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# Bulk Heterojunction Solar Cells – Opportunities and Challenges

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Additional information is available at the end of the chapter

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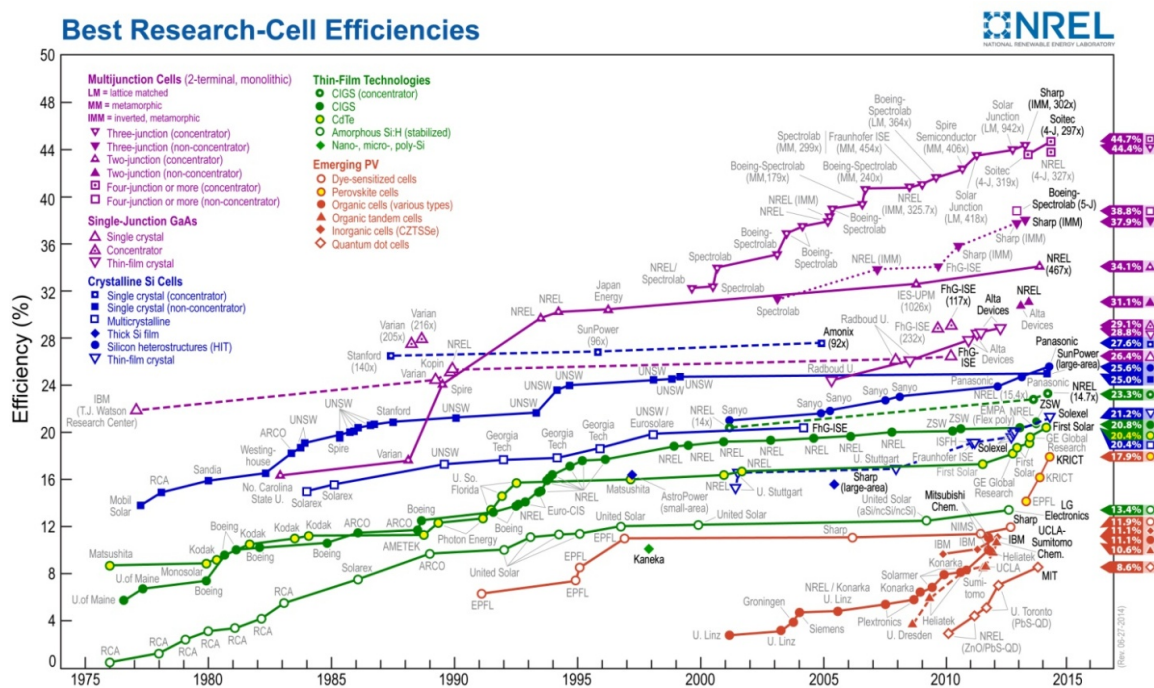
## 1. Introduction

Due to the rising concerns over the exhaust of fossil fuel and the associated environmental consequence of the carbon emission problem, search for renewable energy has become a hot research topic worldwide. Organic semiconducting materials based photovoltaic (PV) technology developments have attracted tremendous attention from both the academic community and the industry. In principle, the organic solar cells employ organic material based light absorbing functional layer to convert sunlight to electricity. Typically the light absorbing layer is made of a blend of donor material and a fullerene based acceptor material. The observation of photovoltaic effect on organic materials began in 1986 with the “Tang cell” [1], which was a two-layer device with a structure of ITO/copper phthalocyanine/perylene diimide/gold. Later in the early 1990s, the discovery of ultrafast charge transfer from polymer to fullerene [2] initiated the research field of bulk hetero-junction (BHJ) solar cells. Over the past two decades, substantial research progress have been made in the development of more robust light harvesting materials, the further modification of the modelling theory of the OPV physics, better understanding and elucidation of the light-to-electricity process and the continuous optimization of the device fabrication process with new strategies employed. This process can be witnessed by the fast growing efficiency data of the OPV cells (Figure 1) and the vast amount of literatures published annually on the topic of OPV technology. Concurrently, the industrial attention is mainly focused on development of robust materials with long lifetime and good efficiency in large scale application, production technique optimization and market exploration for OPV technology. The fast growing research activity on OPV technology involves the collaborative consolidation of knowledge from synthetic chemistry, especially on  $\pi$ -chemistry, semiconductor physics and device engineering. Figure 1 [3] depicts the certified record PCE data of various types of PV technologies that have been continuously optimized

in the past decade. Compared with inorganic PV technologies, organic solar cells have achieved magnificent improvement in terms of efficiency. Currently the record holder is Mitsubishi Chemicals who has demonstrated a reproducible  $10.7 \pm 0.3\%$  organic solar cell.

Compared with the existing mature inorganic based photovoltaic technology, a list of proposed advantages of OPV technology should be mentioned which include 1) short energy payback time [4]; 2) lower production cost compared with inorganic PVs; 3) potential fabrication via continuous printing tools; 4) new market opportunities, such as flexible PV, wearable PV, semitransparent PV window, etc.; 5) low weight and easy integration of the organic PV products. Nevertheless, inorganic based PV technologies, such as silicon, cadmium telluride (CdTe), III-V group semiconductors and copper indium gallium selenide (CIGS), are still dominating the PV market.[5] The reasons why the OPV are short of the market are mainly due to the inferior power conversion efficiency (PCE) and the poor stability of the organic solar cell devices compared with their inorganic analogs. As the ultimate goal of materials research is to apply the material based science and technology into material based products, the applicability and the competitiveness of the technology should always be buried in mind. The economic aspects of the OPV technology have attracted more attention as many companies start to step into the OPV market and create opportunities. The optimization of the OPV device, both in terms of device stability and power conversion efficiency, has become a synergistic work between the academia and the industries. Moreover, the industrial production of OPV modules, which is very different from the lab-scale production step, is also being optimized. All these efforts will be highlight in this Chapter.

With both the advantages and existing disadvantages of OPV technology in mind, we plan to give an overview of how to transform a molecule to a material and finally to a product for OPV technology and we organize this Chapter in the following way. Firstly we will summarize the existing strategies to prepare new and better light harvesting materials by synthetic chemists. Due to the limited space, we focus on the most commonly used polymeric donor-acceptor (D-A) type materials. In the following part, we summarize the recently developed device engineering methods to improve the performance of the OPV materials. This part deserves its own merit because the OPV device engineering process is essential to demonstrate the full potential of a new polymer molecule as a functional light harvesting material. Then we will summarize some aspects of OPV materials which are important for the production development, such as the lifetime/stability of the material and production techniques. Finally we will end up our discussion with a summary and perspective on the future research. There have been many excellent summary works dealing with various aspects of OPV technology, such as the working mechanism and physics of the OPV device [6-9], design principles and synthesis of new light absorbing materials [9-19], thin film morphology control and characterization [20-21], new device architecture development [22-24], interface engineering [25], quantum chemical calculations [26], economical aspects [27-29] and many insightful overviews and perspectives [30-42]. There are also a series of *Photovoltaics Literature Survey* papers by Santosh Shrestha [43] in *Progress in Photovoltaics: Research and Applications* which are useful for readers to catch up current research progress in various aspects regarding PV technology.



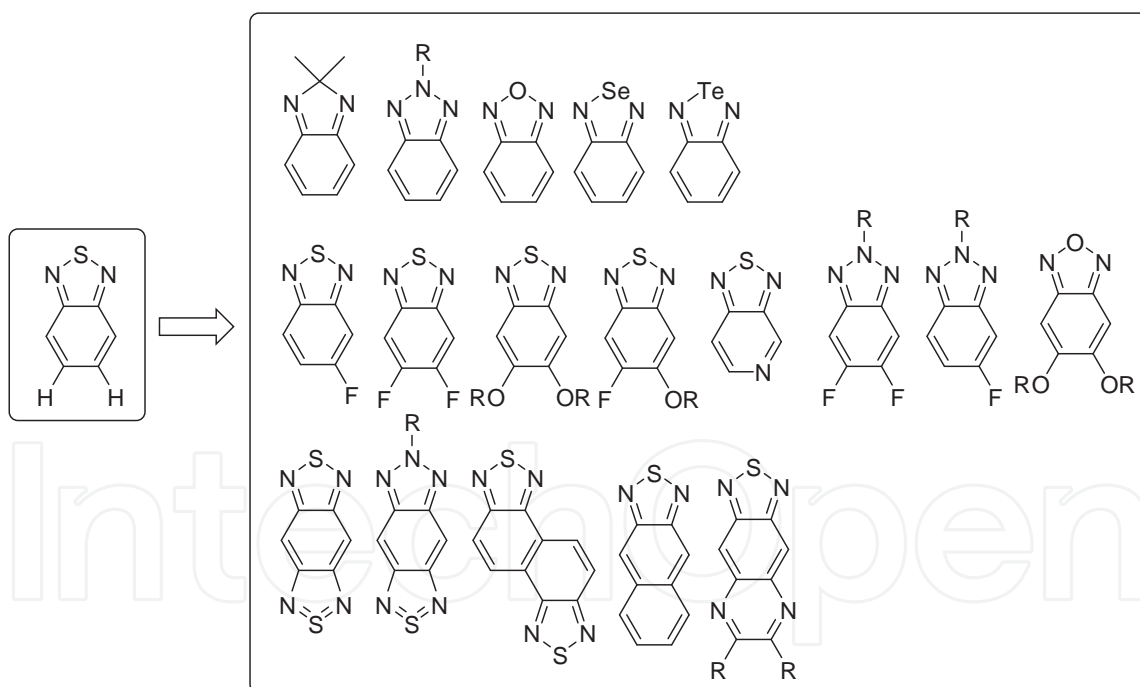
**Figure 1.** Best Research Cell Efficiencies for all types of PV technology. Data from National Renewable Energy Laboratory (NREL).[3]

## 2. Development of new materials

### 2.1. Chromophores with new $\pi$ -structure

In the concept of BHJ solar cells, the active layer is comprised of a blend of electron-donating material and electron-withdrawing material. The electron-donating material can be small molecules [12, 13] or polymeric materials [10,11,14-19] while polymeric materials are more commonly used in the literature. Both types of materials typically follow a Donor-Acceptor (D-A) design principle, in which the conjugated backbone is constructed by covalent linkage of a series of electron rich moieties and electron deficient moieties in an alternative way. This design strategy is especially useful in tuning the physical properties (absorption, frontier orbital energy levels, etc.) of the final materials due to the vast stock of electron rich and electron deficient building blocks. Guo and co-workers [44] have presented a thorough summary of current prevailing donor and acceptor species, which include about 45 donor and 60 acceptor backbones. Note that there are also variations on the solubilizing chains and spacer groups. Hence the actual number of such building blocks would be much larger than the summarized numbers. Given the wide choice of building blocks, there is no surprise that a huge structural diversity of OPV materials exists and a large amount of new materials are coming out every year in the literature. The design principle of the donor material in the BHJ blend has been summarized [45]. Basic considerations include light absorption range, frontier orbital energy levels, charge carrier mobility, favorable blend morphology, stability and solubility.

Concurrently new building blocks are being synthesized to provide more possibilities to further optimize the optical and electronic properties of the final material. Take benzothiadiazole (BT) as an example (Figure 2). Benzothiadiazole (BT) is one of the most commonly used building blocks for the construction of D-A type conjugated polymers. By carrying out structural modification of the backbone, a series of new electron-deficient moieties with different electronic properties can be prepared. One strategy is to replace the sulfur atom in the thiadiazole hetero-cycle with other elements such as carbon [46], oxygen [47,48], nitrogen [49], selenium [50,51], etc. The new building blocks have various electron withdrawing properties and hence are useful in tuning the properties of the polymer materials. The second strategy is to introduce substitutions on the BT unit, such as fluorine atoms [52-60], alkoxy groups [61-65], or replacement of C-H with imine nitrogen [66-69]. More building blocks can be prepared with the combination of these two strategies [70-75]. The third strategy is to extend the  $\pi$ -conjugation of the BT unit to prepare  $\pi$ -extended moieties [76-81]. Extension of the  $\pi$ -backbone is a versatile route to tune the electronic properties of the BT unit; however, the new building blocks typically exhibit poorer solubility and have to be prepared in longer synthetic steps. For example, by fusion of one more thiadiazole ring to the BT unit, bis-benzothiadiazole (BBT) can be prepared and possess much higher electron deficiency but poorer solubility.

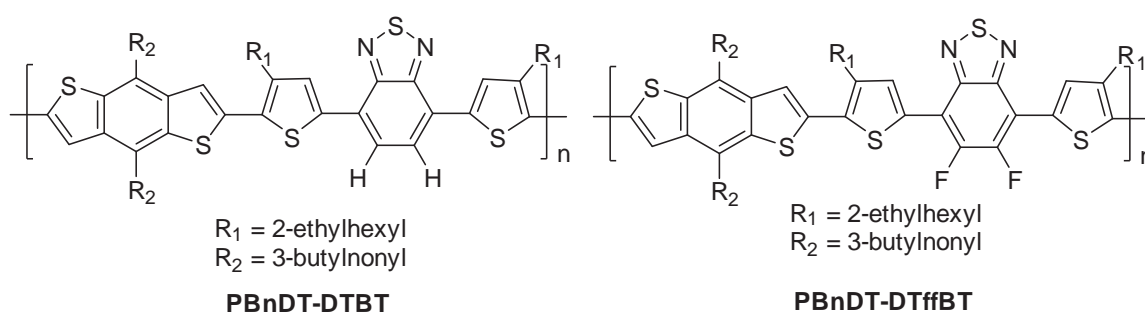


**Figure 2.** Evolution of benzothiadiazole (BT) based electron withdrawing moieties for the preparation of D-A type light absorbing polymers.

Out of all these strategies, the substitution of fluorine atoms on the aromatic backbone turns out to be a very efficient approach to achieve high-performance OPV materials. Introduction of fluorine substitutions has minor influence on the absorption behavior of the polymer; however, it induces a decrease of the frontier orbital energy levels due to its strong electrone-



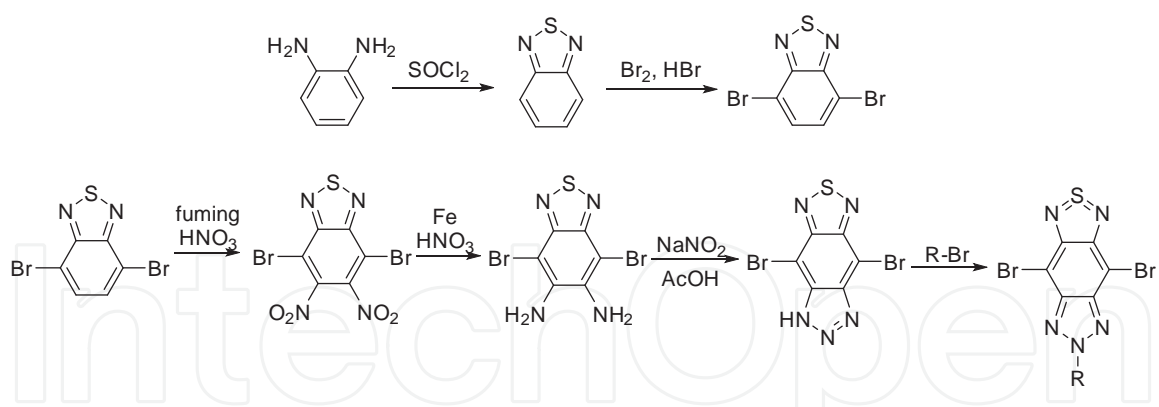
gativity and consequently the fluorinated polymers typically exhibit higher open circuit voltage ( $V_{oc}$ ). The advantages of fluorine in OPV polymer have been demonstrated by Zhou et al. [82] Polymer **PBnDT-DTBT** (Figure 3) exhibits a HOMO and LUMO energy level at -5.20 eV and -2.92 eV, respectively. After addition of two fluorine atoms on the BT unit, the HOMO and LUMO energy level of **PBnDT-DTffBT** decreases to -5.30 eV and -2.97 eV, respectively. **PBnDT-DTBT**/PC<sub>61</sub>BM based solar cell device exhibits the best PCE=5.0% with  $J_{sc}$ =10.03 mA cm<sup>-2</sup>,  $V_{oc}$ =0.87 V and FF=0.57. For **PBnDT-DTffBT**, the best device exhibits PCE=7.2% with  $J_{sc}$ =12.91 mA cm<sup>-2</sup>,  $V_{oc}$ =0.91 V and FF=0.61. It is found that after attachment of the fluorine atoms on the repeating unit, the short circuit current, the open circuit voltage and the factor are all enhanced.



**Figure 3.** Chemical structures of **PBnDT-DTBT** and **PBnDT-DTffBT**.

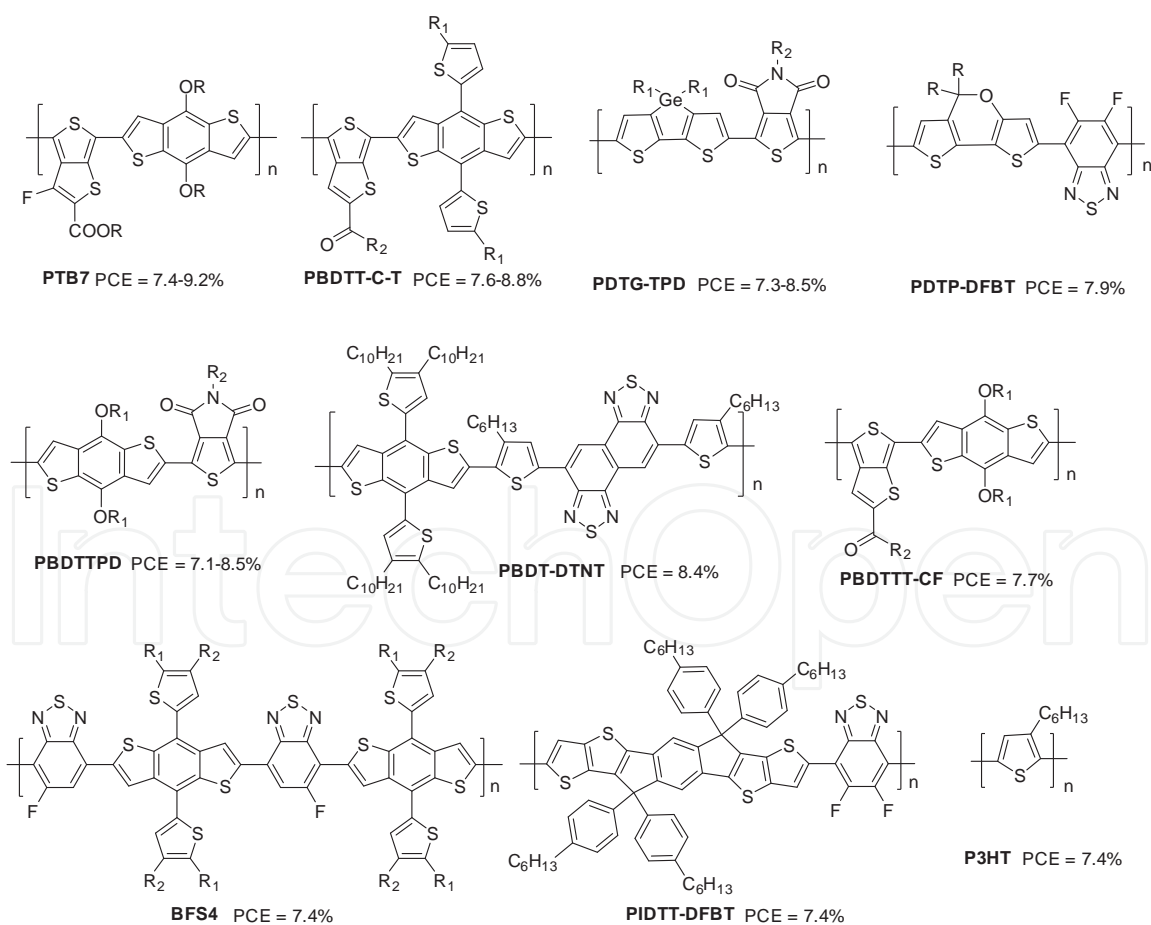
The longer synthesis steps for the more complicated building blocks are also a concern if they are to attract industrial attention. Although achieving materials in a cost-effective way is generally neglected in the academic publication and in many cases the complicated synthesis of a monomer is considered as *novelty* of the work, a simple, high yield and easily scalable synthesis of materials is highly desirable in the industry from the application point of view. For example, 4,7-dibromobenzo[c][1,2,5]thiadiazole can be prepared in three steps from 1,2-phenylenediamine (Scheme 1). As this building block is so commonly used nowadays, it has become commercially available by vendors such as Sigma Aldrich. While for alkylated 4,8-dibromo-[1,2,5]thiadiazole[3,4-f]benzotriazole [83], which is a BT unit fused with a triazole hetero-cycle, is prepared with four more synthetic steps from 4,7-dibromobenzo[c][1,2,5]thiadiazole. According to a recent estimation [84], the cost per gram of the final material increases linearly with the number of synthetic steps needed for the synthesis. The extended synthesis would definitely reduce the potential applicability of the material, as the value of a material is a compromise between the performance and the cost.

A list of D-A type polymers that have demonstrated PCE values > 7% are shown in Figure 4 [85]. It should be highlighted that the high performance of the polymers does not necessarily mean that the embedded building blocks are superior. The power conversion efficiency is determined by a number of factors and the chemical structure of the polymer is just one of them. Even for a classical polymer P3HT, after careful optimization of the device condition, the PCE can also reach 7.4% [86]. Many other factors, like the fabrication conditions, also play



**Scheme 1.** Synthetic routes of 4,7-dibromobenzo[c][1,2,5]thiadiazole and alkylated 4,8-dibromo-[1,2,5]thiadiazole[3,4-f]benzotriazole.

a significant role in determining the overall efficiency of the cell. These factors will be discussed in the following text.



**Figure 4.** Chemical structures of polymers that exhibit PCE > 7%.

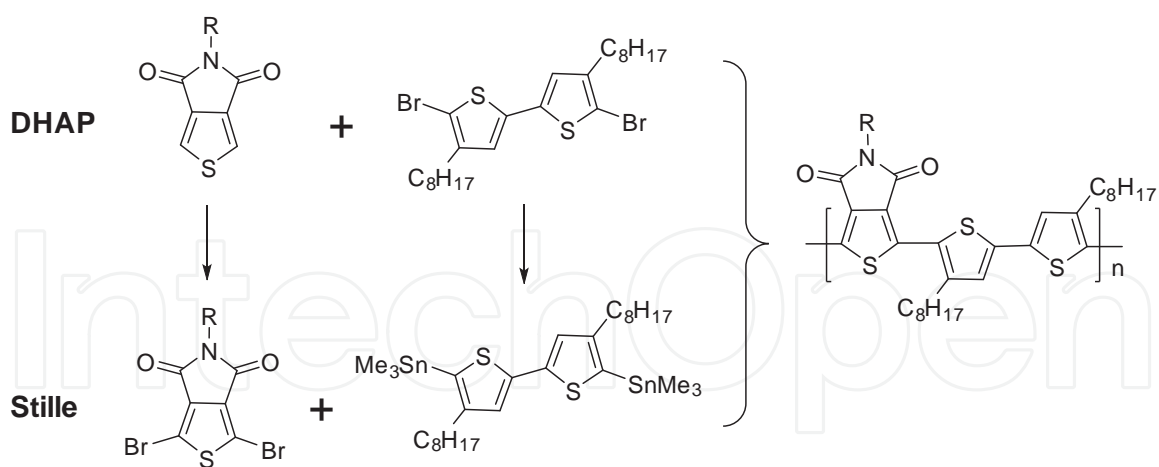
## 2.2. Side chain engineering

Side chains are attached on the rigid aromatic  $\pi$ -backbones to form “hairy rod” type polymers with suitable solubility to allow solution based processing techniques viable. In fact, the role of the side chains are far beyond the solubility concerns. Other physical properties of the polymer, such as absorption, emission, energy levels, molecular packing, charge transport and the morphology of the thin film are critically affected by the side chains attached in many cases. Commonly used side chains include linear alkyl side chains ( $n\text{-C}_n\text{H}_{2n+1}$ ), branched alkyl side chains, electron donating side chains ( $-\text{OR}$ ,  $-\text{SR}$ ,  $-\text{NHR}$ , etc.), electron withdrawing side chains ( $-\text{C}(=\text{O})\text{R}$ ,  $-\text{SO}_2\text{R}$ , etc.), aromatic side chains (4-alkoxyphenyl, etc.), functional side chains (e.g. with cleavable groups on the side chains), ionic side chains, oligoether side chains, fluorinated side chains and so on. A comprehensive discussion on various types of side chains has been presented by Mei and Bao [87]. Side chain engineering has become a routinely used strategy to modify the physical properties, especially the self-assembly of the materials in the thin film, and thus to optimize the light absorbing materials in the OPV device. Given the importance of side chain engineering, it should be noted that as the side chains do not contribute to the light absorption or charge transport in the thin films, a trade-off between the solubility and the performance of the final polymer must be made.

## 2.3. New synthetic methodology

Currently, the D-A type polymers are typically synthesized via palladium catalyzed cross coupling reactions such as Stille coupling [88] and Suzuki coupling reactions [89]. Stille coupling involves C-C bond formation between trialkylstannyl species and aromatic halide species and has been routinely used for the preparation of a large number of high performance polymers. However, the high toxicity of the tin reagent and the associated environmental issue of the generated tin wastes inhibit its wide industrial applications. Recently, a new polymerization method involving direct heteroarylation polymerization (DHAP) between aryl C-H bond and aromatic halides has been developed as a promising greener alternative of Stille coupling for the preparation of conjugated polymers (Scheme 2). Berrouard et al. [90] has demonstrated that the DHAP reaction between 5-alkyl[3,4-c]thienopyrrole-4,6-dione and 5,5'-dibromo-4,4'-dioctyl-2,2'-bithiophene is as efficient as the corresponding Stille approach. As in this direct coupling reaction no organo-tin or organo boron reagents are needed, it shortens the synthesis of final polymer by at least two steps. This strategy has been successfully implemented for the synthesis of OPV polymers [91,92], OFET polymers [92] and EC polymers [93] with reasonable molecular weight and polydispersity after judicious optimization of the coupling condition. Nevertheless, as this polymerization technique is still in its infancy, the reaction is still difficult to control for some substrates and the final polymer might be branched due to unselective C-H activation in the substrate [94,95]. The reaction conditions of the reaction including the catalyst, ligand, base, additive, solvent, temperature and duration have to be carefully controlled and optimized in order to achieve the highest molecular weight.





**Scheme 2.** Synthetic approaches of direct heteroarylation polymerization (DHAP) and conventional Stille coupling reaction.

## 2.4. Molecular weight and purity of the polymer

The molecular weight and the purity of the polymers are issues beyond the molecular architecture of the semiconducting polymers. But both factors have been demonstrated as essential parameters to ensure the good performance of the prepared polymers within the device. A high molecular weight increases the regularity of thin film and in many cases induces enhanced charge carrier transport in the transistor device [96,97] and power conversion efficiency in the BHJ solar cell device [98]. For instance, **P1** (Figure 5) [99,100] with a low molecular weight ( $M_n < 10 \text{ kg mol}^{-1}$ ) exhibits a charge carrier mobility of  $\mu = 5.2 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and power conversion efficiency of  $\eta = 2.7\%$  with  $J_{sc} = 4.2 \text{ mA cm}^{-2}$ ,  $V_{oc} = 0.64 \text{ V}$ , and  $FF = 0.35$ . For **P1** with high molecular weight ( $M_n > 34 \text{ kg mol}^{-1}$ ), it exhibits an enhanced mobility of  $\mu = 3.6 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and power conversion efficiency of  $\eta = 5.9\%$  with  $J_{sc} = 17.3 \text{ mA cm}^{-2}$ ,  $V_{oc} = 0.57 \text{ V}$ , and  $FF = 0.61$ . Similar phenomenon is also observed for **P2** [98]. **P2** with a low molecular weight ( $M_n \sim 46 \text{ kg mol}^{-1}$ ) exhibits an ambipolar behavior with  $\mu_h = 2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and  $\mu_e = 5.2 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and a PCE  $\eta = 5.48\%$  with  $J_{sc} = 12.1 \text{ mA cm}^{-2}$ ,  $V_{oc} = 0.90 \text{ V}$ , and  $FF = 0.50$ . For **P2** with high molecular weight ( $M_n \sim 61.8 \text{ kg mol}^{-1}$ ), the mobility increases to  $\mu_h = 0.15 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and  $\mu_e = 0.064 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and an enhanced PCE  $\eta = 6.79\%$  with  $J_{sc} = 13.7 \text{ mA cm}^{-2}$ ,  $V_{oc} = 0.89 \text{ V}$ , and  $FF = 0.56$ . The improved mobility for high molecular weight samples is ascribed to improved  $\pi$ - $\pi$  stacking, thin-film formation properties and increased inter-chain interactions. The increased  $J_{sc}$  and fill factor are mainly because of the improved hole mobility of the polymer, which facilitates the charge collection and inhibit charge recombination in the blend.

The purity [101-103] and the end group effect [104-106] on the performance of transistor materials and OPV materials have also been investigated. However, as the exact determination of “contaminant” or “purity level” of a given material, especially for polymers, is very difficult to achieve, the attempts to correlate the performance of an “impure” material to the existence of some extrinsic impurity would be questionable. Even though the end capping strategy has been found efficient to improve the performance of the polymer [104-106], it is still not

commonly adopted by research groups, even not routinely used by the groups who claimed the positive effect. Questions such as how the end group influences the performance of the polymer, what kinds of impurities are detrimental to the performance and what kinds of impurities serve as friendly dopants still remain unaddressed. More research effort, for example, intentional doping [107,108], is in need to solve the impurity issue of organic semiconductors in both the theoretical aspect and the practical aspect. But it is commonly believed that tedious and labor-intensive purification processes, such as Soxhlet extraction and silica gel column chromatography is always necessary to ensure sufficient purity of the sample for characterization.

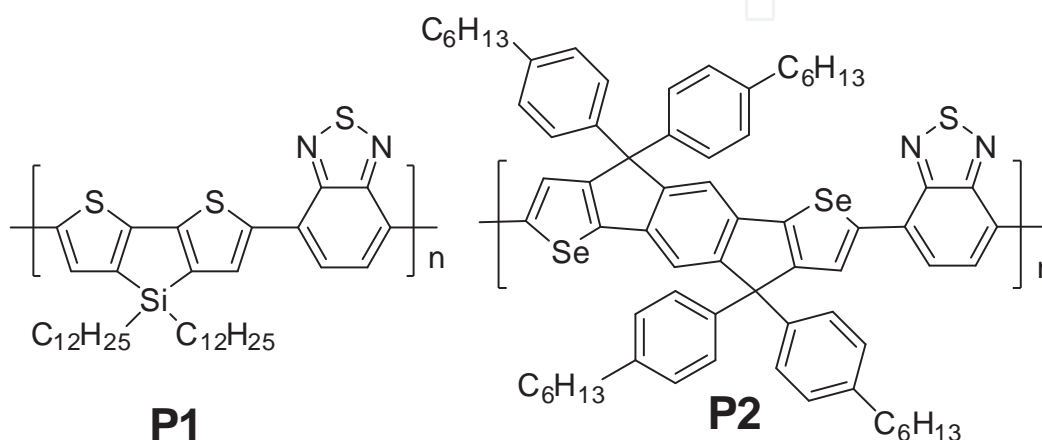
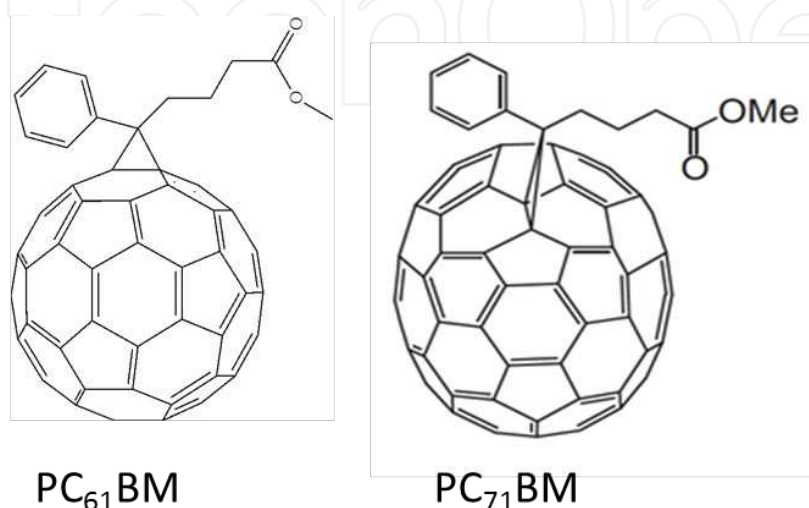


Figure 5. Chemical structures of P1 and P2.

## 2.5. Acceptor

The other important active species in the BHJ blend is the acceptor. The benchmark acceptors are fullerene based derivatives, mainly [6,6]-phenyl- $C_{61}$ -butyric acid methyl ester ( $PC_{61}BM$ ) and [6,6]-phenyl- $C_{71}$ -butyric acid methyl ester ( $PC_{71}BM$ ) (Figure 6) [109,110]. The key features of these sphere-shaped acceptors are their low internal reorganization energy, high polarizability, relatively high dielectric constant, favorable LUMO energy level, reversible redox properties, good electron transport properties and anisotropic charge transport behavior [109,110]. The superior performance of these two acceptors in the BHJ devices renders them as the first choice for most of the newly developed donor materials. Whereas  $PC_{61}BM$  absorbs minimal amount of light in the visible region,  $PC_{71}BM$  is strongly blue and green light absorbing acceptor and is more useful when the absorption of it is complementary to that of the donor so that more sunlight can be captured [111]. Nevertheless, some drawbacks of these fullerene derivatives would hamper their wide application in the industrial production. One is the high production energy cost of these fullerene based acceptors. For  $PC_{71}BM$ , the production energy is approximately  $90 \text{ GJ kg}^{-1}$  [112]. For comparison, the production energy of P3HT is only about  $1.9 \text{ GJ kg}^{-1}$  [113]. The other concern is the relative high price of these fullerene derivatives. A recent analysis by Lewis and Nocera [114] indicates that the OPV system should cost no more than  $\$10 \text{ per m}^2$  to compete with fossil fuels for energy production. The cost of

PCBM at roughly \$500-1000 per m<sup>2</sup> [42] makes the BHJ based PV technology with PCBM problematic for commercialization. Use of technical grade PCBM (~80% PC<sub>61</sub>BM and 20% PC<sub>71</sub>BM) [115] might help relieve the stress but is far away from the desired price range. In fact, various types of small molecule based [116] or polymer based [117] acceptors have been tested to replace fullerene derivatives in OPV cells. But yet the efficiency of these acceptors still cannot surpass that of fullerene based derivatives.



**Figure 6.** Chemical structures of PC<sub>61</sub>BM and PC<sub>71</sub>BM.

### 3. Morphology and device engineering

#### 3.1. Characterization of morphology

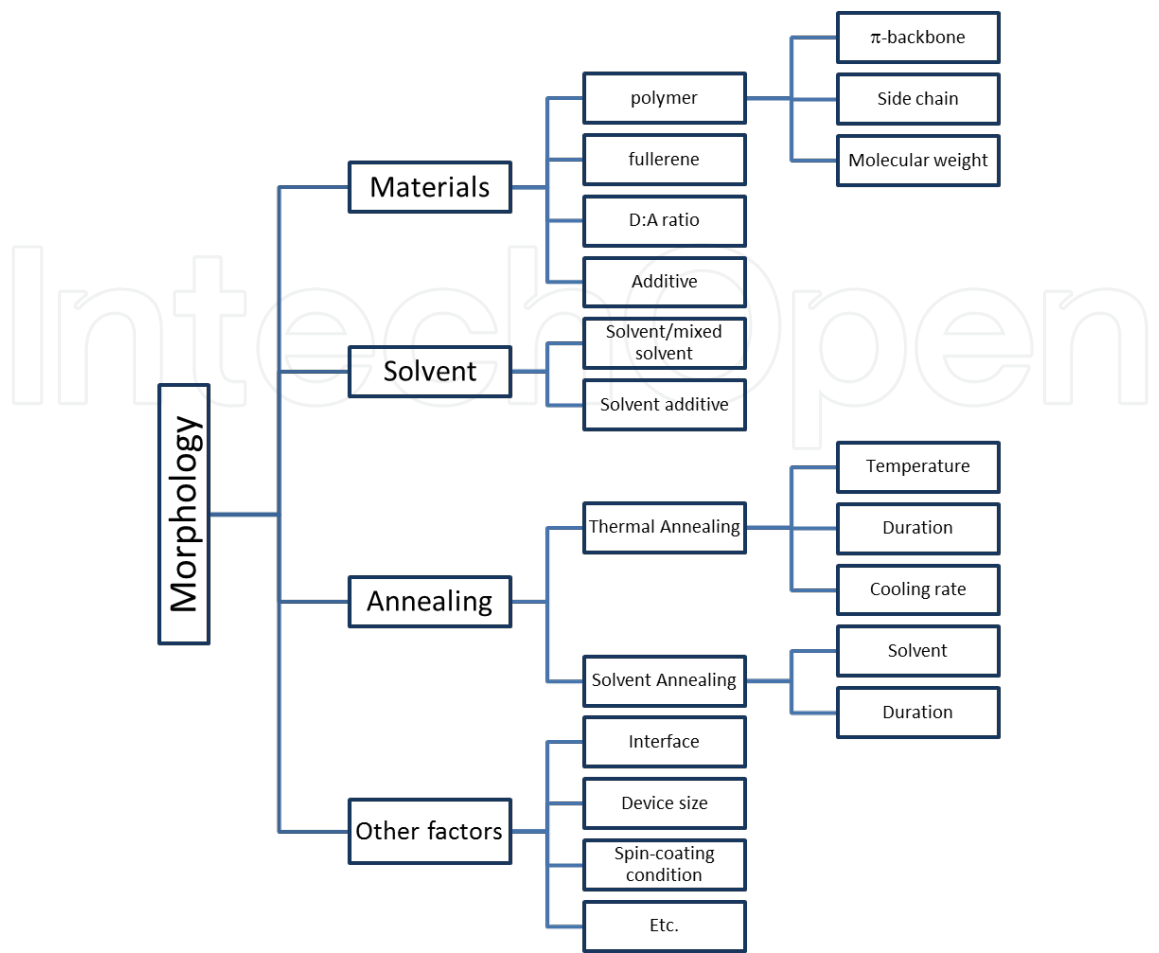
Along with the research effort to prepare D-A type conjugated polymers in BHJ solar cells to achieve the world record efficiency value, studies revealing the importance of the morphology of the polymer/fullerene blend have been carried out and the experience gained on controlling the morphology has become a valuable tool to explore the full potential of a new polymer as light harvesting materials. The thin film morphology characterization tools include grazing incidence wide-angle X-ray scattering, grazing incidence small angle X-ray scattering, resonant soft X-ray scattering, small-angle neutron scattering, transmission electron microscopy, atomic force microscopy, solid-state nuclear magnetic resonance, dynamic secondary ion mass spectrometry, near-edge X-ray absorption fine structure and scanning transmission X-ray microscopy. These analysis techniques are comprehensively summarized by Huang et al. [21]. As so much work has been done to investigate the morphology of the thin film, a rational question to ask is: *what is the best morphology?* Unfortunately, so far a precise answer to this question has not been achieved. One reason is because every characterization technique only sees the film from one aspect and a thorough mapping of the material distribution in the film still remains a challenge [118-119]. Another reason may be due to the fact that the reported

polymers with the highest power conversion efficiency values do not really share exactly the same morphology profile. As a result, the *optimal* morphology and the engineering method to achieve the best performance are case-by-case and mostly obtained in a trial-and-error approach. General descriptions like *homogeneous* and *interpenetrating networks* with *nanoscale phase-separated domains* are routinely used to describe the morphology in the cells with distinct performance.

### 3.2. Morphology optimization by device engineering

A series of parameters that will influence the morphology of the polymer/fullerene thin film are listed in Figure 7. The physical properties of the polymer such as the  $\pi$ -backbone, side-chains, the molecular weight, the identity of the fullerene acceptors used and the mass ratio between the two etc., are factors related to the materials. The determination of the ideal D:A ratio for a new polymer material has been a matter of trial and error, with the ratio 1:1 to 1:4 most commonly used. The solubility of the polymer and the fullerene derivative should be sufficient in the processing solvent. Halogenated solvents (chloroform, chlorobenzene, 1,2-dichlorobenzene, 1,2,4-trichlorobenzene) are routinely used as they possess high solubility for both the donor polymer and the fullerene acceptors. For many reported polymers [20,21], judicious choice of the processing solvent has to be made in order to achieve the optimal morphology and power conversion efficiency. For a specific new polymer, or a new polymer/fullerene blend, the choice of optimal processing solvent is not trivial, normally based on trial-and-error investigations. Recently, more research has been focused on the replacement of halogenated processing solvents with more environmentally friendly solvents, such as toluene, xylenes and long alkanes [120]. This is especially important for the industrial production of OPV modules [121].

Processing additives with low vapor pressure and high boiling point are commonly added in the solvent to optimize the morphology of the polymer/fullerene blend [85]. Commonly used additives include 1,8-diiodooctane, 1,8-octanedithiol and 1-chloronaphthalene (Figure 8). General guideline for selection of the additive is that the solvent additive should be less volatile with higher boiling points than the host solvents. The mechanism how the additive influence the morphology and the overall performance of the device has been discussed by Lee et al. [122]. It should be noted that solvent additives added during the fabrication process might remain in the solar cell and behave as contaminants to hamper the performance of the solar cell. In some case, addition of additives shows no effect [123,124] while in some case the addition of additives is detrimental to the performance [125]. These results indicate that the solvent additive is not an elixir to enhance the PCE performance of all polymers and the detailed effect and mechanism should be made case by case. Moreover, a specific process step must be added to remove the residual deleterious compounds which are obviously unfavorable in the industrial application. Hence, it is more desirable to design high performance polymer/fullerene system with no such additives needed to achieve the good performance. During the production of OPV modules, some other additives, such as rheology modifiers, anti-foaming agents and surface tension modifiers would be added into the ink formulation to make it more suitable for printing technology. The effect of these additives on the solar cell

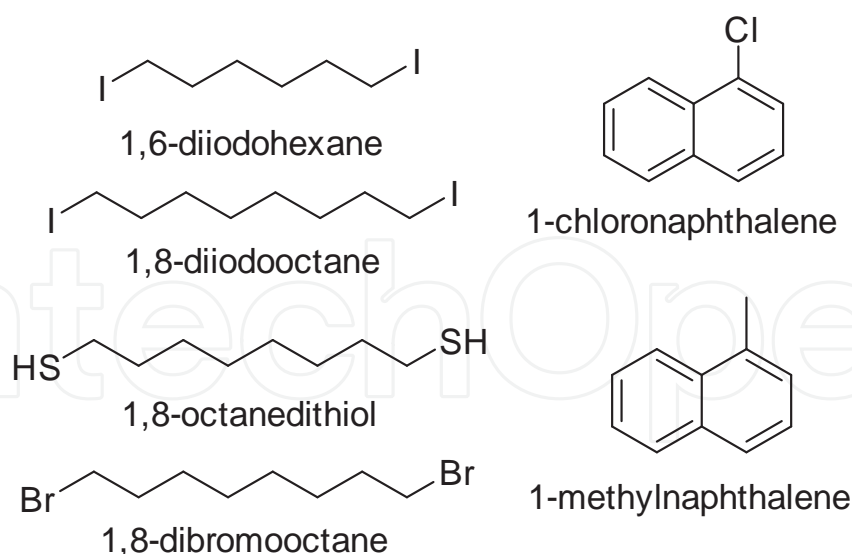


**Figure 7.** Summary of parameters that influence the morphology of the BHJ active thin film.

performance has not yet been well studied. There are research attempts to incorporate various non-solvent additives, such as nanoparticles [126], carbon nanotubes [127], small molecules [128] and polymers [129], to create a ternary blend BHJ solar cell. These strategies have demonstrated how a third component in the polymer/fullerene blend influences the overall morphology and performance of the solar cell, which could be used as a potent routine method to enhance the performance of the device [130].

Thermal annealing is an alternative method for controlling the BHJ morphology and improving the PCEs. By applying thermal energy to the thin film, it helps the reorganization of the polymer/fullerene blends and increases the crystallinity of the film [131]. This processing method has been routinely used to optimize the thin films for transistors [132] and BHJ solar cells [20,21]. The annealing temperature, the annealing duration and the cooling rate are key parameters to optimize the performance of the device and the optimal combination of the thermal treatment is material-dependent. Even for the same material, e.g., P3HT/PCBM blend, the optimal annealing condition differs from lab to lab [20], presumably due to different device structure, different solvent, different purity, different molecular weight, or even different operator. So far there is no general guideline to predict the optimal condition for a new OPV material and the optimal condition is obtained via a tedious trial-and-error approach.





**Figure 8.** Chemical structures of solvent additives for BHJ solar cells.

Solvent annealing refers to the treatment of the BHJ thin film with solvent vapor, typically in a petri dish contained with the solvent. Parameters to optimize include the solvent type and the treatment duration. By exposing the coated thin film with solvent vapors, there is reorganization and further morphological evolution over time. This method has been demonstrated to enhance the morphology, the hole mobility of P3HT [133] and the PCE performance of the P3HT/PCBM solar cell [134]. Treatment of the thin film with polar solvents, such as methanol and ethanol, is also found to improve the morphology and render higher PCE values for P3HT/PCBM [135].

In summary, the morphology of the active polymer/fullerene blend in the BHJ solar cell can be tuned by a number of factors, such as the materials, choice of solvent, solvent additives, annealing condition, etc. The optimal condition to achieve the best device performance is typically material dependent and achieved in a trial-and-error approach. Sometimes, a minor modification of the processing condition can introduce magnificent enhancement of the device performance, for example, addition of processing additives. The complexity of the morphology control and the tedious optimization process would account for the phenomenon that why so many promising polymer materials in the literature with suitable absorption, energy level and solubility possess inferior device performance. Even for the same polymer motif, the OPV performance would vary significantly by different processing methods [136]. This again highlights the importance of device engineering work to explore the full potential of a new polymer in the BHJ solar cell.

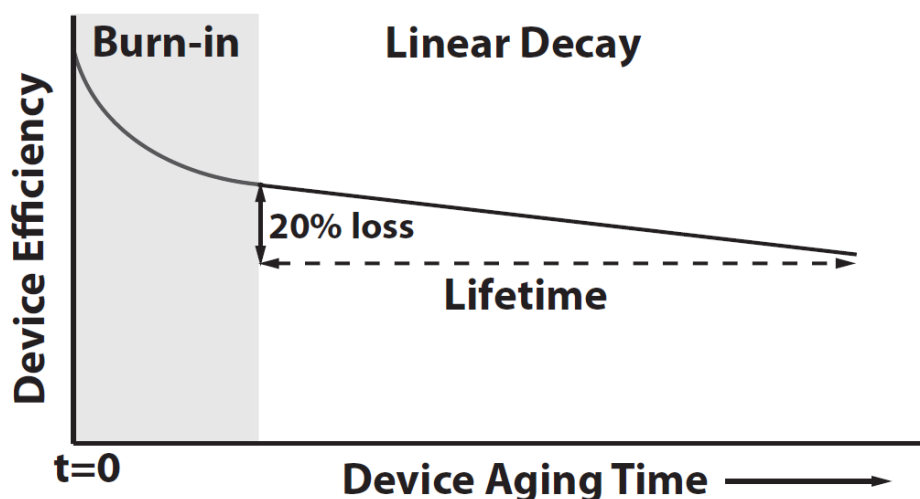
#### 4. Industrial concerns

As the ultimate goal of any material related research and technology development is to apply the material and to fulfill the promises of the material, such stress on the large scale manufac-

turing and product development has also been witnessed for OPV technology. With the fast performance improvement of OPV cells in research labs, the application of OPV technology as a renewable energy source has become more appealing. However, it is never trivial to translate a lab-based technology into a large volume production process. A large number of difficulties and problems have to be overcome to ensure the successful commercialization of the technology. In this session, we will highlight some aspects related to the industrialization of OPV technology.

#### 4.1. The stability and the lifetime issue

The stability issue of the light harvesting material in the solar cell device should be brought into discussion as the OPV technology is aimed to generate electricity from sunlight for a long period of service time. The materials used to construct the OPV module, which include the active layer, the electrode materials and the encapsulating materials, should be robust under the outdoor condition and the performance of the OPV module should be maintained to ensure the power generation efficiency of the technology. The currently known degradation mechanisms of the solar cell device, including morphology degradation, photo-oxidation, interface degradation, physical and mechanical degradation, have been well discussed in a number of review articles [137-139]. It should be highlighted that the active layers and the metal electrode materials are especially prone to degrade upon contact with water and oxygen. Therefore, in real practice the encapsulation of the device is mandatory to guarantee the long-term stability of the device. The water and oxygen transmission properties of the encapsulant materials are thus essential to ensure the stability of the OPV module [29]. The growing concerns over the stability issue on OPV technology and fulfillment of the promise of OPV as a renewable energy technology has initiated the “International Summits on Organic Photovoltaic Stability” (ISOS) [140] to stimulate the research effort to address these issues.



**Figure 9.** Typical decay curve of a polymer solar cell employing a standard device architecture. The lifetime is defined by the point at which the efficiency has dropped by 20% from the start of the linear decay period. [141] Copyright 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

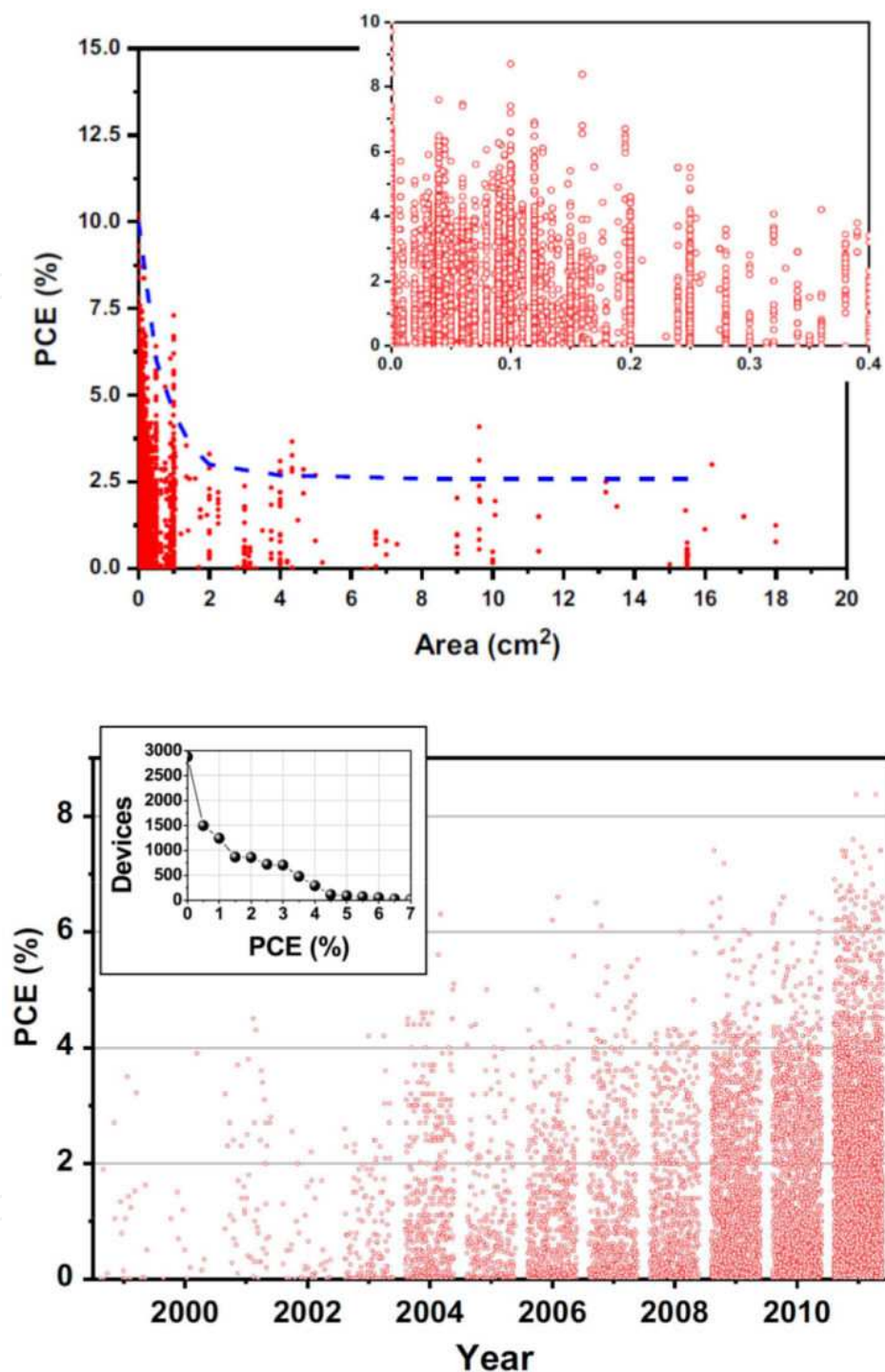
The degradation profile of an OPV module typically follows a trend shown in Figure 9 [141]. The device suffers a *burn-in* degradation process at the early working life which is characterized by an exponential loss in efficiency and then a linear decay process. The lifetime of the device is defined as the time at which the efficiency drops to 80% of the efficiency after *burn-in* process. By appropriate encapsulation, solar cell devices based on poly[9'-hepta-decanyl-2,7-carbazole-alt-5,5-(4',7'-di-thienyl-2',1',3'-benzothiadiazole)] and PC<sub>71</sub>BM blend have demonstrated a lifetime of ca. six years [141]. This lifetime is marvelous in reported lifetime of OPV solar cells [142]. However, such lifetime is still considered insufficient if OPV technology is aimed to compete with the mainstream Si-based PV technology. A silicon based solar cells typically lasts on the order of 25 years and much higher PCE (Figure 1). In this regard, there is still a huge space for OPV technology to improve in order to survive in the PV market.

#### 4.2. Processing technique

As one of the potential advantages, solution based processing methods, such as roll-to-roll printing and ink-jet printing, are suitable for organic solar cell materials [143-145]. So far in the lab scale, the BHJ solar cells are typically fabricated by spin-coating method. As spin-coating turns out to be suitable for the reproducible formation of homogeneous thin films, it is difficult to scale up and a large amount of inks is wasted during the spin-coating process. Wet-printing with a roll to roll production process is a more favorable processing technique for large scale OPV module fabrication. These printing techniques include gravure printing, flexographic printing, screen printing, rotary screen-printing, knife coating, slot die coating, and so on. More details regarding these printing techniques can be found in [144, 145]. Demonstration of large scale printing of OPV modules has been done by Krebs et al. [146] and currently OPV based solar parks have been established to explore the potential this new energy technology. One issue related to the printing technology is the uniformity and reproducibility of the final OPV module since the OPV performance of BHJ blend is very sensitive to the morphology of the thin film whereas the morphology is very sensitive to the processing condition. The materials used and the processing technique should be able to provide an OPV module with lifetime > 10 years with an average power conversion efficiency > 10% to compete with the mature inorganic PV products in the mainstream market. Even though the current start-of-the-art efficiency can reach >10% for small devices in the research lab, the efficiencies of the large area devices by solution processing methods are still low (< 3.5%) [144]. Further optimization of both the materials and the processing methods is urgently needed to fulfill all the advantageous claims of OPV technology.

#### 4.3. The economic potential of OPV technology

One concern regarding the OPV technology is that how cheap the electricity generated by this renewable technology can be. More anxiety appears after the business failures of endeavors in the OPV market [147,148]. As a matter of fact, in the past years only a number of companies (Solarmer Energy Inc., Ossila, DyeSol, Heliatek, G24 Power, Eight19, Mitsubishi, Plextronics, Sharp Solar, Solaronix, SolarPrint, etc.) have ventured into the OPV technology related business, and are struggling to survive in the market. A number of articles have addressed the



**Figure 10.** Top: A plot of the power conversion efficiency versus the active area. Bottom: The PCE values obtained versus the publication year. [30] Copyright Elsevier 2013.

economic potential of OPV technology to estimate the cost of the OPV electricity [4, 27-29, 149-150]. One key factor that dominates the cost is definitely the power conversion efficiency. Figure 10 shows the PCE values of the reported OPV devices vs. the area (top) and the year (bottom) by Krebs et al.[30] It is found that most of the highly promising efficiency data are

only achievable with a device area  $< 1 \text{ cm}^2$ . Furthermore, even though there are promising efficiency data ( $\sim 7\text{-}10\%$ ) of some hero polymers, the majority of the research work exhibits a power conversion efficiency of less than 3%. As the area of the solar cell device increases, the efficiency is expected to be lower. With the current efficiency number for large scale OPV modules ( $< 3.5\%$ ), the applicability as mainstream power generation technology is rather dim. Some potential market and niche products for OPV technology include portable, low weight charger for electronics, PV covered uniforms, backpacks and tents for military usage and OPV integrated windows and walls. One intriguing idea about OPV usage is to serve as top cell in a tandem device with an inorganic bottom cell [151]. The tandem cell design strategy for all organic based materials has been proven efficient to improve the power conversion efficiency [22,24]. Key to the success of this tandem organic/inorganic strategy is the development of OPV modules with comparable lifetimes so that the technology can be used in a time of 5-10 years range. Another aspect is the energy pay-back time. For crystalline silicone PV technology, the energy pay-back time is estimated to be 4.12-2.38 year while for OPV it is about 2.02 to 0.79 year [28]. An even more optimistic estimation of the energy pay-back time of OPV technology is only 1 day [4]. As currently all promising data about OPV technology come from research labs and theoretical work, it is still difficult to conclude on the future and fate of OPV technology. Efficiency and stability are two major obstacles, but may also become opportunities for new business players.

## 5. Summary and outlook

The concept of bulk hetero junction solar cells has been continuously developed over the past two decades. Enormous achievements have been witnessed over the journey and currently the record efficiency of BHJ solar cells has reached over 10% (Figure 1). New materials, especially the donor materials in the blend, have been developed in an expanding rate, with new design strategies, new building blocks and new polymerization methods at the same time. For the acceptor part, fullerene based derivatives,  $\text{PC}_{61}\text{BM}$  and  $\text{PC}_{71}\text{BM}$ , are still the first choice for researchers. As the energy conversion process involves charge transfer over the donor/acceptor interface, the morphology of the donor/acceptor is therefore essential for an efficient power conversion process. The morphology of the thin film, however, is very sensitive to the processing conditions, such as the materials used, solvent, solvent additives, annealing, spin-coating conditions, etc. A tedious but worthwhile optimization process of all these parameters has to be carried out to explore the full potential of any newly synthesized polymer donor material or any new acceptor material. So far, the choice of the best condition is still based on a trial-and-error approach. Furthermore, problems arise as the OPV technology is translated from the lab-scale to industrial scale, e.g., how to achieve the optimal morphology of a  $\text{cm}^2$  device in the industrial scale, how to optimally process the OPV module, and how to improve the device stability by suitable encapsulation. The solutions to these questions are by no means trivial. Most probably a rediscovery process has to be carried out to optimize all the parameters associated with the industrial scale production.



As the OPV technology has gradually become business relevant and quite a number of companies are currently active in the OPV market to cash the promises of OPV researchers, more creative breakthroughs are in urgent need to solve the intrinsic efficiency and stability issues of current OPV technology. Other than further development of more efficient light harvesting materials, some new concepts such as ternary solar cell [23, 130], and modification of the solar cell structures [22,24], e.g., inverted solar cells, tandem solar cells, or tandem organic/inorganic solar cells would pave new ways to improve the efficiency of the solar cell. Further development of encapsulant materials with lower water/oxygen transmission rate would help the solar cells survive longer under ambient conditions [29]. The continuous optimization effort on the industrial roll-to-roll printing techniques would help minimize the gap between the best efficiency data from lab devices and the large scale OPV modules. These developments have to be fast, as tremendous work is spent to optimize current inorganic PV technology as well (Figure 1). Furthermore, BHJ based solar cells also have to compete with other organic material based PV technology, such as dye-sensitized solar cells [152] and perovskite solar cells [153]. There are also issues regarding the marketing of OPV based technology. As it is envisaged that OPV will not be able to compete with inorganic PV technology in the mainstream energy production market in the coming 5 to 10 years [28], niche markets, such as portable electronics chargers, flexible PV and wearable PV, are therefore sought in the short term. The light weight and the flexibility of OPV technology would become advantageous to survive in the market.

To end up our discussion, we will emphasize the nature of OPV research and related materials development. Any science and technology development, if it is aimed at large scale application, it should be robust, reproducible, affordable and efficient in its claimed function. The materials used in the device should be accessed in an easy and cheap way and the production process should be cost-effective. And more importantly, the commercial products should have attractive features to survive in the market. There are still a lot of obstacles for OPV researchers to conquer, but more opportunities in the future.

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