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Solar Energy Materials  
& Solar Cells

Solar Energy Materials & Solar Cells 83 (2004) 125–146

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# A brief history of the development of organic and polymeric photovoltaics

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## Abstract

In this paper an overview of the development of organic photovoltaics is given, with emphasis on polymer-based solar cells. The observation of photoconductivity in solid anthracene in the beginning of the 19th century marked the start of this field. The first real investigations of photovoltaic (PV) devices came in the 1950s, where a number of organic dyes, particularly chlorophyll and related compounds, were studied. In the 1980s the first polymers (including poly(sulphur nitride) and polyacetylene) were investigated in PV cells. However, simple PV devices based on dyes or polymers yield limited power conversion efficiencies (PCE), typically well below 0.1%. A major breakthrough came in 1986 when Tang discovered that bringing a donor and an acceptor together in one cell could dramatically increase the PCE to 1%. This concept of heterojunction has since been widely exploited in a number of donor–acceptor cells, including dye/dye, polymer/dye, polymer/polymer and polymer/fullerene blends. Due to the high electron affinity of fullerene, polymer/fullerene blends have been subject to particular investigation during the past decade. Earlier problems in obtaining efficient charge carrier separation have been overcome and PCE of more than 3% have been reported. Different strategies have been used to gain better control over the morphology and further improve efficiency. Among these, covalent attachment of fullerenes to the polymer backbone, creating so-called double-cable polymers, is the latest. The improved PCE of plastic solar cells combined with increased (shelf and operating) lifetime, superior material properties and available manufacturing techniques may push plastic PVs to the market place within a few years.

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**Keywords:** Organic photovoltaics; Plastic solar cells; Heterojunction; LED; Photocurrent

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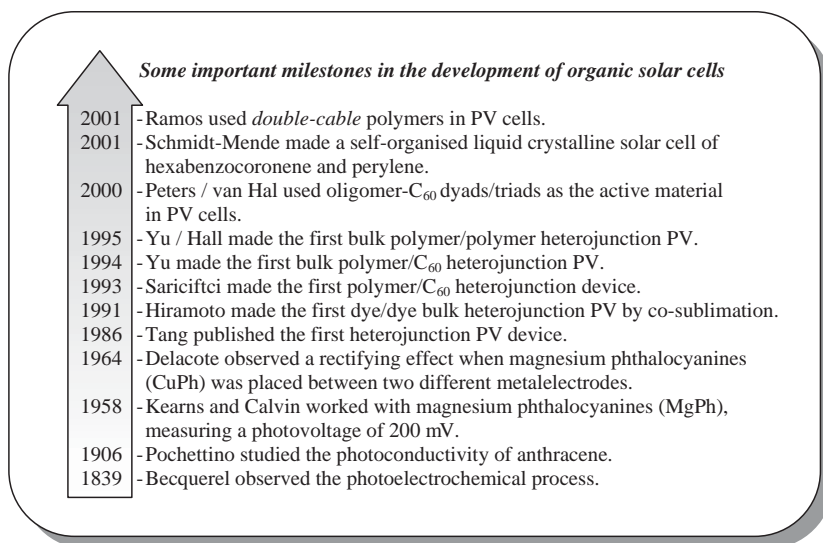


Fig. A

## 1. Introduction

The discovery of the photovoltaic (PV) effect is commonly ascribed to Becquerel (see Fig. A), who discovered a photocurrent when platinum electrodes, covered with silver bromide or silver chloride, was illuminated in aqueous solution (strictly speaking this is a photoelectrochemical effect) [1]. Smith and Adams made the first reports on photoconductivity, in 1873 and 1876, respectively, working on selenium [2]. Anthracene was the first organic compound in which photoconductivity was observed by Pochettino in 1906 [3] and Volmer in 1913 [4]. In the late 1950s and 1960s the potential use of organic materials as photoreceptors in imaging systems was recognized [5]. The scientific interest as well as the commercial potential led to increased research into photoconductivity and related subjects. In the early 1960s it was discovered that many common dyes, such as methylene blue, had semi conducting properties [6]. Later, these dyes were among the first organic materials to exhibit the PV effect [7]. Also, the PV effect was observed in many important biological molecules such as carotenes, chlorophylls and other porphyrins, as well as the structural related phthalocyanines (PC). Despite many improvements over the years organic PVs has not yet reached the market place unlike inorganic solar cells.

The first inorganic solar cell was developed at Bell Laboratories in 1954 [8]. It was based on Si and had an efficiency of 6%. Over the years the efficiency has reached 24% for crystalline Si solar cells in the laboratory [9]. Today Si-based solar cells are by far the most dominating type of PVs used and account for 99% of all PVs [10].

With increasing efficiency and reduced production costs the world PV-market has increased. In the past 20 years, the demand for solar energy has grown consistently with growth rates of 20–25% per year, reaching 427 MW in 2002. Fifty years of research and innovation has dramatically reduced the price of Si PVs to the level possible using existent technology. However, despite much effort of further reducing the price of Si based PVs, this technology is confined to niches. Thus, semiconductor PVs still account for less than 0.1% of the total world energy production.

Organic semiconductors are a less expensive alternative to inorganic semiconductors like Si. Also, organic molecules can be processed by techniques not available to crystalline inorganic semiconductors. Especially conjugated polymers are attractive in this respect. The superior material properties of polymers (plastics) combined with a large number of cheap processing techniques has made polymer based materials present in almost every aspect of our modern society.

In this paper we review the development of organic solar cells from the beginning of the 19th century to the most recent developments, focussing on polymer-based solar cells. Hybrid cells, consisting of both inorganic semiconductors and dye molecules [11], as well as photoelectrochemical (PEC or Grätzel) cells [12] are reviewed elsewhere.

## 2. Principle of operation

Before discussing the development of organic PVs the basic principles are outlined. Almost all organic solar cells have a planar-layered structure, where the organic light-absorbing layer is sandwiched between two different electrodes. One of the electrodes must be (semi-) transparent, often Indium–tin-oxide (ITO), but a thin metal layer can also be used. The other electrode is very often aluminium (calcium, magnesium, gold and others are also used). Basically, the underlying principle of a light-harvesting organic PV cell (sometimes referred to as photodetecting diodes) is the reverse of the principle in light emitting diodes (LEDs) (see Fig. 1) and the development of the two are somewhat related.

In LEDs an electron is introduced at the low-workfunction electrode (cathode) with the balanced introduction of a hole at the high-workfunction electrode (anode). At some point the electron and the hole meets, and upon recombination light is emitted [13]. The reverse happens in a PV device. When light is absorbed an electron is promoted from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) forming an exciton (see Fig. 2). In a PV device this process must be followed by exciton dissociation. The electron must then reach one electrode while the hole must reach the other electrode. In order to achieve charge separation an electrical field is needed, which is provided by the asymmetrical ionisation energy/workfunctions of the electrodes. This asymmetry is the reason why electron-flow is more favoured from the low-workfunction electrode to the high-workfunction electrode (forward bias), a phenomenon referred to as rectification. The light harvesting process along with the positioning of energy levels is depicted in Fig. 2.

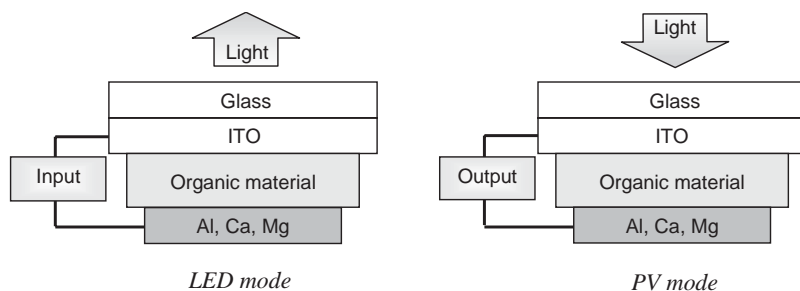


Fig. 1. A PV device (right) is the reverse of a LED (left). In both cases an organic material is sandwiched between two electrodes. Typical electrode materials are shown in the figure. In PVs electrons are collected at the metal electrode and holes are collected at the ITO electrode. The reverse happens in a LED: electrons are introduced at the metal electrode (cathode), which recombine with holes introduced at the ITO electrode (anode).

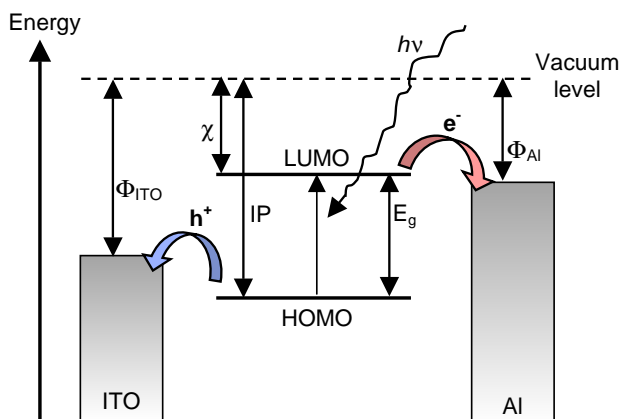


Fig. 2. Energy levels and light harvesting. Upon irradiation an electron is promoted to the LUMO leaving a hole behind in the HOMO. Electrons are collected at the Al electrode and holes at the ITO electrode.  $\Phi$ : workfunction,  $\chi$ : electron affinity, IP: ionisation potential,  $E_g$ : optical band gap.

In the solid phase, the HOMOs and LUMOs of adjacent molecules may interact and form a conduction band (CB) and a valance band (VB) respectively (this will be described below). The shape of the CB and VB changes when the organic material is put into contact with electrodes (see Fig. 3), depending on the conductance of the polymer and on whether the electrodes are connected or not. If the cell is short-circuited the Fermi levels of the electrodes align (B and C), and in doing so the CB and VB are pulled skew. In B the polymer material is an insulator. This gives a field profile that changes linearly through the cell. In C a hole-conducting (p-type) semiconductor is used (most polymers are much better hole conductors than electron conductors). If the material is doped or illuminated charge carriers are generated. Due to the p-conduction properties, the generated holes are allowed to redistribute freely and they will flatten the bands approaching the high-workfunction electrode

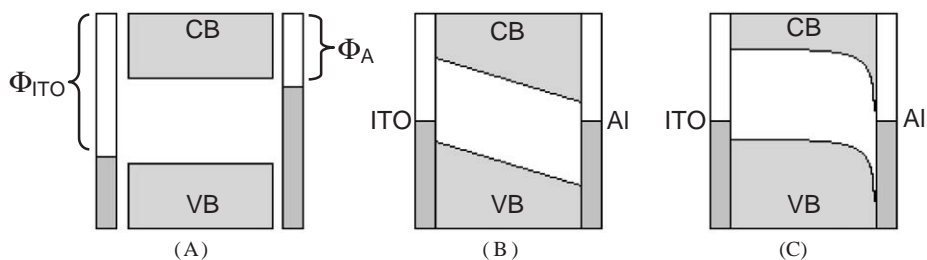


Fig. 3. The relative energy levels of the electrodes, CB and VB are shown in three situations, with no external bias. (A) CB and VB are shown along with the low-workfunction electrode (Al) and the high-workfunction electrode (ITO) when isolated from each other. (B and C) The cell is assembled and short-circuited, causing alignment of the electrode potentials. In (B), an insulating organic material is used. In C a hole-conducting polymer is used forming a Schottky junction at the high-workfunction electrode.

(a Schottky junction). The distance over which the CB and VB exhibit curvature is called the depletion width. In B the depletion width extends throughout the material. In C the depletion width is less than half the material thickness. Under external bias the relative electrode potentials can be changed, depending on the size and direction (forward or reverse) of the bias.

### 2.1. Comparison of inorganic and organic PV

In a crystalline inorganic semiconductor with a 3D crystal lattice the individual LUMOs and HOMOs form a CB and a VB throughout the material. This is fundamentally different from most organic dye semiconductors where the intermolecular forces are too weak to form 3D crystal lattices. Consequently the molecular LUMOs and HOMOs do not interact strongly enough to form a CB and VB. Thus charge transport proceeds by hopping between localised states, rather than transport within a band. This means that charge carrier mobility in organic and polymeric semiconductors are generally low compared to inorganic semiconductors. Also, charge separation is more difficult in organic semiconductors due to the low dielectric constant. In many inorganic semiconductors photon absorption produces a free electron and a hole (sometimes called charge carriers), whereas the excited electron is bound to the hole (at room temperature) in organic semiconductors. Conjugated polymers lie somewhere between the inorganic semiconductors and organic dyes. In general, excitons are considered to be localised on specific chain segments. However, there are cases where excitons seem to be delocalised. In these cases, the excitons are referred to as polarons [14].

In simple PV devices and diodes based on organic semiconductors the primary exciton dissociation site is at the electrode interface (other sites include defects in the crystal lattice, absorbed oxygen or impurities) [15]. This limits the effective light-harvesting thickness of the device, since excitons formed in the middle of the organic layer never reaches the electrode interface if the layer is too thick. Rather they recombine as described above. Typical exciton diffusion distances are on the order of 10 nm.

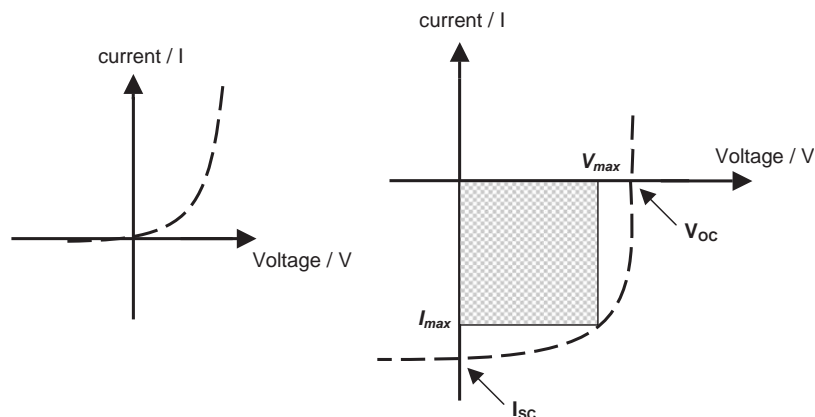


Fig. 4.  $I$ - $V$  curves of an organic PV cell under dark (left) and illuminated (right) conditions. The open-circuit voltage ( $V_{OC}$ ) and the short-circuit current ( $I_{SC}$ ) are shown. The maximum output is given by the square  $I_{max}^*V_{max}$ .

## 2.2. Characteristics of PVs [16]

In Fig. 4 below some of the characteristics of a typical organic PV device is outlined. To the left, the  $I$ - $V$  curve of the cell in the dark is shown. When a cell is illuminated, the  $I$ - $V$  curve is shifted down by the short-circuit current,  $I_{SC}$  (Fig. 4, right). The open-circuit voltage,  $V_{OC}$ , is the maximum voltage difference attainable between the two electrodes, typically around 0.5–1.5 V, which is higher than inorganic cells. The cell is placed in an open circuit and illuminated. Electrons and holes separate and flow towards the low- and high-workfunctions, respectively. At some point the charge build-up will reach a maximum equal to the  $V_{OC}$  that is limited by the difference in workfunctions of the two electrodes [17] (recently Brabec et al. [18] have shown that in some heterojunction cells  $V_{OC}$  is more dependent on acceptor strength than electrode material). The maximum current that can run through the cell is determined by the short-circuit current,  $I_{SC}$ . This quantity is determined by connecting the two electrodes, whereby the potential across the cell is set to zero, and then illuminating the cell while the current flow is measured.  $I_{SC}$  yields information about the charge separation and transport efficiency in the cell. The magnitude of  $I_{SC}$  depends on the illumination strength, but for intensities around 100 mW/cm<sup>2</sup> (AM1.5)  $I_{SC}$  is in the 0.20–80 mA/cm<sup>2</sup> range. The square  $I_{max}V_{max}$  is the maximum work the cell is able to yield. The fill-factor FF is given by  $I_{max}V_{max}/V_{OC}I_{SC}$ , and is typically around 0.4–0.6. The quantum efficiency (QE) is the number of generated electrons per absorbed photon. For single layered organic PV the QE is typically in the order of 1%, while inorganic PV often reaches a QE of 80–90%. The power conversion efficiency (PCE) is the power output divided by the incident light power. For single layered organic PV this is typically below 0.1%, while crystalline Si cells have up to 24%.

### 3. Chemistry and physics at the electrodes [19]

When a pristine conjugated polymer is brought into contact with electropositive metals typically used as electrodes (i.e. Al, Ca, Mg, Mg/In), the interface is never sharp. Rather, chemistry always occurs to a varying extent. In the case of poly(*p*-phenylene vinylene) (PPV) on aluminium XPS studies reveals the formation of a 30 Å thick insulating layer. This layer is thought to be formed as Al atoms diffuse into the polymer matrix where Al reacts with the vinyl groups and disrupt the conjugation (see Fig. 5). The effect of this layer is to increase the electron injection barrier at the interface. Naturally, as the layer becomes thicker and thicker electron extraction becomes impossible rendering the device useless. Different strategies have been investigated to overcome this problem. In LEDs a thin protective layer between an Al-electrode and the organic layer has been found effective and increasing overall performance. Hung et al. [20] demonstrated that a 5–10 Å thin LiF or MgO layer improved efficiency of the Al-electrode by lowering the electron-injection barrier. Greczynski et al. [21] has also investigated the protective properties of LiF in a thorough study done on polyfluorene using UPS and XPS. Both studies indicate that LiF does not dissociate and react chemically, but rather serves as a protecting layer between the electrode and the organic material. Also, Al<sub>2</sub>O<sub>3</sub> has been shown to have favourable properties as a protective layer reducing drive voltage and increasing device performance in LEDs [22]. Very recently Brabec et al. [23] have shown that the advantages of using a protective layer on the negative metal electrode carry well over in PV devices. Indeed LiF, has been reported to increase the FF and stabilise the  $V_{OC}$  in PV cells.

Transparent ITO is the material most used as the high-workfunction material in PV devices and LEDs. The ITO–polymer interface is not well understood or well controlled. There are large variations of the ITO morphology and workfunction from manufacturer to manufacturer and from batch-to-batch [24]. The uneven surface of ITO on glass results in local areas with high fields under operation that may cause rapid polymer degradation. AFM and UPS studies have shown that acid etching and ozone cleaning can be used to control the surface [25]. Similar to the cathode interface, atoms from the anode can react with the organic material. Thus, in one study it was found that oxygen could diffuse into MEH–PPV forming aromatic aldehydes [26]. Also, indium was found to diffuse into the organic layer where it acts as trapping site for charge carriers [27]. One strategy used to minimize indium and oxygen diffusion is to place an interfacial hole-transporting layer, such

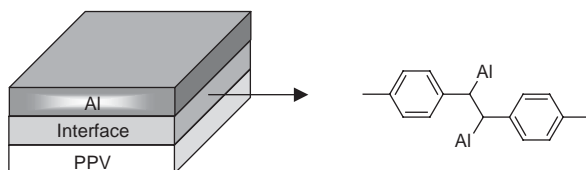


Fig. 5. Aluminium and the pristine polymer will chemically react and form an insulating layer at the interface.

as PEDOT-PSS [28], between ITO and the active material. This layer also serves to smooth out the uneven surface of ITO.

#### 4. Dye solar cells [7]

Photoconductivity was first observed on anthracene (see Fig. 6) in the beginning of the 20th century [3,4]. From the 1950s anthracene was intensively studied, partly because the crystal structure was accurately determined early [29], and high-purity single crystals were readily available [30]. The first real PV investigations were done on porphyrins and PCS, and this class of compounds has remained among the most investigated dyes. The compounds are easy to prepare, highly coloured, and they form crystalline films by vacuum sublimation with good semiconducting properties. Also, they readily form complexes with a number of metal ions. In 1958 Kearns and Calvin worked with magnesium phthalocyanines (MgPc) between two glass electrodes and measured a photovoltage of 200 mV [31]. Six years later in 1964 Delacote et al. [32] observed a rectifying effect when copper phthalocyanines were placed between two different metals. In 1971 Federov and Benderskii re-investigated MgPc. They found that the PV properties of MgPc are very dependent on exposure to oxygen [33]. Five Years earlier Kearns et al. [34] had suggested that oxygen at the crystal surface of anthracene assisted in exciton dissociation and thus played an important role in the photoconductivity of anthracene. The pronounced effect of

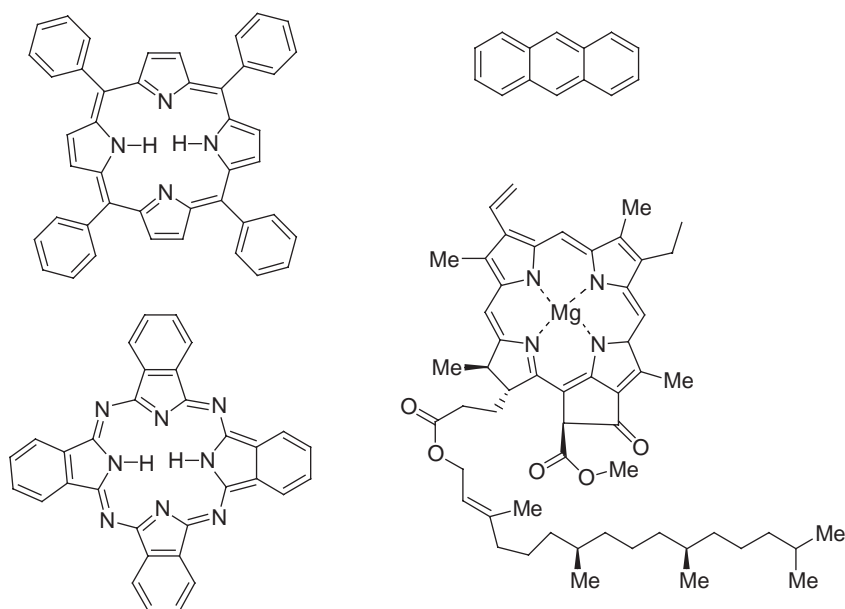


Fig. 6. Some of the early investigated organic molecules. Top: TPP and anthracene. Bottom: phthalocyanine and Chl-a.



oxygen is now known to be related to the electron accepting ability of molecular oxygen. Meilinov et al. [35] worked on chlorophyll-*a* (Chl-*a*) in 1970 and measured a photocurrent quantum yield of 10% in Al/Chl-*a*/Al, which was substantially better than previously reported. In 1975 Tang and Albrecht [35] worked extensively with Chl-*a* (extracted from green spinach) in metal1/Chl-*a*/metal2 cells. By varying the electrode metals they found the optimal cell to be Cr/Chl-*a*/Hg that had a PCE of 0.01% under monochromatic illumination, orders of magnitude larger than most systems at that time. Earlier work by Putseiko et al. [36] had established that Chl-*a* was water sensitive, which Ballschmitter et al. [37] found was related to the formation of a Chl-*a*-H<sub>2</sub>O adduct. The adduct formation plays an important role in the formation of ordered microcrystalline domains in Chl-*a* films. Chlorophyll is still attracting interest, and in 2002 the conducting mechanism of Chl-*a* in Al/Chl-*a*/Ag cells was investigated by Mabrouki et al. [38]. The cells had a PCE of 0.1%, a factor of 10 larger than the cells investigated in 1975 by Tang. Four decades of research have shown that the typical PCE of simple single dye PVs probably will remain below 0.1%. A major breakthrough in cell performance came in 1986 when Tang showed that much higher efficiencies are attainable by producing a double-layered cell using two different dyes [39]. This concept will be described in greater detail below.

## 5. Conjugated polymer cells [40]

One of the most studied photoconducting polymers is poly(vinyl carbazole) (PVK). The first report came in 1958 by Hoegel et al. [41] who proposed its practical use as an electrophotographic agent. In the 1970s it was discovered that certain conjugated polymers, notably poly(sulphur nitride) and polyacetylene (see Fig. 7), could be made highly conducting in the presence of certain dopants [42]. In 1982 Weinberger et al. [43] investigated polyacetylene as the active material in an Al/polyacetylene/graphite cell. The cell had a low open-circuit voltage of only 0.3 V and a low QE of only 0.3%. Later Glenis et al. [44] investigated different polythiophenes. Again the systems suffered low efficiencies and low open-circuit voltages in the 0.4 V range. The low open-circuit voltages have been ascribed to the formation of polarons

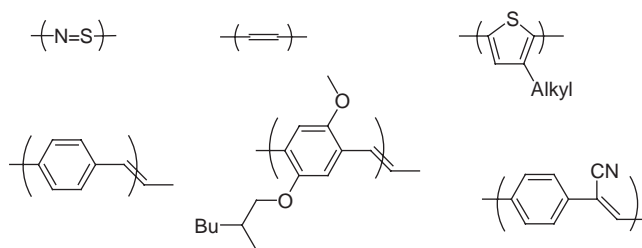


Fig. 7. Some conjugated polymers investigated in PV cells. Top: poly(sulphur nitride) (SN<sub>x</sub>), polyacetylene and poly(3-alkyl-thiophene). Bottom: poly(*p*-phenylene vinylene) (PPV), poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylvinylene) (MEH-PPV), and cyano-PPV (CN-PPV).

(delocalised excitons) that energetically relax in the energy gap, which then becomes smaller than the  $\pi$ – $\pi^*$  gap. This relaxation results in a large spectral shift when the luminescence spectra are compared to the absorption spectra (Stokes' shift). The result of the relaxations is that it limits the attainable voltage and the maximum PCE. Different electrode material have been used but not with success.

Followed by the poly(alkyl-thiophenes) (PATs), PPV and its derivatives is the most investigated conjugated polymer in PV cells. Unlike polyacetylene and polythiophene there is only limited energy relaxation. Karg et al. [45] was the first to investigate PPV in ITO/PPV/Al LEDs and PV devices in 1993. Karg measured  $V_{OC}$  of 1 V and a PCE of 0.1% under white light illumination. In 1994 both Marks et al. [46] and Antoniadis et al. [47] also investigated this system. Interestingly enough they had different views on the depletion width in the cells. Marks found that their cells were completely depleted while Antoniadis' cells formed Schottky type barriers at the Al-interface. This divergent behaviour is probably related to the fact that PPV is very sensitive to atmospheric oxygen as an efficient dopant for PPV. Thus in the presence of oxygen, electron abstraction from PPV increases the conductance orders of magnitude, due to the p-type behaviour of PPV. Other investigated PPV derivatives include MEH–PPV [48] and poly(2,5-diheptyloxy-*p*-phenylenevinylene) (HO–PPV) [49].

## 6. The concept of a heterojunction

As previously described, excitons do not dissociate readily in most organic semiconductors. The idea behind a heterojunction is to use two materials with different electron affinities and ionisation potentials. This will favour exciton dissociation: the electron will be accepted by the material with the larger electron affinity and the hole by the material with the lower ionisation potential.

In the 1950s it was discovered that organic dyes adsorbed on the surface of inorganic semiconductors had an effect on the photoresponse of the semiconductor in the spectral range of the dye. In 1956, for example, Nelson [50] found that the photoconductivity of CdS was increased when sensitised with a cyanine dye in the red spectral range. Nelson argued that the LUMO of the dye was above the CB of the semiconductor. When the dye was excited, the electron in the LUMO of the dye would be transferred to the CB of CdS and thereby enhance the conductivity.

In 1979 Tang [39] filed a patent on his ability to increase PCE to 1% of a bi-layer PV device consisting of copper PC and a perylene derivative, the results was not published until 1986. Tang proposed that the observed synergistic effect of bringing two different semiconductors in contact was caused by the field at the heterojunction interface. This local field aids dissociation of excitons diffusing to the interface. Such a situation is depicted in Fig. 8 where the donor molecule is excited (upward arrow); the electron is promoted from HOMO to LUMO leaving a hole behind. The electron and hole can recombine (downward arrow), yielding e.g. luminescence, or they can dissociate. If the acceptor LUMO is sufficiently lower than the donor LUMO, the excited electron will relax into the acceptor LUMO and in this way separate from the

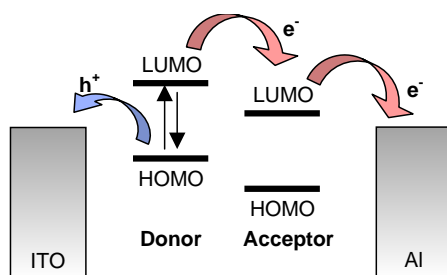


Fig. 8. Exciton dissociation at the donor–acceptor interface. The electron goes to the acceptor while the hole stays on the donor.

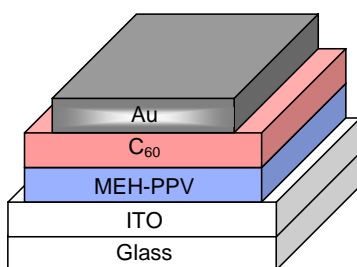


Fig. 9. A two-layer heterojunction photovoltaic cell. The electron accepting C<sub>60</sub>-layer contacts the Au electrode, while the electron donating MEH-PPV layer contacts the ITO electrode.

hole. Indeed charge separation is much more efficient at the donor–acceptor interface than at the electrode interface.

One of the most used acceptors in heterojunction cells is the fullerene molecule C<sub>60</sub> [51]. Besides having a high electron affinity, C<sub>60</sub> is fairly transparent and also has fair electron conductance ( $10^{-4} \text{ Scm}^{-1}$ ). This makes fullerenes a good component in PV cells. The first report of a conducting polymer/C<sub>60</sub> cell came in 1993 by Sariciftci et al. [52]. In one study, fullerene was vacuum sublimed onto a MEH–PPV layer that was spin coated on ITO-covered glass. Au was used as the electron-collecting electrode (see Fig. 9). The cell had a relative high FF of 0.48 and a PCE of 0.04% under monochromatic illumination. The photocurrent increased more than 20 fold when C<sub>60</sub> was added as a second layer, indicating that fullerene strongly assist charge separation. Poly(1,6-heptadiene) and poly(3-octylthiophene) (P3OT) were also studied as donor polymer. The same year Moriata et al. [53] made a similar observation working with poly(3-alkyl-thiophene) (P3AT) and C<sub>60</sub>.

In 1996 Halls et al. [54] made a very thorough study on PPV/C<sub>60</sub> heterojunction. The cell had a FF of 0.48 similar to the MEH–PPV case described above, but the PPV cell achieved an external monochromatic QE of 9%. Halls found that the photocurrent spectrum was inversely proportional (antibatic) with the PPV

absorption spectrum, indicating that light has to reach the PPV/C<sub>60</sub> interface in order to generate a photocurrent. From models, an average exciton diffusion length of 6–8 nm could be derived.

In 1997 Halls [55] also investigated heterojunctions where perylene was the electron acceptor. Bis(phenethylimido)perylene was vacuum sublimed onto PPV films spincoated on ITO covered glass, and Al was used as the counter electrode material. These cells had QE of 6% and PCE of 1% (monochromatic illumination). A high FF value of 0.6 was reported.

It became clear that if absorption at the heterojunction interface were increased the photocurrent from the cell would increase as well. The optical field varies through the cell, the incoming light interfere with reflections from the metal surface and the fullerene/polymer interface resulting in a standing wave. In the optimal situation the standing wave will have a node at the heterojunction interface. In 1999 Pettersson et al. [56] calculated the optical field intensity through a heterojunction multi-layer cell using complex indices of refraction, determined using spectroscopic ellipsometry. The studied cell consisted of PEOPT (poly(3-(4'-(1'',4'',7''-trioxaoctyl)-phenyl)thiophene)) and C<sub>60</sub>. Al was used as the electron-collecting electrode, while ITO was the hole-collecting electrode. The ITO electrode was covered with a PEDOT (poly(3,4-ethylenedioxythiophene))–PSS (poly(styrenesulfonate) layer to improve hole transport. By varying the polymer- and C<sub>60</sub>-thickness the nodes of the standing wave can be moved back and forth through the cell. Pettersson found that the exciton-diffusion range was around 5 nm in PEOPT and around 8 nm in the fullerene domain, thus the node of the optical field becomes very critical. When an 80 nm thick fullerene layer was used the optical field had an antinode at the PEOPT/C<sub>60</sub> interface, but when the fullerene layer was reduced to 35 nm the optical field had a node at the interface. Applying this result, Pettersson constructed a cell with a PEOPT thickness of 40 nm and a fullerene thickness of 31 nm and achieved a peak QE of 21% (using monochromatic 440 nm light), which indicates efficient charge separation.

Very recently in 2003, Durstock et al. [57] used electrostatic self-assembly to control the layer thickness in PPV/C<sub>60</sub> heterojunction cells. The thickness of the fullerene layer could be controlled by alternating immersion of the substrate into baths of water-soluble cationic and anionic C<sub>60</sub> derivatives. In the same way, the PPV layer thickness was controlled by using a PPV precursor as the cation and sulfonated polystyrene (SPS) as the anion. In a subsequent step the films were heated to convert the PPV precursor into PPV. Aluminium and ITO was used as electrode materials. Besides controlling the polymer and fullerene layer, a thin interfacial fullerene/PPV layer was inserted in some of the cells (Fig. 10).

For a fixed SPS/PPV layer thickness of  $z \approx 20$ , varying the fullerene layer thickness gave an optimum cell performance at  $x \approx 50$ . If  $x$  was held at 50, peak performance was around  $z \approx 20$ . If an interfacial layer was inserted the cell efficiency could be further improved. The insertion of only two C<sub>60</sub>/PPV<sup>+</sup> bilayers ( $y=2$ ) increased the short-circuit current by a factor of 3. A further three bilayers ( $y=5$ ) gave a total increase of a factor of 4. The final optimised cell had  $I_{SC}$  around 1.4  $\mu\text{A}/\text{cm}^2$  and  $V_{OC}$  around 0.5 V. For  $y > 5$  the  $I_{SC}$  slowly decreased. From this, Durstock concluded

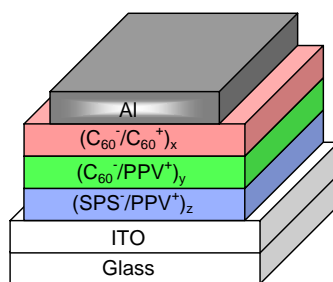


Fig. 10. Electrostatically self-assembled PV cells produced by Durstock. Different layer thicknesses were used in different cells ( $x=0-100$ ,  $y=0-10$  and  $z=0-40$ ).

that the interfacial layer increases the effective donor–acceptor interface leading to increased charge separation, however for increasing interfacial layer thickness the distance to the electron- and hole-conduction layer becomes too large to utilise the increased exciton dissociation. This study demonstrates the importance in controlling the interfaces in heterojunction cells.

Finally polymer/polymer donor–acceptor heterojunction should be mentioned. If this type of cell is fabricated by spincoating the challenge is to find a solvent that will not wash away the first layer when the second polymer is spincoated. Since conjugated polymers typically have poor solubility in normal solvents the available donor–acceptor polymer pairs are limited. In 1999 Tada et al. [58] fabricated a heterojunction cell consisting of the acceptor polymer poly(*p*-pyridylvinylene) (PPyV) and the donor polymer poly(3-hexylthiophene) (P3HT). PPyV was spincoated from formic acid and P3HT could then be spincoated from chloroform without damaging the first layer. The photocurrent increased some three orders of magnitude when the donor layer was present, indicating efficient charge transfer at the interface between the layers.

### 6.1. Dispersed (or bulk) heterojunction

It is clear that exciton dissociation is most effective at the interface in heterojunction cells, thus the exciton should be formed within the diffusion length of the interface. Since typically diffusion lengths are in the range of 10 nm, this limits the effective light-harvesting layer. However, for most organic semiconductors the film thickness should be more than 100 nm in order to absorb most of the light. It follows that thicker film layers increase light absorption but only a small fraction of the excitons will reach the interface and dissociate. This problem can be overcome by blending donor and acceptor, a concept called dispersed (or bulk) heterojunction (see Fig. 11).

One of the inherent problems with dispersed heterojunction is that of solid-state miscibility. Large extended conjugated systems are normally not miscible; this goes for dyes and particularly for conjugated polymers. Thus cell fabrication should be

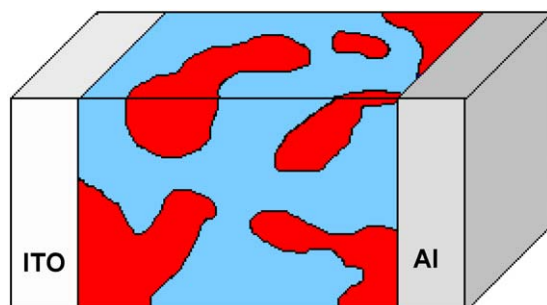


Fig. 11. Dispersed heterojunction between a transparent ITO electrode and an Al electrode.

carried out so equilibrium is never reached, e.g. by spincoating where solvent evaporation is fast.

Hiramoto [59,60] reported the first dye/dye-dispersed heterojunction in 1991. Working with the same class of p- and n-type organic semiconductors as Tang, metal-free phthalocyanine ( $H_2Pc$ ) and a perylene tetracarboxylic derivative, Hiramoto investigated the effect of introducing a third organic layer in the middle of a two-layer heterojunction PV. This middle layer was a mixture of the two dyes made by co-sublimation from different thermal sources. Hiramato found that by introducing a third layer the photocurrent was doubled as compared to the two-layered cell.

In 2001 Schmidt-Mende et al. [61] fabricated PV cells of self-organized discotic liquid crystals of hexaphenyl-substituted hexabenzocoronene (HBC) and perylene. The perylene and HBC  $\pi$ -systems segregated into vertical rods, ideal for efficient charge transport. Al was evaporated onto a 60:40 HBC:perylene blend that was spincoated on ITO. The cell had a peak QE of 34% and a PCE of 2% (at 490 nm). This ranks the cell among the best of the present day non-fullerene organic PV cells.

In 1994 Yu [62] made the first dispersed polymer heterojunction PV cell by spincoating on ITO covered glass from a solution of MEH-PPV and  $C_{60}$  in a 10:1 wt-ratio. Finally, Ca was evaporated onto the organic layer. The cell showed a photosensitivity of 5.5 mA/W, an order of magnitude larger than the photosensitivity of the pure polymer. In 1996 Köhler [63] also used this approach for fabricating PV cells with success. One limitation of this approach is the relative low solubility of fullerenes in normal solvents. This problem was solved when Hummelen et al. [64] synthesised a number  $C_{60}$ -derivatives with increased solubility in 1995, which allowed the fullerene content to be as high as 80% in the prepared films. Using a methano-functionalised fullerene derivative Yu et al. [65] repeated the fabrication procedure with a polymer/fullerene ratio of 20/80, the contacts were made of ITO and Ca, and the cell had a QE of 29% and a PCE of 2.9% (under monochromatic light, intensity at 20 mW/cm<sup>2</sup>). Thus a substantial increase compared to earlier polymer/fullerene mixtures. In 2000 Shaheen et al. [66] reported high QE values of 85% in a PPV-derivative and fullerene heterojunction cell, with a PCE of 2.5%. Very recently Munters et al. [67] showed how the chosen synthetic route towards poly (2-methoxy-5-(3',7'-dimethyl-octyloxy))-p-phenylene (MDMO-PPV) influences the

final cell efficiency when blended with a fullerene derivative. Thus one route gave a PCE of  $\sim 2.5\%$  (AM 1.5) compared to  $\sim 2.9\%$  for an alternative route. The efficiency difference is ascribed to different levels of chain defects in the polymer. Also, the influence of solvent on the crystal structure of phenyl-C61-butyric acid methyl ester (PCBM) has been investigated and related to PV efficiency by Hummelen et al. [68]. Besides PPV derivatives, polythiophenes have been used in fullerene bulk heterojunction cells [69]. In 2003 Brabec et al. [70] showed that very high QE (76%) in poly(3-hexylthiophene)/methanofullerenes bulk heterojunctions are attainable. The limitation seems to be optical loss in the cell, thus QE approaching 100% should be within reach. Geens et al. [71] have shown that sandblasting of the glass substrate can effectively reduce optical loss due to reflection in organic PV cells.

The first reports of polymer/polymer bulk heterojunction PV came independently from Yu et al. [72] and Halls et al. [73] in 1995. Both worked with the same PPV-based derivatives: CN-PPV as acceptor and MEH-PPV as the donor polymer. Halls made a PV cell from a blend of the two polymers in equal amounts by spincoating. ITO and Al were used as electrode materials, and the organic layer was 100 nm thick. Transmission electron microscopy (TEM) showed that the organic layer consisted of an interpenetrating network of a microphase-separated blend with typical domain sizes of  $\sim 10$  nm. The cells had a peak monochromatic QE of 6% and peak monochromatic PCE of 1%. This type of composite cell was found to be three orders of magnitude more efficient than pure cyano-PPV (CN-PPV) and two orders of magnitude more effective than pure MEH-PPV. The effectiveness of this type of polymer-blend is strongly dependent on the morphology. Ideally the microphase domains should be no larger than the exciton diffusion length, which for PPV-type polymers is around 7 nm according to Halls. In addition the network should be bicontinuous, leaving a free path for both holes and electrons so that they can reach the respective electrodes without the necessity for tunnelling through domains. Recently Halls has investigated how the morphology depends on the rate of solvent evaporation [74]. There has been at least one report on polymer/polymer/fullerene bulk heterojunction [75]. The idea behind using an extra polymer is to widen the spectral range and increase the PCE of the cell under white light illumination. While some promising results were reported by Chen et al. there has been limited focus on multiple polymer bulk heterojunctions cells.

## 6.2. Molecular heterojunction

It is clear that the control of morphology in dispersed heterojunction devices is a critical point. The degree of phase separation and domain size depend on solvent choice, speed of evaporation, solubility, miscibility of the donor and acceptor etc. One strategy towards increasing control is to covalently link donor and acceptor. In 2000 Stalmach et al. [76] synthesised PPV- $C_{60}$  diblock copolymers through controlled living radical polymerisation. The same year Peeters et al. [77] synthesised a number of *p*-phenylene vinylene oligomers (OPV) attached to  $C_{60}$  and investigated their use in PV devices. Peeters found that charge separation lifetimes was dependent



on the number of repeating oligomer units. Thus, charge separation lifetimes were much longer for 3–4 units compared to 1–2 repeating units. A cell consisting of the longest oligomer (4 repeating units) between aluminium and a PEDOT-PSS covered ITO electrode had an  $I_{SC}$  of  $235 \mu\text{A}/\text{cm}^2$  and a  $V_{OC}$  of 650 mV, but a relatively low FF of only 0.25. Van Hal et al. [78] made a similar study on fullerene-oligo(thiophene)-fullerene triads varying the number of monomer units. In agreement with Peeters they found that a certain length is needed in order to observe charge transfer upon excitation. Thus photoinduced charge transfer was much more pronounced for 6 monomer units, compared to an oligomer with 3 monomer units. Such model studies are important in understanding charge transfer and light harvesting in greater detail. In 2003 Krebs et al. [79] have made an interesting study on a dyad consisting of a poly(terphenylene cyanovinylene) terminated with an ADOTA dye. The dye is a cation and the assembly thus resembles a soap molecule and have the ability to form LB films. By spincoating the dyad on an ITO covered glass substrate, followed by evaporation of Al on the organic layer, the short circuit current of the dyad was 100 fold larger compared to the pure polymer [80].

While some control is introduced by covalently linking the donor and acceptor in polymer/oligomer- $C_{60}$  assemblies the final morphology may suffer from phase separation and clustering of the fullerene (or dye) units (see Fig. 12), which potentially limits efficient charge separation due to low donor/acceptor interfacial area. Also, increased phase separation may disrupt the continuity of the phases and reduce the charge transport properties of the material, due to inefficient hopping between different domains, reducing overall performance. This may be a critical point, since intramolecular charge recombination might occur at a fast rate.

One way to control a bicontinuous phase separation and insure a large interfacial area between donor and acceptor is to covalently graft fullerene moieties onto the donor-polymer backbone (Fig. 12), so-called *double-cable* polymers (due to their p/n-type conduction properties). These assemblies have been intensively investigated in recent years as promising components in PV devices [81], but they are also interesting as components in molecular electronics [82]. The first reports of polymers bearing fullerene on the side chains came in 1996 by Benincori et al. [83] and in the following year by Ferraris et al. [84]. In both cases the polymer was a polythiophene.

The first use of double-cable polymers in PV devices was reported in 2001 by Ramos et al. [85]. Using a PPV derivative with ITO and Al electrodes an  $I_{SC}$  of  $420 \mu\text{A}/\text{cm}^2$  (AM1.5), a  $V_{OC}$  of 830 mV, a relatively low FF of 0.29, and a peak QE of 6% at 480 nm was obtained. Zang [86] has produced solar cells based on polythiophene double cable polymers with a PCE of 0.6% (monochromatic illumination).

Very recently Cravino et al. [87] synthesised a fullerene-thiophene double-cable and used it in a solar cell. However the PV device had limited cell efficiency due to low levels of fullerene content ( $C_{60}$  was attached to 7% of the repeating units). It is important that the fullerene content reaches the percolation threshold to insure efficient electron transport. Thus as the complexity of the designed systems increase the more critical it becomes to optimise design parameters. Even though the



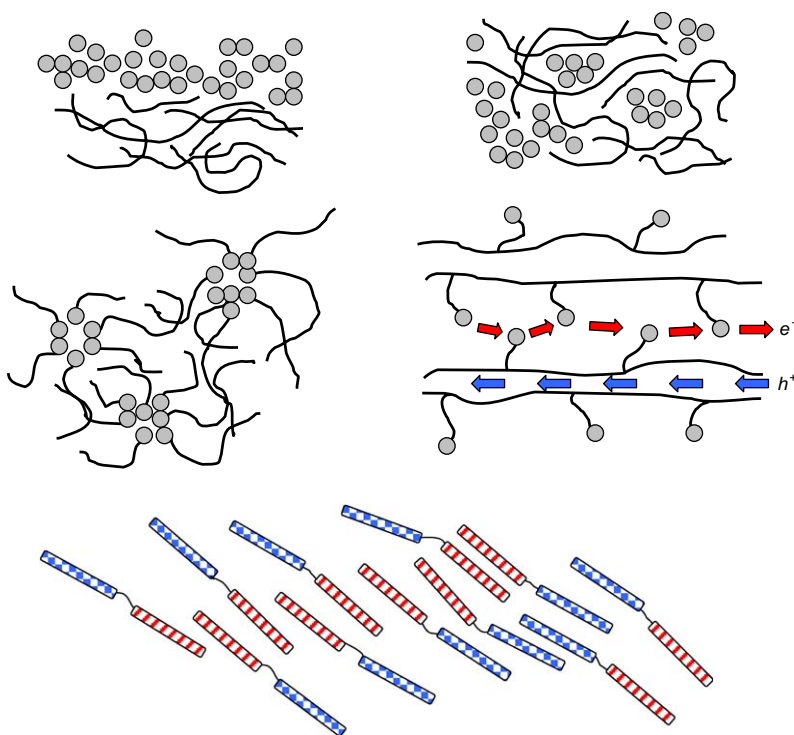


Fig. 12. Different morphologies of heterojunction cells. Top, left: Two-layered structure of fullerenes and polymer chains. Top, right: dispersed heterojunction. Middle, left: fullerenes with polymer chains attached. Middle, right: self-assembled layered structure of double-cable polymers. Bottom: self-assembled layered structure of diblock copolymers. The layered structure of double-cable polymers and diblock copolymers are expected to facilitate efficient electron and hole transport.

synthesised double cable polymers have shown some promising results, we have yet to see the fully optimised double-cable polymers.

An alternative to polymer-fullerene double-cables is block copolymers consisting of a donor and acceptor block. In general block copolymers are known to phase separate and form ordered domains similar to the double-cable polymers. In 2003 Krebs et al. [88] synthesised a block copolymer consisting of an electron acceptor block and an electron donor block. The backbone was polyacetylene, and by using phenyl and pentafluorophenyl as side groups the HOMO and LUMO of the individual blocks could be tuned so that hole or electron conductance is favoured. Recently, Sun [89] has done some preliminary investigations on the use of diblock copolymers in PVs.

## 7. Production issues

Before the potential of plastic solar cells can be exploited there are at least two fundamental problems that must be overcome. First, methods that allow production of

large area devices are needed. Most literature reports employ PV devices with an active area of  $\sim 1 \text{ mm}^2$ . Secondly; the cells have to be protected from oxygen. Typical half-life times of organic PVs are a few hours in air under illumination. Recently, a few reports have emerged that deal with these critical issues. In 1999 Gebeyehu et al. [90] produced rather large solar cells with an active area of  $0.4 \text{ cm} \times 4 \text{ cm}$  by spin coating. Also, Gebeyehu protected the fabricated cells by laminating the cells inside foils. Spin coating becomes less favourable as the area exceeds  $10 \text{ cm} \times 10 \text{ cm}$ . In 2001 Shaheen et al. [91] used screen-printing to produce bulk heterojunction solar cells. However, the produced cells had dimensions of only  $0.12 \text{ cm}^2$ . A PCE of 4.3% was reported for MDMO-PPV:fullerene bulk heterojunctions, which shows that the silk printing technology easily compete with spincoating. Krebs et al. [92] used industrial-scale ( $1 \text{ m}^2$ ) screen-printing equipment to produce large area PV devices (active area  $2 \text{ cm} \times 3 \text{ cm}$ ), and demonstrated that many PV cells of the same size could be connected in series in the same process. The fabrication time is limited by solvent evaporation time, and is complete in approximately 20 s. The cells were laminated in PET using a standard office laminator whereby the aluminium electrode was mechanically protected.

## 8. Outlook

During the last decades organic PV has undergone a major development, with PCE increasing several orders of magnitude. After the breakthrough in 1986 by Tang it seems clear that single component PVs are unable to compete with the heterojunction concept. Effective absorption, charge transfer, electron and hole conduction is simply too much for a single component. When two components are used morphology and miscibility becomes crucial issues. The drive for increasing control has led to the synthesis of covalently linked donor–acceptor systems. The latest and most elaborate include block copolymers and double-cable polymers. Both systems self-assemble into layered structures that aid efficient charge carrier transport. When two-component cells are much more effective than single component cells, it is intriguing to think that the right three-component system may be even more effective. e.g. an extra donor polymer could widen the spectral range of the device as mentioned. Alternatively the extra component could consist of an effective electron transport unit. Of course, more complex systems is much more difficult to synthesise and optimise. However, the elaborate assemblies that have been constructed in recent years are encouraging.

## Acknowledgements

This work was supported by the Danish Technical Research Council (STVF).

## Abbreviations

AM1.5	Air mass 1.5
CB	Conduction band

Chl-a	Chlorophyll-a
CN-PPV	Cyano-PPV
FF	Fill factor
HBC	Hexaphenyl-substituted hexabenzocoronene
$I_{SC}$	Short-circuit current
ITO	Indium-tin-oxide
LED	Light emitting diode
MDMO-PPV	Poly(2-methoxy-5-(3',7'-dimethyl-octyloxy))- <i>p</i> -phenylene)
MEH-PPV	Poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylvinylene)
Pc	Phthalocyanine
PCBM	Phenyl-C61-butyric acid methyl ester
PCE	Power conversion efficiency
PEDOT	Poly(3,4-ethylenedioxythiophene)
PEOPT	Poly(3-(4'-(1'',4'',7''-trioxaoctyl)phenyl)thiophene)
PET	Poly(ethylene terephthalate)
PPV	Poly( <i>p</i> -phenylenevinylene)
PpyV	Poly( <i>p</i> -pyridylvinylene)
PSS	Poly(styrenesulfonate)
PV	Photovoltaics
P3AT	Poly(3-alkylthiophene)
P3HT	Poly(3-hexylthiophene)
P3OT	Poly(3-octylthiophene)
QE	Quantum efficiency
VB	Valence band
$V_{OC}$	Open-circuit voltage

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