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Solides, fluides : propriétés électroniques et optiques/*Solids, fluids: electronic and optical properties*
(Surfaces, interfaces, films/*Surfaces, interfaces, films*)

PHOTONIQUE MOLECULAIRE :
MATÉRIAUX, PHYSIQUE ET COMPOSANTS

MOLECULAR PHOTONICS: MATERIALS, PHYSICS AND DEVICES

Organic photovoltaic materials and devices

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Abstract Organic photovoltaic solar cells bere an important potential of development in the search for low-cost modules for the production of domestic electricity. We review the principles and techniques needed for their development: organic semiconductors, their transport properties and photophysical characteristics, photovoltaic molecule and polymer structures, device technologies, electrical and optical behaviour of the cells, state of the art, limitations and perspectives. Despite some recent record efficiencies, research on organic solar cells is still in its infancy when stability and efficiency have to be compared with the performances of silicon cells. A nominal 10% solar efficiency is the research target for the next few years. ***To cite this article: J.-M. Nunzi, C. R. Physique 3 (2002) 523–542.*** © 2002 Académie des sciences/Éditions scientifiques et médicales Elsevier SAS

photovoltaic solar cell / organic semiconductor / molecular engineering / photogeneration

Résumé Les cellules solaires photovoltaïques organiques sont porteuses d'un potentiel de développement important dans la recherche de modules bas coût pour la production d'électricité domestique. Nous examinons les principes et techniques nécessaires à leur développement : les semi-conducteurs organiques, leurs propriétés de transport et leurs caractéristiques photo-physiques, les matériaux photovoltaïques organiques, la technologie des dispositifs, le comportement électrique et optique des cellules, l'état de l'art, les limitations et les perspectives. Malgré de récents records, la recherche sur les cellules solaires organiques en est toujours à ses débuts lorsqu'on la compare au silicium en termes de performances en stabilité et en efficacité. Un rendement solaire nominal voisin de 10% sera l'objectif des recherches pour les années qui viennent. ***Pour citer cet article : J.-M. Nunzi, C. R. Physique 3 (2002) 523–542.*** © 2002 Académie des sciences/Éditions scientifiques et médicales Elsevier SAS

cellule solaire photovoltaïque / semi-conducteur organique / ingénierie moléculaire / photo-génération

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1. Introduction

Recent progress achieved using organic mono-crystal, multilayered thin film and interpenetrated network technologies permit one 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 past 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 of seeing 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 review, we discuss some of the key technical aspects of the problem.

There is no short term ambition to replace silicon, or 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 an objective becomes feasible now a days, 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-year 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 chapter, we first review the organic materials for the PV application. Emphasis is given on the structure/property relationships which are the guidelines for a molecular engineering strategy. We start with the basic understandings of organic semiconductors, and their essential properties such as charge transport. We give indications aimed at selecting efficient organic PV materials and we review some classes of materials used in the different layers of a PV cell. We then go to an electrical description of organic solar cells. A critical analysis of the physical processes leading to the photovoltaic effect in organic materials permits us to size the maximal and minimal yields achievable using different device structures. This allows also to dimension the main physical parameters permitting the achievement of a 10% solar energy conversion in trial devices. We finally describe materials and device structures in view of such objective.

2. Organic materials for photovoltaic applications

There are several reasons to use organic materials for photovoltaic solar cell applications. Most important is the peculiar advantages of organic materials:

- they can be processed easily using spin coating or doctor blade techniques (wet-possessing) or evaporation through a mask (dry-processing);
- amounts of organic materials are relatively small (100 nm thick films) and large scale production (chemistry) is easier than for inorganic materials (growth processes);
- they can be tuned chemically in order to adjust separately band gap, valance and conduction energies, charge transport, as well as solubility and several other structural properties;
- the vast variety of possible chemical structures and functionalities of organic materials (polymers, oligomers, dendrimers, organo-minerals, dyes, pigments, liquid crystals, ...) favours an active research for alternative competitive materials with the desired PV properties. Original materials and structures can also be covered by patents.

2.1. Structural aspects of organic semiconductors

Organic semiconductors can demonstrate very different structural aspects, depending on the mechanical properties required for processing [6]:

- The polymers are made of a large (10–10^3) number of identical repeat units, all linked together by covalent bonds in a linear way. They are deposited in thin films from a solution (wet process). They can be soluble in various solvents or insoluble if prepared from a precursor route. Polymers can also be attached together: crosslinked. The sol-gel technology gives an example of such cross linked polymers [7]. Thin films made from polymers are usually in a glassy state.
- Small fragments of polymers attached linearly and with a well defined length (2–12) are called oligomers [8]. The longest oligomers bear all the essential electrical and optical properties of the polymers. They can be either soluble or not. Thin films made from oligomers are usually in a polycrystalline state.
- The dendrimers are also made of identical repeat units all linked together by covalent bonds, but in a three dimensional way, like the branches of a star, forming an ellipsoid-like structure with a fractal surface [9]. They can be either soluble or not. Thin films made from dendrimers are usually in a glassy state with a large glass transition temperature (T_g).
- The pigments come from the paint industry. They are small molecules bearing specific properties relevant to light absorption and charge generation. They are processed by evaporation (sublimation) from a solid powder, under vacuum. Pigments usually form polycrystalline thin films.
- The dyes have mainly the same electronic structure and properties as pigments, but they bear ‘side groups’ which make them soluble. They would not form thin films by themselves from a solvent, but they can be sublimated as pigments or be incorporated by mixing into a polymer host [10–12]. They can also be attached chemically to the host polymer [13,14].
- Liquid crystal materials (LCs) can be either polymers, oligomers, dyes or pigments, and they can either be wet or dry processed. Their particularity is that the order which results from the liquid-crystal state (nematic, columnar, smectic, …) permits the adjustment separately of light absorption, charge generation and transport [15] in the same layer.
- Self assembled monolayers (SAM) [16], layer by layer deposited polymer films [17] and Langmuir Blodgett films (LB) [18–21] permit the control of the molecular order in the same way as using the liquid-crystal state. They can be used also to adjust electrode properties: tuning the work function of electrodes for efficient electron or hole extraction [22].

All materials must be carefully purified before use in PV cells. This is mandatory to get optimum efficiency and stability [23]. Wet processed materials can be purified from solvent extraction techniques. The dry processed materials must be purified by sublimation [24]. Train sublimation is the usual technique to improve the performances of small molecules [25].

2.2. Energy bands

Polymers, oligomers, dendrimers, dyes, pigments, liquid crystals, organo-mineral hybrid materials, all organic semiconductors share in common part of their electronic structure. It is based on conjugated π electrons. By definition, a conjugated system is made of an alternation between single and double bonds. Ethene (Fig. 1(a)), butadiene and benzene (Fig. 1(b)) are basic representative elements of conjugated systems [26]. The essential property which comes out from conjugation is that the π electrons are much more mobile than the σ electrons; they can jump from site to site between carbon atoms with a low potential energy barrier as compared to the ionisation potential (Fig. 1(c)). The π electron system has all the essential electronic features of organic materials: light absorption and emission, charge generation and transport.

Each carbon atom in a conjugated system has 3 nearest neighbours with which it forms 3 equivalent σ bonds made from the trigonal sp^2 hybridisation of 3 valence atomic orbitals of the carbon atom: $2s$, $2p_x$ and $2p_y$ for instance (Fig. 1(a)) [27]. For such a hybridisation state, the fourth orbital $2p_z$ lies perpendicular to the σ bond plane. It is the lateral overlap of these out of plane $2p_z$ atomic orbitals which gives the π bonds. In most molecules, unlike in Fig. 1(c), double bonds are localised and the two extreme positions are

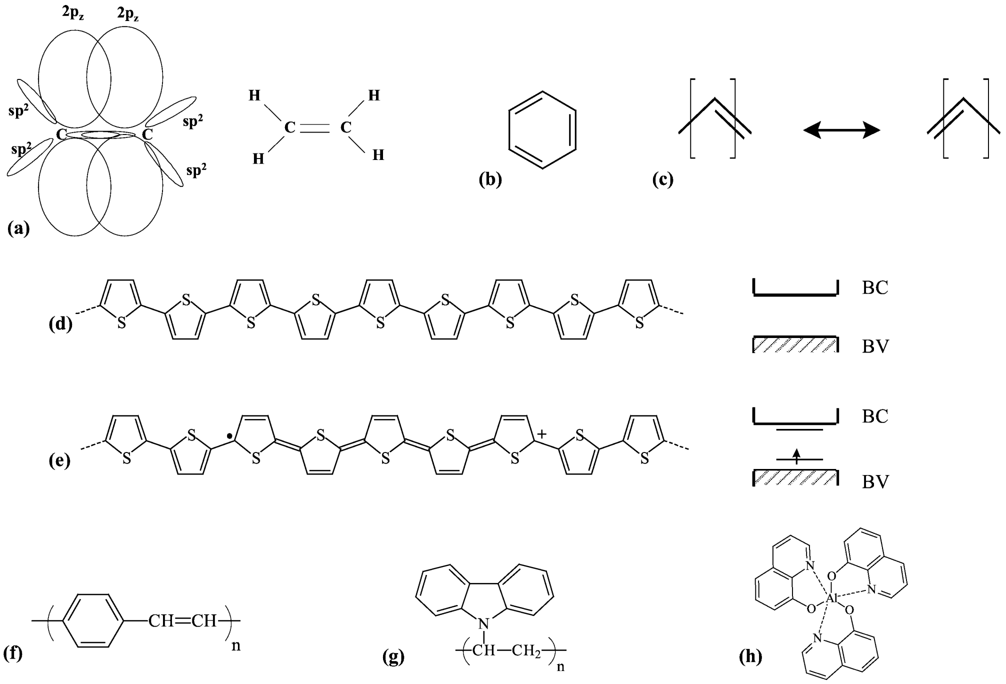


Figure 1. Model conjugated molecules and polymers: (a) ethylene with its σ and π orbitals; (b) benzene; (c) a conjugated bond with no alternation; (d) polythiophene; (e) a charged polaron in polythiophene and corresponding energy levels; (f) PPV; (g) PVK; (h) Alq$_3$.

usually not equivalent. A more general definition of a conjugated system would be an ensemble of atoms whose p-orbitals overlap.

When the carbon chain length is increased, the molecule becomes a polymer. It has been proved experimentally, in the case of thiophen (Fig. 1(d)) [28], phenyl–vinyl oligomers [29], for instance, and theoretically in the case of phenyl–vinylen oligomers for instance [30], that oligomers with more than 5 to 8 repeat units bear all the essential electronic properties of the infinite polymer chains as concerns absorption and emission of light.

Electronic properties of polymers can be described in terms of semiconductor physics [31]. The particular framework of one dimensional periodic media is well suited to the basic understanding of an isolated polymer chain [32]. Polymers are bonded by strong covalent bonds. As π-orbitals overlap is weaker than s-orbitals overlap, the energy spacing (band gap) between bounding and antibounding molecular orbitals is larger for the π–π^* difference than for the σ–σ^* one. One can thus, in a first approach, limit the band study to the π–π^* molecular orbitals. Those are respectively the HOMO (for Highest Occupied Molecular Orbital) and LUMO (for Lowest Unoccupied Molecular Orbital), in terms of molecular physics. They are also the usual valance (VB) and conduction bands (CB) of semiconductor physics, respectively (Fig. 1(d)). σ-bonds then only contribute to the stability of the molecular structure [33]. As an example, the case of the infinite polyparaphenylene (PPP) chain is treated in a pedagogical manner by Moliton [27] within the Hückel theory. PPP (with molecular formula –$(C_6H_4)_n$–) is a chain of benzene rings (Fig. 1(b)) attached in the para position. The problem is simply parameterised using the benzene resonance integral t_0 (or exchange integral between two adjacent carbon atoms inside a ring) and the inter-ring resonance integral t_1. In the case of benzene, the HOMO–LUMO band-gap is $E_\mathrm{g} = 2t_0 = 5.5$ eV, as determined experimentally. In the case of the PPP polymer chain, the π and π^* orbitals split into two bands: the valance VB and conduction CB bands, with a band gap $E_\mathrm{g} = 2t_0 - 4t_1 = 3$ eV, as determined experimentally. Both band widths are given by Hückel theory as $4t_1 = 2.5$ eV. This width is close to the experimentally determined values, using electron energy loss spectroscopy. A more rigorous description of PPP energy levels confirms the validity of this simplified approach [34].

When the chain length is reduced, the maximum absorption of PPP shifts continuously to the blue, according to an experimental law $E_{\max} = (3.36 + 3.16/n)$ eV [35], where n is the number of repeat units (benzene rings) of the oligomer. The maximum absorption $E_{\max}$ given here is larger than the band gap E_{g}. The same type of law applies to all the so-called alternated conjugated polymers (polymers in which double bonds are localized). This implies that in a 'real' conjugated polymer with random length, corresponding to what most chemical synthetic routes deliver, the bands are broadened and the band gap is apparently reduced.

In a real material also, 3-dimensional interactions play a major role in transport properties, even dominating the transport which becomes an interchain hopping process.

Small molecules are bounded by weak interactions in the condensed state: Van der Waals forces. There results a weak coupling between them, the resonance integral t_1 is thus small (tenth of eV at most) [36], resulting in narrow flat bands. Mobility is thus a priori smaller in small molecules, owing to a large effective mass

$$m^* = \frac{\hbar^2}{2}\left(\frac{\partial^2 E}{\partial k^2}\right)^{-1}.$$

There can of course be exceptions to such a rule, the interdistance spacing can be small and molecular materials can in fact possess a rather large mobility. The first electrically pumped injection organic laser was indeed made from small molecules (a tetracene single crystal) [37].

2.3. 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 [38]. Energy levels of the charges are usually determined by cyclic voltametry for materials in solution. They can be characterized by XPS or UPS (X-ray and UV photoelectron spectroscopies) for 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 [39]. Polarons may be regarded as defects in conjugated polymer chains (Fig. 1(e)). 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. 2(a)). One must distinguish between intramolecular charge transport along a conjugated polymer chain and intermolecular charge transport between adjacent molecules or polymer chains (Fig. 2(b)). The former which is specific to conjugated polymers is the most efficient. Charge mobility in organics is field dependent, especially in the law mobility materials in which it usually follows phenomenologically a Poole–Frenkel law: $\mu \propto \exp(\sqrt{E})$ [40]. Mobility can be experimentally determined by photo-current transients (time of flight) [41], field effect transistor saturation currents [42], space charge limited currents [43] or impedance spectroscopy [44]. Mobilities in organic semiconductors are usually rather small: from 10^{-2} in well ordered conjugated polymers (liquid crystalline polyfluorene) [45], down to 10^{-8} $\mathrm{cm}^2/(\mathrm{V{\cdot}s})$ in guest–host polymer systems (dye doped poly-vinylcarbazole – PVK, Fig. 1(g), for instance) [12]. 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 – Alq_3 (Fig. 1(h)) [41] – as well as in conjugated polymers such as the famous poly-paraphenylvinylene – PPV (Fig. 1(f)) [44]. The lowest mobilities are usually dispersive, which is the result of a distribution of mobilities [46]. Mobility can increase by up to two decades upon applying a voltage, being eventually very large above 1 MV/cm in conjugated polymers [47]. Mobility is increased by orders of magnitude when the molecular packing is improved. This is achieved by molecular ordering. Single crystals have the

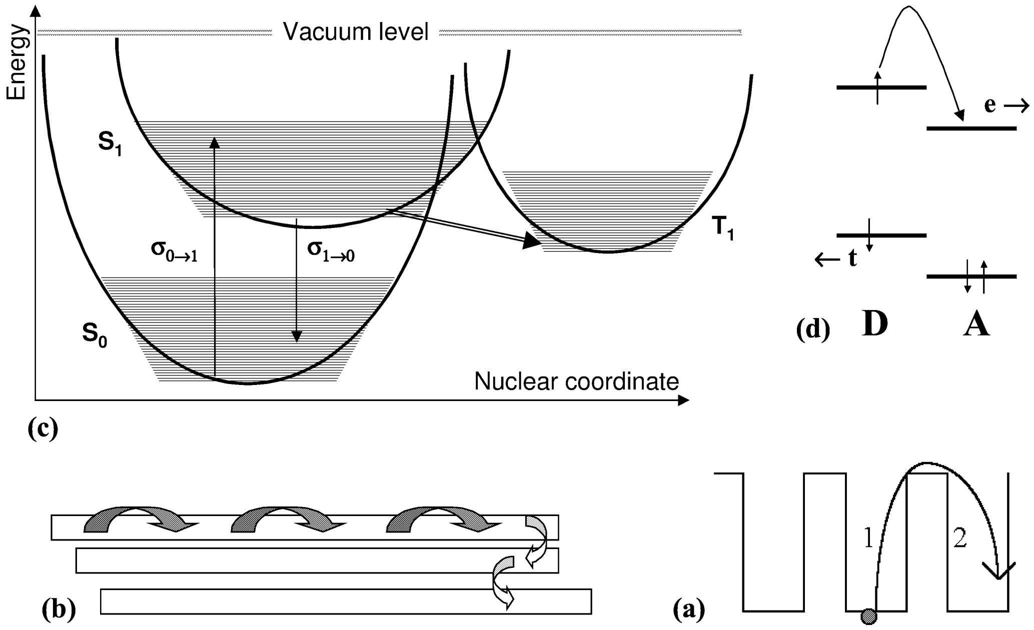


Figure 2. Photophysics of organic semiconducting materials: (a) hopping process between molecules 1 and 2; (b) intra- (full arrows) and intermolecular (broken arrows) charge-transport; (c) absorption ($S_0 \to S_1$), luminescence ($S_1 \to S_0$) and inter-system crossing ($S_1 \to T_1$); (d) charge separation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

best performances [37], electron mobility in fullerene C_{60} single crystals is 2.1 $\mathrm{cm}^2/(\mathrm{V{\cdot}s})$ [48], but it is reduced by at least 3 orders of magnitude by imperfect purification and uncontrolled crystallization [49], as well as by oxygen traps [48]. With this in mind, mobility in photovoltaic materials can be improved by using liquid crystals made from molecules (columnar LCs [15]) or polymers (nematic LCs [45]). Mobility is also increased by orders of magnitude, up to 0.1 $\mathrm{cm}^2/(\mathrm{V{\cdot}s})$, between a random polymer (poly-3-alkylthiophene – P3AT) and its regioregular analogue [50,51], the latter leading to supraconductivity at low temperature in a field-effect device [52]. Charge transport is also improved by purification or deposition conditions; for instance, mobility becomes non-dispersive in Alq_3 upon purification (oxygen induces traps) [53] and it becomes non-dispersive in soluble PPV derivatives upon selection of the solvent used for deposition [54]. Mobility is usually low and dispersive in randomly distributed polar molecules, but it is increased significantly when the dipoles are organized [55]. A record non dispersive electron mobility of up to $2 \cdot 10^{-4}$ $\mathrm{cm}^2/(\mathrm{V{\cdot}s})$ was recently achieved in an air stable amorphous glassy molecular material [56]. Another record non dispersive hole mobility of 10^{-2} $\mathrm{cm}^2/(\mathrm{V{\cdot}s})$ was also achieved in an amorphous glassy molecular material [57], together with the guidelines for developing such promising materials. It is important that the mobility always drops by at least 2 orders of magnitude with impurities or defects (traps).

2.4. Photophysics

Light absorption by organic materials can also be rationalized using photophysics concepts [58]. It is from the optically excited state that the neutral excitation (exciton) can gives rise to a free charge pair (Fig. 2(d)). Absorption and photoluminescence usually involve the same energy levels: the fundamental S_0 and first excited S_1 singlet states (Fig. 2(c)). Upon light absorption, molecules are excited from the fundamental to the excited state with a cross section $\sigma_{0\to 1}$. 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 $\sigma_{1\to 0}$ which is almost the same as $\sigma_{0\to 1}$ (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). The speed of this decay is almost proportional to $N!$ where N is the number of vibration quanta ν_{vib} (stepladders in Fig. 2(c)) needed to decay down to the lower electronic state: $N \approx (\lambda_{\max} \cdot \nu_{\mathrm{vib}})^{-1}$. Another exciton decay channel is through inter system crossing (ISC) to the lower triplet state T_1 (Fig. 2(c)). 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 dramatically 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.

2.5. Charge generation

Exciton dissociation into a pair of charges occurs under large electric fields which can compete with the 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:

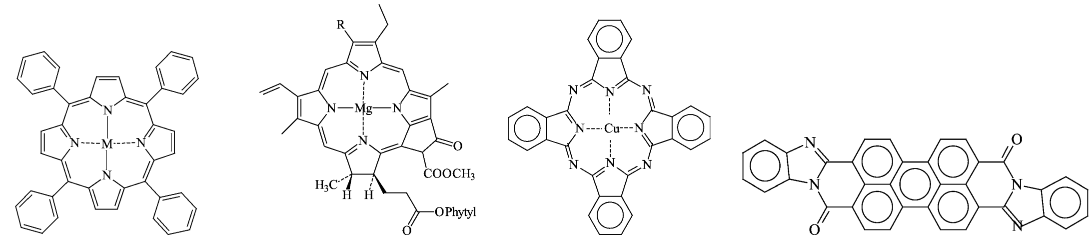
$$\phi = \phi_0 \exp\left(-\frac{r_{\mathrm{c}}}{r_0}\right)\left[1 + \frac{r_{\mathrm{c}} e E}{2! k_{\mathrm{B}} T} + \cdots\right],$$

with $r_{\mathrm{C}} = e^2/4\pi\varepsilon k_{\mathrm{B}} T$ 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. 2(d)). A partner of the donor acceptor pair can simply be an impurity (O_2, for instance, is an acceptor [5]). 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.

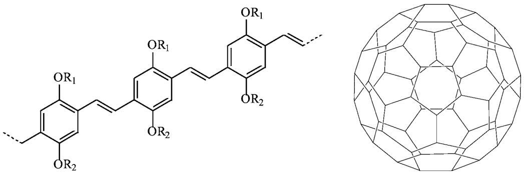
2.6. Materials

Excellent reviews on semiconductor materials are available: general reviews [59], polymer specific reviews [60], molecule specific reviews [25], molecular engineering [61], and reviews describing the sate of the art of materials used in commercial or pre-commercial electronic devices [62]. Most of the materials currently used in electroluminescent diodes or in photocopying machines (xerographic materials) are now commercially available from different suppliers, for different quantities and qualities (Covion, Syntec, American Dyes, H.W. Sands, Aldrich, ...). Some of them can be readily used as PV materials. C_{60} (Fig. 3(f)) and its derivatives [63] are excellent acceptor molecules, with a sizable electron mobility. Perylen pigments (Fig. 3(d)) are also acceptors, with a larger near-IR absorption. The phtalocyanins, porphyrins and related molecules (Fig. 3(a)–(c)) are good donors with a sizable electron mobility. Additionally, all the above molecules can be doped, in order to improve charge transport and junction extension. The MEH-PPV is a polymer whose luminescence is efficiency quenched by charge transfer to C_{60} in the so-called ‘interpenetrated networks’ [64]. Several photovoltaic molecules are described in [65].

Importantly, organic molecules have a donor or an acceptor character, which is an intrinsic property. They can be independently *p* or *n* doped by impurities, which is an extrinsic property. They can also be



(a) Tétraphénylporphyrin (b) Chlorophyl (c) Cu Phtalocyanin (d) Perylen pigment



(e) MEH-PPV polymer (f) C_{60}

Figure 3. Model materials for photovoltaic cells: (a)–(e) are donors (A), (d) and (f) are acceptors.

efficient electron or hole transporters, which is a kinetic property determined by orbital overlap in the solid state. However, an ideal donor should also permit efficient hole transport and eventually be p-doped. An ideal acceptor should also permit efficient electron transport and eventually be p-doped. Deviations from this rule would make poor PV cells.

3. Physics of organic photovoltaic solar cells

3.1. The photovoltaic effect

The production of electric energy from sun-light is the result of a chain process (Fig. 4). Sunlight photons are absorbed inside the device (A), carriers are then generated from exciton dissociation (G), carriers are collected by the electrodes and driven into the external circuit (C). These are the productive events of the PV process [66]. A more detailed analysis permits us to understand and eventually improve the different steps of the PV effect (Fig. 5) [6].

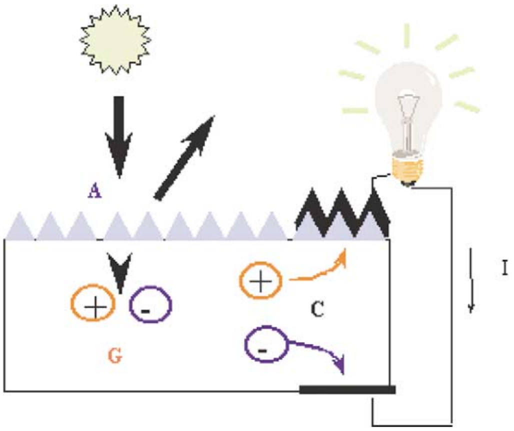


Figure 4. The photovoltaic process: absorption of photons (A), generation of carriers (G), collection of carriers (C).

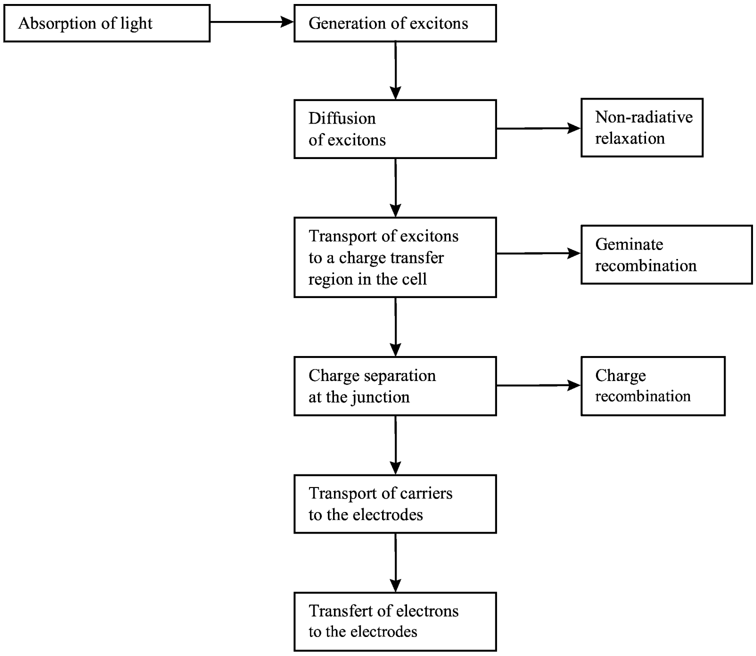


Figure 5. Conversion steps and loss mechanism of light power into electric power. Light which is not converted to electricity is converted to heat and eventually contributes to damage.

Incident solar energy = Electricity + Heat

3.1.1. *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 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 in 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.

3.1.2. *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. 4.

3.1.3. *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.

3.1.4. *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.

3.1.5. *Charge transport*

The transport of charges is affected by recombination during the journey 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.

3.1.6. *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. 6) permits an evaluation of most of its photovoltaic performances as well as its electric behaviour [67]:

- 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 $|I_{\max} \times V_{\max}|$. This 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:

$$\mathrm{FF} = \frac{P_{\max}}{V_{\mathrm{oc}} \times I_{\mathrm{sc}}} = \frac{V_{\max} \times I_{\max}}{V_{\mathrm{oc}} \times I_{\mathrm{sc}}};$$

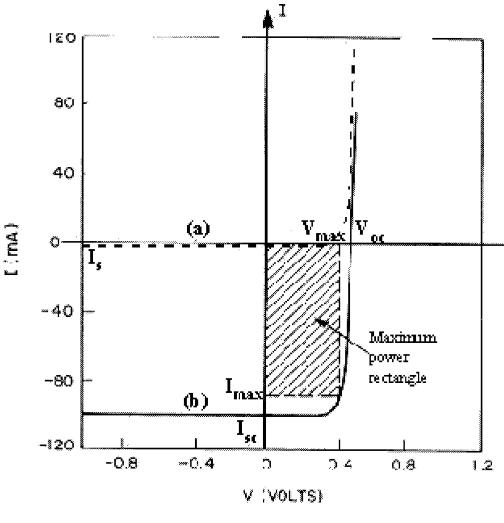


Figure 6. *I–V* characteristics of an ideal solar cell in the (a) dark, and (b) under illumination.

- 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

  $$\mathrm{IPCE} = \frac{J_{\mathrm{sc}}}{G \times \lambda} \times \frac{hc}{e},$$

  with J_{sc} the short-circuit current density, or numerically in a very simple manner: $\mathrm{IPCE} = 1.24 J_{\mathrm{sc}}/(G \times \lambda)$, with J_{sc} in $\mathrm{A{\cdot}cm^{-2}}$, G in $\mathrm{W{\cdot}cm^{-2}}$ 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:

  $$\eta = \frac{P_{\mathrm{max}}}{S \times G}$$

  (it is often expressed as a percentage). Conversion yield is the key parameter as concerns cells productivity. It must be evaluated carefully [68], and not be confused with ICPE.

3.3. Equivalent circuit

Dark characteristics of the cells is a standard diode one. The sign and value of the applied voltage determines blocking and conducting regimes. The cell conducts when the voltage exceeds a threshold V_{s}. An ideal cell can follow the thermionic injection model [69]:

$$I = I_{\mathrm{s}}\left(\exp\left(\frac{eV}{kT} - 1\right)\right),$$

where I_{s} is the saturation current under reverse bias.

Under light, the cell can be represented by the equivalent circuit in Fig. 7. It is described as a current source in parallel with the junction. I_{L} originates from charge generation by the illumination. R_{L} is the charge resistance of the external circuit. Ideally, current in the circuit is modelised as

$$I = I_{\mathrm{s}}\left(\exp\left(\frac{eV}{kT} - 1\right)\right) - I_{\mathrm{L}}.$$

In real devices, the circuit must be modified to account for serial R_{s} and shunt R_{sh} resistance losses. An 'ideality factor' n is also introduced (it is 1 for an ideal diode). Currents becomes determined by the equation

$$I\left(1 + \frac{R_{\mathrm{s}}}{R_{\mathrm{sh}}}\right) - \frac{V}{R_{\mathrm{sh}}} + I_{\mathrm{L}} = I_{\mathrm{s}}\left(\exp\left(\frac{e}{nkT}(V - IR_{\mathrm{s}})\right) - 1\right).$$

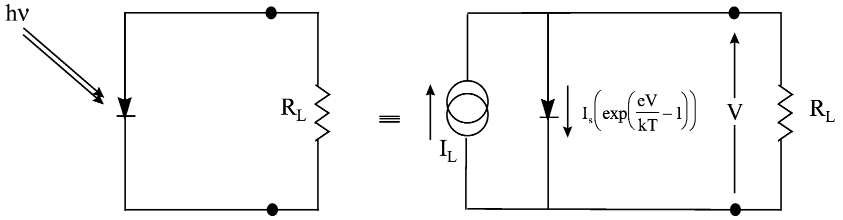


Figure 7. Equivalent circuit of an ideal cell under light. I_{L} is a current source whose intensity depends on G. R_{L} is the charge resistance [69].

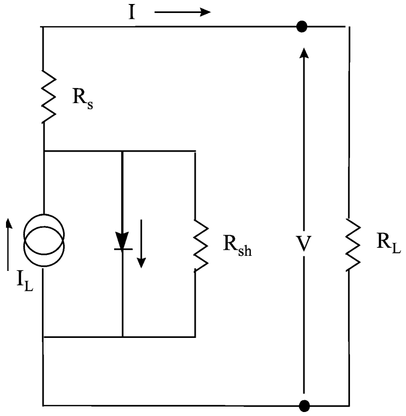


Figure 8. Equivalent scheme of a real PV cell under light. R_{S} and R_{sh} are the series and shunt resistances. R_{L} is the charge resistance of the external circuit.

The equivalent circuit is that of an imperfect current generator, with shunt and series resistances (Fig. 8). Series resistance depends on the material's resistivity, the electrodes' resistivity, and the metal–organic interfaces at the electrodes. The shunt resistance (several kΩ) corresponds to leaks and shorts in the diode. The slope around zero bias is a measure of the shunt resistance [70].

The relation between V_{oc} and I_{sc} can be determined when it is assumed that $R_{\mathrm{S}} = 0$ and $R_{\mathrm{sh}} = \infty$, with $I = 0$ and $I_{\mathrm{L}} = I_{\mathrm{sc}}$:

$$V_{\mathrm{oc}} = \frac{nkT}{e} \ln\left(\frac{I_{\mathrm{sc}}}{I_{\mathrm{s}}} + 1\right).$$

A small shunt resistance R_{sh} will reduce V_{oc}. Additionally, the cell will not deliver any voltage under low illumination G. I_{sc} is essentially reduced by the series resistance R_{S}.

3.4. The 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: $\eta = \phi \cdot A \cdot \mathrm{FF} \cdot eV_{\max}/h\nu$. The fill factor can be almost close to 1 (or 0.8), provided shunt resistance is large ($R_{\mathrm{sh}} > 25$ kΩ) and series resistance is small ($R_{\mathrm{S}} < 50$ Ω). 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 [71–73] (see Section 2.5). In an homogeneous layer, this would require an exciton diffusion length close to the thickness of the diode, which is also possible in some pigments [74]. Organic colorants have an absorption in the visible range greater than $\alpha \geqslant 10^7\ \mathrm{m}^{-1}$ over a 100 to 200 nm bandwidth. 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* (Section 2.4) and the *charge mobility* (Section 2.3). Both are sizable:

- This is presumably the improvement of the exciton diffusion length which has recently permitted reaching a 3.6% solar efficiency with a bi-layer molecular cell [75] analogous to the original Tang cell [1]. 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) [76], 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 (1–3 $\mathrm{cm}^2/(\mathrm{V}\cdot\mathrm{s})$) which may explain the exceptional solar efficiency obtained in pentacene crystals [2]. 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 $J = 20\ \mathrm{mA/cm}^2$ current extracted out of the cell. Space charge limited current follows the law:

$$J_{\mathrm{sc}} = \frac{9}{8}\varepsilon\mu\frac{V^2}{L^3},$$

in which V is the working voltage and L the organic semiconductor thickness. We get a lower limit for the mobility: $\mu \geqslant 2\cdot 10^{-4}\ \mathrm{cm}^2/(\mathrm{V}\cdot\mathrm{s})$. This can be an electron or a hole mobility which must reach this value, or both, depending on the cell structure.

3.5. 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. 2(d)) if they are intrinsic (undoped). Several examples are given in [77].

A junction will result from the equalization of the chemical potential of the electron (Fermi level in inorganic semiconductors) in the two different materials [77]. The case of a Schottky cells for the contact between a metal and a p-type semiconductor is illustrated in Fig. 9. Let ϕ_{m} be the ionisation potential (IA)

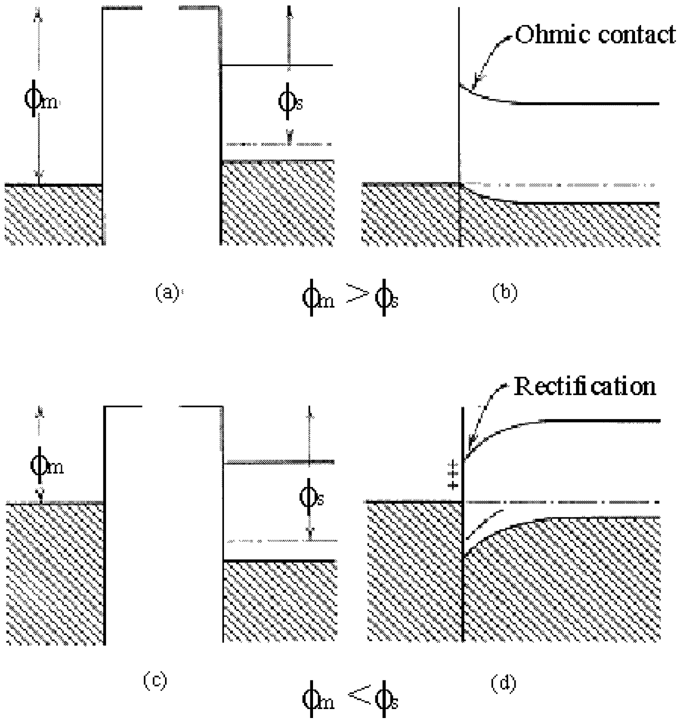


Figure 9. Energy levels of a metal – p-type semiconductor contact. Before and after contact for (a), (b) $\phi_{\mathrm{m}} > \phi_{\mathrm{S}}$; and (c), (d) for $\phi_{\mathrm{m}} < \phi_{\mathrm{S}}$.

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:

- 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 [5,6,66,77]

In order to meet the specific requirement for efficient photon to charge conversion, different device architectures have been developed. Figure 10 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 work-function (typically ITO) and the acceptor-material with the lower work-function electrode (typically Al). Of course, as the height of the work-function of ITO is between Al and Au (Al < ITO < Au), the structure is inverted in Fig. 10. The different architectures are now given.

4.1.1. *Single layer cells*

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 ohmic in 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 photoexcited charges may travel through the same material recombination losses are generally high. Such cells are currently used for screening and evaluation purposes.

4.1.2. *Double layer cells*

Double layer cells benefit from separated charge transport layers that ensure connectivity with the correct electrode and give a separated charge carrier only a small 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 become dissociated.

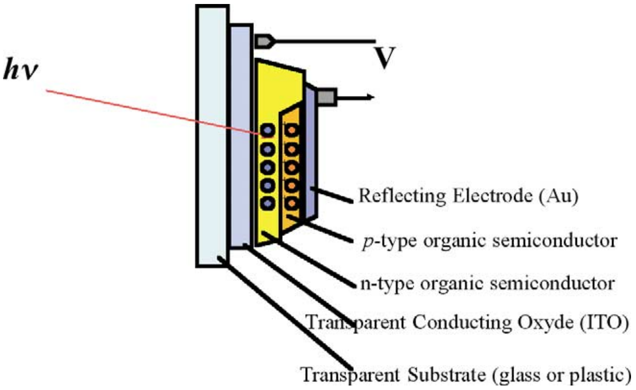


Figure 10. Typical bi-layer organic solar cell design.

4.1.3. *Blend cells*

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 [78].

4.2. Emerging technologies

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 [79]. 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. 11 [80]. The efficiency of such a diode is limited to almost 1% [1]. This difficulty was recently overcome in a CuPc/C_{60} cell designed with improved electrodes, yielding a 3.6% efficiency [75]. This proves that bi-layer cells can be good candidates for an efficient energy conversion [71].

In the year 2000, the Lucent group got a 4.5% efficiency with an halogen (Br or I_2) doped pentacene monocrystal ($C_{22}H_{14}$) [81]. The efficiency was even larger, 5%, by considering only the surface of the cell and not the crystal efficiency. 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 $\mathrm{cm}^2/(\mathrm{V\cdot s})$;
- 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 of building single layer solar cells for an efficient PV conversion. However, absorption cannot cover all the solar spectrum with a single layer of an homogeneous organic material, so that a bi-layer diode remains a potentially attractive device [82]. Additionally, halogen doped crystals may be highly unstable materials, but this also can be overcome using controlled molecular doping with strong acceptor molecules [83]. Promising structures which combine some advantages of the crystalline diodes with the processablility of multilayer devices are the columnar liquid crystal cells [73, 84], or any other self-organized device structure [85,86].

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 trial was achieved more than 10 years ago with dye-sensitised solar cells [87] (the so-called Grätzel cells). The concept was applied more recently with success to a solid single-layer polymer solar cell. It is based on the efficient – ultrafast – charge transfer which occurs between C_{60}-derivatives as charge acceptor and semiconducting polymers as charge donor [88,89]. Such cells exceed 3% solar efficiency. From a chemical point of view, the advantage is that materials do not

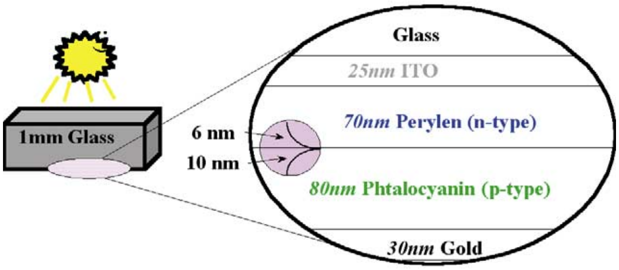
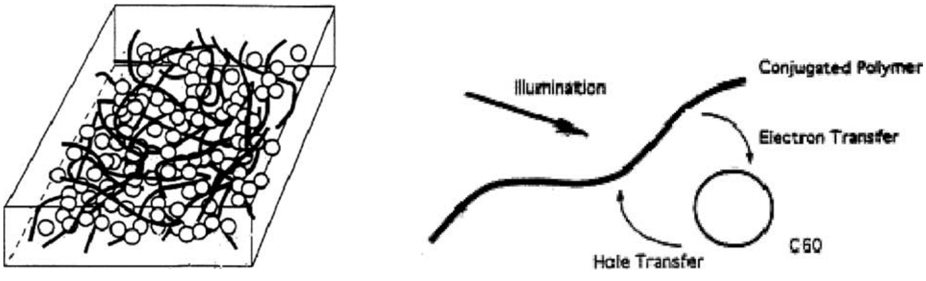


Figure 11. Scheme of a bi-layer *p–n*-type molecular PV cell showing the extension of the photoactive region in which excitons dissociate, around the junction [80].



(a) (b)

Figure 12. (a) Scheme of an interpenetrating network of a donor polymer and an acceptor C_{60}-derivative, showing (b) the detail of an ultrafast charge transfer event [64].

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. 12). From a topological point of view, the effective surface of the junction is significantly improved by the interpenetrated network. The difficulty lies in the fabrication of a doubly connected network made of an electron transport material (conjugated polymer) and a hole transport material (C_{60}) [90]. Attempts have been made to link the donors and acceptors chemically, but experimental results do not yet show any significant progress in this direction [91,92]. Another actual difficulty lies in the stability of the cells: both structural and photochemical stability [93]. There is still many room for improvement in the technology of interpenetrated networks [94]: some attempts consist in replacing C_{60} by inorganic semiconductor nano-materials (so-called hybrid cells) [95,96], as a strategy for further improvement of stability and performances 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) [97]. 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 [55,98]. 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

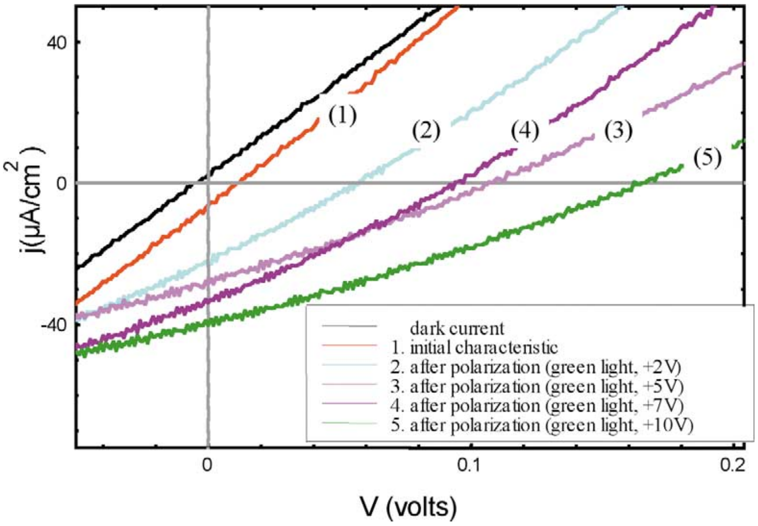


Figure 13. Current density/voltage characteristics recorded in the dark and under 12.5 mW/cm^2 red light illumination through ITO for an ITO/P3BT(25%wt) + copolymer MMA-DR1 (50%wt) + PR3072 (25%wt)/Au device, before and after different polarization sequences at room temperature (curves 1–5) [102].

absorption of light and transport of excitons and charges, as do liquid crystals; the latter permits in addition the induction of an internal polarization field [99,100]. This field improves exciton dissociation inside the cell (Section 2.5) as well as charge mobility [55]. 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 [100–102]. A two orders of magnitude efficiency improvement was obtained in a blended polythiophene structure (Fig. 13). 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.

4.3. Degradation

The degradation issue has made enormous progress in the recent years in the field of organic electroluminescent devices. Their lifetime now reaches 20 000 hours under nominal working conditions. However, a photovoltaic device should be exposed to sun light for a period larger than 10 years in order to become a competitive alternative to silicon. That is more than 10 000 hours of sun, this is not an easy task. The causes of degradation have different origins:

- photochemically [93]: it can be an intrinsic property of the molecules or an extrinsic one (photo-oxydation with oxygen for instance [58]);
- electrochemically: ionic impurities or water may promote redox reactions at the electrodes. Such degradation may eventually be recovered [103];
- structurally: low-T_g materials may reorganise, recrystallise, or diffuse one into another, owing to repeated heating and cooling in outdoor conditions [104];
- electrodes: they can react with the molecules, metal diffusion from ITO into polymers for instance [105].

Improvement of the stability of organic PV cells requires the choice of intrinsically stable materials (stable under storage, under sunlight and under reduction or oxidation conditions), the use of efficient purification methods, the choice of high-T_g materials and structures (stable under outdoor cooling or heating), a water an oxygen free fabrication technique (under a glove box, for instance), encapsulation of the structures after fabrication, etc. Also, the fabrication of efficient solar cells, because unconverted light heats and eventually damages the cells (Fig. 5).

5. Conclusions

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 the orientation of future generations of photovoltaic solar cells [106] toward a low cost technology (with a typical 1 €/W target). Several laboratories are now implicated in this research, increasing the rate of improvement and breakthrough in the domain of organic photovoltaic materials and devices.

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