
An overview on P3HT:PCBM, the most efficient organic solar cell material so far.

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Abstract

It is not news that organic polymers have been used as solar cell materials. They have a couple of advantages over conventional semiconductors. However, their efficiency remains relatively low due to limited absorption spectra and poor charge mobility. Among these materials, fullerene derivates shows great potential being effective electron acceptor. A combination of narrow-band donor and fullerene derivate is a possible approach to efficient organic cells, including the most efficient organic cell P3HT:PCBM. Here I'll discuss the ways to increase solar efficiency and give a brief description of efforts made for P3HT:PCBM.

key words: organic solar cell, P3HT:PCBM

Introduction

Solar cell or Photovoltaic cell (or PV cell for short), is the device that converts the radiation of the sun to electricity. Every leaf of a green plant does something similar --- they convert sunlight to chemical energy. Actually, a group of solar cells, the so-called "organic cells", started by borrowing the idea from leaves. Pigments (including chlorophyll[1]) were used to sensitize titanium-based materials[1,2]. The importance of developing efficient solar cells is obvious. The sun supplies us a clean and unlimited resource of energy, helping us relieve the energy crises and world pollution. The source is out of question while the approach to efficiently utilize it remains a challenge.

Ever since 1954, when the first modern Si p-n junction solar cell is invented at bell lab[3], many attempts have been done looking for a high-efficiency low-cost solar cells, leaving several significant milestones. In 1970, Zhores Alferov's team at USSR developed first highly effective GaAs heterostructure cell. In 1980, the first thin-film cell using

Cu₂S/CdS was developed at the University of Delaware with efficiency of 10%. In 1991, the first dye-sensitized cell was invented. In 1994, there came the first cell that exceeds 30% conversion efficiency using GaInP/GaAs. And in 2006, the "40% efficient barrier" was broken. Besides material research, much has been done for increasing sunlight concentration, carrier collection, and cell stability[4]. Moreover, researches have gone beyond the inorganic world. Despite their low efficiency, the organic polymers have attracted much interest. The poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C₆₁-butyric acid methylester (PCBM) blends is one of the promising organic solar cell materials. It is the most efficient fullerene derivate based donor-acceptor copolymer so far[5,6].

P3HT:PCBM has reported an efficiency as high as 5%, which is unusual in the organic cell material. Their structures are as shown (Fig 1). PCBM is a fullerene derivative. Because of high hole mobility, it plays the role of electron acceptor in many organic cells. P3HT is among the Polythiophene family,

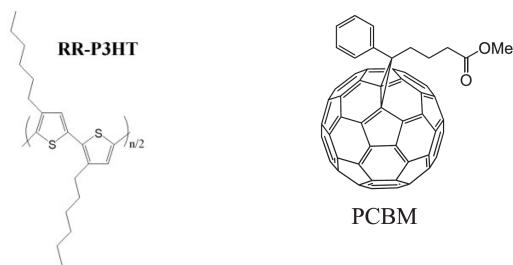


Fig 1: chemical structure of PH3T and PCBM

which is a kind of conducting polymer. It is the excitation of the π -orbit electron in P3HT that gives the photovoltaic effect in the blend. [7]

General Principle

Here I'll briefly introduce the microscopic working steps of a solar cell as well as its macroscopic parameters such as short circuit I_{SC} , open circuit voltage V_{OC} , Fill Factor FF, and characteristic resistance.

Generally a solar cell operates through four major steps. The first step is to absorb incident photons, which is affected by the macroscopic surface property. Then, the electron-hole pair, the so-called exciton, is produced. This is directly determined by the material's band structure. The third step is separation of the pairs, determined by the charge distribution inside the cell. And in the end, the generated charge would be collected at electrodes. The major factors of the efficiency of a solar cell is the number of independent charge carriers produced through the procedure. Thus, the second and third steps are mostly focused on.

(1) Exciton generation

The basic idea how the incident light produces charge carriers seems easy to comprehend. When a photon incidents on a certain material, it would be either scattered or absorbed. For the latter case, the photon

should have a minimum energy. Then an electron would be excited to a higher energy state. For example, in alkali metals, the metal got ionized when incident by (UV) beams, and “photoelectric” current is produced. “Photovoltaic” materials operates in a similar way. For example, in a semiconductor, when the incident photon has an energy $\hbar\nu \geq E_g$, an electron in the valence band would be excited to the conducting band, leaving a hole in the valence band. This electron-hole pair is called *exciton*. In organic materials, E_g equals to the difference between energy of lowest unoccupied molecular orbit (LUMO) and highest occupied molecular orbit (HOMO). Extra energy ($\hbar\nu - E_g$) would be wasted in the form of heat.

Thus, an efficient solar cell should have a wide absorb spectrum, so as to create as many pairs as possible. A multiband material would be a good choice. With smaller gaps, the cell can operate in the dark using infrared spectrum. On the other hand, larger gaps leaves little extra energy for UV photons, so that the energy wasted in the form of heat is minimized. Additionally, low optical reflectance is desired.

Why not choose an alkali metal as a solar cell material, then, as they also produce charge carrier after illuminated? The reason is quite obvious: energy gap. In a band-structured material, electrons excited to conducting band or LUMO have to cross energy barrier before recombination with holes. In a metal where no

such gap exists, electrons and holes would instantly recombine unless the metal is ionized. Besides higher energy requirement to ionize the metal, vacuum and external field supply is desired to collect all the photoelectrons. In band-structured materials, on the other hand, potential difference naturally builds up when illuminated. So that's a better material to convert solar energy to electricity, despite the fact that surface resistivity would somewhat impair the production of current. It is the energy gap that mainly leads to the difference of "photovoltaic" materials and "photoelectric" materials, the former of which we choose to make solar cell.

"Photovoltaic effect" is more than just photoelectric effect, although the physics for photon-charge transmission is the same. Experiments show that photovoltaic potential is only proportional to light intensity at low intensity. With the increase of the intensity, it would then go up in a logarithm behavior then reaches a steady maximum. On the other hand, simple photoelectric effect goes directly proportional to light intensity[8]. This might be the result of a limited charge carrier supply. Moreover, photoelectric cells goes to higher potential when illuminated while photovoltaic cells can have reversed polarity[8], which means not only electrons, but also holes, can be the charge carriers. Furthermore, to produce a photoelectric current needs external potential, which is not necessary for photovoltaic cells[8], indicating the existence of internal field in photovoltaic cells, which usually occurs in the vicinity of junctions and are essential to exciton separation.

The actual energy to create an exciton is actually less than E_g , considering the fact that electron and hole are paired through screened Coulomb interaction instead of none. On the other hand, we have to supply this energy to separate the excitons, which would be

discussed later. It's easy to calculate the binding energy E_b using hydrogen model, replacing the reduced mass m by reduced effective mass m^* and electronic charge by e^2/ϵ , where ϵ is the dielectric constant, we got $E_b = \frac{m^2}{me^2} E_0$, $E_0=13.6\text{eV}$ [9]

(2) Exciton separation

Separation of exciton is the major difference of various kinds of solar cell materials: semiconductors, dye-sensitized materials, and organic polymers. First difference lays in the binding energy. In semiconductors where ϵ is large, $E_b \sim 0.1\text{ eV}$, the pair is easy to separate. Meanwhile, the change in the band structure is trivial. In dye-sensitized materials, the electron is excited to the conducting band, leaving the dye molecule in an ionized state. The ionized dye is regenerated by electron transfer from the surrounding environment[10]. In other words, the dye-sensitized material separates the pair by extracting the hole with electron supplied from the environment. In organic polymers, however, things have been different. Dielectric constants ϵ are small [11]. This shifts the absorption spectrum to longer wavelength but brings difficulties to separate excitons.

Excitons can be separated if they meet with electric field within their diffusion range ($\leq 20\text{nm}$ [12]). The internal field exists in the vicinity of junctions, the boarder where two regions meet. It is the result of thermal equilibrium of the contacted materials. When two materials with different work functions were brought into contact, electrons would flow from the one with lower work function to the other until the Fermi surface matches. This builds up an internal field near the contact surfaces. Here's some typical junctions.

Schottkey junctions occurs at the

interface of metal and semiconductors, or between metal and p-type organic polymers. Due to high resistivity of organic polymers, only the excitons created within the diffusion range from the interface can be separated.

Most common solar cells were based on the single p-n junctions, which is the interface of similar semiconductors. This can be achieved by doping one single crystal with different dopants diffused from each end. The field of the p-n junction is shown in Fig 3b.

When two dissimilar layers are in contact, heterojunction forms. As the gaps are not of same width, there can be either staggered gap (Fig 3c) like common p-n junctions, or straddling gap (Fig 3d). Ideally the band offsets can be calculated by Anderson's rule.

However, due to lattice distortion at the interface, in real cases it becomes more complicated. Heterostructures have many interesting properties, like superinjection and window effect. The former increases carrier number and the latter prevents photon absorption at surface defects, both largely improving the photoelectron productivity [13]. In organic materials, the most basic heterostructure is a bilayer of donor and acceptor, and the exciton is separated when the charge carrier moves from LUMO of donor to LUMO of acceptor. However, due to short diffusion range, this is still inefficient.

To address this problem, bulk junction structure has been introduced to replace bilayer, so that the interface between the donor

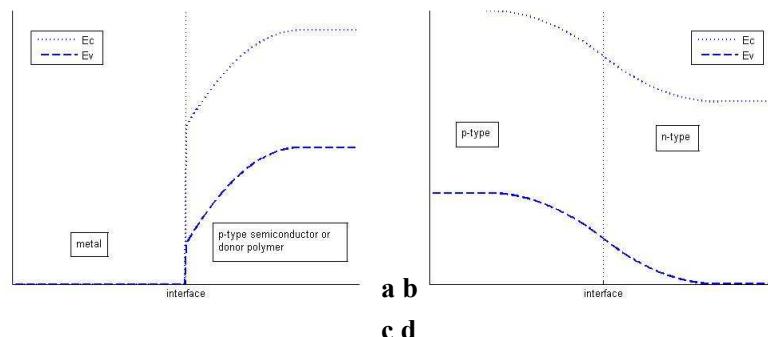


Fig 2. schematic plot of junctions.

- a. Schottkey**
- b. p-n**
- c. heterojunction, staggered**
- d. heterojunction, straddled**

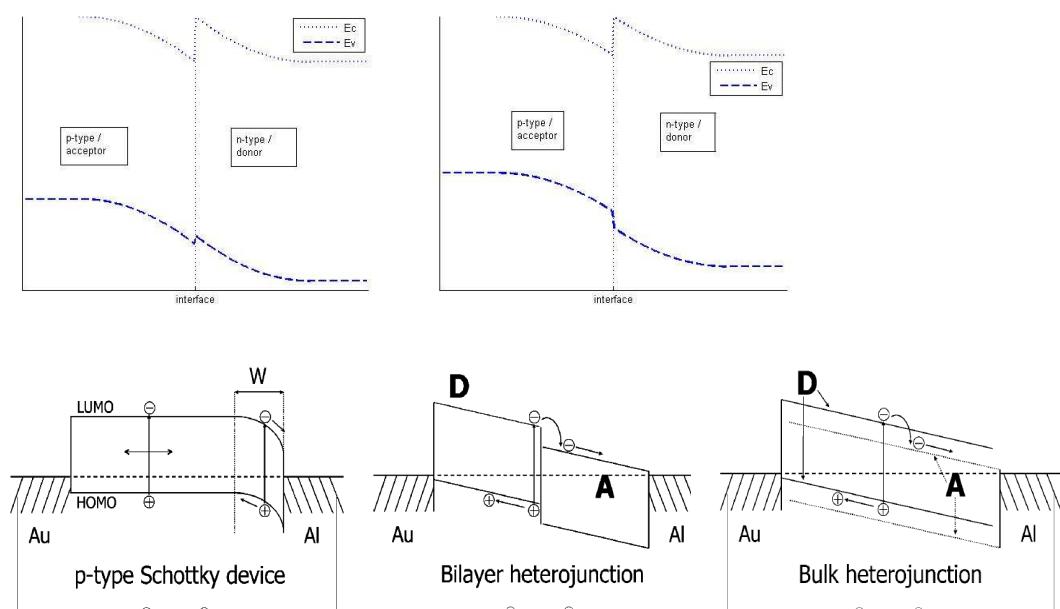


Fig 3. schematic junction structures for organic polymer [12]

and acceptor is enlarged. For example, instead of depositing a polymer layer on metal surface, small conducting particles were brought into polymers. But in this case, localized plasma instead of some “bulk Schottkey junction” enhanced the polymer’s performance [14]. There’s also bulk heterostructure by copolymerization of the donor and acceptor materials. Thus, excitons have more chances to diffuse into an internal field and got separated [12].

Additionally, exceeding energy ($h\nu - E_g$) can help with exciton separation[15].

(3) Exciton collection

As has discussed above, bulk heterostructure helps to increase the exciton separation percentage. However, the high charge separation efficiency of bulk junction structure is achieved at the cost of charge mobility and collection efficiency[16]. It results from lower driving force from polymer to acceptor compared to bilayer, where charge layers are built. So efforts like diffuse bilayer heterojunction, which combines bilayer and bulk architecture has been tried[12]. Another way is to decrease surface resistivity, for example, by utilizing some inorganic materials [17]. PCBM is a material that have higher hole mobility[18]. Experiments has show that better-organized morphology helps charge transport[19,20]. And more efficient charge collection approaches are being sought. For example, thin films of partially oxidized carbon nanotubes are applied to facilitating hole-extraction[21].

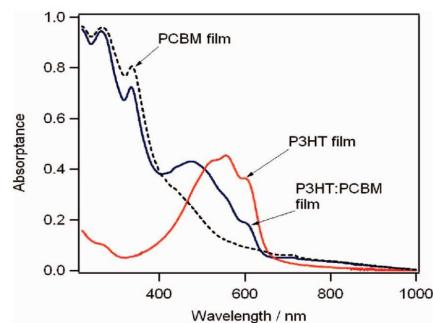


Fig 4 Absorptance spectrum of P3HT film, PCBM film, and P3HT:PCBM film [16]

(4) macroscopic parameters of a “good ” cell

In application, several parameters were measured to test the performance of a solar cell. The most commonly used parameters are: short circuit current I_{SC} , open circuit voltage V_{OC} , fill factor FF, and characteristic resistivity (parallel, series, and shunt). From the basic principles discussed above, it is easy to see these parameters’ link with microscopic mechanism. I_{SC} is nothing more than charge carriers, which is determined by the efficiency of exciton generation and separation, and charge collection. V_{OC} is related to gap, in organic polymers the difference between LUMO of acceptor and HOMO of donor. FF describes the part of energy loss in the form of Joule heat, which mainly determined by surface resistivity. So is all characteristic resistibility. Moreover, R_{Shunt} is further affected by the bending of cathode’s work function at the interface with the active layer, usually caused by diffusion of metal atoms at the cathode into the active layer.

PH3T:PCBM

(1) Absorption spectrum

Organic polymers have wider gap than semiconductors. Thus they give an efficient absorption at near UV part. So is PH3T:PCBM blends. The gap of the blend is approximately 1.8eV. So the longest absorption wavelength should be around 650 nm, as fig 4 indicates.[16]

One of the interesting features of organic polymer is that the band gap can easily be altered without changing its chemical components. It has been discovered that a Head-Tail alignment of P3HT has narrower gap than a Head-Head alignment [16]. It has also been discovered that in several materials, the different arrangement in lateral chains can also result in different band gap structures[16]. Moreover, changing the ratio of P3HT:PCBM can change the gap as well [16].

(2) charge generation[16]

Like in many other OSC materials, bulk heterojunction structure has been adopted in the P3HT:PCBM blends so that the DA interface is enlarged.

Ultrafast studies have been carried out to study the charge-generation mechanism in the material. It is shown that in the presence of P3HT, the PCBM excitons are effectively split quite fast and produced P3HT^+ and PCBM^- . The rate of charge transfer is faster than other possible decaying of the PCBM in excited state, which means the excitons got separated before the recombination of electron and hole. From the measured rate of charge transfer, the Gibbs free energy change during splitting can be calculated using the Marcus-Hush theory. It is approximately 1eV, i.e. over half of the absorbed photon energy ($\sim 1.8\text{eV}$). This is also larger than the binding energy of the excitons ($\sim 0.3\text{-}0.5\text{eV}$), indicating that a large portion of photon energy is wasted in heat. Thus, charge generation would be impeded or even completely stopped due to a fast transfer rate. This challenge points out a possible direction to further increase the efficiency that materials with similar structure but less transfer rate can be exploited.

(3) Increasing efficiency: morphology and other ways

Nanoscale morphology is important in improving cell efficiency. Experiments show that when P3HT:PCBM blends adopts an organized morphology, the cell's performance is improved. It is found that the absorption spectra is widened, I_{SC} increases, while V_{OC} slightly decreases. Moreover, surface resistivity decreases.

There're several advantages taking this more organized morphology, where all P3HT aligns parallel and PCBM adopts nanocrystal structure. Firstly, probably the gap is narrowed and the absorption spectrum is consequently widened. This is in agree with a lowered V_{OC} . But the change in V_{OC} is insignificant compared with the change in absorption spectrum. It is likely to be a result from change in both donor and acceptor's band structures. This is supported by the fact that when applying electric field in synthesizing the organized structure, an increase in V_{OC} is achieved, indicating certain kind of polarized structure occurs in the material. With a widened absorption spectrum, more excitons can be produced. Moreover, this morphology gives a large interface, increasing separate percentage. And experiment have also shown that there's a preferred orientation, which provides charge carrier channel, enhancing charge mobility, and decreases surface resistivity. This factors above combined give an increased I_{SC} . The power conversion can achieve as high as 5%, a record for organic solar cell materials[22].

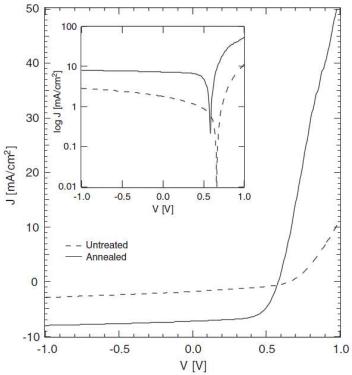


Fig 5. I-V curve of P3HT:PCBM blends before and after annealing [19]

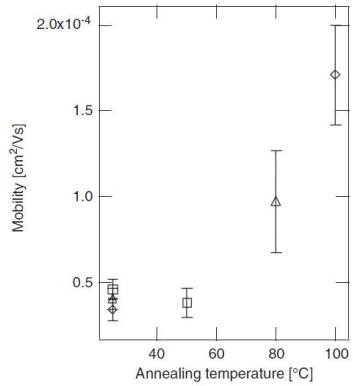


Fig 6. Hole mobility, as-produced and after annealing [19]

Thermal annealing is a method commonly used to optimize the material's morphology. Experiments show that after thermal annealing, the P3HT:PCBM blends adopts a better-organized structure. P3HT forms long and thin fibre while PCBM crystalline become more homogeneous, as shown in Fig. 7[20].

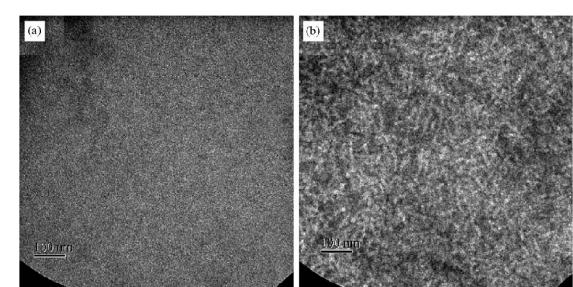
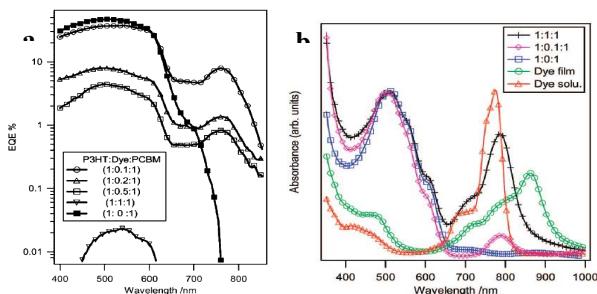


Fig 7: TEM images of a P3HT:PCBM 1:1 blend (a) before and (b) after annealing at 100 °C for 5 min [19]

A study on the phase diagram of the blends[23] gives that the change of conformation occurs as a single glass transition, where T_g is associated with the concentration of PCBM. And this T_g gives lowest annealing temperature. Actually, the crystallization of the two components are inhibited at the presence of each other, and by thermal annealing, they resume better crystalline structures. However, the phase diagram also indicates instability at working temperature. Moreover, when P3HT chains are crystallized, nucleation sites were provided for PCBM [24]. Then the components of the blends grow through a self-organization process. Thus, the growth of such ordered conformation on a larger area is possible.

Besides morphology, various approaches have been tried to enhance the cell's efficiency.

Dye has been introduced to increase near IR region photoconversion [25]. As Fig 8 shows, with proper dye concentration, the absorption at long wavelength region of the



**Fig 8: a) external quantum efficiency with different dye concentration.
b) absorption spectra [25]**

material increases. But when the concentration goes too high, the efficiency decreases because the efficient charge separation rate has go down.

Hole-extraction layer has been applied[26-28]. ITO anode[26], PEDOT:PSS modifier and anode[27], and carbon nanotube[28] have been used. So far, ITO anode provides good efficiency and is highly transparent. And the other two has shown no significant advantage in efficiency but would probably be a good alternative when the cost of ITO is kept high by limited source of tin.

Buffer layer between the active layer and the electrodes has been tried, as well [29,30]. A buffer layer at the cathode [29] can increase R_{Shunt} by preventing diffusion of the cathode material into the active layer. A buffer layer at the anode [30] plays an optical role, increasing the intensity at the active layer. However, these do not show significant success.

(4) Stability of P3HT:PCBM cell

Despite the prediction from the phase diagram, the P3HT:PCBM module is quite stable [31]. Experiments show that under accelerated light soaking conditions in the laboratory, it remains good light stability, and over a year of outdoor exposure.

Ratio of components, morphology, and cathode material would affect stability [32,33]. Besides higher efficiency, a more ordered microscopic structure also gives better stability [33]. With Ca/Ag cathode the blend film can retain its sufficiency for a significantly longer time than using LiF/Al cathode [32]. Moreover, inspired by biological structures, a special family of organic materials, efforts on self-repair and defect-tolerating materials have been done [11].

(5) Synthesis

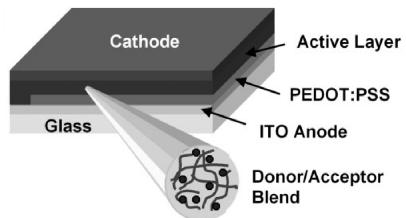


Fig 9: Schematic of a polymer/fullerene bulk heterojunction [34]

The construction of a piece of BHJ solar cell is as shown (Fig. 9). To construct organic thin films, wet processing, is useful. Methods such as spin coating, Knife-over-edge coating, spray coating, slot-die coating, rotogravure printing, and screen printing were introduced. [35-37] These approaches provides possible ways to process low-cost large-area cells. Designed patterns can easily be reproduced by these highly repeatable methods. This can lead to mass-integrated cells where identical units were arranged in one piece[35][38].

Moreover, there're technical reasons adopting these wet processing methods. First of all, many organic polymers have poor heat stability [12]. They might decompose before evaporate. So the choice of solvent becomes important for these technique. Additionally, it is also shown that different solvent can even give different efficiency and stability [35], probably ligands have played a role in crystallization process. Another reason is that drying process provides conditions for annealing to optimize morphology. Moreover, the required condition is not so strict. Experiments showed that even a contaminated environment can the printing procedure be operated. [37]

Summary

To achieve an efficient solar cell, several factors can be improved. First is to enlarge the absorption spectrum. Organic solar cell absorbs UV efficiently. With the aid of dye molecules, the absorption of near-IR region can be increased. If this is finally put to application, then the organic cells can also work in the dark. Second is to find a more efficient way to separate excitons. Bulk junction is a good solution so that more excitons can be separated in a field within their diffusion range. In P3HT:PCBM, UV photons provide sufficient energy for a rapid and completed separation. However, this is inefficient because the number of excitons generated is thus lowered. Hence, some improvement might be introduced to slow down exciton separation in the material. Third is to increase charge mobility. In better organized morphology, charge transport is facilitated.

A glance at the polymer's synthesis and fabrication gives proof to the fact that organic cells are much easier to construct. It is true that organic polymers are hard to crystallize. However, when proper solvent is chosen, with the aid of thermal annealing, those amorphous or nanocrystalline structures would rearrange

to adopt better-organized morphology via self-organization process. After thermal annealing, both efficiency and stability are enhanced. Thus, the growth conditions for pristine blends are not as hard as, say, for monocrystalline silicon.

P3HT:PCBM is quite stable especially when adopting a more ordered structure. Besides the blend, proper choice of cathode can prolong the solar cell's lifetime.

In summary, organic solar cells are still quite promising. A major advantage is that their morphology are relatively easy to optimize. Meanwhile, flexibility, large area, light-weight, and the ability to self-repair are all attractions for research. The largest challenge remains in the low efficiency mainly due to poor charge mobility. Utilization of whole spectrum and a more efficient use of UV energy are also possible points for breakthrough.

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