25.1 INTRODUCTION

25.1.1 Photovoltaic Devices for Solar Energy Conversion

Solar energy has primary importance among all renewable energy resources. It is a remarkable fact that sun gives to the earth surface in one hour so much energy that it would be enough to cover the annual need of the present population of our planet. Photovoltaic devices allow for the most simple and efficient conversion of the solar energy to electricity. The power conversion efficiencies of the best laboratory devices based on silicon reach 24.4% [1]. The first generation of solar cells based on crystalline silicon is known since the middle of the last century (1954 by AT&T Bell Labs). However, for a long time, wide-scale distribution of such devices has been limited to aerospace applications by their extremely high cost. Today, the crystalline silicon modules can be installed at the cost of 2–3 USD per every watt of nominal power generated at maximal (peak) (denoted as watt-peak, Wp) [2].

The second generation of solar cells is based mainly on the amorphous and multicrystalline silicon and metal chalcogenides such as CdTe, CuInGa(1-x)Se2 (CIGS) and other similar thin-film absorbers. The best devices of the CIGS type yield power conversion efficiencies of 15–20% [3]. The power conversion efficiencies of such cells in general stay below the level achieved for the first-generation solar cells. However, second-generation solar cells are less expensive than the devices of the first generation. Therefore, the resulting economical effect is quite significant. The price of the generated energy becomes much lower, which stimulated growth of the thin-film photovoltaic technologies market [4]. Unfortunately, toxicity of cadmium telluride or gallium arsenide and expected shortage of indium and gallium world production will have to be considered for these technologies as an energy solution for the future [5]. At the same time, the efficiency of the cells based on amorphous silicon remained stuck at around 10.1%, which resulted in decrease of their market share since 2009–2010 [6].

The tandem and triple-junction solar cells are expected be able to operate at potentially ultrahigh light power conversion efficiencies (>50%) for concentrated sun light. Power conversion efficiencies of the best tandem solar cells are near 43% while their price remains much higher than the target 100–150 USD/m2 in spite of using inexpensive solar light concentrators [7].

Organic solar cells offer another alternative that yields moderate power conversion efficiencies of 8–10% at very low module costs (40–60 USD/m2) and lifetimes of 5–10 years. Indeed, laboratory prototypes of organic solar cells with the active areas as large as 1–8 cm2 demonstrated certified power conversion efficiencies of 8–10% (see Table 25.1 below). Lifetimes of 7 years were projected for conjugated polymer-based devices using accelerated tests [8]. At the same time, Heliatek confirmed continuous operation lifetimes of 16,000 hr (100 mW/cm2, AM1.5) for their small molecular-based double-junction devices [9]. Further improvements of organic solar cells in terms of performance, lifetime, module design and production technologies might lead to a breakthrough in the renewable energies. Ultimately, the energy generated by solar light conversion should become less expensive than the energy produced by combustion of fossil fuels.
In this chapter, we will focus on the organic semiconductor nanomaterials used for construction of efficient bulk heterojunction solar cells. The content of this chapter and provided citations are organized for didactical purposes only and do not reflect the chronology of the research in the field and/or have no claim of completeness. The further-interested reader is referred to monographs and reviews addressing different aspects of organic photovoltaics [10–15].

25.1.2 Construction of Bulk Heterojunction Solar Cell

The bulk heterojunction concept was invented in 1992 and was reported in a patent application [16]. A fast photoinduced charge separation between the [60]fullerene (or its functionalized derivatives) and conjugated polymer was revealed and the first p–n bulk heterojunction plastic solar cell was realized [17, 18]. According to the bulk heterojunction concept, p-type and n-type materials are mixed together and self-organize on nanoscale to form three-dimensional interpenetrating networks capable of efficient charge generation and transport. The strongest advantage of bulk heterojunction solar cells is significantly increased interface between p-type and n-type materials compared to the planar heterojunction devices known before [19, 20]. Typically, a size of the interconnected grains formed by the two phases should stay in the range of the exciton diffusion length (5–20 nm). Such nanomorphology allows more or less all excitons generated in the active layer to reach the interface and contribute to the generation of free charge carriers. That is why internal quantum efficiency of some bulk heterojunction solar cells approaches 100% [21].

A schematic layout of the architecture of an organic bulk heterojunction solar cell is shown in Figure 25.1. The active layer of this device comprises interpenetrated phases of electron donor material and electron acceptor material capable of efficient hole and electron transport in opposite directions toward respective electrodes. In order to avoid charge recombination at the electrodes, some buffer layers of pristine materials (or some other charge selective materials) should be introduced under the electrodes. For instance, the positive electrode, which extracts holes from the active layer, should form a direct contact only with a p-type material. At the same time, just a pure phase of the n-type material should be adjacent to the negative electron-collecting electrode.

Bulk heterojunction solar cells were explored intensively during the last decade. Many different materials were evaluated as p-type and n-type semiconductor components for construction of the devices. Blending p-type and n-type materials together produced polymer/polymer, polymer–small molecule, polymer–carbon nanotube, and polymer–inorganic nanoparticles, as well as small-molecule–small-molecule composites. Several types of these composite systems showed comparably high performances in organic solar cells (Table 25.1).

25.1.3 Operation Principle of Organic Bulk Heterojunction Solar Cells

Here we describe the operation principle of organic bulk heterojunction solar cells just briefly. The interested reader might be referred to specialized reviews and monographs [43, 44]. Any organic bulk heterojunction solar cell comprises a blend of p-type and n-type semiconductor materials which harvests photons and generates free charge carriers. Organic p-type material typically serves as electron donor, while an n-type component works as an electron acceptor. Photoinduced charge separation between donor and acceptor is a fundamental principle of operation of organic photovoltaic devices as well as the natural photosynthetic systems.

At the first step (step I in Figure 25.2), absorption of photons in the donor–acceptor blend leads to the generation of excitons D∗ and A∗. In an ideal case, donor and acceptor components have complementary absorption spectra, and both contribute significantly to the photon harvesting. However, typical electron acceptor components such as [60]fullerene and its derivatives are quite poor visible light absorbers because they have symmetry-forbidden transitions above 450 nm. On the contrary, [70]fullerene and its derivatives possess relatively strong absorptions in the visible range (up to ~700 nm) that make them very promising n-type materials for organic photovoltaics. Unfortunately, high costs of [70]fullerene and its functional derivatives limit industrial application of this type of materials. The excitons D∗ and A∗ have to diffuse in order to reach the interface between the donor and acceptor materials where charge separation might take place (Step II in Figure 25.2). Therefore it is crucially important to adjust the morphology of

![FIGURE 25.1. Schematic layout of bulk heterojunction solar cell.](image-url)
### TABLE 25.1. Some Advanced Material Composite Systems Used in Bulk Heterojunction Solar Systems

<table>
<thead>
<tr>
<th>Description of the Materials</th>
<th>Power Conversion</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fullerene/Polymer</td>
<td></td>
<td></td>
</tr>
<tr>
<td><img src="fullerene_polymer_structure.png" alt="Fullerene/Polymer structure" /></td>
<td>7.1 22</td>
<td></td>
</tr>
<tr>
<td><img src="fullerene_polymer_structure.png" alt="Fullerene/Polymer structure" /></td>
<td>7.4 23</td>
<td></td>
</tr>
<tr>
<td><img src="fullerene_polymer_structure.png" alt="Fullerene/Polymer structure" /></td>
<td>8.37 24</td>
<td></td>
</tr>
<tr>
<td><img src="fullerene_polymer_structure.png" alt="Fullerene/Polymer structure" /></td>
<td>7.7 25</td>
<td></td>
</tr>
<tr>
<td><img src="fullerene_polymer_structure.png" alt="Fullerene/Polymer structure" /></td>
<td>7.3 26</td>
<td></td>
</tr>
<tr>
<td>Undisclosed material combination from Konarka Technologies</td>
<td>8.3 27</td>
<td></td>
</tr>
</tbody>
</table>

(Continued)
<table>
<thead>
<tr>
<th>Description of the Materials</th>
<th>Power Conversion Efficiency (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Solution Processible Small Molecule/Small Molecule</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Chemical Structure]</td>
<td>5.2</td>
<td>28</td>
</tr>
<tr>
<td>[Chemical Structure] + Undisclosed fullerene derivative (proprietary of Mitsubishi Chemical)</td>
<td>9.2–10.2</td>
<td>29, 30</td>
</tr>
<tr>
<td><strong>Evaporation Processible Small Molecule/Small Molecule</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Chemical Structure]</td>
<td>4.9</td>
<td>31</td>
</tr>
<tr>
<td>[Chemical Structure] + [Chemical Structure]</td>
<td>5.2</td>
<td>32</td>
</tr>
<tr>
<td>Undisclosed material combination from Heliatek, double-junction device</td>
<td>8.3</td>
<td>27</td>
</tr>
<tr>
<td><strong>Polymer/Nanoparticle</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P3HT + CdSe QDs</td>
<td>2.9</td>
<td>33</td>
</tr>
<tr>
<td>P3HT + PbS QDs + MWCNT</td>
<td>3.03</td>
<td>34</td>
</tr>
</tbody>
</table>
TABLE 25.1. (Continued)

Polymer/Polymer

$\text{P3HT} + \text{PbS QDs}$

3.8 35

$\text{P3HT} + \text{CdSe QDs}$

3.13 36

$\text{P3HT} + \text{SWCNT}$

0.22 37, 38

$\text{P3HT} + \text{SPFGraphene}$

0.6–0.8 39, 40

$\text{P3HT} + \text{Graphene QDs}$

1.28 41

$\text{P3HT} + \text{F8TBT}$

1.8 42
these devices so that more or less all excitons can reach the donor–acceptor interface and contribute to the charge generation [45]. This can be achieved by keeping the size of the $p$-type and $n$-type material domains comparable to the exciton diffusion length which stays near 5–20 nm for organic materials [46–48].

The exciton $D^*$ is quenched via electron transfer to the LUMO level of the acceptor molecule ($A^0$) at the donor–acceptor interface (step III in Figure 25.2). On the contrary, exciton $A^*$ is quenched via hole transfer to the HOMO level of the donor molecule ($D^0$). Both pathways result in the formation of the same charge-separated state $D^+ \cdots A^-$. Positive and negative charges in this ion pair are bound by Coulomb attraction forces and are also denoted as a “geminate polaron pair” [49–51]. This pair can dissociate in the electric field induced by the potential jump at the heterojunction and/or by the difference in the electrode work functions. At the same time, the energy difference between the donor and acceptor LUMO levels (in the case when electron transfer takes place) or HOMO levels (in the case of hole transfer) released as a heat also helps to some extent with dissociation of geminate polaron pairs [52].

The charges generated in the blend should be transported to the respective electrodes (step IV in Figure 25.2). Holes should move in the phase of $p$-type material while electrons are transported in the $n$-type counterpart. Therefore it is essential to form percolated pathways for charge transport in both phases (see Figure 25.1).

At the final stage (step V in Figure 25.2) the generated charges have to be collected at the electrodes. In bulk heterojunction devices the lower work function metal (e.g., calcium, lithium, magnesium, barium, etc.) should match well the LUMO energy level of the acceptor component to collect negative charges (electrons) easily. At the same time, the high work function electrode (e.g., gold, platinum, nickel) should be adjusted to the HOMO energy level of the donor component to collect positive charge carriers (holes) without large barriers [43, 44]. However, the choice of electrode materials is somewhat complicated in the case of real devices. For instance, an indium–tin oxide electrode (ITO) can extract both positive and negative charges from the active layer of the device. At the same time, top electrodes composed of aluminum or silver can also extract both holes and electrons. Such poor selectivity of the charge collection results in a low photovoltaic performance of the device because of the massive charge recombination at the electrodes. To avoid this loss, some buffer layers should be introduced at the interfaces between the electrodes and the active layer. Electron blocking layers composed of evaporated or solution-processed vanadium (V) oxide, molybdenum (VI) oxide, tungsten (VI) oxide, and nickel (II) oxide were extensively utilized [53–55]. Titanium dioxide, cesium
carbonate, zinc oxide, or fullerene derivatives behave as electron-transporting and hole-blocking materials [55–60]. There are recent reviews summarizing information on the available buffer layer materials used in organic bulk heterojunction devices [61–64]. Optimized bulk heterojunction cells with appropriate buffer layers can give high fill factors of 65–75% typically providing also high-power conversion efficiencies.

25.1.4 Characterization of Organic Photovoltaic Devices

The main tool for characterization of organic photovoltaic cells is measuring their current–voltage characteristics (I–V curves) in the dark and under illumination. Under standard conditions the light-on curves of the photovoltaic devices should be measured using standardized light sources (solar simulators) with a known irradiation spectrum which has to be close as much as possible to the true AM1.5 (Air Mass 1.5) spectrum. The light intensity should be set to 100 mW/cm², and the photovoltaic cell should be kept at 25°C. From the experimental I–V curve (Figure 25.3a) it is possible to extract all main parameters of the device: short-circuit current density \( I_{SC} \), which is determined as current at the zero applied voltage; open-circuit voltage \( V_{OC} \), which is measured at the point where current is equalized to zero; fill factor, determined using the equation shown as inset in Figure 25.3a; and, finally, the power conversion efficiency of the device (\( \eta \)). The power conversion efficiency of photovoltaic cell is calculated as electrical power produced by the device, divided by the power of the light irradiating the device area. The electrical power is calculated as a maximal product of the current and voltage in the fourth quadrant. The current and voltage at the maximal power point on the \( I-V \) curve are defined as \( I_{max} \) and \( V_{max} \), respectively.

The characterization of photovoltaic devices remains incomplete without measuring their \textit{external quantum efficiency (EQE) spectra}, also called \textit{incident photon to collected electron efficiency (IPCE) spectra}. To obtain such spectra, the devices are irradiated with monochromatic light of known intensity, which generates a photocurrent that has to be measured with high accuracy. The calculation of an average fraction of incident photons that produced free electrons collected at the device electrodes gives us EQE (IPCE) values at each wavelength (see example in Figure 25.3b). If we recalculate the fraction of the produced in the device charge carriers per every absorbed (but not incident) photon, we can obtain \textit{internal quantum efficiency (IQE) spectra}. IQE is always higher than EQE because it does not account for the optical losses (e.g., scattering, reflection). Integration of an EQE spectrum of a photovoltaic device over a known AM1.5 solar irradiation spectrum provides a very precise way for calculation of the device short-circuit current density. This method should always be used for checking the \( I_{SC} \) values.

**FIGURE 25.3.** (a) Typical current–voltage characteristic of organic P3HT–PCBM solar cell, along with equation used for calculation of the maximal light power conversion efficiency \( \eta \). (b) The external quantum efficiency (EQE), also called incident photon to collected electron efficiency (IPCE) spectrum, of a typical P3HT–PCBM device, along with a simple equation used for calculation of EQE at each wavelength. Reproduced from reference 14, with permission of Wiley–VCH.
obtained from the $I-V$ measurements, which appear to be less accurate because of the non-accounted spectral mismatches between the irradiation of the used light sources (solar simulators) and true AM1.5 spectrum.

25.2 MAJOR TRENDS IN THE DESIGN OF NOVEL PHOTOACTIVE MATERIALS FOR BULK HETEROJUNCTION SOLAR CELLS

Efforts of the research are focused mainly on achieving higher power conversion efficiencies in the devices by using novel materials and their combinations while the stability issue remains non-addressed in the vast majority of publications. Since the power conversion efficiency depends linearly on short-circuit current, open-circuit voltage and fill factor, each of these parameters also should be increased.

The short-circuit current density in organic photovoltaic cells is limited by a number of photons absorbed in the active layer of the device. Therefore, the active layer materials should exhibit wide absorption spectra to harvest the solar light efficiently and to produce high current densities. Absorption profiles of such well-known material combinations as MDMO-PPV-[60]PCBM and P3HT-[60]PCBM cover only a small part of the solar irradiation spectrum as illustrated in Figure 25.4. Design of low-bandgap electron donor materials capable of the efficient light harvesting has been one of the most intensively developing research directions during the last decade [65].

Considering the overlap between the absorption spectrum of the device active layer of a certain thickness and the solar AM1.5 emission spectrum, it is possible to estimate numerically the maximal short-circuit current density of any photovoltaic device [66–68].

The maximal open-circuit voltage in bulk heterojunction organic solar cells is defined by the energy offset between the HOMO level of the donor material ($p$-type component) and the LUMO level of the acceptor ($n$-type component) (Figure 25.5) [69]. However, real $V_{OC}$ values are lower than theoretically predicted ones by approximately 0.3 eV [70]. This dependence was well-illustrated using sets of fullerene derivatives with different LUMO energy levels and electron donor polymers with different HOMO energy levels [70,71].

The fill factor of photovoltaic devices depends strongly on (a) the charge transport characteristics of the photoactive blend and (b) charge transfer through the interfaces between the active layer and the electrodes. In general, reasonably high fill factors can be obtained only for the systems where electron and hole mobilities are balanced in the photoactive blend (means close to each other as much as possible) [32, 72, 73]. At the same time, the energy levels of buffer layers and work functions of the electrode materials have to be well-aligned to facilitate collection of each type of charge carrier [74]. The fill factors of 65–75% are reached for organic photovoltaic devices [12].

For a certain combination of electron donor and electron acceptor materials with known electronic properties, it is possible to estimate maximal short-circuit current and
open-circuit voltage. Taking these values into account and assuming some reasonable fill factor (FF = 65%) and external quantum efficiency (EQE = 65%) values, it is possible to calculate theoretically achievable power conversion efficiency. Extensive modeling was performed by many groups, which allowed estimating ultimate efficiencies of single-junction and double-junction organic bulk heterojunction cells [70, 75, 76].

For a single-junction cell, the most illustrative diagram shows a correlation between the bandgap of the donor component and offset between the LUMO level energies of the donor and acceptor materials (Figure 25.6). This diagram shows that optimal electron donor material should have a bandgap of \( \sim 1.5 \) eV, which corresponds to the absorption band edge of \( \sim 820 \) nm. At the same time, the offset between the LUMO level energies of the donor and acceptor components should be minimized to 0.2–0.3 eV to enable maximal \( V_{OC} \) achievable for the system. The modeling performed recently by Kotlarski and Blom [76] suggests that the optimal donor bandgap is \( \sim 1.7 \) eV and the optimal active layer thickness should be around 100 nm. The optimized composite system (with donor–acceptor LUMO offset of 0.3 eV) is expected to yield \( V_{OC} = 1.0 \) V, \( J_{SC} = 15.6 \) mA/cm\(^2\), FF = 74\%, and \( \eta = 11.5\% \). The second efficiency maximum of 9.9\% was found for the systems with the donor bandgap of 1.9 V (similar to the bandgap of P3HT) and the active layer thickness of 200 nm.

It is very likely that on-grid applications of organic solar cells will become feasible only when the module efficiencies will reach 10% in combination with the lifetime of 10 years and the cost below 100 USD/m\(^2\) [77]. The power conversion efficiencies of single cells have to be boosted up to 13–15% to meet this severe module efficiency requirement. It is clear that classical organic single junction devices will fail to produce 13–15% efficiencies. Therefore, the research community pays more and more attention to tandem organic solar cells, especially the double-junction devices. Theoretical modeling suggests that indeed double-junction organic solar cells can produce power conversion efficiencies of 14–15% if optical and electronic properties of the materials in both subcells are optimized.

The diagram shown in Figure 25.7 suggests that 14% efficiency can be obtained for double-junction organic solar cells whose subcells are composed of the materials with the bandgaps of 1.60–1.65 eV and 1.20–1.25 eV (the first maximum) or 1.75–1.80 eV and 1.30–1.35 eV (the second maximum) [75].

Somewhat different modeling results for double-junction organic solar cells were reported by Kotlarski and Blom [76]. First of all, they confirmed that in the optimal situation the front cell (one that is closer to transparent electrode) should have a higher bandgap compared to the back cell (one that is closer to the reflecting metal electrode). The optimal bandgap for the front-cell donor component was estimated to be around 1.9 eV, and the optimal active layer thickness was around 150 nm. At the same time, the back cell should have the bandgap of 1.5 eV and the thickness of the light absorbing layer has to be near 90 nm. These results are comparable to the ones reported by Ameri et al. [75] and presented in Figure 25.7, though the absolute values of the bandgaps are somewhat different.
(\(E_g = 1.9\) eV). However, the thickness of the front cell active layer (40 nm) should be much smaller compared to the back cell active layer (200 nm) to provide the maximal efficiency of 13.1%.

The presented modeling results are very useful guidelines for material chemists who design novel photoactive electron donor and electron acceptor materials for bulk heterojunction organic solar cells. It becomes clear what kind of electronic and optical properties one should attain by synthesizing, for instance, a new donor polymer that is supposed to be used in organic solar cells in combination with the fullerene-based material [60]PCBM. Assuming that the LUMO level energy of PCBM is equal to \(-3.9\) eV as reported \([78,79]\), the optimal LUMO and HOMO energies of the polymer should be around \(-3.6\) eV and \(-5.1\) eV, respectively (taking optimal polymer bandgap of 1.5 eV according to references 70 and 75). If we assume the lower LUMO energy for PCBM (\(-4.3\) eV according to the report of Scharber et al. [70]), the optimal LUMO and HOMO energies of the donor component will transform to \(-4.0\) and \(-5.5\) eV.

Unfortunately, the correlations between the theoretical predictions and the experimental data are not always perfect. A good illustration of this disagreement between the theory and the experiment is reported by Blouin et al. [80]. A range of carbazole-based electron donor polymers was synthesized and investigated in bulk heterojunction solar cells in combination with [60]PCBM. Some polymers possessing optimal frontier energy levels were good candidates for 8–10% efficient organic solar cells. However, the experimental power conversion efficiencies were 5–10 times lower than the theoretically estimated ones. This situation is illustrated by Figure 25.8, where the black numbers on the diagram correspond to the solar cells efficiencies experimentally obtained for every polymer. It is seen from the Figure 25.8 that only one polymer (PCDTBT) shows the performance that corresponds well to the theoretical predictions.

The theoretical modeling results of Scharber et al. [70] and Ameri et al. [75] were based on the assumption of high external quantum efficiency (EQE = 65%) and high fill factors (FF = 65%) that experimentally are not achievable for many systems. Insufficiently high fill factors and EQEs typically account for the disagreement between the theoretically predicted efficiencies and experimental results. Nanomorphology of the active layer in each case determines the charge carrier mobility in the bulk and therefore has to be optimized.

**25.3 ACTIVE LAYER NANOMORPHOLOGY AS A MAJOR FACTOR LIMITING PHOTOVOLTAIC PERFORMANCE OF BULK HETEROJUNCTION SOLAR CELLS**

Importance of the active layer nanomorphology of organic solar cells was first recognized in 2001 for the solar cells based on the MDMO-PPV/[60]PCBM composite. The power conversion efficiency of the devices was increased from 0.9% to 2.5% simply by replacing the solvent used for active layer casting from toluene to chlorobenzene [81]. In the subsequent study by Hoppe et al. [82] it was demonstrated that MDMO-PPV/[60]PCBM films cast from toluene are rather inhomogeneous and comprise round-shaped distinct features approaching in size 500–600 nm which were later shown to be the PCBM crystallites [83]. On the contrary, films cast from chlorobenzene were much more homogeneous, and the cluster size in that case did not exceed 50 nm. Illustrative AFM images recorded for the toluene-cast
and chlororobenzene-cast MDMO-PPV–[60]PCBM films are shown in Figure 25.9.

It was mentioned above that the charge generation in bulk heterojunction solar cells occurs at the interface between the donor (in this case MDMO-PPV) and acceptor ([60]PCBM) components of the blend. The excitons generated in the active layer have to diffuse to the interface where charge separation takes place. It is known that characteristic exciton diffusion lengths in organic semiconductors typically do not exceed 20 nm [46–48]. Therefore, the domains of individual materials formed in the blend as a result of the phase separation should not be larger than the exciton diffusion lengths ($L_{ex}$) in these materials. The round-shaped clusters in the case of the toluene-cast MDMO-PPV/[60]PCBM films are at least 25–30 times larger than the typical $L_{ex}$ values. Therefore a vast majority of excitons generated inside these clusters recombine since they cannot reach the donor–acceptor interface where charge separation takes place. The situation is much more positive in the case of chlororobenzene-cast films where the average cluster size matches quite well the $L_{ex}$ value. The smaller degree of phase separation in this case allows the majority of excitons to reach the fullerene–polymer interface and contribute to the charge carrier generation. Improved morphology of the chlororobenzene-cast MDMO-PPV–[60]PCBM blends results in the superior device performances: EQEs approach 50% and light power conversion efficiencies come close to 2.5% [81].

It has been shown recently that the morphology of the MDMO-PPV-based composites can be controlled by changing the molecular structure of the fullerene derivatives [68]. Indeed, small variations in the length of alkyl chains attached to the carboxylic group in the structures of investigated [70]fullerene derivatives induce significant changes in the composite morphology as concluded from the AFM images of the blends (Figure 25.10). It was shown experimentally that both short-circuit current density, and power conversion efficiency of the devices decrease rapidly with increase in the lateral size of the clusters (round-shaped features) revealed on the surface of the films by AFM.

A clear correlation between the solar cell parameters ($I_{SC}$ and $\eta$) and the size of the clusters in the fullerene–polymer composites observed in reference 68 is a good experimental confirmation of the theoretical considerations presented above. Indeed, recombination of excitons inside the large clusters leads to the expectable drop in the device current density and power conversion efficiency.

Next generation of organic solar cells based on the P3HT–[60]PCBM blends is also governed by the active layer morphology. Padinger et al. [84] have shown that thermal annealing of P3HT–[60]PCBM solar cells results in a dramatic improvement of their performance providing power conversion efficiency of 3.5% for the first time. This work attracted tremendous attention in the field and stimulated subsequent investigation of the P3HT–[60]PCBM composite solar cells. It was shown that morphology of P3HT–[60]PCBM solar cells can be tuned by thermal annealing [85], solvent vapor annealing [86, 87], and use of chemical additives [88].

Electron tomography has revealed a three-dimensional structure of the P3HT–[60]PCBM blends with nanometer resolution [89]. It was demonstrated that thermal and solvent vapor annealing results in the formation of genuine 3D nanoscale interpenetrating networks of donor and acceptor materials with high crystalline order (Figure 25.11). These favorable morphological changes account for a considerable increase in the power conversion efficiency of the devices after thermal or solvent-assisted annealing. Electron tomography allows for precise determination of concentration gradients of both P3HT and [60]PCBM through the thickness...
of the photoactive layer. It has proved in particular that the concentration of P3HT is higher at the ITO–PEDOT:PSS electrode for the annealed blend films.

A thorough understanding of the morphology effects in organic bulk heterojunction solar cells based on the P3HT–[60]PCBM composite resulted in gradual improving of their light power conversion efficiency up to the level of 4.0–4.5% [66, 90–91]. Unusual results came out from a systematic study of a library of fullerene derivatives in bulk heterojunction solar cells in combination with P3HT [92]. It was found that all fullerene derivatives presented in Figure 25.12 have virtually the same frontier energy levels (in particular, LUMO energies affecting $V_{OC}$ of solar cells) regardless the structure of organic addend attached to the cages of fullerenes C$_{60}$ and C$_{70}$. However, even very slight modifications of the molecular structures of fullerene derivatives induce significant changes in their physical properties such as solubility in organic solvents. This is well illustrated by the solubility values measured for all fullerene derivatives in chlorobenzene which are presented in Figure 25.12 near numbers of the compounds in brackets.

The solubility of the fullerene derivatives affected strongly the morphology of their blends with P3HT (Figure 25.13). For instance, the films composed of the least-soluble fullerene derivative 7 (solubility $S = 5$ mg/mL) and P3HT showed large aggregates approaching 30–100 μm in size. An increase in the solubility of the fullerene component by a factor of two for the compound 6 ($S = 10$ mg/mL) resulted in the remarkable decrease in the cluster size in the blend films by a factor of 10. Use of the fullerene-based materials with the solubility of 22 mg/mL (compound 9) and 30 mg/mL (compound 10) led to further improvement of the blend...
ACTIVE LAYER NANOMORPHOLOGY AS A MAJOR FACTOR LIMITING PHOTOVOLTAIC PERFORMANCE

FIGURE 25.11. Results of electron tomography applied to P3HT–[60]PCBM photoactive layers: as spin-coated, thermally annealed at 130°C for 20 min (TA), and solvent-assisted annealing for 3 h (SAA). The first three rows contain slices taken out of a reconstructed volume of the corresponding film. All slices are lying in the horizontal (X, Y) plane of the film at a different depth (Z location): one slice close to the top of the film (i.e., to the electron collecting electrode), another one in the middle of a film, and the third one close to the bottom of the film (the hole collecting PEDOT:PSS/ITO electrode). The dimensions of the slices are around 1700 nm × 1700 nm. Images in the fourth row are snapshots of the corresponding film’s whole reconstructed volume—that is, a stack of all of the slices through the whole thickness of a film, with dimensions of around 1700 nm × 1700 nm × 100 nm. Reproduced from reference 112, with permission of the American Chemical Society.

morphology erasing any signs of the phase segregation at least on the micrometer scale.

Strong variation of the film morphology induced by different solubility of the fullerene derivatives (molecular structures are shown in Figure 25.12) affected significantly photovoltaic performance of the P3HT–fullerene composites. Rather clear correlations of the short-circuit current density, open-circuit voltage, fill factor, and light power conversion efficiency with the solubility of the fullerene-based materials were revealed (Figure 25.14).

The presented examples prove that supramolecular assembling of the fullerene derivative and the polymer in the blends is governed by relative solubility of the materials. In the case of P3HT, the best solar cell performances were obtained with the use of fullerene derivatives that exhibited solubility values close to the solubility of P3HT itself (70–90 mg/mL). Therefore it was suggested that balanced active layer morphology in fullerene–polymer composites can be achieved through a combination of electron donor and electron acceptor materials with similar solubilities. As a main consequence of this conclusion, any novel electron donor material might require a specific fullerene counterpart with fitting solubility to be combined in order to achieve the highest photovoltaic performance.

Further investigation of the library of fullerene derivatives in combination with poly(3-alkylthiophenes) with different side chains revealed unexpected results [93]. It was found that the dependence of the solar cell parameters upon the fullerene component solubility might have an unexpected double-branched shape as shown for poly(3-pentylthiophene) in Figure 25.15. The fullerene derivatives with the solubility fitting the range of 20–60 mg/mL form two separate groups. One group of the fullerene-based compounds clearly outperforms another one in solar cells as follows from the Figure 25.15. Moreover, very similar dependences were revealed for poly(3-alkylthiophenes) with heptyl, octyl, decyl, and dodecyl side chains as well.

The obtained results suggest strongly that the morphology and photovoltaic performance of the fullerene/polymer composites is governed to a large extent by supramolecular interactions between the components. On the one hand, the best-performing systems (upper “branch” in Figure 25.15) comprise fullerene derivatives that are well compatible (like 8–P3DT composite above) with the polymer due to some attractive intermolecular interactions. On the other hand, the worse performing systems (lower “branch” in Figure 25.15) are based on badly compatible fullerene and polymer components (like 3–P3DT composite above) that might be a consequence of some missing intermolecular interactions between the components.

It would not be a big exaggeration to say that there are several thousands of known conjugated polymers that were synthesized and applied or were supposed to be applied as
FIGURE 25.12. Molecular structures of fullerene derivatives forming a library of acceptor materials investigated in solar cells in combination with P3HT. Solubility values determined in chlorobenzene are given in parentheses near the numbers of the compounds. Reproduced from reference 115, with permission of Wiley–VCH.

FIGURE 25.13. Optical microscopy images for the blends of four different fullerene derivatives with P3HT. Obvious improvement of the active layer morphology with increase in the solubility of the fullerene derivatives can be observed. Reproduced from reference 115, with permission of Wiley–VCH.

electron donor components in organic bulk heterojunction solar cells. However, nearly all these polymers were investigated in solar cells in combination with conventional commercially available fullerene derivatives [60]PCBM and [70]PCBM (molecular structures are shown in Figure 25.4). In the view of the experimental results reported in references 92 and 93, it is very unlikely that two conventional fullerene derivatives ([60]PCBM and [70]PCBM) have appropriate solubility and good compatibility making them suitable electron acceptor components for a very broad range of electron donor polymers. It has already been shown that replacement of PCBM with better suiting fullerene counterpart might improve photovoltaic performance of some conjugated polymers by a factor of 2–3 [93,94]. One more example

1We relate the term “good compatibility” to the existence of attractive intermolecular interactions between the fullerene derivative and the polymer, preventing large-scale phase separation like it was illustrated above for 3/P3DT composite. On the contrary, the term “bad compatibility” refers to the systems with insufficient attractive interactions between the components that finally result in their large-scale segregation in the blends.
ADVANCED ELECTRON ACCEPTOR MATERIALS FOR BULK HETEROJUNCTION SOLAR CELLS

25.4 ADVANCED ELECTRON ACCEPTOR MATERIALS FOR BULK HETEROJUNCTION SOLAR CELLS

Fullerene derivatives [60]PCBM and [70]PCBM were running horses for many years in the field of the research related to the polymer–fullerene bulk heterojunction solar cells. However, many promising electron donor conjugated polymers were developed that are characterized by insufficiently low LUMO energies that result in considerably large $\Delta E_{ET} = E_{LUMO(D)} - E_{LUMO(A)}$ energy band offset (D states for donor polymer and A for acceptor fullerene derivative). As shown in Figure 25.6, the optimal $\Delta E_{ET}$ should be $\sim 0.3$ eV to ensure efficient electron transfer. The systems with the larger

is provided by the polymer AnE-PV_stat, which yields power conversion efficiencies of 2.4–3.5% in solar cells in combination with [60]PCBM and [70]PCBM. However, the composites of this polymer with fullerene derivatives 8 and 18 showed power conversion efficiencies of 5.0–5.1% in optimized bulk heterojunction solar cells (Figure 25.17). The superior device performance using fullerene derivatives 8 and 18 was correlated with the improved active layer morphology [95]. It seems that every conjugated polymer requires its own fullerene-based counterpart with optimized molecular structure (to provide necessary compatibility) and appropriate solubility. This is an important message suggesting the need for revisiting many theoretically promising electron donor copolymers that showed power conversion efficiencies of 1–3% with PCBM and consequently were discarded. It is very probable that many previously abandoned polymers will show state-of-the-art solar cell performances if appropriate fullerene-based counterparts are provided.

FIGURE 25.14. The short-circuit current ($I_{SC}$), open-circuit voltage ($V_{OC}$), fill factor (FF), and light power conversion efficiency ($\eta$) as functions of the solubility of the fullerene-based materials. Reproduced from reference 115, with permission of Wiley–VCH.

FIGURE 25.15. Unusual double-branched dependence of the solar cell power conversion efficiency upon the solubility of the fullerene derivatives combined with poly(3-octylthiophene) as a donor polymer. Reproduced from reference 116, with permission of the authors.
ΔE_{ET} values suffer from the losses in the open-circuit voltage. The P3HT–PCBM is one of the most illustrative systems where high LUMO energy of P3HT limits severely the V_{OC} of the P3HT–PCBM solar cells. If we take HOMO–LUMO energy levels for [60]PCBM and P3HT given in reference 70, the maximal obtainable V_{OC} in the solar cells based on this system is ~0.8 V (Figure 25.18). At the same time, the ΔE_{ET} is unnecessary large and approach ~1.1 eV.

The experimental V_{OC} values (V_{OC}(exp)) for the reasonably efficient P3HT–PCBM cells vary in the range of 0.58–0.68 V [91]. We believe that the experimental V_{OC} values are described with a reasonably good accuracy by the model of Vandewal et al. [96], who proposed the following empiric equation for estimating V_{OC}(exp):

\[ V_{OC}(exp) \approx \frac{E_g}{e} - 0.43V \]  

where \( E_g \) is a bandgap of the charge-transfer state formed in the polymer–fullerene system, which is also ~0.1–0.2 eV smaller than the LUMO(A)–HOMO(D) offset defining \( V_{OC}(max) \).

Therefore, we can modify Eq. (25.1), leading to a more convenient equation:

\[ V_{OC}(exp) \approx V_{OC}(max) - (0.53 \div 0.63)V \]  

If we take the LUMO energy value of −3.9 eV for PCBM (following references 78 and 79), we can obtain more optimistic \( V_{OC}(max) = 1.2 \) V and the ΔE_{ET} = 0.7 eV. Following the Eq. (25.2), we can obtain \( V_{OC}(exp) = 0.57–0.67 \) V, which shows excellent agreement with the values published in the literature [91].

To make efficient P3HT-based organic solar cells, one needs to design fullerene derivatives with higher LUMO level energies to bring ΔE_{ET} value as close to the desired 0.3 eV as possible. This idea was first illustrated in 2001 by Brabec et al. [69]. A set of fullerene derivatives demonstrating higher open circuit voltage in solar cells compared to [60]PCBM was designed by Kooistra et al. [97] in 2007. The best V_{OC} of 925 mV was provided in MDMO-PPV based solar cells by the compound F1 (Figure 25.19) bearing

\[
\begin{align*}
\text{FIGURE 25.16.} & \quad \text{The blends of fullerene derivatives 3 and 8 with P3DT reveal very different morphologies in spite of the similar solubility of these compounds in chlorobenzene. Molecular compositions of the blends are shown (on the left side) together with the height AFM images and their 3D profiles (on the right side). Reproduced from reference 116, with permission of the authors.}
\end{align*}
\]
three methoxy groups attached to the PCBM phenyl group. The reference [60]PCBM provided a \( V_{OC} \) of 870 mV. Unfortunately, no solar cells efficiencies are given in reference 97, which strongly suggests that the observed improvement in \( V_{OC} \) was counterbalanced by decreased FF and/or \( I_{SC} \) values.

A much more successful attempt to design superior fullerene-based acceptor materials was reported by Riedel et al. [98] in 2005. The developed material \( \text{F2} \) (Figure 25.19) showed in combination with P3HT the \( V_{OC} \) value of 0.65 V, which is \( \sim \)100 mV higher than the \( V_{OC} \) obtained for the [60]PCBM–P3HT blends under identical conditions. However, the power conversion efficiency of the \( \text{F2}/\text{P3HT} \) devices did not exceed 2.3% due to the lowered current densities. A similar compound \( \text{F3} \) (Figure 25.19) reported recently produced \( V_{OC} \) of 690 mV and power conversion efficiency of 2.6% in solar cells with P3HT used as an electron donor component [99].

A dramatic progress was made by application of bis-functionalized derivatives of C60 and C70 fullerenes as electron acceptor components in organic solar cells. The first success in this field was reported in a patent application filled in 2007 by a joint team of inventors from Plextronics and Nano-C companies [100]. They reported, in particular, bisindene fullerene adduct \( \text{F4} \) (Figure 25.20) providing for \( V_{OC} = 0.84 \) V, \( I_{SC} = 9.43 \) mA/cm\(^2\), FF = 64%, and \( \eta = 5.1\% \) in bulk heterojunction solar cells based on its composite with P3HT. Virtually the same results were reported by independent group in 2010 [78]. Subsequent efforts allowed the same group to bring the efficiency of the \( \text{F4}/\text{P3HT} \) solar cells up to the level of 6.5% [101], which, up to our best knowledge, was never certified or independently reproduced. The Yang group investigated the \( \text{F4}/\text{P3HT} \) system [102] and reported the efficiency of 4.5%, which is close to the values of 5.1–5.4%, reported in references 78 and 100.

There is some uncertainty regarding the other types of bis-functionalized fullerene derivatives—in particular, bis-[60]PCBM \( \text{F6} \) (Figure 25.20). Bis-PCBM was reported in 2008 by Lennes et al. [103] as a fullerene-based material yielding improved photovoltaic performance in solar cells with P3HT.

The theoretical modeling performed by Nelson and co-workers [104] suggests an existence of a considerable energetic disorder in the mixtures of bis-PCBM isomers possessing somewhat different LUMO level energies. The energetic disorder is expected to lead to the charge trapping in the system reducing FF and \( I_{SC} \) values of the devices. This conclusion was supported by experimental data reported by different groups [105, 106]. A number of other explored products bearing two to four cyclopropane addends on the fullerene cage (\( \text{F7–F12} \)) produced poor performances in organic bulk heterojunction solar cells [107, 108].

A family of different cyclopentadiene-type fullerene derivatives was synthesized and investigated by Niinomi et al. [111]. It was shown that LUMO energies of the compounds \( \text{F13–F20} \) (Figure 25.21) range from \(-3.4 \) eV to \(-3.3 \) eV, thus approaching very closely the LUMO energy of P3HT \((-3.2, -3.3 \) eV). The resulting driving force \( \Delta E_{ET} = 0.1 \pm 0.2 \) eV might still be sufficient for the efficient electron transfer in the view of the results reported.

![Figure 25.18](image-url) Frontier energy level diagram for a P3HT–PCBM system.

![Figure 25.19](image-url) Molecular structure of diphenylmethanofullerenes that showed improved open-circuit voltages in organic bulk heterojunction solar cells compared to the reference [60]PCBM material.
FIGURE 25.20. Molecular structures of some fullerene bis- and polycycloadducts applied as electron acceptors in bulk heterojunction solar cells.

FIGURE 25.21. Molecular structures of some cyclopentadiene-type fullerene derivatives with high LUMO level energies investigated as electron acceptor materials in bulk heterojunction solar cells.
TABLE 25.2. The Parameters of Photovoltaic Cells Based on P3HT and Different Fullerene Derivatives

<table>
<thead>
<tr>
<th>Fullerene Derivative</th>
<th>$I_{SC}$ (mA/cm²)</th>
<th>$V_{OC}$ (V)</th>
<th>FF (%)</th>
<th>η (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[60]PCBM</td>
<td>10.6</td>
<td>0.64</td>
<td>55</td>
<td>3.7</td>
<td>92</td>
</tr>
<tr>
<td>F4</td>
<td>9.43</td>
<td>0.84</td>
<td>64</td>
<td>5.1</td>
<td>100</td>
</tr>
<tr>
<td>10.61</td>
<td>0.84</td>
<td>72</td>
<td>6.5</td>
<td>101</td>
<td></td>
</tr>
<tr>
<td>F5</td>
<td>8.5</td>
<td>0.82</td>
<td>65</td>
<td>4.5</td>
<td>102</td>
</tr>
<tr>
<td>F6</td>
<td>11.34</td>
<td>0.81</td>
<td>63</td>
<td>5.79</td>
<td>109</td>
</tr>
<tr>
<td>F7</td>
<td>10.6</td>
<td>0.85</td>
<td>74</td>
<td>6.7</td>
<td>110</td>
</tr>
<tr>
<td>F8</td>
<td>9.14</td>
<td>0.724</td>
<td>68</td>
<td>4.5</td>
<td>103</td>
</tr>
<tr>
<td>F9</td>
<td>5.86</td>
<td>0.77</td>
<td>34</td>
<td>1.53</td>
<td>107</td>
</tr>
<tr>
<td>F10</td>
<td>5.91</td>
<td>0.72</td>
<td>41</td>
<td>1.72</td>
<td>108</td>
</tr>
<tr>
<td>F11</td>
<td>1.88</td>
<td>0.64</td>
<td>28</td>
<td>0.34</td>
<td>108</td>
</tr>
<tr>
<td>F12</td>
<td>0.48</td>
<td>0.57</td>
<td>32</td>
<td>0.09</td>
<td>108</td>
</tr>
<tr>
<td>F13</td>
<td>0.2</td>
<td>0.25</td>
<td>43</td>
<td>0.02</td>
<td>111</td>
</tr>
<tr>
<td>F14</td>
<td>1.9</td>
<td>0.72</td>
<td>34</td>
<td>0.45</td>
<td>111</td>
</tr>
<tr>
<td>F15</td>
<td>2.8</td>
<td>0.76</td>
<td>51</td>
<td>1.08</td>
<td>111</td>
</tr>
<tr>
<td>F16</td>
<td>0.2</td>
<td>0.30</td>
<td>34</td>
<td>0.02</td>
<td>111</td>
</tr>
<tr>
<td>F17</td>
<td>0.8</td>
<td>0.42</td>
<td>37</td>
<td>0.12</td>
<td>111</td>
</tr>
<tr>
<td>F18</td>
<td>3.8</td>
<td>0.63</td>
<td>38</td>
<td>0.91</td>
<td>111</td>
</tr>
<tr>
<td>F19</td>
<td>2.5</td>
<td>0.73</td>
<td>38</td>
<td>0.68</td>
<td>111</td>
</tr>
<tr>
<td>F20</td>
<td>2.1</td>
<td>0.61</td>
<td>32</td>
<td>0.40</td>
<td>111</td>
</tr>
</tbody>
</table>

recently by Gong et al. [112]. However, the composite systems comprising P3HT and fullerene derivatives F13–F20 showed rather poor photovoltaic performance. The origins for poor performance of these compounds are still poorly understood.

Table 25.2 summarizes the data on photovoltaic performance of different fullerene derivatives possessing higher LUMO level energies compared to [60]PCBM. It is seen from this table that only the fullerene derivatives F4 and F5 bearing two indene fragments attached to the C60 and C70 cages, respectively, outperform clearly [60]PCBM in bulk heterojunction solar cells using P3HT as an electron donor component. All other adducts show either comparable (like F6) or lower performances compared to the reference [60]PCBM. Even though the efficiency of ~5.0% seems to be the most realistic value for the F4/P3HT and F5/P3HT solar cells, there is no doubt that F4 and F5 are superior fullerene-based materials compared to [60]PCBM and [70]PCBM.

25.5 ADVANCED ELECTRON DONOR MATERIALS FOR BULK HETEROJUNCTION SOLAR CELLS

It was shown above that the optimal LUMO and HOMO energies of the electron donor counterpart for [60]PCBM (or [70]PCBM) should be around −3.6 eV and −5.1 eV, respectively (taking optimal polymer bandgap of 1.5 eV according to references [70 and 75] as illustrated in Figure 25.6). The design of such material with well-matching energy levels is a challenge for material chemists. The evolution of conjugated polymers during the last few years resulted in the development of many different promising structures. It is not possible to discuss all of them in the present chapter; therefore we will focus below mainly on the materials that provided power conversion efficiencies above 6.0% in bulk heterojunction solar cells.

The carbazole–thiophene–benzothiadiazole copolymer P1 (abbreviated as PCDTBT) designed by the Leclerc group [80] was the first disclosed polymer providing certified power conversion efficiencies of 6.0% in bulk heterojunction solar cells [21] (Figure 25.2). This material has low HOMO energy resulting in high open-circuit voltages in bulk heterojunction solar cells using PCBM as the electron acceptor component. At the same time, it has approximately the same bandgap as P3HT, thus enabling appreciably high short-circuit current densities of 8–10 mA/cm². A thorough investigation of P1–[70]PCBM composites showed recently that their morphology can be turned by introducing small amounts of polar solvents to the blend solutions used for film casting. Recently, the additives of DMSO (methylsulfoxide) and DMF (dimethylformamide) boosted the efficiency of the solar cells based on the P1–[70]PCBM composites up to the level of 7.0%. Very similar efficiency has been achieved for the P1/[70]PCBM system by Cao group using additional charge selective buffer layer and Al negative electrode [24]. An excellent environmental stability of P1 is a strongest
advantage of this polymer. The solar cells comprising P1 as an electron donor polymer showed estimated operation lifetime of 7 years in accelerated tests [8].

A group of very promising conjugated polymers comprising alternating thieno[3,4-b]thiophene and benzodithiophene units was introduced by Yu et al. [113, 114]. Starting with appreciably high initial efficiencies of ∼5.0%, subsequent structural evolution of these materials resulted in the development of conjugated polymers P2 and P3 providing power conversion efficiencies well above 7.0%. A record certified efficiency of 8.37% has been reported recently for the solar cells based on P2–[70]PCBM composite modified with the charge-selective buffer layer at the interface between the photoactive blend and electron-collecting Al electrode [24]. It is obvious that polymers P2 and P3 are capable of giving high
Efficiencies of organic bulk heterojunction solar cells. However, the operation stability of these materials and devices remain poorly investigated.

Another promising electron donor material P4 is a copolymer of Si-modified cyclopentadithiophene and 5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (DOPT) [115]. A family of cyclopentadithiophene-based copolymers P6 and P7 has been intensively studied since 2006 [116]. However, the maximal power conversion efficiencies of bulk heterojunction solar cells based on these polymers were in the range of 5–6% [117–119]. The replacement of the benzothiadiazole unit in P7 with DOPT block resulted in P4 polymer which showed power conversion efficiency of 7.3% after substantial device and polymer optimization [26]. At the same time, a similar polymer P5 comprising alternating cyclopentadithiophene and DOPT units showed appreciably high power conversion efficiency of 6.4% [120].

Somewhat lower power conversion efficiencies (5.0–6.5%) were obtained for the copolymers P8 [121], P9 [122], P10 [123], P11 [124], and P12 [125]. Very elegant chemical structures and relatively simple synthetic routes developed to produce these conjugated polymers make them promising electron donor materials for organic photovoltaic cells potentially available in bulk quantities.

Directed chemical structure design plays an important role in the development of novel conjugated polymers for photovoltaic applications. One of the illustrative examples is provided by the polymers P13 and P14 [126]. The dithienobenzene–benzothiadiazole copolymer P13 showed moderate performance in organic bulk heterojunction solar cells defined by the solar light power conversion efficiency of 5.0%. The introduction of two fluorine atoms in the benzothiadiazole ring in the polymer P13 resulted in a new polymer P14. Such modification has changed the electronic structure of the polymer: The HOMO level of P14 is lowered by 0.14 eV compared to P13, while the LUMO level of P14 is 0.2 eV lower than that of P13. Such modification of the electronic structure of the polymer brought an expected increase in the V oc from 0.87 V to 0.91 V accompanied also by the considerable improvements in the short-circuit current density and the fill factor (Table 25.3) resulting in the power conversion efficiency of 7.2%.

The data presented in Table 25.3 give an overview of the current status of the research in the field of organic fullerene–polymer solar cells. It is clearly seen that the intensive development of novel conjugated polymers during the last 5 years resulted in tremendous progress in the field and brought the solar cell efficiencies from 4.0–4.5% level (the best P3HT-based devices) to the current level of 7–8%.

It would be unfair not to mention low molecular weight materials that boosted the performance of organic bulk heterojunction solar cells well beyond 8–9% recently [29, 30]. Many low molecular weight materials are not soluble in organic solvents, however their inherent stability allows one to purify and process them by vacuum sublimation. Some merocyanine dyes showed promising performances when used as electron donor materials in organic solar cells. In particular, the D1/C60 combination (Figure 25.23) provided power conversion efficiencies close to 5.0% [31]. Similar performances were obtained using oligothiophene donor molecule D2 and diphenylamine–thiophene–benzothiadiazole hybrid D3 also combined with C60 [127].

A tandem bulk heterojunction solar cell structure based on coevaporated C60 fullerene, fluorinated phthalocyanine D4, and oligothiophene D5 bearing dicyanovinyl groups was reported recently [128]. A power conversion efficiency of 6.0% was achieved in solar cells based on these simple

### Table 25.3. Performance of Organic Bulk Heterojunction Solar Cells Based on the Selected Combinations of Electron Donor Polymers and Fullerene Derivatives

<table>
<thead>
<tr>
<th>Polymer–Fullerene</th>
<th>$I_{SC}$ (mA/cm²)</th>
<th>$V_{OC}$ (V)</th>
<th>FF (%)</th>
<th>η (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1–[70]PCBM</td>
<td>11.8</td>
<td>0.91</td>
<td>66</td>
<td>7.1</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>12.1</td>
<td>0.90</td>
<td>62</td>
<td>6.55</td>
<td>24</td>
</tr>
<tr>
<td>P2–[70]PCBM</td>
<td>15.75</td>
<td>0.756</td>
<td>70.15</td>
<td>8.37</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>14.5</td>
<td>0.74</td>
<td>69</td>
<td>7.4</td>
<td>23</td>
</tr>
<tr>
<td>P3–[70]PCBM</td>
<td>15.2</td>
<td>0.76</td>
<td>67</td>
<td>7.7</td>
<td>25</td>
</tr>
<tr>
<td>P4–[70]PCBM</td>
<td>12.2</td>
<td>0.88</td>
<td>68</td>
<td>7.3</td>
<td>115</td>
</tr>
<tr>
<td>P5–[70]PCBM</td>
<td>14.1</td>
<td>0.75</td>
<td>61</td>
<td>6.4</td>
<td>120</td>
</tr>
<tr>
<td>P6–[70]PCBM+ODT</td>
<td>16.2</td>
<td>0.62</td>
<td>55</td>
<td>5.5</td>
<td>119</td>
</tr>
<tr>
<td>P7–[70]PCBM</td>
<td>12.7</td>
<td>0.680</td>
<td>55</td>
<td>5.1</td>
<td>118</td>
</tr>
<tr>
<td></td>
<td>14.9</td>
<td>0.576</td>
<td>61</td>
<td>5.2</td>
<td>117</td>
</tr>
<tr>
<td>P8–[70]PCBM</td>
<td>10.5</td>
<td>0.89</td>
<td>64</td>
<td>6.0</td>
<td>121</td>
</tr>
<tr>
<td>P9–[70]PCBM</td>
<td>10.3</td>
<td>0.8</td>
<td>65</td>
<td>5.5</td>
<td>122</td>
</tr>
<tr>
<td>P10–[70]PCBM</td>
<td>13.3</td>
<td>0.7</td>
<td>69</td>
<td>6.3</td>
<td>123</td>
</tr>
<tr>
<td>P11–[70]PCBM</td>
<td>12.3</td>
<td>0.722</td>
<td>70.5</td>
<td>6.26</td>
<td>124</td>
</tr>
<tr>
<td>P12–[70]PCBM</td>
<td>9.9</td>
<td>0.89</td>
<td>70</td>
<td>6.2</td>
<td>125</td>
</tr>
<tr>
<td>P13–[70]PCBM</td>
<td>10.03</td>
<td>0.87</td>
<td>57.3</td>
<td>5.0</td>
<td>126</td>
</tr>
<tr>
<td>P14–[70]PCBM</td>
<td>12.91</td>
<td>0.91</td>
<td>61.2</td>
<td>7.2</td>
<td>126</td>
</tr>
</tbody>
</table>

**Note:** The table provides an overview of the performance of organic bulk heterojunction solar cells based on the selected combinations of electron donor polymers and fullerene derivatives. The values in columns represent the current density ($I_{SC}$), open-circuit voltage ($V_{OC}$), fill factor (FF), and efficiency (η) for each polymer–fullerene combination.
FIGURE 25.23. Molecular structures of some low molecular weight compounds applied as electron donor materials in organic bulk heterojunction solar cells.

Heliatek has certified 8.3% organic double-junction solar cells[27]. An improved efficiency of 9.8% has been claimed by Heliatek for small-molecular photovoltaic cells very recently [129]. Unfortunately, the material combinations used to produce these high-efficiency devices are not disclosed by now.

Small electron donor molecules might possess reasonably high solubility in organic solvents, enabling wet
processing of organic photovoltaic devices. A combination of diketopyrrolopyrrole compound D6 with [70]PCBM was initially one of the most efficient low-molecular-weight material combinations developed for this purpose [130, 131]. However, recently reported squaraine dye D7 outperformed D6 significantly in bulk heterojunction solar cells with [70]PCBM [132]. Similarly high performances were reached also using oligothiophene donor molecule D8 modified with cyanovinyl units on both sides [133].

A very elegant and highly promising approach to design solution-processible organic solar cells was demonstrated by Matsuo et al. [28]. The key material is a soluble porphyrin precursor D9 that eliminates ethylene upon heating, producing insoluble tetrabenzo porphyrin D10 (Figure 25.25). When the composite of D9 with the fullerene derivative SIMEF was subjected to annealing, a highly ordered columnar structure was formed (Figure 25.26). Such composite morphology is very favorable for photovoltaic applications. To build a photovoltaic device, a soluble precursor D9 was spin-coated on a PEDOT:PSS-covered ITO slide and then converted to insoluble D10 by thermal annealing at 180°C thus producing a continuous bottom donor D10 layer. A 3:7 w/w blend of D9 and SIMEF was spin-coated above the bottom D10 layer. The resulting film was also sintered at 180°C thus forming intermediate bulk heterojunction layer with permanently fixed morphology. The morphology of the composite can be easily revealed by washing the fullerene component SIMEF away and exposing a well-ordered columnar network of the D10 material (Figure 25.26). The device was completed by the deposition of the top SIMEF layer followed by the hole-blocking layer of bathocuproine or similar material and aluminum top electrode. The fabricated devices yielded an impressive power conversion efficiency of 5.2% with an EQE of 35–45% in the whole visible range. Subsequent research of Mitsubishi Chemical in that direction brought record power conversion efficiencies of 9–10% in 2011 [29, 30]. The devices produced using this approach are expected to enter a commercialization stage rather soon.

New soluble small-molecule D11 featured by the Heeger group provided a power conversion efficiency of 6.7% when combined with [70]PCBM in organic solar cells [136]. Very similar material D12 yielding a solar cell power conversion efficiency of 5.84% was reported recently by Zhou et al. [135].

An overview of small-molecule-based solar cells presented in Table 25.4 proves that low-molecular-weight compounds have a large and still not fully explored potential to be used as advanced photoactive materials for construction of efficient bulk heterojunction devices.

Finally, we would like to mention a recent work of C. Tang and co-workers [32] which featured Schottky barrier-type photovoltaic devices based on organic semiconductors. The efficiency of the devices based on a C70/MoO3 Schottky junction exceeded 5% when a small amount (5%) of organic dopant D13 was added to the layer to improve its electrical properties. The emerging Schottky barrier approach promises to bring the efficiency of organic solar cells closer to the performance of conventional photovoltaic cells based on inorganic semiconductors.

25.6 CONCLUSION AND OUTLOOK

The last 5–10 years of intensive research resulted in the development of many novel photoactive p-type and n-type organic semiconductors, which are key materials for organic solar cells. At the same time, the OPV community learned how to manage the nanoscale ordering of the materials to create the appropriate nanoscale p–n heterojunctions in the entire volume of the active layer of the device. New materials and new knowledge brought up commercially interesting certified solar cell efficiencies of 8–10% reported recently by several independent groups.
FIGURE 25.26. (a) Technology for the solar cell construction based on SIMEF and D9/D10. (b) Top view (left) and side view (right) SEM images of the exposed porphyrin D10 network after removing SIMEF material. Reproduced from reference 49, with permission of the American Chemical Society. See color insert.

<table>
<thead>
<tr>
<th>Material Combination</th>
<th>Processing Route</th>
<th>$I_{SC}$ (mA/cm²)</th>
<th>$V_{OC}$ (V)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1–C₆₀</td>
<td>Evaporation</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>4.9</td>
<td>31</td>
</tr>
<tr>
<td>D2–C₆₀</td>
<td>Evaporation</td>
<td>11.1</td>
<td>0.97</td>
<td>49</td>
<td>5.2</td>
<td>127</td>
</tr>
<tr>
<td>D3–C₆₀</td>
<td>Evaporation</td>
<td>14.68</td>
<td>0.79</td>
<td>50</td>
<td>5.81</td>
<td>134</td>
</tr>
<tr>
<td>D4–C₆₀ + D5–C₆₀</td>
<td>Evaporation</td>
<td>6.18</td>
<td>1.589</td>
<td>61</td>
<td>6.07</td>
<td>128</td>
</tr>
<tr>
<td>D6–[70]PCBM</td>
<td>Solution</td>
<td>10.0</td>
<td>0.92</td>
<td>48</td>
<td>4.4</td>
<td>130</td>
</tr>
<tr>
<td>D7–[70]PCBM</td>
<td>Solution</td>
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<td>0.92</td>
<td>50</td>
<td>5.5</td>
<td>132</td>
</tr>
<tr>
<td>D8–[70]PCBM</td>
<td>Solution</td>
<td>10.74</td>
<td>0.86</td>
<td>55</td>
<td>5.1</td>
<td>133</td>
</tr>
<tr>
<td>D10–[70]PCBM</td>
<td>Solution</td>
<td>10.3</td>
<td>0.75</td>
<td>65</td>
<td>5.0</td>
<td>28</td>
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<tr>
<td>D11–[70]PCBM</td>
<td>Solution</td>
<td>14.4</td>
<td>0.78</td>
<td>59.3</td>
<td>6.7</td>
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<tr>
<td>D12–[70]PCBM</td>
<td>Solution</td>
<td>11.5</td>
<td>0.80</td>
<td>64</td>
<td>5.84</td>
<td>135</td>
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<tr>
<td>D13–C₇₀–MoO₃</td>
<td>Evaporation</td>
<td>11.43</td>
<td>0.91</td>
<td>50.23</td>
<td>5.2</td>
<td>32</td>
</tr>
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</table>
FIGURE 25.27. Progress of organic bulk heterojunction solar cells.

The progress in organic photovoltaics is reflected on the graph shown in Figure 25.27. If this trend continues in future, the organic solar cells will reach the level of amorphous silicon and go beyond it within the next couple of years, presenting serious competition to the classic solar energy conversion technologies.

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