

## Review Article

# Recent Advances in Organic Solar Cells

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Solar cells based on organic semiconductors have attracted much attention. The thickness of the active layer of organic solar cells is typically only 100 nm thin, which is about 1000 times thinner than for crystalline silicon solar cells and still 10 times thinner than for current inorganic thin film cells. The low material consumption per area and the easy processing of organic semiconductors offer a huge potential for low cost large area solar cells. However, to compete with inorganic solar cells the efficiency of organic solar cells has to be improved by a factor of 2-3. Several organic semiconducting materials have been investigated so far, but the optimum material still has to be designed. Similar as for organic light emitting devices (OLED) small molecules are competing with polymers to become the material of choice. After a general introduction into the device structures and operational principles of organic solar cells the three different basic types (all polymer based, all small molecules based and small molecules mixed with polymers) are described in detail in this review. For each kind the current state of research is described and the best of class reported efficiencies are listed.

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## 1. INTRODUCTION

Organic photovoltaic devices have gained a broad interest in the last few years due to their potential for large-area low-cost solar cells. From the first reports on molecular thin film devices more than 30 years ago, their power conversion efficiencies have increased considerably from 0.001% in 1975 [1] to 1% in 1986 [2] and more recently to 5.5% in 2006 [3–6]. The progresses in efficiency will possibly make them a competitive alternative to inorganic solar cells in the near future. Different concepts have been published using either small molecules [1–4, 7], conjugated polymers [7–17], combinations of small molecules and conjugated polymers [18–20], or combinations of inorganic and organic materials [21] as the active layer. “Active layer” refers here to the layer in which the majority of the incident light is absorbed and charges are generated. Small molecules and polymers differ in their molecular weights. Commonly, macromolecules with a molecular weight larger than 10 000 amu are called polymers, whereas lighter molecules are referred to as “oligomers” or “small molecules.”

Historically, small molecules were mainly deposited by vacuum deposition techniques since they showed limited solubility in common solvents. In contrast to these small molecule thin films, the preparation of thin polymer layers does not require high vacuum sublimation steps. Large

polymer thin film areas can be deposited by several methods, such as spin-coating, screen printing, spray coating, or ink jet printing, allowing for large-area, ultrathin, flexible, and low-cost devices. Currently, there is a head-to-head race going on between solution processed and sublimed organic solar cells, but the ease of processability may finally tip the balance in favour of polymers or small molecules blended with polymers. Although it should be noted that currently there are some efforts to develop soluble oligomers to allow for cost efficient solution processing techniques, the concept of efficient complete small molecules-based devices prepared from solution processing has yet to be proven.

## 2. DEVICE STRUCTURE AND OPERATION

Organic semiconductors differ from classical crystalline inorganic semiconductors (e.g., silicon) in many fundamental aspects.

First of all, the mobilities of organic semiconductors are several orders of magnitude less than those found in crystalline inorganic semiconductors [22]. Transport processes in organic semiconductors are best described by hopping transport in contrast to the band transport in most crystalline inorganic semiconductors. Even the highest reported hole mobilities ( $\mu_h$ ) for organic semiconductors reach currently only about  $15 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for single crystals of small

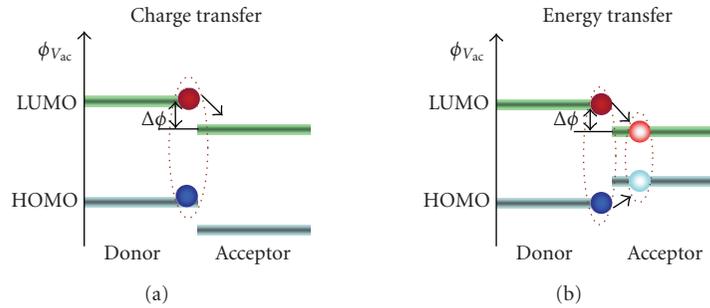


FIGURE 1: The interface between two different semiconducting polymers (D = donor, A = acceptor) can facilitate either charge transfer by splitting the exciton or energy transfer, where the whole exciton is transferred from the donor to the acceptor.

molecules [23] and  $0.6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  for liquid crystalline polymers [24] (silicon:  $\mu_h = 450 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ). Highest electron mobilities ( $\mu_e$ ) for organic materials are typically lower, hovering around  $0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  reaching higher values only in particular TFT structures using highly crystalline small molecules [25, 26] (silicon:  $\mu_e = 1400 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ). The mobility values for amorphous organic materials as used most commonly in organic solar cells are even several magnitudes lower. These low mobilities limit the feasible thicknesses of the organic layer in solar cells to a few hundred nanometres. Fortunately, organic semiconductors are very strong absorbers in the UV-VIS regime. Thus only *ca.* 100 nm thick organic layers are needed for effective absorption.

Second, the exciton binding energy in organic semiconductors is much higher than, for example, in silicon. Upon absorption of a photon of sufficient energy by the organic semiconductor, an electron is promoted into the lowest unoccupied molecular orbital (LUMO), leaving behind a hole in the highest occupied molecular orbital (HOMO). However, due to electrostatic interactions, this electron-hole pair forms a tightly bound state which is called singlet exciton. The exact binding energy of this exciton is still under debate but it is expected to be in a range of 200–500 meV [27, 28]. Hence, the exciton binding energy for organic semiconductors is roughly one order of magnitude larger than for inorganic semiconductors like silicon, where photoexcitations typically lead directly to free carriers at room temperature. The thermal energy at room temperature ( $\sim 25 \text{ meV}$ ) is not sufficient to efficiently generate free charge carriers in organic materials by exciton dissociation, even at typical internal electric fields ( $\sim 10^6\text{--}10^7 \text{ V/m}$ ) [29]. For example, in the widely used Poly(2-methoxy-5-(2'-ethyl-hexyloxy)-p-phenylene vinylene) (MEH-PPV) [30] experiments revealed that only 10% of the excitons dissociate into free carriers in a pure layer [31], while the remaining excitons decay via radiative or nonradiative recombination pathways. Thus, the energy efficiencies of single-layer polymer devices remain typically below 0.1% [27, 32].

The most important discovery on the route to high-efficiency organic solar cells was the finding that solar cells containing a heterojunction between hole and electron accepting organic materials exhibited performances far superior to single component devices [2, 8–10]. Using the het-

erojunction approach, photogenerated excitons (bound electron-hole pairs) in the polymer layer can be efficiently dissociated into free carriers at the interface, whereas in single component devices most excitons recombine after a short time. The charge separation occurs at the interface between donor and acceptor molecules, mediated by a large potential drop. After photo-excitation of an electron from the HOMO to the LUMO, the electron can jump from the LUMO of the donor (the material with the higher LUMO) to the LUMO of the acceptor if the potential difference  $\Delta\Phi$  between the ionisation potential of the donor and the electron affinity of the acceptor is larger than the exciton binding energy (see Figure 1). However, this process, which is called photoinduced charge transfer, can lead to free charges only if the hole remains on the donor due to its higher HOMO level. In contrast, if the HOMO of the acceptor is higher, the exciton transfers itself completely to the material of lower-band gap accompanied by energy loss.

For efficient exciton dissociation at the heterojunction, the donor and acceptor materials have to be in close proximity. The optimum length scale is in the range of the exciton diffusion length, typically a few tens of nanometres. On the other hand, the thickness of the active layer should be comparable to the penetration length of the incident light, which for organic semiconductors is typically 80–200 nm.

A heterojunction can be realised in several ways (see Figure 2). The most straightforward approach is the preparation of a bilayer by subliming or by spin-coating a second layer on top of the first, resulting in a more or less diffused bilayer structure [11, 33, 34]. If polymers are used and both materials are soluble in the same solvents, laminating techniques can be used [10, 35]. This bilayer geometry guarantees directional photoinduced charge transfer across the interface. Since both types of charge carriers travel to their respective electrodes in pure *n*-type or *p*-type layers, the chances for recombination losses are significantly reduced. However, the interfacial area and thus the exciton dissociation efficiency are limited. Higher interfacial areas and thus improved exciton dissociation efficiencies can be achieved if layers containing both the electron donor and electron acceptor in a mixture are prepared. These so-called bulk heterojunctions can be deposited either by cosublimation of small molecules or by spin-coating mixtures of polymers.

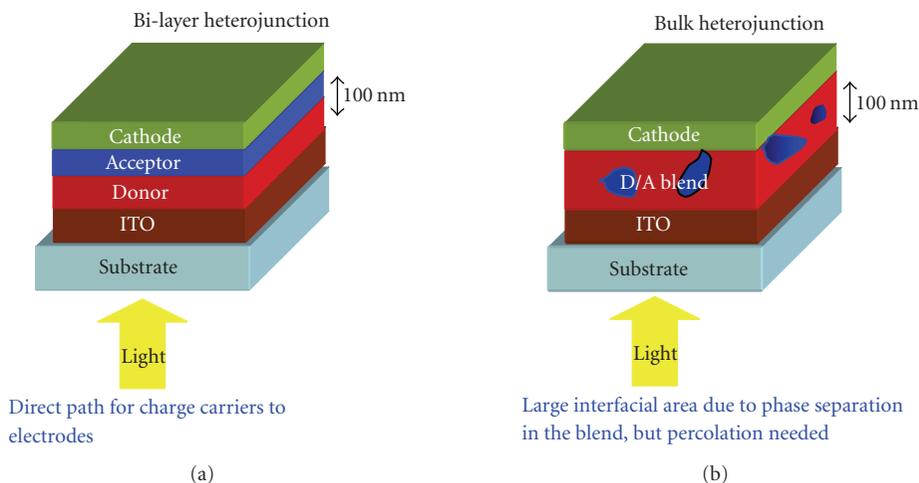


FIGURE 2: Two approaches to heterojunction solar cells.

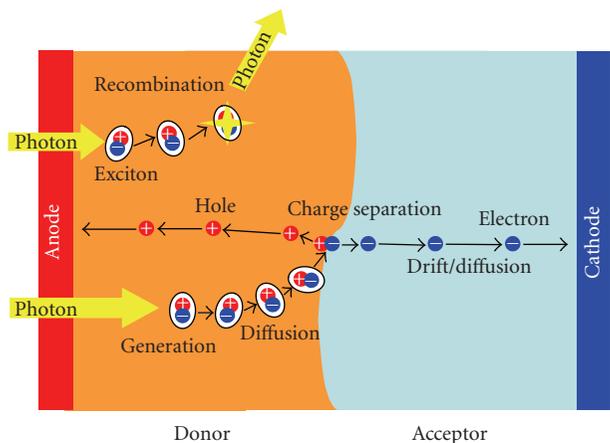


FIGURE 3: Principle of charge separation in a solar cell.

The drawback of the bulk heterojunction structure is that a percolating pathway for the hole and electron transporting phase to the electrodes is needed in order that the separated charge carriers can reach their corresponding electrodes.

If the individual layer thicknesses (in case of a bilayer structure) or the phase separated domains (in case of a blend layer) is larger than the exciton diffusion length, then most excitons will recombine (Figure 3). If, however, the excitons are generated in close proximity to an interface, they have a chance to be separated into free charge carriers which may diffuse or drift to the corresponding electrodes. The overall efficiency of this process is described by the incident photon to converted electron efficiency (IPCE). The IPCE is calculated by the number of electrons leaving the device under short circuit condition per time and area divided by the number of photons incident per time and area:

$$\text{IPCE} = \frac{\# \text{ extracted electrons}}{\# \text{ incident photons}}. \quad (1)$$

Note that the IPCE is a measure of the external quantum efficiency, meaning that losses due to reflection at the surface or transmission through the device are included in the IPCE value. Subtracting these two loss channels would lead to the internal quantum efficiency, which is, however, rarely used to compare solar cells.

Solar cells are further characterised by measuring the current-voltage  $I(V)$  curve under illumination of a light source that mimics the sun spectrum. A typical current-voltage  $I(V)$  curve of a polymer solar cell is shown in Figure 4. Since organic semiconductors show very low intrinsic carrier concentration, the metal-insulator-metal (MIM) [36] model seems to be best suited to explain this characteristic. The characteristic points used to characterise a solar cell are labelled in Figure 4. In addition, for each of these points, the energy diagram for a single-layer cell with an indium tin oxide (ITO) anode and aluminium cathode is displayed.

- The current delivered by a solar cell under zero bias is called short circuit current ( $I_{sc}$ ). In this case, exciton dissociation and charge transport is driven by the so-called built-in potential. In the MIM picture, this potential is equal to the difference in work function ( $W_f$ ) of the hole- and electron-collecting electrodes. For polymer solar cells, the transparent ITO electrode is often chosen ( $W_{f,ITO} = 4.7 \text{ eV}$ ) in combination with a low work function material ( $W_{f,Ca} = 2.87 \text{ eV}$ ,  $W_{f,Mg} = 3.66 \text{ eV}$ ,  $W_{f,Al} = 4.24 \text{ eV}$ ) [37] as counter-electrode to achieve a high internal field [38–41]. For example, the difference in work functions between ITO and Ca is approximately 2 eV.
- The voltage where the current equals zero is called open circuit voltage ( $V_{oc}$ ). In the MIM picture this situation is described by the case where the band is flat, since the applied voltage equals the difference in the work function of the electrodes. (Note that diffusion effects are neglected in this simplified picture.)
- When  $V > V_{oc}$ , the diode is biased in the forward direction. Electrons are now injected from the low work

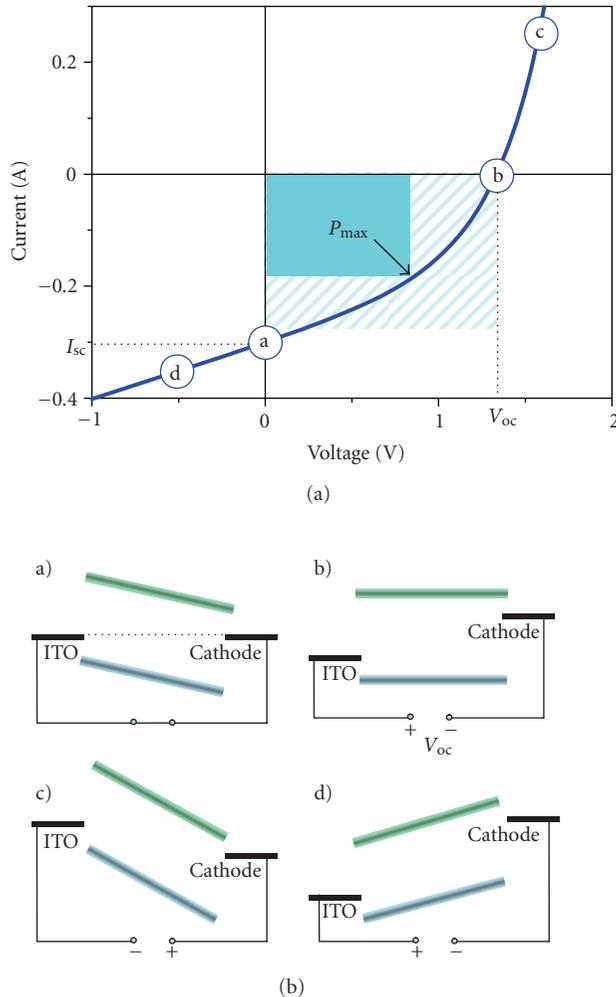


FIGURE 4: Current (voltage) characteristics of a typical organic diode shown together with the metal-insulator-metal (MIM) picture for the characteristic points. (a) Short circuit condition. (b) Open circuit condition. (c) Forward bias. (d) Reverse bias.

function electrode into the LUMO and holes from the high work function electrode into the HOMO of the organic layer, respectively.

- (d) When  $V < 0$ , the diode is driven under a reverse biased condition the solar cells works as a photodiode. The field is higher than in (a) which often leads to enhanced charge generation and/or collection efficiency.

The point where the electrical power  $P = I \times V$  reaches the maximum value represents the condition where the solar cell can deliver its maximum power to an external load. It is called the maximum power point. The ratio of this maximum electrical power  $P_{max}$  to the product of the short circuit current and the open circuit voltage is termed the fill factor (FF):

$$FF = \frac{P_{max}}{I_{sc} \times V_{oc}}. \quad (2)$$

Ideally, the fill factor should be unity, but losses due to transport and recombination result in values between 0.2–0.7 for

organic photovoltaic devices. As an example, a constant slope of the  $I(V)$  characteristic corresponds to  $FF = 0.25$ .

The photovoltaic power conversion efficiency ( $\eta$ ) is then calculated for an incident light power  $P_{light}$ :

$$\eta = \frac{I_{sc} \times V_{oc} \times FF}{P_{light}}. \quad (3)$$

### 3. SMALL MOLECULE-BASED SOLAR CELLS

The first efforts to fabricate organic photovoltaic devices using small molecules date back to 1975, however efficiencies did not reach more than 0.001% at that time. The work of Tang [2] in 1986 is commonly cited as the groundbreaking discovery that sparked the current interest in the field. Using copper phthalocyanine (CuPc) as the electron donor and a perylene derivative, 3,4,9,10-perylene tetracarboxylic bis-benzimidazole (confusingly referred to as PTCBI, PV, or PBI), as the electron acceptor in a simple bilayer structure, a power conversion efficiency of 1% was reported. The open circuit voltage reached 450 mV and the fill factor of 65% indicated excellent charge transport. For the past 20 years, CuPc has been the donor of choice in most small molecule solar cells due to its high stability, high mobility, and widespread availability. The device physics of small molecule solar cells is described in a review paper of Peumans et al. [42]. The original Tang structure was improved by cosublimation of CuPc and PTCBI leading to a blend structure followed by an annealing step [43]. Due to the improved interfacial area, a higher efficiency ( $\eta = 1.5\%$ ) was obtained. Later in 2005, a novel deposition method called vapour phase deposition (VPE) helped to increase the efficiency for this system further since a highly intermixed donor-acceptor interface could be obtained [44, 45]. The interfacial area was increased by a factor of four compared to a bilayer structure while still maintaining  $n$ -type and  $p$ -type percolating pathways, and a power conversion efficiency of 2.2% was reported [44, 45].

Although C60 (fullerene) does not show strong absorption properties in the visible region, its much larger exciton diffusion length compared to PTCBI is favorable to achieve higher efficiencies. Devices based on incorporating CuPc:C60 bulk heterojunctions reached power conversion efficiencies of up to 5% [3, 6, 46]. The highest efficiency for an organic solar cell so far was reached by Xue et al. [4] for a stacked solar cell comprising two CuPc:C60 bulk heterojunction cells separated via a layer of silver nanoclusters, which served as a charge recombination layer.

The drawback of using CuPc as an electron donor is that only relative small open circuit voltages ( $<0.6$  V) can be reached with perylenes or fullerenes as acceptors, since a large portion of photon energy is wasted when the photo-generated electron on CuPc transfers to C60 or perylene. The open circuit voltage could be increased by using boron subphthalocyanine (SubPc) instead of CuPc [47]. The HOMO level of SubPc (HOMO:  $-5.6$  eV) is shifted by approximately 400 meV compared to CuPc (HOMO:  $-5.2$  eV). As a result, the  $V_{oc}$  increased by the same amount to nearly 1 V. The SubPc:C60 device reached a power conversion efficiency of 2.1% leaving room for further improvement. If CuPc is

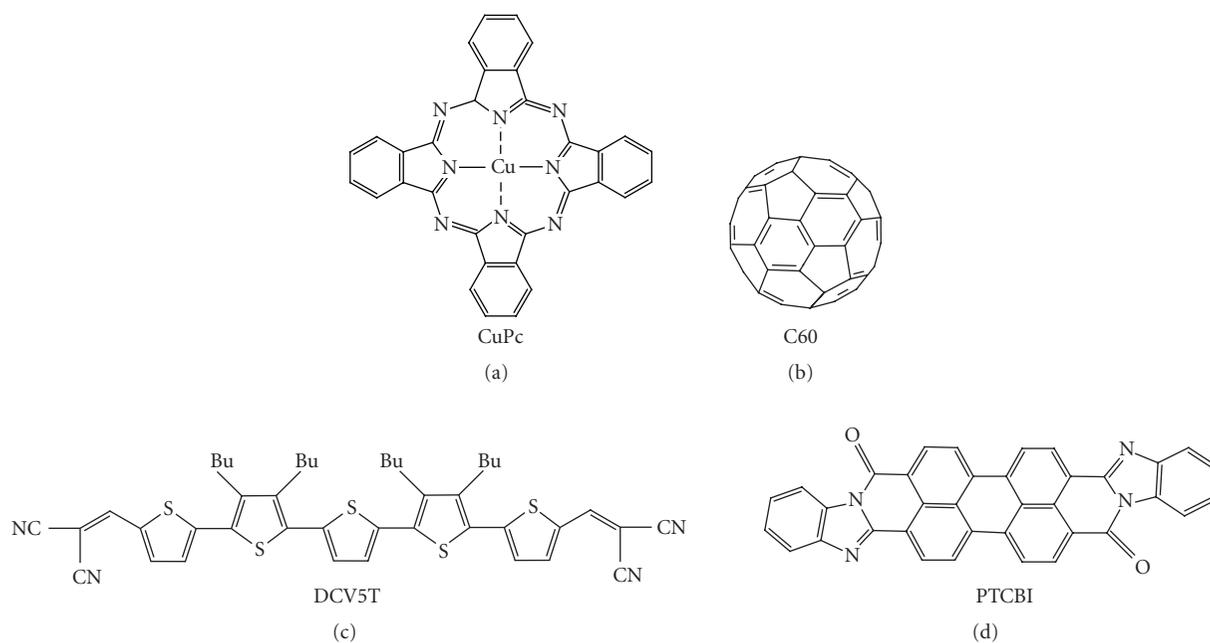


FIGURE 5: Chemical structures of most important small molecules used for organic solar cells.

substituted by tin(II) phthalocyanine (SnPc), the photoreponse increases from 800 nm to nearly 1000 nm [48]. However, the hole mobility in SnPc is very low limiting the device power conversion efficiency to around 1%.

A promising alternative to CuPc or phthalocyanines in general was presented by Schulze et al. [49] using  $\alpha,\alpha$ -bis(2,2-dicyanovinyl)-quinquithiophene (DCV5T) as electron donor in combination with C60 (see Figure 5 for the chemical structure). Since the HOMO level of DCV5T is sufficiently low ( $-5.6$  eV), open circuit voltages of 1 V could be obtained. The IPCE reached values as high as 52% leading to a high overall efficiency of 3.4%. In another approach, a glass forming thienylenevinylene triphenylamine [50] was used in combination with C60 for devices with open circuit voltages as high as 1.15 V. However, the power conversion efficiency was limited to 1.9% by its small fill factor.

An overview of small molecules solar cells can be found in Table 1.

## 4. POLYMER-BASED SOLAR CELLS

### 4.1. Introduction

For most of their history, polymers have been considered as electrical insulators. It was the discovery in 1977 by the group of Heeger, Shirakawa, and MacDiarmid that doped polyacetylene could achieve metallic conductivity which initiated intense research on conjugated polymers [53]. The work of these three pioneers was later honoured with the Nobel Prize in Chemistry in 2000 [54–56]. From this earlier work, it was not till the late 1990s that highly purified and soluble conjugated polymers became widely available. While initial research was concentrated mostly on improving the conductivity of conjugated polymers by chemical doping, serious

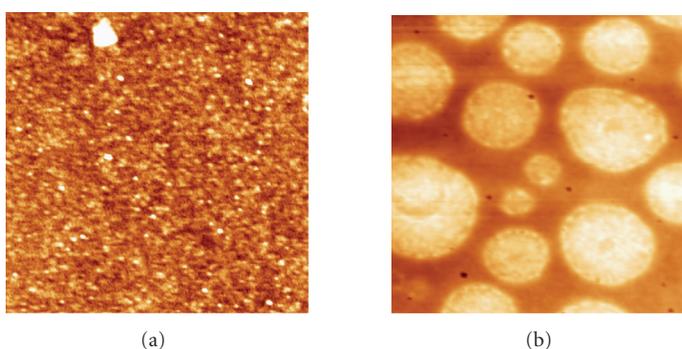
interest also grew in intrinsically semiconducting and highly soluble polymers. From then on, the application of conjugated polymers for a wide range of semiconductor devices such as light emitting diodes (LEDs) [30, 57], solar cells, and thin film transistors (TFTs) [58] was systematically investigated.

The conjugated systems of these polymers usually consist of chains and rings of carbon atoms in  $sp^1$  and  $sp^2$  hybridisation, leading to a framework of alternating double- or triple- and single-bonds. In this representation, single bonds are  $\sigma$ -bonds, and double bonds contain a  $\sigma$ -bond and a  $\pi$ -bond. However, in reality, the  $\pi$ -electrons are not constricted to the individual bonds, but rather are delocalised over the entire molecule. Thus conjugated polymers can be regarded as quasi one-dimensional semiconductors. The extent of the  $\pi$ -orbital overlap together with the bond alternation defines the band gap.

Layers containing a mixture of an electron donating and an electron accepting polymer (so-called polymer blends) can be prepared by spin-coating from a solution containing both polymers in the same solvent [8, 13, 14]. Since the entropy of mixing is generally low for polymers, solid polymer blends tend to phase-separate, leading to a distributed bulk heterojunction. A large donor-acceptor interface is formed without any additional processing steps. If donor and acceptor components are intimately mixed such that the length scale of the phase separation is in the range of the exciton diffusion length ( $<10$  nm), nearly all excitons can be separated. Moreover, when a thin layer of immiscible polymers is deposited from solution, the resulting morphology strongly depends on various parameters such as the individual solubility of the polymers in the solvent, the interaction with the substrate surface, the layer thickness, the deposition method, and the drying process [59–65]. Therefore, the adjustment

TABLE 1: Best in class solar cells: small molecule-based solar cells.

Donor	Acceptor	$\eta$	$V_{oc}$	FF	IPCE	Reference
CuPc	C60	5.7%	1.0 V	59%	NA	Xue et al. [4]
CuPc	C60	5.0%	0.6 V	60%	64%	Xue et al. [6]
MeO-TPD, ZnPc (stacked)	C60	3.8%	1.0 V	47%	NA	Drechsel et al. [51]
CuPc	C60	3.5%	0.5 V	46%	NA	Uchida et al. [46]
DCV5T	C60	3.4%	1.0 V	49%	52%	Schulze et al. [49]
CuPc	PTCBI	2.7%	0.5 V	58%	NA	Yang et al. [44, 45]
SubPc	C60	2.1%	1.0 V	57%	NA	Mutolo et al. [47]
MeO-TPD, ZnPc	C60	2.1%	0.5 V	37%	NA	Drechsel et al. [51]
TDCV-TPA	C60	1.9%	1.2 V	28%	NA	Cravino et al. [50]
Pentacene on PET	C60	1.6%	0.3 V	48%	30%	Pandey and Nunzi [52]
SnPc	C60	1.0%	0.4 V	50%	21%	Rand et al. [48]

FIGURE 6: The AFM height images (size  $2.8 \times 2.8 \mu\text{m}$ ) reveal different phase-separated morphologies for blends of PFB and F8BT (1 : 1 ratio by mass) spin-coated from (a) chloroform and (b) xylene.

of the length scale of phase separation in thin layers is often arbitrary and based on trial-and-error.

The tendency for demixing lies in the macromolecular nature of the polymers. One driving force for phase separation is the different polarity or polarisability of the polymer repeat units making the contact between identical polymers energetically favourable. However, many dissimilar molecules, such as water and ethanol, mix in any ratio. For these small molecules, the increase in entropy upon mixing overcomes the enthalpic interaction. To describe the mixing properties of a pair of polymers, the Flory and Huggins theory can be applied [66]. However, the real situation for thin blend films is much more complicated since the interactions of the two polymers with the surface and the substrate as well as the influence of the solvents and the solvent evaporation rate have to be taken into account [61, 67]. Therefore, the interplay of mixing and dewetting makes the prediction or even control of the morphology difficult.

The best studied conjugated polymer system so far is the blend of PFB [poly(9,9-dioctylfluorene-2,7-diyl-*co*-bis- $N,N'$ -(4-butylphenyl)-bis- $N,N'$ -phenyl-1,4-phenylenediamine)] [68] and F8BT [poly(9,9-dioctylfluorene-2,7-diyl-*co*-benzothiadiazole)] [69]. The correlation between layer composition, morphology, and photovoltaic properties for devices prepared from various organic solvents has been studied in detail for this model system [35, 64, 70–75]. F8BT has a LUMO of  $-3.2 \text{ eV}$  and an HOMO of  $-5.9 \text{ eV}$ , whereas

the LUMO and HOMO energy levels of PFB are  $-1.9 \text{ eV}$  and  $-5.1 \text{ eV}$ , respectively. Apparently, there exists a relatively large offset of  $1.3 \text{ eV}$  for the LUMO levels and of  $0.8 \text{ eV}$  for the HOMO levels, which guarantees very efficient electron dissociation at the interface. Investigations concerning its blend morphology in relation to the solar cell properties revealed that the length scale on which phase separation occurs strongly depends on the solvent used, on the interaction with the substrate, and on the deposition conditions. For example, spin-coating a 1 : 1 PFB:F8BT solution in xylene leads to phase separation at the micrometre scale whereas the length scale of the phase separation for films prepared from chloroform is less than  $100 \text{ nm}$ , as shown in the atomic force microscopy (AFM) image in Figure 6. This phenomenon was due to the more rapid evaporation of the low boiling point solvent chloroform compared to xylene which prevented large-scale reorganisation and diffusion of the polymer chains and thus leads to a finer scale of the phase separation. Heating of the substrate during spin-coating leads to a phase separation on an even smaller scale due to the more rapid evaporation, thus freezing out the onset of spinodal composition [70]. Interestingly the phase-separated morphology of the PFB:F8BT blend layer spin-coated from xylene revealed a substructure at the nanometre scale in addition to micrometre sized features.

Based on AFM and Raman microscope investigations, it was proposed that one phase is composed of almost equal

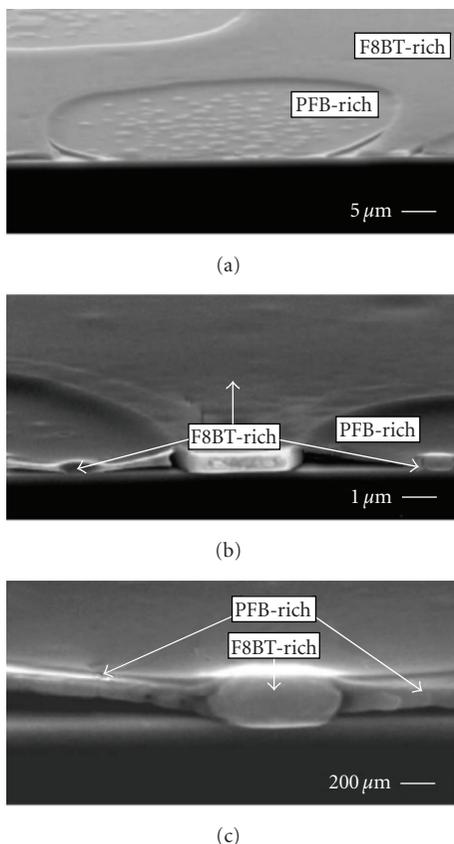


FIGURE 7: Environmental scanning electron microscopy (ESEM) images of the cross-section of an F8BT:PFB film spin-coated from a xylene solution at magnifications of (a) 4528 $\times$ , (b) 14 622 $\times$ , and (c) 58 489 $\times$  taken from [74].

proportions of PFB and F8BT whereas the second is F8BT rich and consists of 80% F8BT and only 20% PFB [74, 76]. This second phase was also found to be of larger thickness. Further analysis revealed that the blend layers can be described as PFB-rich cylinders surrounded by an F8BT-rich matrix as shown in Figure 7.

As expected, the solar cell properties depended strongly on preparation conditions. For the PFB:F8BT (1 : 1) blends the IPCE was *ca.* 2 times higher for layers spin-coated from chloroform (IPCE = 2–4.5%) solution compared to xylene solutions (IPCE = 0.5–1%) [70, 75]. This was attributed to a larger phase separation for the layers prepared from xylene. In subsequent studies, photovoltaic devices were studied with varying ratios of PFB and F8BT in layers prepared from xylene solution. It was found that the phase separation and the external quantum efficiencies were strongly dependent on the layer composition. Highest efficiencies were reported for devices containing 5 times more of the electron transporting F8BT than PFB.

In a more recent study investigating the photocurrent generation with near field photoconductivity measurements, it was found that the photocurrent is not increased at the interface of both domains. It was rather proposed that pho-

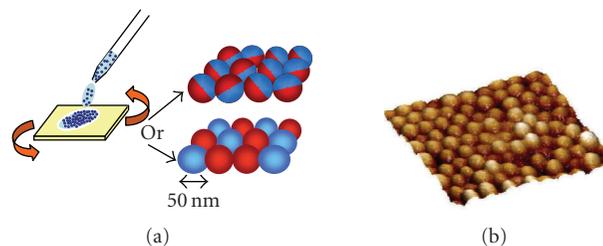


FIGURE 8: The nanoparticles allow for the preparation of nanostructured layers of conjugated polymers as shown in the AFM image on the right for particles of 50 nm diameter.

tocurrent is generated in both phases, while the phase with the smaller height seems to be more efficient [72, 77].

In conclusion, these studies clearly showed that the preparation conditions as well as the layer composition have a profound and, in part, unpredictable effect on the photovoltaic properties of the device. Moreover, since the meso-scale phase separation has been shown to depend strongly on the blend ratio, an investigation for a given length scale of phase separation but different blend ratios was not possible by using layers spin-coated from organic solvents. A method for a defined control of the phase separation formed in polymer blends would hence be highly desirable.

The most straightforward approach for a defined phase separated D-A polymer nanostructure would be to use linear block copolymers [78]. However, the drawback of this approach is that both components, A and D, with their different chemical and electronic structures have to be connected via a covalent bond, which limits the availability of possible A-D pairs. In fact, only a few examples of block copolymers containing two semiconducting polymers have been reported and solar cell efficiencies are still quite low [79–83]. Another method to obtain a nanostructured conjugated polymer layer with defined structure size in the 40–100 nm range is the nanoparticle approach as shown in Figure 8 [84–88]. Here in the first step, solid polymer nanoparticles with well-controllable size are prepared via the formation of a miniemulsion of the polymer solution in water. In addition, blend nanoparticles can be prepared by starting with a solution of both polymers. Spectroscopic investigations revealed that the latter approach indeed leads to nanospheres containing both polymers in each particle. The nanoparticles approach allows for the preparation of blend layers in two ways: either a mixture of nanoparticles of pure polymers (nanoparticle blend) or the blend nanoparticles are spin-coated on a substrate.

#### 4.2. Polymer solar cell devices

The first report on all polymer solar cells with moderate efficiencies dates back to 1995 with two independent reports from Yu and Heeger [9] and Halls et al. [89]. In both cases, MEH-PPV (Poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene-vinylene)) was used as the electron donor and CN-PPV (cyano-para-phenylenevinylene) as the electron acceptor. External quantum efficiencies were still low

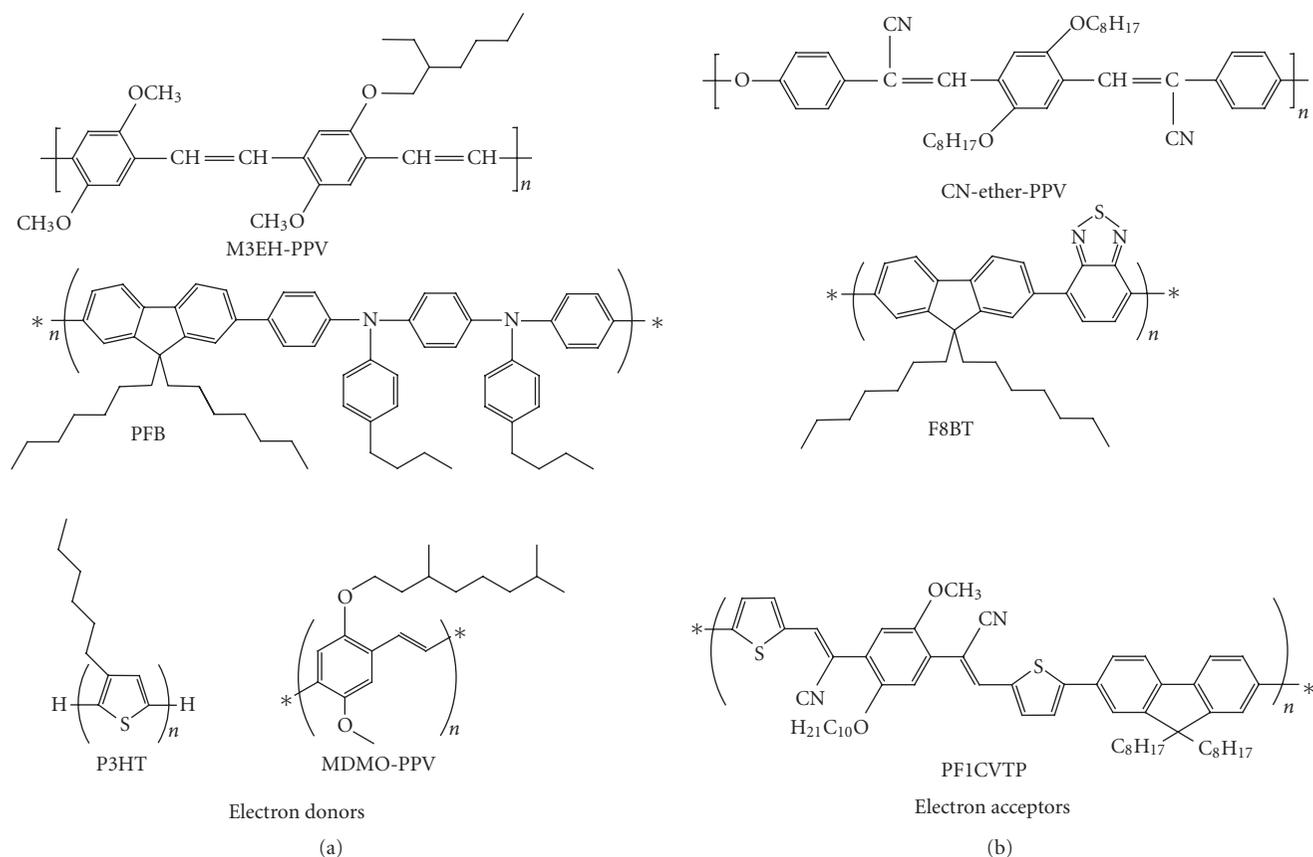


FIGURE 9: Chemical structures of conjugated polymers used in organic solar cells.

(around 5-6%), most likely due to the nanomorphology not being optimized. A big efficiency jump was obtained after the CN-PPV was modified by introduction of an ether group to increase solubility [90]. Using the copolymer M3EH-PPV (see Figure 9 for the chemical structures) as donor and CN-Ether-PPV as acceptor, Breeze et al. [91] demonstrated in 2000 external quantum efficiencies of 24% corresponding to 0.6% power conversion efficiency. Even higher efficiencies were published by the same authors in 2004 [12]. In that work, it was demonstrated for the first time that 1% power conversion efficiency could be reached in a polymer-polymer blend device. The open circuit voltage was 1 V, however the low fill factor of 25% left room for further improvement. The highest power conversion efficiency so far for solar cells composed of polymer blend was reached in 2005 by Kietzke et al. [92] using the same materials coupled with improved processing. It could be shown that annealing the layer leads to an improvement of the efficiency by a factor of two compared to the prepared layers [93]. An open circuit voltage of 1.36 V and a white light conversion efficiency of 1.7% were obtained. The fill factor reached 35% indicating improved charge transport. Photophysical studies on PPV-based blends revealed that the exciplex formation in this system might have been a major loss factor [92-94].

Recently Koetse et al. [95] reported solar cells based on MDMO-PPV as donor and a novel acceptor copolymer

PF1CVTP. A high quantum efficiency of 42% was achieved. However, the power conversion efficiency could not set a new record, since the conversion efficiency decreased at higher light intensities typical for solar illumination.

Several approaches have also been investigated for polymer bilayer structures. Alam and Jenekhe [96] reported devices based on insoluble PPV as donor and BBL as electron acceptor. BBL was deposited from methanesulfonic acid. The devices showed extremely high quantum efficiencies of up to 62%. Unfortunately, the device efficiency decreased at higher light intensities dramatically. The power conversion efficiency dropped from record breaking 5% at very low light intensities to 1.5% under standard 1 sun. Similar efficiencies could be reached for M3EH-PPV as donor and CN-Ether-PPV as acceptor.

Polymer solar cells have much room for optimization (the characteristic parameters of the best of their kind are in Tables 2 and 3). Both the fill factor and the quantum efficiency need to be doubled in order to reach 6-7% power conversion efficiency. Recent experiments indicated that the device performance is currently limited largely by the low dissociation efficiency of the photogenerated excitons into free charge carriers. Even after dissociation, the electrons tend to localise near the heterointerface in the electron accepting polymers due to their amorphous nature. To proceed to higher efficiencies more crystalline electron acceptor polymers with larger electron mobilities are needed [93].

TABLE 2: Best in class solar cells: polymer-polymer (blend) solar cells.

Donor	Acceptor	$\eta$	$V_{oc}$	FF	IPCE	Reference
M3EH-PPV	CN-Ether-PPV	1.7%	1.4 V	35%	31%	Kietzke et al. [92]
MDMO-PPV	PF1CVTP	1.5%	1.4 V	37%	42%	Koetse et al. [95]
M3EH-PPV	CN-Ether-PPV	1.0%	1.0 V	25%	24%	Breeze et al. [12]

TABLE 3: Best in class solar cells: polymer-polymer (bilayer) solar cells.

Donor	Acceptor	$\eta$	$V_{oc}$	FF	IPCE	Reference
PPV	BBL	1.5%	1.1 V	50%	62%	Alam and Jenekhe [96]
MDMO-PPV:PF1CVTP	PF1CVTP	1.4%	1.4 V	34%	52%	Koetse et al. [95]
M3EH-PPV	CN-Ether-PPV	1.3%	1.3 V	31%	29%	Kietzke et al. [97]
MEH-PPV	BBL	1.1%	0.9 V	47%	52%	Alam and Jenekhe [96]
M3EH-PPV	CN-PPV-PPE	0.6%	1.5 V	23%	23%	Kietzke et al. [97]

## 5. BLENDS OF POLYMER AND SMALL MOLECULES

After the discovery in 1991 [98] that the transfer of photoexcited electrons from conjugated polymers to fullerenes is very efficient, it took 10 years more until organic solar cells reaching 2.5% efficiency were reported [65]. Since C60 showed a strong tendency to crystallise in the polymer matrix, a new fullerene derivative called PCBM was developed. The increased solubility of PCBM resulted in the formation of smaller crystallites in the blend. It was a poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV):PCBM (weight ratio 1 : 4) device that eventually reached the 2.5% power conversion efficiency benchmark. Of crucial importance was the type of solvent used because of the different nanostructures formed for the same reasons explained in the previous paragraph for polymer-polymer blends. In the following years, PCBM-based solar cells attracted much attention with more than 200 refereed papers published on this topic. Regioregular P3HT (poly-3-hexylthiophene) soon became the material of choice as electron donor, as P3HT is able to absorb photons at longer wavelength compared to PPV derivatives. In addition a more balanced weight ratio of P3HT and PCBM (1 : 0.8) was sufficient to obtain high efficiencies. Due to the efforts of several groups worldwide [5, 13, 14, 99–103], a record power conversion efficiency of 5% could be reached in 2005 [5]. The most important finding was that slow drying of the P3HT:PCBM layer leads to increased mobilities, thus preventing the build up of space charge inside the device [104–110]. Also, the degree of regioregularity, the polydispersities, and molecular weights of P3HT seems to have an important influence on the device efficiency [111]. Highest efficiencies were recorded for P3HT with very high regioregularity due to improved molecular order which translates to higher mobilities [112]. For an excellent summary of the device physics PCBM:polymer solar cells see Blom et al. [113].

As shown in Figure 10, from 2001 to 2005 the number of published papers on PCBM-based solar cells correlate well with the published efficiencies obtained with the same year. However, it seems that the reported efficiencies stagnated in 2005. The reason is that the internal quantum efficiency for

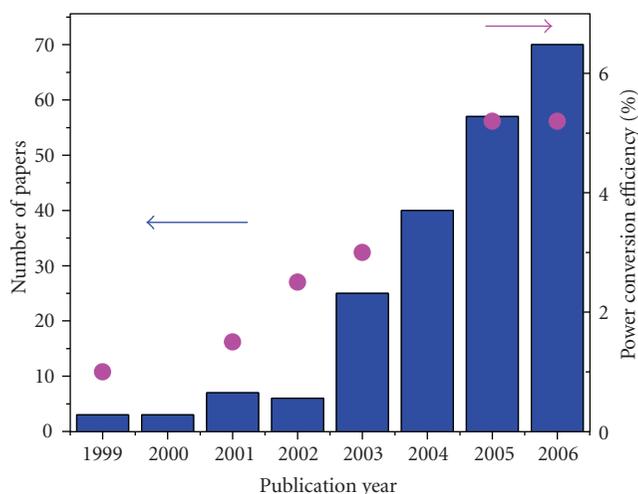


FIGURE 10: Correlation between reported solar cell efficiencies for polymer:PCBM blends and a number of papers published in this field. The information was obtained by searching ISI web of knowledge on 16.12.2006 for the terms “polymer” and “PCBM.”

the 5% efficient P3HT:PCBM devices is already nearly unity, leaving little space for further optimisation of this system.

Two main factors limit the device efficiency of the P3HT:PCBM system to 5%. First, the open circuit voltage reaches only 0.7 V, which is quite small compared to the bandgap of P3HT (1.9 eV). A large amount of energy is lost when the photoexcited electron transfers from the LUMO of P3HT (around  $-3$  eV) to the LUMO of PCBM ( $-3.8$  eV).

Recently it was pointed out that 10% efficiency may be in reach with polymer:fullerene blends if the relative energy levels could be better aligned [108, 130]. Either the PCBM LUMO level had to be raised to about 3.3 eV or both the LUMO and HOMO of the donor polymer had to be lowered sufficiently assuming that all other parameters remained unchanged.

Recently, a few P3HT-based solar cells where PCBM was replaced by an alternative electron acceptor have been reported (compare Table 5). Unlike PCBM, electron acceptors

TABLE 4: Best in class solar cells: blends of polymers and fullerene derivatives.

Donor	Acceptor	$\eta$	$V_{oc}$	FF	IPCE	Reference
P3HT	PCBM	5.0%	0.6 V	68%	NA	Ma et al. [114]
P3HT	PCBM	4.9%	0.6 V	54%	NA	Reyes-Reyes et al. [5]
P3HT	PCBM	4.4%	0.9 V	67%	63%	Li et al. [115]
MDMO-PPV	PC <sub>71</sub> BM	3.0%	0.8 V	51%	66%	Wienk et al. [17]
MDMO-PPV on PET	PCBM	3.0%	0.8 V	49%	NA	Al-Ibrahim et al. [116]

TABLE 5: Best in class solar cells: blends of polymers and nonfullerene-based oligomers.

Donor	Acceptor	$\eta$	$V_{oc}$	FF	IPCE	Reference
P3HT	V-BT	0.45%	0.7 V	37%	16%	Shin et al. [117, 118]
P3HT	PDI	0.19%	0.4 V	43%	7%	Li et al. [119]
P3HT	PDI-C8	0.18%	0.4 V	38%	19%	Shin et al. [120]
P3HT	BT1	0.07%	1.0 V	19%	NA	Camaioni et al. [121]

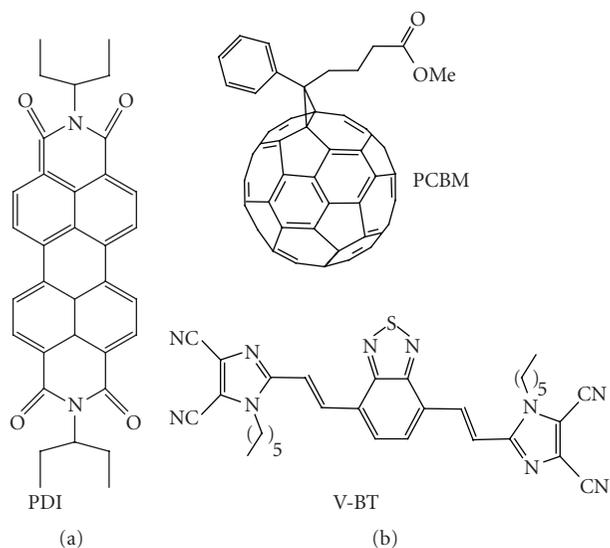


FIGURE 11: Soluble small molecules used in blends with conjugated polymers.

such as soluble perylene derivatives are advantageous as they absorb visible light strongly. However, reported efficiencies are currently a factor of 10 lower compared to P3HT:PCBM devices. The highest efficiency was achieved using a vinazene derivative (V-BT) (see Figure 11 for the chemical structure) as electron acceptor ( $\eta = 0.5\%$ ). Since not much work has been done so far on alternative acceptors, it is expected that higher efficiencies will be reported in the future.

The second factor limiting the efficiency of P3HT:PCBM cells is the absorption range of P3HT. P3HT absorbs visible light until about 650 nm, meaning that most of the red portion of the visible spectrum and all infrared photons cannot be harvested. Efforts have been undertaken to increase the absorption range by synthesizing novel low-bandgap polymers. Contrary to expectations, the low bandgap polymers synthesized with bandgaps as low as 1 eV did not result in devices with higher efficiency (see Table 6). One major problem

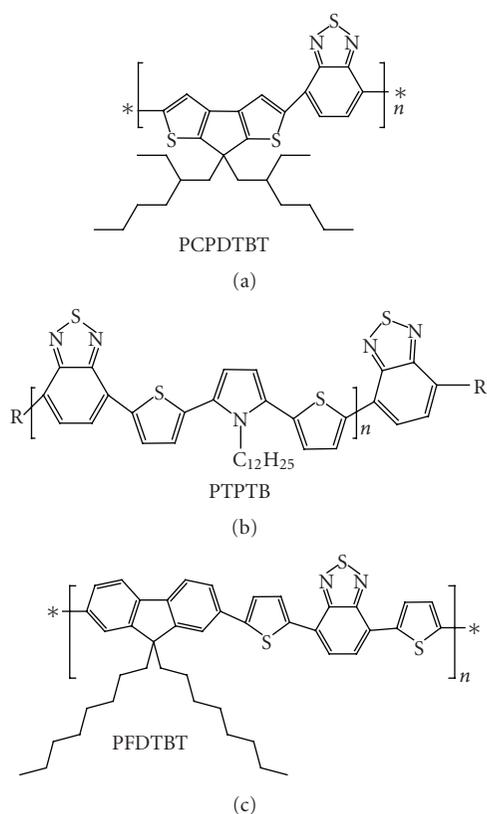


FIGURE 12: Low-bandgap polymers based on benzothiadiazole units.

with these low band-gap polymers was their low mobilities, which limited the efficiency. The mobility plays an important role especially for low-bandgap polymers, since at longer wavelength much thicker layers are needed for absorption of sunlight and the build up of a space charge has to be prevented to achieve high fill factors and short circuit voltages.

The first milestone of a 1% efficient low-bandgap solar cell was finally achieved for a polymer consisting of alternating electron-rich N-dodecyl-2,5-bis(2'-thienyl) pyrrole

TABLE 6: Best in class solar cells: blends of low-bandgap polymers and nonfullerene derivatives.

Donor	Acceptor	$\eta$	$V_{oc}$	FF	IPCE	Reference
PCPDTBT	PC <sub>71</sub> BM	3.2%	0.7 V	47%	38%	Mühlbacher et al. [122]
PCPDTBT	PCBM	2.7%	0.7 V	NA	31%	Mühlbacher et al. [122]
PFDTBT	PCBM	2.2%	1.0 V	46%	40%	Svensson et al. [123]
APFO-Green1	PCBM	2.2%	0.6 V	44%	38%	Zhang et al. [124]
PTBEHT	PCBM	1.1%	0.6 V	41%	15%	Wienk et al. [125]
PTBTB	PCBM	1.0%	0.7 V	37%	20%	Dhanabalan et al. [126], Brabec et al. [101]
APFO-Green1	BTPF70	0.3%	0.5 V	32%	8%	Wang et al. [127]
APFO-Green1	BTPF	0.7%	0.5 V	35%	28%	Wang et al. [128]
PDDTT	PCBM	0.1%	0.4 V	39%	NA	Xia et al. [129]

(TPT) and electron-deficient 2,1,3-benzothiadiazole (BT) units, called PTPTB (see Figure 12 for the chemical structure) [101, 126]. The photoresponse in combination with PCBM reached 800 nm.

The most promising low-bandgap material so far is poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b]-dithiophene)-*alt*-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT) reported by Mühlbacher et al. [122]. In combination with PCBM or PC<sub>71</sub>BM, a photoresponse extending to the infrared region exceeding 900 nm was measured. The high fill factor 47% found for this device demonstrates good charge transport capabilities leading to an overall power conversion efficiency of  $\eta = 3.2\%$ .

## 6. TANDEM SOLAR CELLS

Since it seems unlikely that a single organic material can absorb efficiently from the blue to the infrared region, tandem structures were proposed, where different subcells absorb different wavelength regions. The difficulty in designing tandem solar cells is that the current of each subcell has to be matched, since the total current in the device is limited by the lowest current generating subcell. First attempts have been made to prepare organic tandem cells. One example is the tandem cell where one subcell is made of P3HT:PCBM and the second of ZnPc:C60 [131]. The open circuit voltage was nearly doubled, but the conversion efficiency is still lower than what can be reached with a P3HT:PCBM cell alone. Shrotriya et al. [132] demonstrated LiF (1 nm)/Al(2.5 nm)/Au(12.5 nm) cathodes with a transparency between 50% and 80% in the visible region. By simply stacking an MEH-PPV:PCBM cell on a similar cell with a transparent electrode, a power conversion efficiency of 2.4% and an open circuit voltage of 1.64 V could be reached. Recently Kim et al. [133] reported tandem solar cells exceeding 6% conversion efficiency by using a TiOx interlayer to separate the two subcells.

## 7. SUMMARY

Recently, organic solar cells have broken the 5% power conversion efficiency barrier. While currently small molecules (e.g., CuPc) and polymers (e.g., P3HT) are similarly well

suiting as electron donor materials, these high efficiencies cannot currently be obtained using polymeric electron acceptors due to the low electron mobilities in these materials. Fullerenes and fullerene derivatives like PCBM are currently needed to reach 5% efficiency. However, it seems that P3HT:PCBM or CuPc:C60 devices have already been pushed fairly close to their theoretical efficiency limits, with quantum efficiencies greater than 80% already quite common. Therefore, it seems sure that new materials are needed to push the efficiencies into the 10% region, which is the generally agreed upon benchmark for economically viable photovoltaic devices. Either the open circuit voltage has to be raised by better matching of the energy levels of donor and acceptor materials or a broader spectrum of the sunlight needs to be absorbed using low-bandgap absorbers.

Developing novel crystalline electron acceptors with high electron mobilities and tunable energy levels to replace fullerene derivatives might be one promising direction for the future to achieve higher open circuit voltages, especially since not much research has been done in this direction. The tandem approach might be the key for harvesting a broader fraction of the sunlight in conjunction with novel low-bandgap materials.

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