

Flexible Conjugated Polymer-Based Plastic Solar Cells: From Basics to Applications

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Invited Paper

Triggered by the outstanding worldwide growth of the photovoltaic market as well as by the need of alternative energy sources in future, organic solar cells are the object of vivid interest from both industrial and academic sides. Based on the semiconducting properties of organic conjugated macromolecules, these devices possess the potential to be processed by common printing techniques. Besides being easily upscalable on rigid as well as on flexible substrates, they open the route of roll-to-roll production of low cost renewable energy sources. Today, up to 5% power conversion efficiencies are reported in this kind of plastic solar cells.

Keywords—Conjugated polymers, flexible, fullerenes, solar cells.

I. INTRODUCTION

The expansion trend of the photovoltaic (PV) industry as one of the most promising renewable energy sources was exhibited in the last five years by a module production growth of 30% annually, reaching a volume of 560 MW_p in 2002 [1]. This sector represented in the same year an overall market estimated at about \$3.5 billion. As shown in Fig. 1, this evolution is observed not only in Japan, but in the United States and Europe as well. Besides, most Japanese, U.S., and European roadmaps seem to agree on one point: this tendency is expected to last at least for the next 30 years to come [1]. This statement implies that the installed capacity of solar energy may grow the same way (Fig. 2). In 2030, a significant capacity of about 140 GW_p should be operational around the globe. This number is the equivalent of 100 state-of-the-art nuclear power plants.

More than 85% of the current world production of PV cells involve crystalline silicon. Nevertheless, after several

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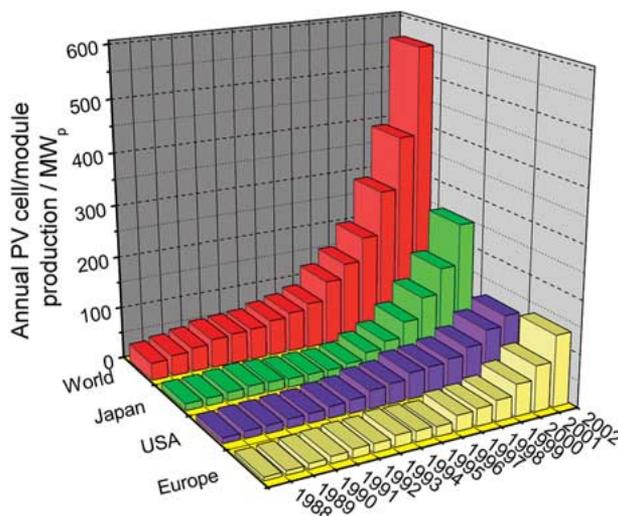


Fig. 1. Annual PV cell/module production from 1988 to 2002 (data from [1]).

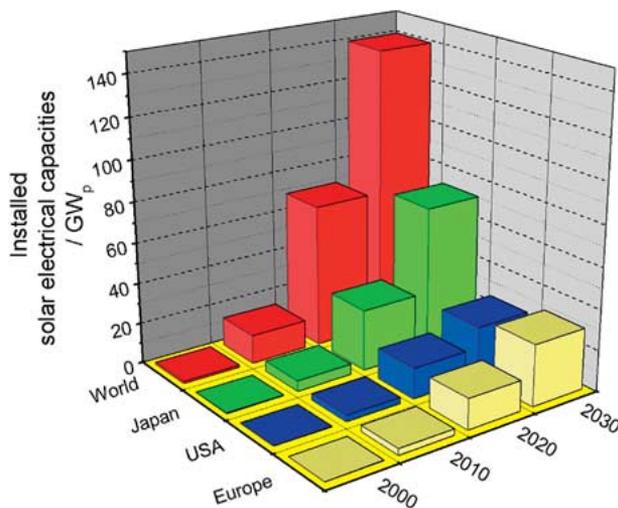


Fig. 2. Estimation of present and future installed solar capacities expressed in GW_p (sources: Japanese, U.S. and EPIA roadmaps [1]).

years of intensive research and development, a new generation of devices is in transition from pilot to large-scale pro-

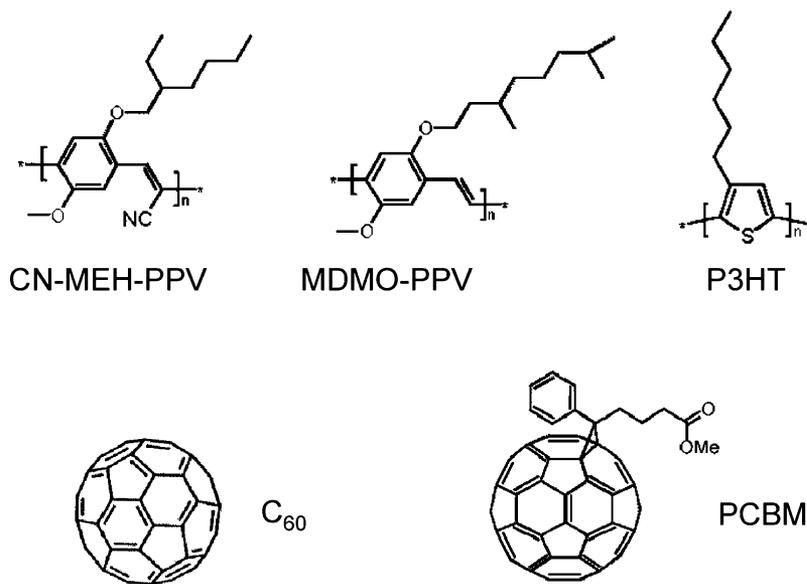


Fig. 3. Chemical structures of some common materials used in conjugated polymer-based solar cells.

duction. This one is based on inorganic materials like CdTe and CuInSe (CIS), etc. [2]. But beyond this second generation, a third one is intensively considered. This latter calls upon an entirely new type of materials, namely, the organic semiconductors [3].

Comprising “small molecules” [4] and conjugated polymers [5], the organic semiconductors enjoy major advantages as compared to their inorganic counterparts. Indeed, their light weight, mechanical flexibility, and semitransparence open new opportunities for PV cell design. Moreover most conjugated polymers possess a processing advantage [6]: they are soluble in common organic solvents [7] and hence can be deposited by simple solution processing and printing technologies. Thus, their production can be much easier and consequently much less costly than the inorganic semiconductor devices. Thin films on flexible or nonflexible substrates are achievable by well known and widespread printing methods like screen- [8], ink-jet- [9], offset-, or flexo printing. Therefore, mass production by roll-to-roll process can be technologically envisaged. In summary, the conjugated polymer-based PV device production would possess the following advantages:

- light weight of the product;
- easy processibility on flexible substrates: flexible product;
- semitransparence and/or choice of color of the product;
- cost-effective upscaling by roll-to-roll printing techniques;
- significant reduction of production energy consumption (in respect of the global energy balance);
- clean processing for environmental considerations.

Nevertheless, to achieve a product viable on the market and competitive with the other available technologies, polymer-based solar cells have to fulfill the standard requirements: cost, efficiency, and lifetime [10]. Today, conjugated polymer-based PV devices have been reported to exhibit

efficiencies up to 5% and are expected to enter the market in 2005 [11], [12].

II. WORKING PRINCIPLES OF CONJUGATED POLYMER SOLAR CELLS

A. Conjugated Polymers

Conjugated polymers essentially comprise a backbone of sp^2 -hybridized carbon atoms linearly attached. The electron in the p_z orbital of each sp^2 -hybridized carbon atom form π bonds with neighboring p_z electrons in a linear chain of sp^2 -hybridized carbon atoms. After the dimerization (Peierls distortion), an alternating single- and double-bond structure appears. Due to the isomeric effect, these π electrons are of a delocalized nature. Besides, the presence of an excited state on the backbone induces a local rearrangement of the chain geometry. Therefore, a strong coupling exists between electronic excitations and/or charge carriers and the bond lengths in the material (electron–phonon coupling) [13].

The interest in conjugated conducting polymers dates back to the report of metallic properties in chemically doped polyacetylene. A. Heeger, A. MacDiarmid, and H. Shirakawa were awarded the Nobel Prize for Chemistry in 2000 for this discovery [14]. This work paved the way to a wide range of semiconducting polymers, from insulators to metallic-like materials. Exhibiting in certain cases charge carrier mobilities [15] (hole mobility of around $\mu \approx 0.1 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ [16]) as high as the one of pentacene ($1 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ [17]), diodes [18] and organic FETs (OFETs) [19] fabricated with these materials were rapidly developed [20]. The observation [21] of electroluminescence in poly(p-phenylene vinylene) (PPV) and its soluble derivatives [7], [22] triggered the development of polymer-based organic LEDs (PLEDs) [23]. With their mechanical flexibility [24] enhancing their overall application potential, these devices actually entered the market a few years ago.

Currently, PLEDs and OFETs are merging, resulting in the so-called all-organic active matrix displays, in which each

single pixel is addressed by one individual OFET. This combination has been achieved on flexible substrates using the ink-jet printing [9] and embossing techniques [25].

B. Primary Photoexcited States in Conjugated Polymers

An important difference between inorganic and organic solar cells resides in the nature of the primary photoexcited state [26]. In the former ones, the absorption of photons leads directly to the creation of free electrons and holes at room temperature. The charge carriers can then diffuse and/or drift to their respective collective electrodes.

In organic semiconductors the situation is somewhat different and still the object of strong debate within the scientific community [27]. It is generally accepted that the absorption of a photon induces mainly excitons with binding energies ranging from 0.05 to >1 eV [28]. According to the Onsager theory [29] that can be invoked as a first approximation in organic semiconductors, photoexcited electrons and holes are coulombically bound and perform a brownian random walk [28], [30]. Once excitons have been created by the absorption of photons, they can diffuse over a length of approximately 5–15 nm [31]. Then they decay either radiatively or nonradiatively. The former route gives rise to luminescence that occurs within 500–800 ps for singlet excitons (fluorescence) and several hundreds of nanoseconds for triplet excitons (phosphorescence) at room temperature.

C. Photoinduced Charge Transfer

For PV purposes, excitons have to be separated into free charge carriers before they decay. That can be achieved by several different ways.

- Trap sites in the bulk of the material [26].
- An externally applied electric field [32].
- The “hot exciton” [33] states: the excess energy of the photons can quickly be distributed over the conjugation segment of the polymer leading to local temperatures high enough for a very short period (in the femtosecond range [34]) to provide the activation energy for exciton dissociation.
- Breaking the exciton at the discontinuous potential drops at the interfaces between donors and acceptors as well as between semiconductors and metals [35], [36].

Indeed, it has been observed that when an exciton reaches the interface between a conjugated polymer (donor) and a C_{60} -based material (acceptor) an ultra-fast electron transfer occurs. This releases an electron from the lowest unoccupied molecular orbital (LUMO) of the “donor” to the lower lying LUMO of the “acceptor,” leaving a hole on the highest occupied molecular orbital (HOMO) of the “donor” [37]. Electrons and holes are separated, and the produced free charges can diffuse/drift in their respective environment during their lifetime (up to a millisecond). The forward electron transfer was observed to happen within 45 fs [38], that is, much faster than any competing relaxation process. Therefore, its efficiency is about 100%. This phenomenon hence quenches the photo- and electroluminescence of

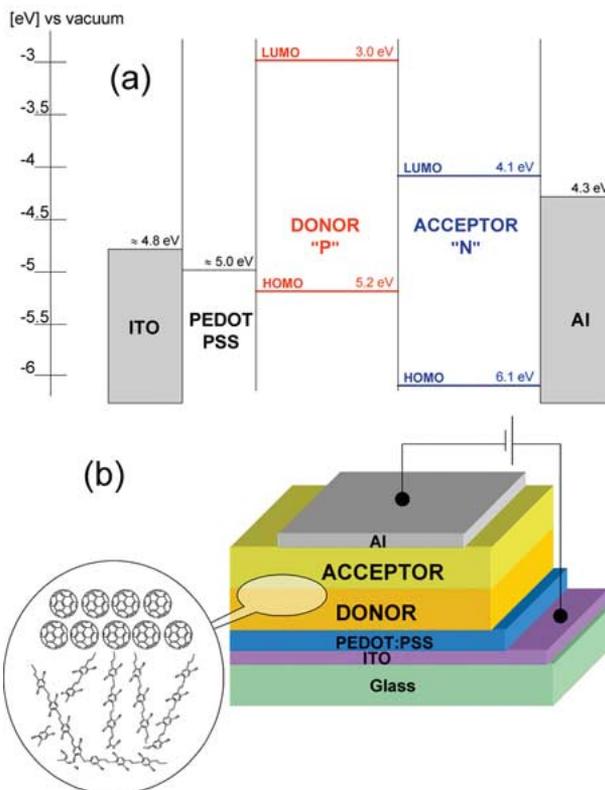


Fig. 4. (a) Energetic diagram and (b) cross section of a bilayer polymer solar cell. The energetic levels given in (a) for the donor and the acceptor correspond to MDMO-PPV and PCBM, respectively.

conjugated polymers like PPV [37] and increases their steady-state photoconductivity by orders of magnitude. This photoinduced electron transfer is described also as photodoping [39]. One might argue that an intermediate state can be distinguished between excitons and free charge carriers, namely, geminate pairs (GP). These consist in excitons dissociated into positive and negative charges still coulombically bounded [40]. Nevertheless, it has been observed that these GPs play a minor role in polymer : fullerene solar cell with high concentrations of acceptors [41], [42]. Therefore, we will neglect their contribution in the rest of the discussion.

Finally, it has to be mentioned that photoinduced charge transfer is observed and studied not only between conjugated polymer and fullerenes [42], but as well between two conjugated polymers with different electron affinities and ionization potentials [i.e., poly(2-methoxy-5-(2'-ethyl-hexoxy)-1,4-phenylene-vinylene) (MEH-PPV) and a cyano-poly(p-phenylene-vinylene) (CN-PPV)] [43], [44].

D. Bilayer Heterojunction Versus Bulk Heterojunction

The simplest structure of an organic polymer solar cell appears to be the superposition of donor and acceptor materials on top of each other, providing the interface needed to ensure the charge transfer. Fig. 4(a) presents the schematic energy diagram of such a bilayer solar cell: the excitons photogenerated in the donor or in the acceptor can diffuse to the interface where they are dissociated; the released electrons are

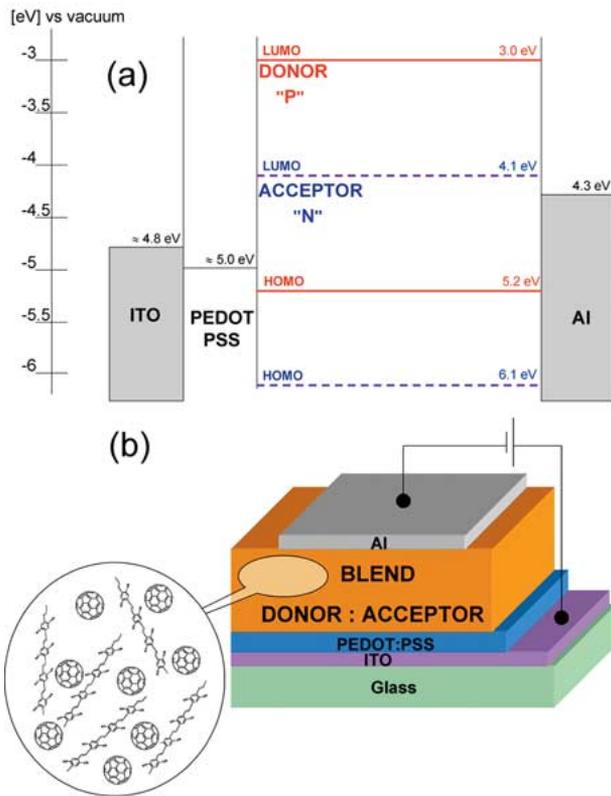


Fig. 5. (a) Energetic diagram and (b) cross section of a bulk-heterojunction polymer solar cell. The energetic levels given in (a) for the donor and the acceptor correspond to MDMO-PPV and PCBM, respectively.

transferred to the fullerene (acceptors); holes and electrons then diffuse or drift in their respective environment to their respective electrode [45].

The main drawback of this concept resides in the rather short diffusion length of excitons (5–15 nm). Indeed, only those that are created within a distance from the sharp donor–acceptor interface shorter than their diffusion length [Fig. 4(b)] may contribute to the photocurrent [46]. This limits drastically the photocurrent and hence the overall efficiency of the bilayer solar cells. To overcome this limitation, the surface area of the donor–acceptor interface needs to be increased. This can be achieved by creating a mixture of donor and acceptor materials with a nanoscale phase separation resulting in a three-dimensional interpenetrating network: the “bulk heterojunction” (Fig. 5). The discovery of 1-(3-methoxycarbonyl) propyl-1-phenyl[6,6]C₆₁ (PCBM) [47], a soluble and processable derivative of fullerene C₆₀, allowed the realization of the first bulk-heterojunction solar cell by blending it with poly(2-methoxy-5-(2'-ethyl-hexoxy)-1,4-phenylene-vinylene) (MEH-PPV) [48]. Fig. 5(a) illustrates the energetic diagram under open circuit (OC) condition for a poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene-vinylene) (MDMO-PPV) : PCBM bulk-heterojunction. Contrary to the situation in Fig. 4(a), excitons experience dissociation wherever they are created within the bulk. Indeed, the next interface between donor and acceptor phases is present within the exciton diffusion length everywhere

in the device. After having been created throughout the bulk, the free carriers have to diffuse and/or be driven to their respective electrode. Despite the fact that the photoluminescence of the MDMO-PPV : PCBM blend is already quenched for PCBM concentration as low as 1%, the onset of the photocurrent was shown to appear for acceptor amount about 17% weight (assuming similar densities, this corresponds to volume %). Interestingly this number corresponds to the calculated percolation ratio of spherical metallic particles embedded in a continuous matrix [49]. In other words, to be efficient, the bulk heterojunction has to ensure a bicontinuous path for electrons and holes to their respective electrode. The photocurrents achieved by bulk heterojunction devices are up to several milliamperes per square centimeter, improving drastically the efficiencies of bilayer cells [45], [48].

III. CHARACTERISTICS OF BULK HETEROJUNCTION SOLAR CELLS

A. Operating Modes

Conjugated polymer thin films (<100 nm) sandwiched between two metal electrodes are usually described using a metal–insulator–metal (MIM) picture [50]. As illustrated in Fig. 6(a), the vacuum levels (E_{vac}) of the stacked materials shall align themselves (Shottky–Mott model). This argument is currently under strong debate within the scientific community [51], since it has been reported that interface dipoles [52] can appear between metal and organic semiconductors [53], inducing E_{vac} discontinuity, strong local field, and Fermi level alignment. Nevertheless, the MIM picture provides a first approximation allowing one to draw a simple scheme of the energetic levels within the device.

Fig. 6(a) represents the energetic diagram of a bulk-heterojunction solar cells in OC condition. The E_{vac} of the different materials are aligned as explained above, and no electrical field is present within the device. Fig. 6(b) shows the short-circuit condition: the Fermi levels of the two electrodes align themselves and a built-in field appears in the bulk, resulting in a constant slope for the HOMO and LUMO levels of the donor and acceptor (respectively, HD, LD, HA, and LA) and for the E_{vac} .

When polarized in the forward direction (high work function electrode (HWFE) connected to \oplus and low work function electrode (LWFE) connected to \ominus) as in Fig. 6(c), electrons can be injected from the LWFE to LA and holes from HWFE to HD. The effective field in the device will ensure the drift of electrons from LWFE to HWFE and hole from HWFE to LWFE. Actually, the efficiency of the charge injection is driven by the energetic mismatch (ϕ_b) between the Fermi levels of the electrodes and the level of the band in which the charge are to be injected. If the contact is ohmic ($\phi_b = 0$ [54]), the injection is mostly space charge limited (SCL) [55]: the electrode supplies more charge carriers per unit time than the organic semiconductor can transport; space charges appear in the vicinity of the electrode due to low mobilities. On the other hand, if ϕ_b is important, the injection is limited by thermally assisted hopping from the

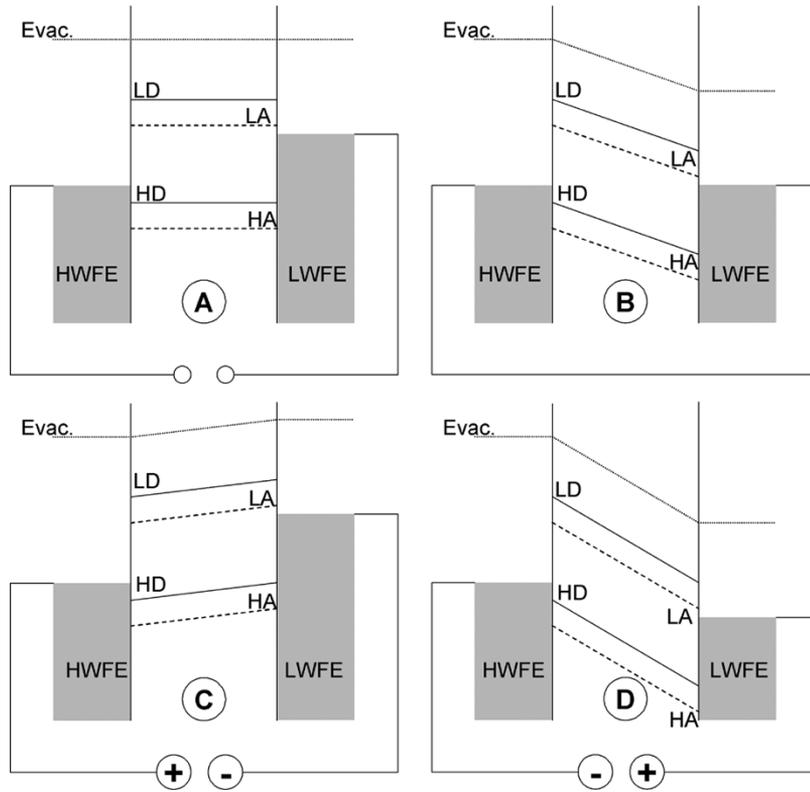


Fig. 6. Operating modes of a simple diode made out of a donor–acceptor blend sandwiched between HLWE and LWFES. (a) OC condition. (b) Short-circuit condition. (c) Forward bias. (d) Reverse bias.

Fermi level of the electrode into localized states of the semiconductor [56], [57]. These states are usually described as belonging to a Gaussian density of states (DOS) broadened by energetic disorder [58].

Finally, when the device is polarized in the reverse direction [HWFE connected to \ominus and LWFE connected to \oplus ; Fig. 6(d)], charge injection is hindered by the field present in the device.

Solar cells are operated between OC and short-circuit condition (fourth quadrant in the current–voltage characteristics), as shown in Fig. 7. It has to be mentioned that in this particular region, the driving force of charge collection in bulk-heterojunction solar cells still remains under discussion. The built-in field present in the device seems to induce a drift current in the device [59]. The charge carriers photo-generated at a distance $d < \mu\tau E$ are then collected [60] (μ : mobility of the charge carriers; τ : lifetime of the charge carriers; E : field across the device). However, for high light intensities, the field may be screened by the large concentration of free charge carriers (up to 10^{19} cm^{-3} at AM1.5 conditions) in the volume. The charge carrier collection may then be dominated by diffusion, triggered by a concentration gradient, and selectivity of the electrodes. Actually, the driving force can be generally assigned to the gradient in electrochemical potential present within the device [28], [61].

B. Equivalent Circuit

The macroscopic equivalent circuit of a solar cell is sketched in the inset of Fig. 7. It comprises the following.

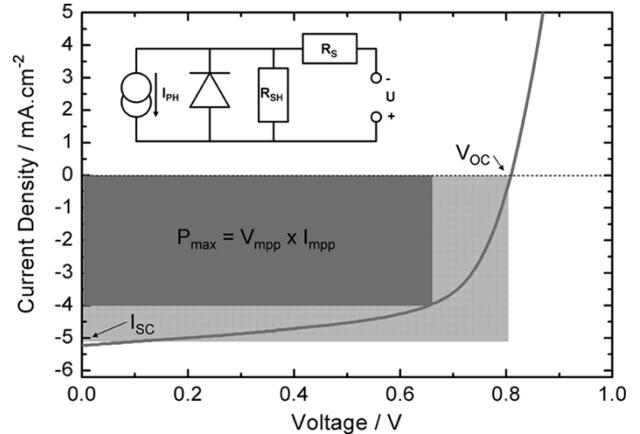


Fig. 7. First and fourth quadrant of a typical I - V curve observed for a GLASS/ITO/PEDOT : PSS (90 nm)/MDMO-PPV : PCBM(1 : 4, 150 nm)/Al (100 nm) solar cell. Shown are the short-circuit current (I_{SC}), the OC voltage (V_{OC}), the voltage (V_{mpp}), and current (I_{mpp}) at maximum power point (P_{max}). The inset illustrates the equivalent circuit of a solar cell comprising series (R_S) and parallel (R_{SH}) resistances as well as a current photogenerated (I_{PH}) and the internal diode.

- A current source that represents the photocurrent generated within the cell. This current flows in opposite direction compared to the forward one of the diode and depends on the voltage across the device [60].
- A voltage source.
- A series resistance R_S that gathers the ohmic contributions of the electrode and the contact between the organic semiconductor and the metal.

Besides, R_S reflects the capability of the organic bulk to transport charge carriers. R_S has to be lowered to ensure a maximum efficiency. Typically R_S decreases with decreasing thickness [62], increasing temperature [63] and increasing light intensity.

- A shunt resistance R_{SH} that illustrates the potential leakage current through the device, that is the overall quality of the thin film. Unlike R_S , R_{SH} has to be maximized to reach high efficiency cells. It has been observed that R_{SH} increases with decreasing thickness [62], is stable with changing temperature, and decreases drastically with increasing light intensity [64].

The overall efficiency of a solar cell can be expressed as follows:

$$\eta = \frac{V_{OC} \cdot I_{SC} \cdot FF}{P_{in}}$$

where V_{OC} is the OC voltage (voltage for $I = 0$), I_{SC} is the short-circuit current (current for $V = 0$), and P_{in} is the incident light power, which is preferably standardized (see Section III-E). The fill factor (FF) is given by

$$FF = \frac{I_{mpp} \cdot V_{mpp}}{V_{OC} \cdot I_{SC}}$$

where I_{mpp} and V_{mpp} represent the current and voltage at the maximum power point (P_{max}) in the fourth quadrant, respectively (Fig. 7).

Even if all these different values influence each other, they deserve to be described separately.

C. OC Voltage V_{OC}

According to the MIM picture, V_{OC} should simply reflect the difference of the metal electrodes' work functions (ϕ_{ME}). On this basis, a typical MDMO-PPV : PCBM bulk-heterojunction sandwiched between indium-tin-oxide (ITO) ($\phi_{ITO} \approx 4.7 - 4.9$ eV) and aluminum ($\phi_{Al} \approx 4.3$) is expected to show a maximum V_{OC} of about 0.4–0.6 V. In reality, V_{OC} reaches values up to 0.8 V in this case. Actually, the maximum value of V_{OC} appears to be limited by the energy difference between the HOMO of the donor and the LUMO of the acceptor. Indeed, they represent respectively the lowest and highest values that the pseudo-Fermi levels of holes and electrons can potentially reach, whereas splitting of these levels should account for the V_{OC} [26], [65]. It has been observed that in the case of ohmic contact, the V_{OC} of MDMO-PPV : fullerene cells varies almost linearly with the first reduction potential (LUMO level) of the acceptor [66]. In the same idea, combining different PPV derivatives with always the same acceptor (PCBM in this case) was shown to induce V_{OC} that follow linearly the evolution of the HOMO of the donor [67].

Nevertheless, for nonohmic contacts, the picture is slightly more complicated. On the bottom side, it has been observed that the work function of polyethylene dioxythiophene-poly-styrene sulfonate (PEDOT : PSS) shows an impact on V_{OC} with a proportionality factor of 0.8 [68]. The realization of an “inverted” solar cell by choosing a dedoped PEDOT having a work function smaller than the LUMO of the

PCBM confirmed the validity of the MIM picture in this case. On the top side, the work function of the electrode metal was found to influence only very slightly the V_{OC} [69] of MDMO-PPV : PCBM cells, contrary to the prevision of the MIM model. This has been explained in terms of “pinning effect” [70]: the work function of the metal is believed to be pinned near the LUMO of the electron acceptor [71]. But other explanations can be invoked, like the existence of surface dipoles as mentioned above, especially in the case of gold, for example [72].

Finally, it is important to notice that since V_{OC} is due to the splitting of the respective pseudo-Fermi level of electrons and holes, it increases with increasing light intensity. It usually follows a logarithmic evolution until it reaches a saturation [63].

D. Short-Circuit Current I_{SC}

The electric current delivered by a solar cell corresponds to the number of photocreated charges that are collected by the electrodes and is directly proportional to

$$I_{SC} \propto \eta_{abs} \cdot \eta_{diss} \cdot \eta_{out}$$

where η_{abs} is the absorption efficiency in the active material, η_{diss} is the efficiency of exciton dissociation (in the case of polymer/fullerene blends, this approaches unity), and η_{out} is the collection efficiency of free carriers that reach the electrode. Each of these factors will be discussed separately.

- η_{abs} : This value depends on the absorption spectrum of the active material as well as on the interference effects of the thin-film-device structure. Absorption coefficients in organic materials are generally very high (for dyes, typically $\geq 10^5$ cm⁻¹). But the spectrum has to fit the terrestrial solar emission spectrum. This matching to the solar spectrum is actually not perfect in the case of MDMO-PPV : PCBM blends, since their absorption onset appears around 550 nm while the maximum of the sun emission spectrum (photon flux) is located around 800 nm. Moreover, polymer solar cells comprise a thick transparent substrate on which several semitransparent layers with different refractive indexes [73] are stacked. Besides, this pile ends up with a strongly reflective metallic electrode. Therefore, constructive and destructive optical interferences occur within the device [74]. A careful optimization of layer thicknesses is necessary to place the maximum of the optical field in the photoactive material and maximize absorption of incident photons [75].
- η_{diss} : An efficient exciton dissociation requires an optimized interface between donor and acceptor. The interfacial area in bulk heterojunctions strongly depends on the nanoscale morphology of the bicontinuous phases. This point will be more extensively discussed in Section V-B
- η_{out} : like η_{diss} , η_{out} is strongly dependant on the 3-D interpenetrating network, since electrons and holes should find continuous pathways to reach their respective electrodes. Moreover, η_{out} is drastically limited

by the quite low charge carrier mobility observed in organic semiconductors [17]. The conduction mechanism in conjugated polymers is believed to occur via thermally assisted intermolecular hopping of highly localized charge carriers [76]. Thus, mobilities generally increase with applied electric field (E) and temperature (T) [77], showing a Poole–Frenkel-like form

$$\mu(E) = \mu_0 \cdot \exp(\gamma\sqrt{E})$$

where the prefactor γ and μ_0 vary with T , μ_0 being the mobility at zero field. Hence, I_{SC} usually increases with increasing temperature, since the charge carrier mobility is thermally enhanced [78]. Pure MDMO-PPV typically shows a hole mobility of about $5 \cdot 10^{-7} \text{ cm}^{-2} \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ [79], while the electron mobility in PCBM is around $2 \cdot 10^{-3} \text{ cm}^{-2} \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ [80]. Nevertheless, it has been observed that hole and electron mobilities are more balanced in MDMO-PPV:PCBM bulk heterojunctions. Indeed, such blends present hole mobilities about two orders of magnitude higher than pristine MDMO-PPV [81].

Finally, if the device does not experience bimolecular recombination, I_{SC} varies linearly with the light intensity.

E. FF and Efficiency η

FF represents the overall quality of the diode as a device and is mainly influenced by R_{SH} and R_S . Therefore, device optimization requires a continuous effort for lowering R_S and increasing R_{SH} . The introduction of a thin ($\approx 90 \text{ nm}$) layer of PEDOT:PSS between ITO and the active material was found to drastically improve the diode quality [82]. Furthermore, the addition of a very thin layer of LiF (0.6 nm) between the active organic layer and the metallic top electrode significantly improves the collection efficiencies of devices [83]. Initially applied in PLEDs [84], this intermediate ionic salt layer does not only increase FF but also V_{OC} .

Thus, the efficiency of a solar cell results from a synergistic effect of all the different parameters described above. An overall increase of power conversion efficiency with increasing temperature was reported [85] up to 60°C .

Finally, it has to be mentioned here that the accepted standard for solar cell testing is the so-called AM 1.5 [86], which is a $100 \text{ mW} \cdot \text{cm}^{-2}$ white light with a spectral intensity distribution matching that of the sun on the earth's surface at a tilted angle of 37° .

IV. EXPERIMENTAL CONSIDERATIONS

A. Production Scheme

The ITO-coated glass ($\approx 10 \Omega/\square$) or poly(ethylene-terephthalate) (PET, $\approx 60 \Omega/\square$) substrates are cleaned subsequently in acetone and iso-propanol. The transparent substrate is first coated by a thin ($\approx 90 \text{ nm}$) PEDOT:PSS layer (dispersion in water, Baytron, Bayer AG). On top of it, the active layer (mixture of donor conjugated polymer



Fig. 8. Picture of a flexible $6.5 \times 4.1 \text{ cm}^2$ MDMO-PPV:PCBM solar cell realized on a PET substrate.

and acceptor soluble fullerene derivative like PCBM) is deposited. Solutions based on organic solvent are typically stirred overnight at 50°C . For laboratory scale samples ($1.5 \times 1.5 \text{ cm}^2$), PEDOT:PSS and active layers are deposited by spin casting. However, for large-scale surface areas, doctor blading or screen printing are the preferred methods. Finally, LiF and a metallic top electrode are vacuum evaporated through a shadow mask.

B. Flexible Conjugated Polymer Solar Cells for Indoor Applications

Not only usable under natural solar light, PV devices can be as well considered for indoor applications. For example, widespread usual fluorescent lamps provide a light made of six main lines. Four of them (545, 485, 435, and 405 nm) can participate in light-to-electricity conversion in classical bulk-heterojunction solar cells.

Fig. 8 shows a picture of a $6.5 \times 4.1 \text{ cm}^2$ polymer solar cell processed on a $175\text{-}\mu\text{m}$ -thick ITO-coated PET substrate. It can be observed that the device is entirely flexible and semitransparent with an orange–reddish color. Here the solar cell comprises 12 individual and independent pads, whose active dimension is $3 \times 24 \text{ mm}$. Under AM 1.5 ($110\,000 \text{ lx}$ of white light), one pad of this PET/ITO/PEDOT:PSS/MDMO-PPV:PCBM/Al structure shows a V_{OC} of about 650 mV, I_{SC} of 1.25 mA ($1.75 \text{ mA} \cdot \text{cm}^{-2}$), and FF of 0.38. The quite low I_{SC} and FF result both from a nonoptimized electrode design and quite high R_S due to the low conductivity of ITO deposited on PET substrate ($\approx 60 \Omega/\square$). Besides, the V_{OC} can be increased by LiF.

Fig. 9 illustrates the evolution of V_{OC} , V_{mpp} , I_{SC} , and I_{mpp} for various standard fluorescent lamp illuminances. Interestingly, in spite of the logarithmic decrease of V_{OC} with decreasing lighting, V_{mpp} is almost constant. This phenomenon takes its origin in the increase of FF with decreasing illuminance induced by a lower contribution of R_S . Thus, flexible polymer solar cells can still easily deliver a V_{OC} of about 500 mV at usual indoor fluorescent light intensity (1000 lx). Moreover, the current intensity

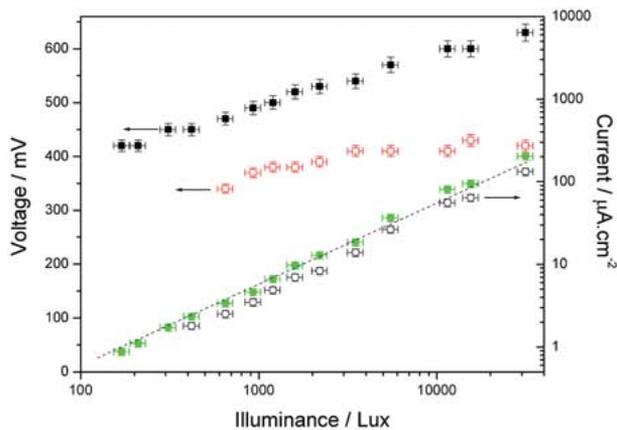


Fig. 9. V_{OC} (■), V_{mpp} (□), I_{SC} (●), and I_{mpp} (○) of a flexible PET/ITO/PEDOT:PSS (90 nm)/MDMO-PPV:PCBM (1 : 4, 150 nm)/Al (100 nm) solar cell for various fluorescent lamp illuminances.

that follows a perfect linear evolution with illuminance still shows decent values at 1000 lx: I_{SC} is about $4.7 \mu\text{A}\cdot\text{cm}^{-2}$.

It appears then that even under rather low illuminance (500–2000 lx), flexible conjugated polymer solar cells provide useful power output under indoor artificial light: at 1000 lx (fluorescent lamp), the maximum power point is located about $V_{mpp} = 375 \text{ mV}$ and $I_{mpp} = 3.5 \mu\text{A}\cdot\text{cm}^{-2}$. Thus, these PV cells are suitable to charge batteries of low energy consumption devices like remote controls, watches, small displays, and backup security systems.

V. STRATEGIES FOR IMPROVEMENTS

A. Controlling the Nanomorphology

As mentioned above, the nanomorphology of the donor–acceptor blend influences the dissociation efficiency of excitons and collection efficiency of the free charge carriers. It has been shown that MDMO-PPV:PCBM (1 : 4) blend prepared in chlorobenzene gives three times better solar cells than blends prepared in toluene [87]. Indeed, atomic force microscope data show the finer dispersion of the donor–acceptor phases in films cast from chlorobenzene in contrast to films cast from toluene in which PCBM is less soluble, resulting in a coarse phase separation [88], [89]. The coarse phase separation can also be observed in films from chlorobenzene with higher concentration of PCBM ($\geq 90\%$ [90]) decreasing the efficiency of the solar cells. The evaporation kinetics of solvents also influences the final morphology of the films. Indeed, drop casting typically leads to larger aggregates than spin casting because the evaporation time is much longer [91]. Besides, the spin speed itself can influence the homogeneity of the active layer, since it plays an important role in the determination of the solvent evaporation kinetic [92].

Finally, knowing that deposition methods like spin casting lead to metastable morphologies frozen by a fast solvent evaporation, it is predicable that thermal treatments trigger a reorganization of the donor–acceptor blend. This is particularly the case for annealing temperature above the glass

transition (T_g) of conjugated polymers. In the case of MDMO-PPV, T_g is known to be about 80°C . For thermal treatments above these temperatures, PCBM diffusion occurs: after a few hours, large PCBM monocrystals appear with sizes in the micrometer range [88].

B. Increasing the Photon Harvesting

Despite the quite large optical gap of MDMO-PPV (2.2 eV), efficiencies up to 2.5% under AM 1.5 were reported for MDMO-PPV:PCBM blends [87]. However, these cells just harvest the photons that have wavelength below 550 nm, which is a very small part of the solar spectrum. One obvious route to increase the solar cell efficiency is to chemically engineer the bandgap [93] of the macromolecules.

Polythiophene derivatives like poly(3-hexylthiophene) (P3HT) were found to give higher efficiency solar cells. Indeed, having an optical gap of 2 eV, its external quantum efficiency (EQE) onset is observed at about 650 nm, that is, 100 nm above that of MDMO-PPV, with a 76% maximum at 550 nm [94]. This important increase in photon harvesting leads to a much higher I_{SC} ($8.5 \text{ mA}\cdot\text{cm}^{-2}$) and an overall efficiency above 3% under AM 1.5 [95].

Currently, intensive efforts are invested by synthetic chemists in order to create new materials that do absorb light in the red and IR region, i.e., low-bandgap materials [96].

C. Increasing Device Lifetime

The lifetime of polymer solar cells like the PPV-based ones is rather poor in the ambient environment, since photodegradation induced by oxygen and moisture occurs [97]. Moreover, top electrode materials are usually chosen among the low work function metals like Al in order to optimize the V_{OC} . These metals undergo severe oxidation when exposed to air, leading to the formation of insulating thin oxide barriers [98] that hinder electrical conduction.

The degradation effect is significantly decreased when the polymer is mixed with fullerenes [99], [100]. Nevertheless, hermetical encapsulation is necessary for this type of devices.

The simplest encapsulation consists in superimposing two glass plates and sealing them with low permeation glue. This ensures lifetimes up to several thousand hours, thus allowing PLEDs to be now on the market. However, the mechanical flexibility is sacrificed in this case. Commercially available polymer foils like PET possess oxygen and moisture permeation rates that are six to seven orders of magnitude too high to properly protect conjugated polymer-based devices. Moreover, the deposition of one single layer of impermeable material like ITO or SiO_x on the polymer substrate decreases these permeation value by a factor of only 500 [101]. Smart solutions based on alternatively stacked layers of inorganic barrier (Al_2O_3 , SiO_x , etc.) and polyacrylate deposited on thin ($175 \mu\text{m}$) PET or poly(ethylene-naphthalate) (PEN) substrates can drastically decrease the diffusion of oxidative gas [102]. Actually, flexible films with permeability as low as that of glass are now achievable, allowing a several-thousand-hour lifetime for flexible organic LEDs [103].

VI. CONCLUSION

The efficiency of polymer solar cells is increasing steadily, today reaching 5%. Extensive efforts are currently underway by chemists in order to produce new low-bandgap materials to harvest more photons and increase the light-to-electricity conversion efficiency. Moreover, processability of conjugated polymers that can be deposited from liquid solutions at low temperature render them suitable for large scale production on flexible substrates at low cost roll-to-roll process. Thus, conjugated polymer solar cells are announced to enter the market in the near future, for example, implemented in portable devices to recharge cell phones.

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