BATLOGG, *Science*, No.288, 656, 2000.
23. J.H. SCHÖN, S. BERG, C. KLOC, B. BATLOGG, *Science*, No.287, 1022, 2000.
24. I. SEGUY et. al., An all-columnar bilayer light-emitting diode, *Synth. Metals*, Vol.111-112, 15, 2000.
25. G. JUSKA, K. ARLAUSKAS, R. OSTERBACKA, *Synth. Metals*, Vol.109, 173, 2000.
26. H. SIRRINGHAUS, P.J. BROWN, R.H. FRIEND, M.M. NIELSEN, K. BECHGAARD, B.M.W. LANGEVELD-VOSS, A.J.H. SPIERING, R.A.J. JANSSEN, E.W. MEIJER, *Synth. Metals*, Vol.111-112, 129, 2000.
27. J.H. SCHÖN, A. DODABALAPUR, Z. BAO, CH. KLOC, O. SCHENKER, B. BATLOGG, *Nature*, No.410, 189, 2001.
28. G.G. MALLIARAS, Y. SHEN, D.H. DUNLAP, H. MURATA, Z.H. KAFABI, *Appl. Phys. Lett.*, Vol.79, 2582, 2001.
29. A.R. INIGO, C.H. TAN, W. FANN, Y.-S. HUANG, G.-Y. PERNG, S.-A. CHEN, *Adv. Mater.*, Vol.13, 504, 2001.
30. C. SENTAIN, C. FIORINI, A. LORIN, J.M. NUNZI, *Adv. Mater.*, Vol.9, 809, 1997.
31. H. MURATA, G.G. MALLIARAS, M. UCHIDA, Y. SHEN, Z.H. KAFABI, *Chem. Phys. Lett.*, Vol.339, 61, 2001.
32. H. KAGEYAMA, K. OHNISHI, S. NOMURA, Y. SHIROTA, *Chem. Phys. Lett.*, Vol.277, 137, 1997.
33. J. TURRO, *Modern Molecular Photochemistry*, University Science Books, Mill Valley, Ca 1991.
34. G.A. CHAMBERLAIN, Organic solar cells: a review, *Solar Cells*, Vol.8, 47, 1983.
35. K. PETRITSCH, *Organic Solar Cell Architectures*, PhD thesis, Graz 2000.
36. L. SICOT, *Etude et réalisation de cellules photovoltaïques en polymère*, PhD thesis, Orsay 1999.
37. J. ROSTALSKI, D. MEISSNER, Monochromatic versus solar efficiencies of organic solar cells, *Sol. Energy Mat. Sol. Cells*, Vol.61, 87, 2000.

38. T. TSUZUKI, Y. SHIROTA, J. ROSTALSKI, D. MEISSNER, The effect of fullerene doping on photoelectric conversion using titanyl phthalocyanine and a perylene pigment, *Sol. Energy Mat. Sol. Cells*, Vol.61, 2000.
39. T. FROMHERZ, F. PADINGER, D. GEBEYEHU, C. BRABEC, J.C. HUMMELEN, N.S. SARICIFTCI, Comparison of photovoltaic devices containing various blends of polymer and fullerene derivatives, *Sol. Energy Mat. Sol. Cells*, Vol.63, 61, 2000.
40. L. SCHMIDT-MENDE, A. FECHTENKÖTTER, K. MÜLLEN et al. , Self-Organized Discotic Liquid Crystals for High-Efficiency Organic Photovoltaics, *Science*, No.293, 1119, 2001.
41. T. Stuebinger, W. Bruetting, Exciton diffusion and optical interference in organic donor-acceptor photovoltaic cells, *J. Appl. Phys.*, Vol.90, 3623, 2001.
42. P. PEUMANS and S. R. FORREST, Very-high-efficiency double-heterostructure copper phthalocyanine/C60 photovoltaic cells, *Appl. Phys. Lett.*, Vol.79, 126 2001.
43. M. POPE, E. SWENBERG, *Electronic Processes in Organic Crystals*, Clarendon Press, Oxford 1982.
44. D. WÖHRLE, D. MEISSNER, *Adv. Mat.*, Vol.3, 129, 1991.
45. M. GRANSTROM, K. PETRITSCH, A.C. ARIAS, A. LUX, M.R. ANDERSSON, R.H. FRIEND, Laminated fabrication of polymeric photovoltaic diodes, *Nature*, No.395, 257, 1998.
46. D. MEISSNER, Plastic solar cell, *Photon*, Vol.2 (1999)
47. J. ROSTALSKI, D. MEISSNER, Photocurrent spectroscopy for the investigation of charge carrier generation and transport mechanisms in organic p/n-junction solar cells, *Sol. Energy Mat. Sol. Cells*, Vol.63, 37, 2000.
48. J. H. SCHÖN, CH. KLOC, E. BUCHER, B. BATLOGG, Efficient organic photovoltaic diodes based on doped pentacene, *Nature*, No.403 (2000) 408
49. L. SICOT, B. GEFFROY, A. LORIN, P. RAIMOND, C. SENTEIN, J.-M. NUNZI, Photovoltaic properties of Schottky and p-n type solar cells based on polythiophene, *J. Appl. Phys.*, Vol.90, 1047, 2001.
50. M. PFEIFFER, A. BEYER, T. FRITZ, K. LEO, Controlled doping of phthalocyanine layers by cosublimation with acceptor molecules: a systematic Seebeck and conductivity study, *Appl. Phys. Lett.*, Vol.73, 3202, 1998.
51. I. SEGUY, R. MAMY, P. DESTRUEL, P. JOLINAT, H. BOCK, Photoemission study of the ITO / triphenylene / perylene / Al interfaces, *Appl. Surf. Sci.*, Vol.174, 310, 2001.
52. S.-G. LIU, G. SUI, R.A. CORMIER, R.M. LEBLANC, B.A. GREGG, Self-organizing liquid crystal perylene diimide thin films: spectroscopy, crystallinity, and molecular orientation, *J. Phys. Chem.*, Vol.B106, 1307, 2002.
53. A.-J. ATTIAS, C. CAVALLI, B. DONNIO, D. GUILLON, P. HAPIOT, J. MALTHETE, Columnar mesophase from a new disclike mesogen based on a 3,5-dicyano-2,4,6-tristyrylpyridine core, *Chem. Mater.*, Vol.14, 375, 2002.
54. N.S. SARICIFTCI, Polymeric photovoltaic materials, *Current Opinion in Solid State and Materials Science*, Vol.4, 373, 1999.
55. B. O'REGAN, M. GRÄTZEL, *Nature*, No.353, 737, 1991.

56. N.S. SARICIFTCI, L. SMILOWITZ, A.J. HEEGER, F. WUDL, *Science*, No.258, 1474, 1992.
57. C.J. BRABEC, N.S. SARICIFTCI, J.C. HUMMELEN, Plastic solar cells, *Adv. Funct. Mater.*, Vol.11, 15, 2001.
58. J. LIU, Y. SHI, Y. YANG, Solvation-induced morphology effects on the performance of polymer-based photovoltaic devices, *Adv. Funct. Mater.*, Vol.11, 420, 2001.
59. W. GEENS, T. AERNOUITS, J. POORTMANS, G. HADZIOANNOU, Organic co-evaporated films of a PPV-pentamer and C₆₀: model systems for donor-acceptor polymer blends, *Thin Solid Films*, Vol.403-404, 438, 2002.
60. J.-F. ECKERT, J.-F. NICOUD, J.-F. NIERENGARTEN, S.-G. LIU, L. ECHEGOYEN, F. BARIGELLETTI, N. ARMAROLI, L. OUALI, V. KRASNIKOV, G. HADZIOANNOU, Fullerene-Oligophenylenevinylene hybrids: synthesis, electronic properties, and incorporation in photovoltaic devices, *J. Am. Chem. Soc.*, Vol.122, 7467, 2000.
61. M. ANGELES HERRANZ, N. MARTIN, A new building block for diels-alder reactions in p-extended tetrathiafulvalenes: synthesis of a novel electroactive C60-based dyad, *Organ. Lett.*, Vol.1, 2005, 1999.
62. H. NEUGEBAUER, C. BRABEC, J.C. HUMMELEN, N.S. SARICIFTCI, Stability and photodegradation mechanisms of conjugated polymer / fullerene plastic solar cells, *Sol. Energy Mat. Sol. Cells*, Vol.61, 35, 2000.
63. J.S. MILLER, Interpenetrating lattices-materials of the future, *Adv. Mater.*, Vol.13, 525, 2001.
64. A.C. ARANGO, L.R. JOHNSON, V.N. BLIZNYUK, Z. SCHLESINGER, S.A. CARTER, H.-H. HÖRHOLD, Efficient titanium oxide/conjugated polymer photovoltaics for solar energy conversion, *Adv. Mater.*, Vol.12, 1689, 2000.
65. X. PENG, L. MANNA, W. YANG, J. WICKHAM, E. SCHER, A. KADAVANICH, A.P. ALIVISATOS, Shape control of CdSe nanocrystals, *Nature*, No.404, 59, 2000.
66. W.U. HUYNH, J.J. DITTMER, A.P. ALIVISATOS, Hybrid nanorod-polymer solar cells, *Science*, No.295, 2425, 2002.
67. C. SENTEIN, C.FIORINI, A.LORIN, J.-M.NUNZI, *Dispositif semiconducteur en polymère comportant au moins une fonction redresseuse et procédé de fabrication d'un tel dispositif*, European Patent, 1997.
68. C. SENTEIN, C. FIORINI, A. LORIN, L. SICOT, J.-M. NUNZI, Study of orientation induced molecular rectification in polymer films, *Optical Materials*, Vol.9, 316, 1998.
69. L. SICOT, C. FIORINI, A. LORIN, P. RAIMOND, C. SENTEIN, J.-M. NUNZI, Improvement of the photovoltaic properties of polythiophene-based cells, *Sol. Energy Mat. Sol. Cells*, Vol.63, 49, 2000.
70. C. SENTEIN, C. FIORINI, A. LORIN, J.M. NUNZI, P. RAIMOND, L. SICOT, Poling induced improvement of organic-polymer device efficiency, *Synth. Metals*, Vol.102, 989, 1999.

71. J.-M. NUNZI, C. SENTEIN, C. FIORINI, A. LORIN, P. RAIMOND, Oriented polymer photovoltaic cells, *SPIE proceedings*, 4108, 41, 2001.
72. A. GOETZBERGER, C. HEBLING, Photovoltaic materials, past, present, future, *Sol. Energy Mat. Sol. Cells*, Vol.62, 1, 2000.

