

CHAPTER 8

Sequential Processing: A Rational Route for Bulk Heterojunction Formation via Polymer Swelling

Matthew T. Fontana, Taylor J. Aubry, D. Tyler Scholes,
Steven A. Hawks and Benjamin J. Schwartz

*Department of Chemistry and Biochemistry,
University of California, Los Angeles,
Los Angeles, CA 90095-1569, United States*

1.1. Introduction: The Development of Sequential Processing

Constructing solar cells based on organic materials such as conjugated polymers holds great potential for low-cost and lightweight power generating applications. Although organic materials are inexpensive and readily amenable to scale-up, successfully incorporating organic solar cells into the energy sector requires understanding their underlying physics and using this knowledge to increase their efficiency. In contrast to inorganic solar cells, a limitation facing organic solar cells is the inability to produce free charge carriers following light absorption. To overcome this, polymer-based photovoltaics are typically based on a blend of two materials: a conjugated polymer, which acts as the light absorber and electron donor, and an electron acceptor, which is often a fullerene derivative such as phenyl- C_{61} -butyric acid methyl ester (PCBM).^{36,87,136,166}

In polymer-fullerene solar cells, light absorption by the semi-conducting polymer produces an excited-state electron and leaves

2 *World Scientific Handbook of Organic Optoelectronic Devices*

behind a corresponding hole. The electron and hole remain strongly Coulombically-bound in organic materials, and thus are collectively referred to as an exciton. Once the photoexcited electron undergoes charge transfer to the fullerene acceptor (exciton dissociation), the Coulomb attraction between the electron and hole is reduced and the electron and hole effectively become free charge carriers. For this to happen, the polymer and fullerene components must be blended well enough to ensure the close polymer/fullerene contact needed to promote charge separation via electron transfer. But once the charges are separated, both carriers must see a continuous pathway to reach the appropriate electrode in order to collect a photocurrent: the electron must be able to hop between neighboring fullerenes to reach the cathode, while the hole must move along a network of adjacent polymer chains to reach the anode. This means that some degree of phase separation of the two components is required. A polymer-fullerene mixture that simultaneously satisfies the intimate blending needed for charge separation and the bicontinuous interpenetrating network needed for charge transport is referred to as a bulk heterojunction (BHJ).^{8,13,30,36,44,59,61,81,104,143}

Clearly, forming an ideal BHJ morphology is critically important for producing high-performance, polymer-fullerene organic photovoltaics. Research from many groups has determined that the typical size of the polymer and fullerene domains in a BHJ architecture must be on the order of the exciton diffusion length of the polymer (typically ~ 10 nm)¹⁴² to ensure efficient exciton splitting; coarser mixing than this leads to inefficient exciton dissociation and thus poor production of charge carriers, while finer mixing reduces transport to the electrodes^{55,127} and increases losses due to the recombination.¹⁴⁵ When both the materials and the resulting BHJ morphology are optimized, high-performance, single-junction, polymer-fullerene BHJ devices have power conversion efficiencies approaching 12%.¹⁷¹

The most widely used method for fabricating the active layer of organic photovoltaics is blend casting (BC). This processing technique constructs the BHJ morphology by co-dissolving the polymer donor and fullerene derivative acceptor and spin-casting the resulting solution into a solid film; this method relies on the

kinetics of solvent evaporation and spontaneous phase-separation of the two materials to form the requisite BHJ.⁵⁹ This means that achieving optimized BHJ morphologies through BC is not trivial. Film formation depends on several interdependent factors related to the active layer materials, including: the miscibilities of the two components in the host solvent and with each other, each component's propensity to self- or co-crystallize,¹⁰² each component's surface energy,¹⁰¹ each component's molecular mobility and diffusivity, and the solvent drying kinetics for a given set of casting conditions.³⁴ Because of this, BHJ formation is hyper-sensitive to subtle changes in either processing conditions or the polymer or fullerene's molecular structure. Processing parameters that can be used to tune the BHJ morphologies formed by BC include thermal annealing,^{7,77,78,99,167} solvent annealing,^{79,172} changing the host solvent,¹⁵⁰ and adding a co-solvent or solvent additive.^{54,73,86,94,114,115,171} Unfortunately, despite well over a decade of intense work, no clear design rules have emerged.^{59,98} Indeed, many donor-acceptor pairs promise efficient devices on paper, but for reasons still unknown simply do not form the requisite BHJs needed to work in the laboratory.⁹⁸

The sensitivity of polymer-based photovoltaic performance to the nm-scale BHJ is further underscored by the eventual need to scale up such devices if they are ever to be commercially practical. This is because the formation kinetics of large-area polymer films by blade coating or roll-to-roll fabrication are quite different from those produced on the laboratory scale by spin-coating. This means that BHJ morphologies produced in large-area devices are different from those in smaller devices, so that work done on optimizing BHJ formation in the laboratory does not necessarily translate when scaled up.^{25,65,72,119} As a result, even though blend-cast organic solar cells are making strides towards higher-efficiency devices because of intense Edisonian effort, there are still no commercial devices available from these materials, which is a direct result of BC's inability to rationally control the BHJ nanomorphology during device processing.

To address these difficulties associated with producing polymer solar cells by BC, we developed an alternative processing method that forms the desired BHJ through sequential deposition of polymer

4 World Scientific Handbook of Organic Optoelectronic Devices

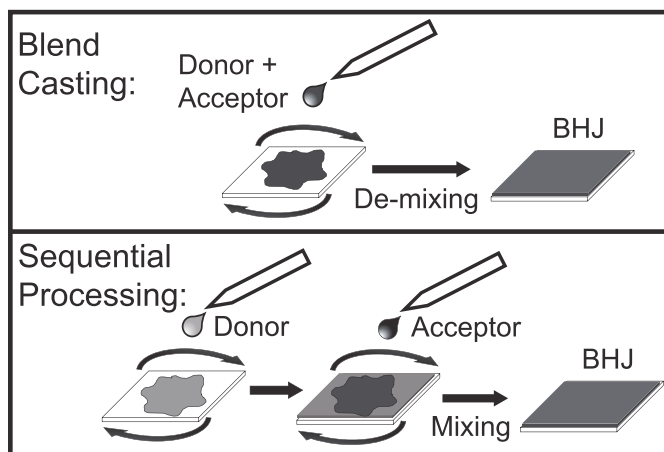


Fig. 1. Comparison of BHJ active-layer formation via BC and SqP techniques. In BC, the donor and acceptor are spin-coated from a mixed solution in a single step whereas with SqP the donor is spun first followed by the acceptor in separate steps. The traditional BC method relies on the spontaneous de-mixing kinetics of donor and acceptor materials, which are poorly understood and difficult to control. Our two-step SqP method involves the interdiffusion of acceptor material into a pre-formed donor matrix, the extent of which can be controlled via swelling and mass action.

and fullerene layers; we refer to this method as sequential processing (SqP).^{6,153} The BC and SqP techniques are illustrated in Fig. 1, with BC in the upper panel and SqP in the lower panel. In SqP, a film of the pure conjugated polymer is spun first, with casting conditions chosen to tune the polymer morphology to what is desirable for a given device. Then, in a second processing step, the fullerene is cast from a solvent that is chosen to swell the underlying polymer layer but not dissolve it.³ Mass action drives fullerenes from the solution used in the second step into the swollen polymer underlayer, forming a BHJ with a fullerene network that is guaranteed to be connected to the top of the film (since the fullerene enters only from the top rather than starting dispersed throughout the film). Therefore, BHJ morphology is determined by the concentration of the fullerene solution, which tunes the mass action driving force for fullerenes to enter the film, and the thermodynamics of how the fullerene solvent swells the polymer, which alters the free volume in

the swollen polymer that allows fullerenes to intercalate. Since mass action and swelling are thermodynamic rather than kinetic effects, this means that SqP provides significantly greater reproducibility and control over the BHJ morphology needed to produce highly efficient polymer solar cells.^{2,3}

It is worth noting that when we originally developed SqP, we were unaware of the extent to which the solvent in the second step could swell the underlying polymer layer, and indeed our initial goal with SqP was to prepare clean polymer-fullerene bilayers. In fact, the fullerene-casting solvent we initially chose, dichloromethane (DCM), is a relatively poor swelling solvent for our initially-studied conjugated polymer, poly(3-hexylthiophene-2,5-diyl) (P3HT).⁶ When we first spun PCBM from a DCM solution onto a pre-cast P3HT film, we found that the top surface was enriched with PCBM crystallites, and that the photovoltaic devices had relatively poor power conversion efficiency. Neutron reflectometry investigations, however, revealed that significant amounts of fullerene mixed into the interior of the polymer film, so that the morphology was more of a quasi-bilayer than either a clean bilayer or a BHJ.^{77,78} Subsequent thermal annealing of the SqP-produced P3HT:PCBM quasi-bilayer caused PCBM to further diffuse into the polymer layer, forming a well-mixed BHJ with greatly improved photovoltaic device efficiency.^{78,96,158} The change in morphology caused by thermal annealing is caused by two predominant effects: (1) PCBM is a higher surface energy material than P3HT, so thermal annealing tends to drive PCBM towards the bottom of the active layer,¹⁰¹ better distributing the PCBM throughout the polymer and improving device performance;^{43,96,139} (2) Thermal annealing enhances the crystallinity of the components in the active layer, particularly P3HT, which improves device efficiency by increasing carrier mobilities.^{7,77,78,99,167}

Although using thermal annealing to drive fullerenes deposited via SqP into a polymer underlayer might seem like a viable approach to BHJ formation, the improvement in sequentially-processed device performance seen upon thermal annealing is unique to P3HT; most modern high-efficiency low band gap polymers degrade or form a homogeneous disordered blend with too little phase separation

6 *World Scientific Handbook of Organic Optoelectronic Devices*

upon thermal treatment.^{9,11,52,87} For this reason, early studies of SqP focused almost exclusively on P3HT.^{9,29,87,98,113} Despite this early limitation, a wealth of morphological studies investigating BHJ formation via SqP have highlighted the differences in BHJ morphology between devices prepared through BC and those made via SqP.^{2,5,21,24,28,43,47,48,57,77,78,82,83,90,95,96,106,110,112,120,134,139,146–149,152,153,154,159,161,167,174} More recently, SqP has been successfully applied to the fabrication of organic solar cells based on high-performing, push-pull polymers.^{3,23,26,93,126,159} Additional studies also have extended SqP to ternary organic blends and the use of alternative fullerene derivatives, such as 1',1'',4',4''-Tetrahydro-di[1,4]methanonaphthaleno [1,2:2',3',56,60:2'',3''] [5,6]fullerene-C₆₀ (ICBA).^{23,82,84,85,137} It is also worth noting that SqP can be used for the infiltration of molecular dopants instead of fullerenes into a polymer underlayer, providing a substantial advance in the quality of doped conjugated polymer films,^{124,125} as discussed further below.

One key advantage of SqP is its ability to take advantage of polymer swelling, which makes SqP applicable to any polymer system. Polymer swelling provides a systematic, rational and tractable avenue towards optimal BHJ construction, including for polymers that, unlike P3HT, cannot be thermally annealed.³ In this sense, the degree of polymer swelling is what allows for precise tuning of the BHJ morphology by SqP.³ If the fullerene-casting solvent poorly swells the underlying polymer, the fullerene will not intercalate within the film, leaving large fullerene domains deposited on top of the polymer underlayer.^{6,31,77,78,120,134,152} Conversely, a solvent that interacts too favorably with a polymer can dissolve or wash away part or all of the underlying polymer film.³ Therefore, optimal BHJ formation requires swelling of the polymer without dissolution. As will be discussed further in Sec. 1.2, this places significant constraints on the choice of fullerene-casting solvent, which must simultaneously possess both high fullerene solubility and yield optimal polymer swelling. In light of this, we have proposed the use of binary solvent blends that can be tuned to create optimal SqP solvents for casting the fullerene.³ With solvent blends and other advances, SqP has produced numerous single-junction, polymer-fullerene, photovoltaic devices with high power conversion efficiencies.^{3,10,20,23,26,31,49,68,75,89,93,126,144,154,157,162}

One of the key features of SqP is that swelling is inherently selective to amorphous regions and does not strongly affect the crystalline regions of a polymer film.^{14,121} Therefore, achieving optimal polymer swelling largely depends upon the degree of polymer crystallinity. Selecting different casting solvents and varying the originally-cast film's drying conditions are well known to control the crystallinity of a spin-cast conjugated polymer film.^{3,57} Thus, SqP provides many experimental "knobs" that can be independently tuned for optimizing BHJ formation, as discussed fully in Sec. 1.2, including controlling the crystallinity of the polymer underlayer and thus the manner in which it swells. This allows for a better opportunity to choose organic semiconductors that have other essential properties that are requisite for high performance (e.g., favorable energy level alignments, absorption spectra, etc.).

In addition to providing a rational pathway for BHJ optimization, SqP provides a route to systematically investigate the mechanisms underlying BHJ formation and to develop design rules that can be extended to any polymer system. For example, the use of solvent additives such as 1,8-diiodooctane (DIO) has become quite commonplace when fabricating blend-cast devices,^{59,64,73,76,86,88,114,171} but the mechanism by which these additives improve BHJ formation was poorly understood. Using SqP, we have found that solvent additives such as DIO act primarily as non-evaporating swelling agents, as discussed in more detail in Sec. 1.3. Overall, SqP is clearly a more tractable technique for BHJ formation because it avoids the problems inherently associated with BC. Thus, SqP not only opens new pathways towards BHJ construction, but also facilitates fundamental investigations into the process of BHJ formation.

1.2. Quantification of Polymer-Solvent Swelling Interactions as the Key to Polymer Solar Cell Design

The advantage of SqP is its ability to controllably tune the degree of polymer swelling such that the acceptor is appropriately dispersed into the polymer layer, creating an ideal BHJ morphology. Quantifying the degree of swelling required to achieve the ideal morphology and optimal performance in any given polymer-solvent

system is important so that the processing conditions can be chosen based on simple measurements instead of trial-and-error. To this end, our approach has been to use porosimetry-ellipsometry measurements to characterize polymer-solvent interactions, making BHJ device optimization predictable.^{3,16,39,62,107,109,111}

In porosimetry-ellipsometry measurements, a polymer film is placed in a porosimeter and swelled by exposure to solvent vapor, and spectroscopic ellipsometry is used to precisely measure the change in thickness and index of refraction of the vapor-swollen film. The experiment also can be done without a porosimeter by simply exposing the polymer film to the saturated solvent vapor of interest during ellipsometry. The ellipsometry-measured change in thickness gives the free volume available in the swollen film for fullerene intercalation. Moreover, the ellipsometry-measured change in index of refraction of the film, combined with the effective medium approximation, provides a means to determine the volume fraction of polymer, ϕ_p , in the swollen film.^{15,18,109,130} With the volume fraction of the polymer in hand, one can calculate the Flory-Huggins χ parameter from^{39-41,62,109}:

$$\ln\left(\frac{p}{p_{\text{sat}}}\right) = \chi\phi_p^2 + \ln(1 - \phi_p) + \phi_p\left(1 - \frac{1}{N}\right), \quad (1)$$

where N is the degree of polymerization and p/p_{sat} is the pressure of the solvent vapor the film is exposed to relative to the solvent's saturated vapor pressure. Lower χ values are associated with stronger solvent-polymer interactions. That is, the lower χ is, the more likely a solvent is to swell (and eventually dissolve) the polymer. In Sec. 1.2.1, we argue that there is a range of optimal χ values that lead to desired BHJ formation and thus improved device performance.

Although there are many factors that influence the value of χ , we focus on two that can be directly controlled to allow SqP to be used to great effect in controlling BHJ morphology: the choice of solvent and the degree of polymer crystallinity. As mentioned above, a solvent in which the polymer is more soluble will act as a better swelling agent than a solvent in which the same polymer is less soluble. However, the same solvent can give different χ values for the same polymer if the microcrystalline structure of the polymer film is

different. This is because the amorphous regions of a polymer film are highly susceptible to swelling by a solvent, whereas crystalline regions can be treated as effectively cross-linked and thus poorly swell.^{3,121} In what follows, we explore systems in which solvent choice and polymer crystallinity are controllably varied to illustrate how SqP can follow design rules that can rationally be used to optimize the performance of BHJ solar cells without the need for trial-and-error.

1.2.1. *Design rules: Controlling swelling via sequential processing solvent choice*

Finding an ideal solvent for the second casting step in SqP is imperative if the method is to be general for any polymer-acceptor system. As mentioned above, the solvent for this step must both wet³ and optimally swell the polymer underlayer without dissolving it,⁵⁷ and also must have high solubility for the acceptor molecule in order to infiltrate meaningful amounts into the polymer film.¹⁴⁴ It is highly unlikely that any single solvent would fulfill all these requirements, particularly for different combinations of polymers and fullerenes. However, we have shown that binary solvent blends can be logically chosen to simultaneously satisfy all of these criteria. The basic idea is to choose a base solvent in which the infiltrant of interest (fullerenes for polymer BHJ solar cells) is highly soluble, and then mix this base solvent with a co-solvent to adjust the degree of swelling for a particular polymer. If the base solvent dissolves the polymer of interest, the co-solvent can be a non-solvent for the polymer, with enough added to stop polymer dissolution and raise χ into the optimal range. Conversely, if the base solvent inadequately swells the polymer, the chosen co-solvent should be a good solvent for the polymer, so that χ can be lowered into the optimal range.³

Through a series of measurements, we have found the values of χ that lead to optimal polymer swelling (to an extent sufficient for fullerene intercalation without dissolving) are in the range of 1.5 to 2.0.³ This is readily achievable for any polymer:fullerene system by using a solvent blend for the fullerene-casting step in SqP because the χ value for a solvent blend is roughly the mole-fraction-weighted χ values for the individual components interacting with the polymer.

Thus, as long as the fullerene is sufficiently soluble,¹⁴⁴ a series of simple swelling measurements provides a recipe for designing an appropriate solvent blend to produce polymer:fullerene BHJs by SqP without trial-and-error.

Although there are several potentially good choices as base solvents for fabricating polymer:fullerene BHJs by SqP, we decided to focus on 2-chlorophenol (2-CP), which has high a solubility for PCBM (112 mg/mL)¹⁰⁰ and a relatively low solubility for most conjugated polymers. As examples of how to tune a solvent blend with 2-CP to produce the optimal χ for BHJ production, we recently focused on applying SqP to produce solar cells from both PTB7, a slightly crystalline and highly soluble polymer,^{56,86} and PSDTTT,^{3,132} a completely amorphous polymer with low solubility in most common organic solvents;¹³² see Fig. 2 for the chemical structures of these polymers. We measured the swelling of both polymers ellipsometrically upon exposure to isopropyl alcohol (IPA) vapor, a non-solvent for conjugated polymers, and to toluene vapor, which is generally a good solvent for conjugated polymers. Figure 2 shows that, as expected, the swelling by of both PTB7 and PSDTTT with toluene (dark circles and dark squares, respectively) is greater than with IPA (light circles, light squares), and that PTB7 (circles) swells about four times more than PSDTTT (squares) since the latter has poor solubility even in “good” solvents such as toluene. Figure 2(d) shows the calculated χ values for these polymer film-solvent pairs extracted from the ellipsometric data. The data clearly show lower χ values for the polymer-toluene interactions compared to those with IPA, and higher χ values for PSDTTT than for PTB7 in a given solvent. It is worth noting that pure toluene cannot be used as a second-step SqP solvent for either polymer as its χ value is low enough that films of either of these polymers would be dissolved during the fullerene-casting SqP step, and pure IPA cannot be used because the χ is too high to promote sufficient swelling. Alternatively, pure 2-CP slightly dissolves PTB7 (χ too low) and does not dissolve PSDTTT (χ too high). Therefore, we can blend 2-CP with IPA to bring χ into the optimal range for PTB7, or blend 2-CP with toluene to bring χ into the optimal range for PSDTTT.³

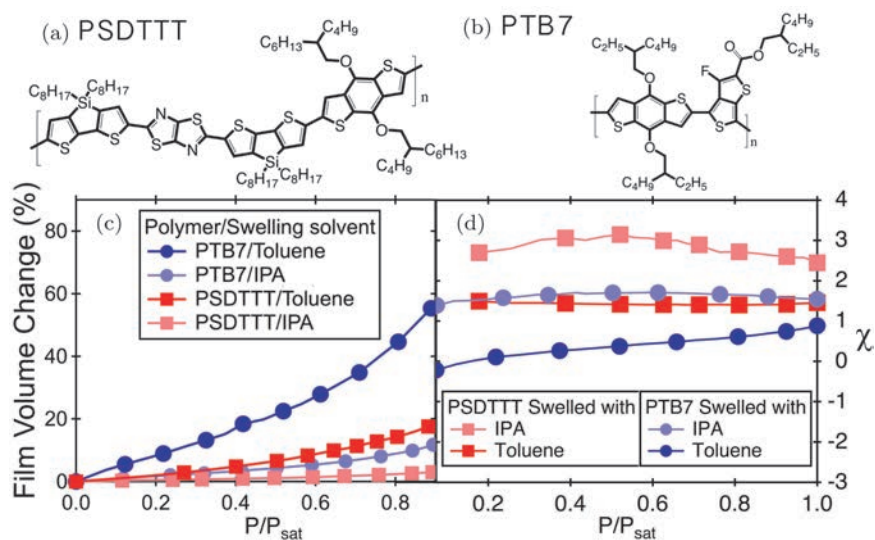


Fig. 2. Chemical structures of (a) PSDTTT^{3,132} and (b) PTB7^{64,86}; (c) Swelling of PSDTTT and PTB7 upon exposure to toluene and isopropanol (IPA) vapor measured by porosimetry-ellipsometry. Being more soluble than PSDTTT, PTB7 swells more with both solvents: toluene (dark circles) and IPA (light circles). Since PSDTTT is poorly soluble it swells less with toluene (dark squares) and IPA (light squares); and (d) Calculated χ parameters for PSDTTT (light squares for IPA-swelling and dark squares for toluene-swelling) and PTB7 (light circles for IPA-swelling and dark circles for toluene-swelling) films using the ellipsometric swelling data and the effective medium approximation to obtain ϕ_p in Eq. 1.³

Figure 3 shows the performance of the photovoltaic devices fabricated with solvent blends by SqP. With the optimized co-solvent ratio for PSDTTT:PCBM of 35% 2-CP to 65% toluene (triangles), device efficiencies of 3.8% were achieved, which exceeded the 3.6% efficiency of blend-cast devices made with these same materials.³ As a control experiment, we also see that PSDTTT devices with the fullerene deposited from a 2-CP:IPA blend (vertical diamonds) perform terribly since IPA can only raise χ relative to 2-CP. For PTB7, the amount of IPA needed to raise the χ high enough so as to not dissolve the polymer underlayer was so large that the fullerene solubility in the solvent blend decreased dramatically. This resulted in insufficient fullerene being driven into the film by mass action and sub-optimal device performance, as seen by the low fill

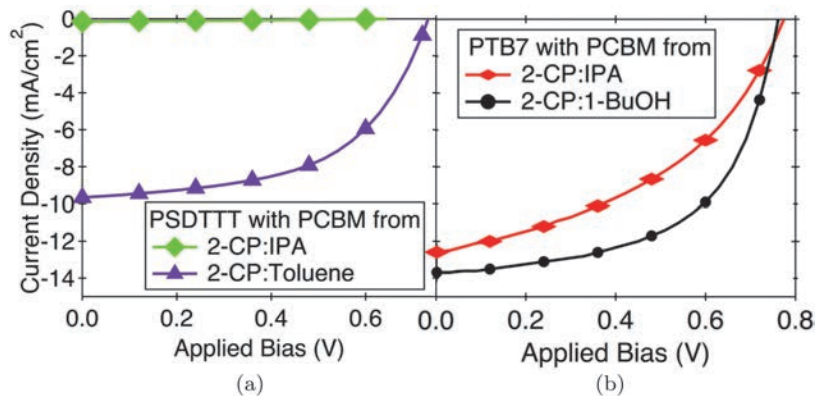


Fig. 3. Device performance of (a) PSDTTT and (b) PTB7 sequentially-processed devices with optimally-designed solvent blends for the fullerene-casting step. For PSDTTT, the fullerene was cast from 70:30 2-CP:IPA (vertical diamonds) and 35:65 2-CP:Toluene (triangles). For PTB7, the fullerene was cast from 70:30 2-CP:IPA (horizontal diamonds) and 50:50 2-CP:1-BuOH (circles). For PTB7, the mixture of 2-CP:IPA has a χ that is still too low and slightly dissolves the film (adding additional IPA leads to too low a PCBM solubility), but blending 2-CP with the higher- χ non-solvent 1-BuOH yields optimal performance.

factor (horizontal diamonds). Since polymer solubility decreases (χ increases) with increasing solvent alcohol chain length, we then tried 1-butanol (1-BuOH) as the fullerene casting co-solvent. With the optimal 50:50 2CP:1-BuOH ratio (circles), we obtained excellent SqP device performance with a photovoltaic power conversion efficiency of 6.0%, exceeding the 5.9% of the blend-cast equivalent device.³ It is important to note that SqP fabrication required neither trial-and-error adjustment of the processing conditions nor the use of any solvent additives such as DIO (as discussed further in Sec. 1.3).

In addition to our work, van Franeker *et al.*¹⁴⁴ examined the influence of swelling interaction, fullerene solubility and evaporation rate of the fullerene-casting solvent on BHJ device performance. They found that nearly all the aromatic solvents they examined similarly swelled the polymer films. However, only solvents with high fullerene solubility (≥ 200 mg/mL) produced devices with efficiencies that were similar to those of traditional blend-cast devices. This result emphasizes the importance of mass action for driving in fullerene

when selecting an SqP swelling solvent: the fullerene solubility must be high enough that the fullerene infiltrates the polymer film once swollen; without a high fullerene solubility the fullerene will not go into the swollen regions.^{68,93,144} Furthermore, too low a fullerene solubility in SqP causes the formation of droplet-like features and/or dendritic fullerene crystallites on top of the polymer film, or a quasi-bilayer structure. If there is insufficient fullerene intercalation, this not surprisingly leads to poor electron mobility and thus lousy photovoltaic performance.^{1,2,17,102}

SqP not only has been demonstrated for an increasingly wide variety of material combinations,^{3,25,68,93,126,152} but also provides a route toward potential commercial scale-up. This is because blend-casting relies on spontaneous de-mixing that occurs during film formation, and drying kinetics change with device area. Moreover, commercial production of polymer-based photovoltaics is highly unlikely to be based on spin-coating, the preferred technique at laboratory scales. This is because the kinetics of solvent evaporation are different with industrial processes such as blade-coating or roll-to-roll processing. Indeed, the limited studies on scalability show that as the active area increases, the performance of blend-cast devices suffer.^{65,72} Fortunately, SqP, which is based on the thermodynamics of swelling, avoids these problems with scale-up.^{2,3,6,57} Figure 4 compares the performance of thickness- and composition-matched P3HT:PCBM devices produced by BC (circles) and SqP (diamonds) at two different size scales. In the small-area devices ($\sim 7 \text{ mm}^2$) shown in Fig. 4(a), the BC and SqP devices perform similarly with slightly better performance from the SqP devices at $3.4 \pm 0.2\%$ compared to $2.9 \pm 0.2\%$. For the identically-prepared larger-area devices ($\sim 34 \text{ mm}^2$) in Fig. 4(b), not only do the SqP devices exhibit superior device efficiency ($2.5 \pm 0.2\%$ versus $2.0 \pm 0.4\%$), but their performance is more consistent, as indicated by the lower standard deviation (error bars) for 20 devices of each type.² Most of the decrease in SqP device performance on increasing the device area results from the sheet resistance of the ITO used for the cathode in these devices, not from changes in the nm-scale architecture of the BHJ active layer.

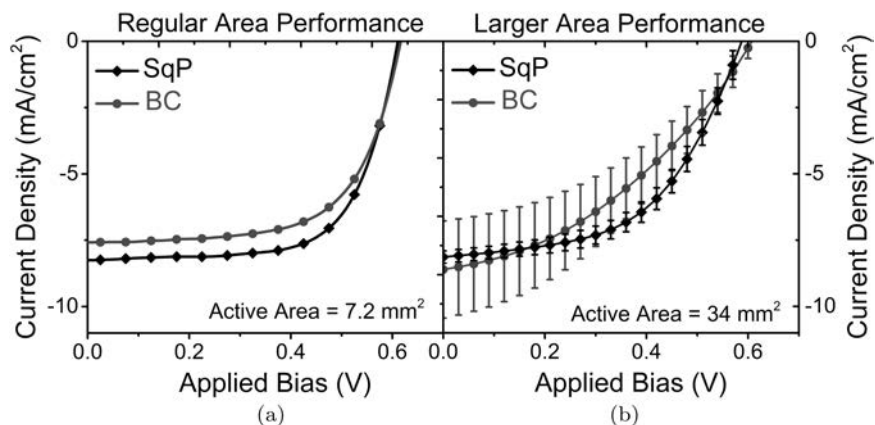


Fig. 4. Comparison of BC (circles) and SqP (diamonds) P3HT:PCBM photovoltaic performance in (a) regular-area ($\sim 7 \text{ mm}^2$) and (b) larger-area ($\sim 34 \text{ mm}^2$) devices. This data makes clear that SqP is more amenable to scale up since large-area SqP devices are not only better performing, but also are more reproducible.

1.2.2. *Design rules: Using SqP to control polymer crystallinity*

A clear benefit of SqP is the ability to quantify, using χ , the swelling induced by a given solvent or solvent blend and thus understand the resulting interpenetrating BHJ network that is formed. As mentioned above, χ is not only affected by the choice of solvent, but also by the polymer crystallinity.^{14,121} Generally, higher polymer crystallinity is better for polymer-based photovoltaics since the regular chain packing provides for improved charge transport. Increasing polymer crystallinity is difficult with blend-cast BHJs, because the presence of fullerenes in the originally-cast film inhibits polymer crystallization (and as mentioned above, most modern push-pull polymers will not tolerate thermal annealing). Fortunately, by separating the polymer and fullerene casting steps, SqP provides a route to independently controlling the polymer crystallinity.

As a demonstration of this type of control, we varied the crystallinity of P3HT films by changing the solvent from which the polymer was cast, and also by thermally annealing the films

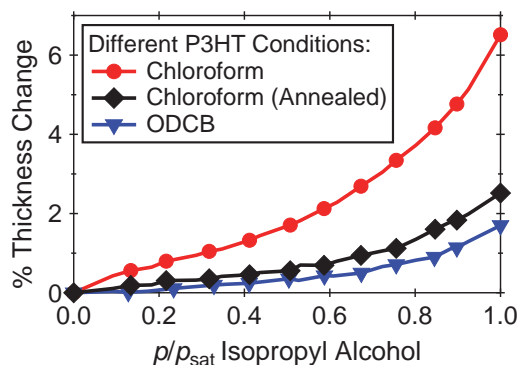


Fig. 5. Porosimetry-ellipsometry measured swelling of P3HT films cast from different solvents; the chloroform-cast films (circles) are much less crystalline than the thermally-annealed (diamonds) or ODCB-cast (triangles) films. The more amorphous chloroform-cast film swells more than twice as much with IPA as the more crystalline films.

(as P3HT is one of the few polymers for which thermal annealing is advantageous).^{7,80,99} When we cast P3HT from a high vapor pressure solvent, such as chloroform, the resulting films are highly amorphous, whereas casting from a slower-drying solvent, such as *ortho*-dichlorobenzene (ODCB), creates P3HT films that are significantly more crystalline, as could be seen by examining both the UV-Visible absorption spectroscopy and X-ray diffraction of the films.^{3,6,79,158,160} Figure 5 shows the results of swelling these P3HT films of varying crystallinity with IPA vapor. We found that the more amorphous films cast from chloroform (circles) exhibit larger volume changes compared to the more crystalline films cast from ODCB (triangles). This is consistent with the idea that crystalline regions are effectively impenetrable to swelling solvents and thus do not participate in the volume expansion of the film. If we thermally anneal a chloroform-cast P3HT film (diamonds), we see that its swellability is reduced to be similar to that of an ODCB-cast film. As a result, the calculated χ value for chloroform-cast P3HT is lower than the nearly-matched χ values for the ODCB-cast and chloroform-cast-annealed P3HT films.³ Thus, SqP allows us to preserve the crystallinity of an ODCB-cast or annealed P3HT film, as long as we

choose a solvent with the second casting step that has an appropriate χ to allow for fullerene intercalation.

With the control over both the polymer crystallinity and the degree of fullerene intercalation that SqP affords, it is interesting to compare the differences in the crystallinity of devices made via BC and SqP. We studied the crystallinities of a series of composition- and thickness-matched P3HT:PCBM BHJs using grazing-incidence wide-angle X-ray scattering (GIWAXS).⁵⁷ From the GIWAXS images shown in Fig. 6, it is clear that sequentially-processed BHJs (diamonds) have a much higher degree of P3HT crystallinity, as evidenced by the much stronger diffraction peaks compared to BC (circles).⁵⁷ Furthermore, electron-energy-loss filtered TEM (EF-TEM) tomography images of composition and thickness-matched sequentially-processed and blend-cast P3HT:PCBM films also show that the morphology obtained by the BC approach has larger and less ordered domains compared to that obtained using SqP.⁵⁷

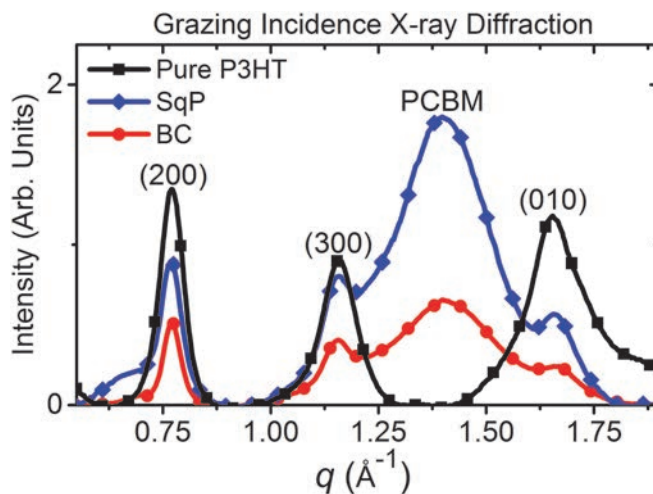


Fig. 6. GIWAXS from a pure P3HT film (squares) cast from ODCB and from composition-and-thickness-matched P3HT:PCBM BHJs produced by both SqP (diamonds) and BC (circles). The SqP film retains more of the pure P3HT crystallinity compared to the BC film in which crystallization is hindered by the presence of fullerene.

As mentioned above, BC nearly always leads to lower polymer crystallinity because the presence of fullerene inhibits polymer crystallization.^{118,135} SqP, on the other hand, can preserve the higher degrees of crystallinity in pure polymer films since the crystalline regions are not disrupted during BHJ formation, providing a route to independently tuning and optimizing this crystallinity.⁵⁷

1.3. Using SqP to Understand How Solvent Additives Improve BHJ Formation

As mentioned in Secs. 1.1 and 1.2.2, thermal annealing improves BHJ morphology for semi-crystalline polymers such as P3HT^{7,99} and other thiophene-based polymers,⁶⁶ but thermal treatment tends to degrade high-performing push-pull conjugated polymers.^{9,29,87,98,113} As a partial solution to this problem, a wealth of literature has demonstrated that adding small amounts of particular co-solvents (so-called solvent additives) to blend-cast donor-acceptor solutions dramatically improves the BHJ morphology and thus device performance.^{73,88,98} Indeed, such additives are required for most high-performing, polymer, blend-cast, photovoltaic systems.^{54,58,64,76,86,94,103,114,168,171}

The first solvent additive shown to improve the BHJ morphology was octanedithiol (ODT). Adding small volumes (typically only a few %) of ODT to the polymer-fullerene blend solution led to large improvements in the photoconductive response and carrier mobilities in the resulting cast films.¹¹⁵ Perhaps more importantly, the addition of just a few percent ODT when fabricating blend-cast films for the active layer of BHJ solar cells led to a doubling of the power conversion efficiency.¹¹⁴ After screening numerous liquids, 1,8-diiodooctane (DIO) emerged as the most promising additive for achieving the best BHJ photovoltaic efficiencies.⁷⁶ Furthermore, DIO's reputation as the additive-of-choice was solidified after numerous reports of devices based on new high-performing polymers that required DIO to achieve reasonable efficiencies.^{54,58,86,94,168,171} Thus, DIO remains as the most frequently-used additive, even though other additives such as ODT and 1-chloronaphthalene (CN) are also known to work with different polymer/fullerene materials combinations.^{73,88}

1.3.1. *Controversy surrounding the solvent additive mechanism of BHJ improvement*

Because of their reputation for significantly enhancing device efficiencies, solvent additives have received considerable attention, although the mechanism by which they improve the BHJ morphology and thus device performance is still not well understood. Moreover, although numerous additives exist and are well-documented in the literature, there is no clear guiding principle for either additive selection or optimal additive concentration.^{59,73} What is known is that in a few select cases, the use of solvent additives leads to morphology improvement by increasing the degree of phase separation of over-mixed polymer-fullerene BHJs.^{22,51,52,73,76,97,114,117} But in the majority of systems, additives work by improving mixing of the overly phase-separated morphologies that are naturally formed with most push-pull conjugated polymers.^{4,12,33,53,60,74,86,103,131,170,171,175} This is because most high-performing, push-pull polymers naturally over-phase segregate when blended with fullerenes. Overall, however, determining whether or not adding a few percent of an additive such as DIO, ODT or CN will increase or decrease the domain size is still determined empirically, by trial-and-error.

One interesting observation is that DIO, the most widely used solvent additive, demonstrates a PCBM solubility that is quite high (> 120 mg/mL).¹⁵⁶ Because of this, it has been postulated in the literature that the BHJ morphology control offered by solvent additives is connected with differential solubility:^{12,76,86,97,171,175} the idea is that keeping the fullerenes better suspended in solution during film formation somehow promotes improved phase separation. This idea, however, is not consistent with the fact that DIO can either improve mixing or promote phase separation depending on the system at hand, or that ODT also favorably improves BHJ morphology,^{22,91,114} but only has a PCBM solubility of 19 mg/mL.¹⁶³ It is also worth noting that the use of solvent additives is neither a scalable nor a desirable avenue towards device optimization: in general, solvent additives are difficult to work with, with only very small amounts required for optimal performance (and an optimal

amount that changes upon scale-up).^{25,73,133} DIO is particularly difficult to work with since it is sensitive to light and air; with its low vapor pressure, DIO tends to remain in the polymer film, leading to degradation of the device performance once this additive begins to break down.^{138,140,164}

1.3.2. *Solvent additives are non-evaporating swelling agents*

Perhaps the one common feature among the various solvent additives used to improve BHJ morphology is that nearly all of them have high boiling points. Shin *et al.*¹²⁸ demonstrated that adding small amounts of ODT or CN to blend solutions of P3HT:PCBM significantly extended the film solidification time, and that increasing the amount of additive produced films with greater thickness.¹²⁸ The increased thickness likely arises simply from the fact that these slowly-evaporating solvent additives remain in the film; indeed, the thickness of films cast with solvent additives decreases over long periods of time as the additive evaporates, approaching the additive-free thickness.¹¹⁸ The fact that solvent additives remain in a polymer BHJ film and increase its thickness has led us to suggest that solvent additives improve device performance by acting as non-evaporating swelling agents, effectively turning BC into SqP.³

Our conclusion that solvent additives function by swelling is based on experiments where we spun pure P3HT from solutions containing no solvent additive, 3% DIO, 3% ODT and 3% CN and then measured the thickness of the resulting films using spectroscopic ellipsometry.^{16,111} We found that the P3HT films cast with both DIO and ODT additives were thicker than those cast without additives by hundreds of nanometers (i.e., the small amounts of solvent additive more than doubled the film thickness).⁴² The films cast from the solution with the CN additive were only marginally thicker than the additive-free films, but since CN has the lowest boiling point out of the three solvent additives, we believe that the CN simply evaporated between the time the films were cast and the ellipsometry measurements.

To understand what the presence of so much solvent additive does in a conjugated polymer film, we fabricated sequentially-processed BHJ solar cells by spin-coating PCBM (dissolved in DCM) onto P3HT films cast with and without solvent additives, as described above. As discussed in Sec. 1.1 above, DCM is a poor swelling solvent for P3HT, so as a result, devices with no solvent additive have poor performance because PCBM is not well-mixed throughout the polymer film. When the P3HT film is pre-swollen by solvent additives, as in the case of ODT and DIO, however, the device performance increased significantly. This suggests that when fullerene is deposited in the second SqP step, the fact that the polymer film was pre-swollen by the additive facilitates more-complete mixing of polymer and fullerene, resulting in an improved BHJ morphology.⁴² Thus, non-evaporating solvent additives present another avenue for optimally swelling polymer films via SqP: if the polymer film is pre-swollen, the fullerene-casting solvent no longer needs to have the optimal value of χ to produce BHJs by fullerene infiltration. Moreover, since DCM removes DIO, sequential deposition of PCBM simultaneously removes the majority of DIO, which otherwise is a separate step required after BC of a BHJ film that uses a solvent additive.¹⁴⁰

The idea that DIO acts as a non-evaporating swelling agent is also consistent with a report by Kong *et al.*⁷¹ In their work, Kong *et al.*⁷¹ created BHJ films from several conjugated polymers and then spun a DIO solution (a few % DIO dissolved in a marginal polymer solvent) on top of the films. They found that the BHJ morphology was reorganized, leading to significantly improved device performance. Since the DIO in this case was introduced after the BHJ was formed and the fullerene was solidified, this provides further evidence that differential solubility of the polymer and fullerene is not the main mechanism for BHJ improvement with solvent additives. But the observed improvement in device performance is consistent with the idea of solvent additives acting as a non-evaporating swelling agent: DIO swells the BHJ and remains in the polymer film, giving plenty of time and free volume for the fullerene to reorganize within the BHJ and form more ideal domains.

Overall, we believe that solvent additives work by essentially converting BC into SqP. When there is a small amount of solvent additive present in a blend-cast solution, the resulting BHJ film ends up swollen by the slowly-evaporating additive that remains in the film. This gives the fullerene time to reorganize within the polymer film even after the main solvent has evaporated; the BHJ morphology is improved in essentially the same manner as in the experiments of Kong *et al.*⁷¹ The reason that blend-cast morphologies are so sensitive to the amount of solvent additive is that different polymers have different χ values with different additives, and as with SqP, it is critical to adjust the amount of polymer swelling to allow for the proper degree of fullerene reorganization. Finally, ODT, CN and other liquids work as solvent additives because they are also good swelling agents for conjugated polymers and have high boiling points, not because they have high fullerene solubility (as ODT does not).

1.4. Doping Conjugated Semiconducting Polymers by the Sequential Processing Approach

The same SqP methodology and design rules described in Sec. 1.2 to create polymer-fullerene BHJs also can be applied to inserting other small molecules into a pre-cast conjugated polymer film. If the molecule of interest has a LUMO level comparable to the polymer HOMO level, charge transfer occurs, resulting in *p*-type doping of the polymer.¹⁶⁵ Since semiconducting polymers have intrinsically low carrier densities and mobilities, molecular doping can be beneficial as it allows electrical properties such as conductivity to be tuned over several orders of magnitude, thereby enabling these materials to be used for a wider variety of applications.^{27,123,165}

Similar to BC in OPVs, molecular doping has traditionally been achieved by co-dissolving the dopant and polymer and using the solution to cast a film.^{38,116,165,169} At low dopant concentrations, BC is a completely adequate preparation method for creating doped conjugated polymer films. As the dopant concentration increases, however, the presence of the charges created on the polymer backbone greatly

decreases the solubility of the polymer in organic solvents, causing the polymer to aggregate and eventually crash out of the solution used to co-dissolve the polymer and dopant.^{37,45,46,105,124} This is why it has been exceedingly difficult to produce high-quality, scalable highly-doped conjugated polymer films via blend-cast doping.^{32,37,169}

Given the success we had using SqP to control BHJ morphologies with conjugated polymer-fullerene blends, we found that we could also use SqP to successfully dope conjugated polymer films with a high degree of morphology control.^{124,125} By simply tuning the concentration of dopant in the selected solvent that appropriately swells the underlying polymer, we were able to achieve high doping levels that were only limited only by the solubility of the dopant in the chosen swelling solvent.¹²⁴ Several groups have subsequently taken advantage of this idea, using SqP doping of conjugated polymer films for patterning or to improve conductivity.^{50,63,67,70} Figure 7 shows our use of SqP to dope P3HT by oxidation with 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4 TCNQ), achieving some of the highest-reported conductivities for this particular materials combination. More importantly, since the quality of the doped

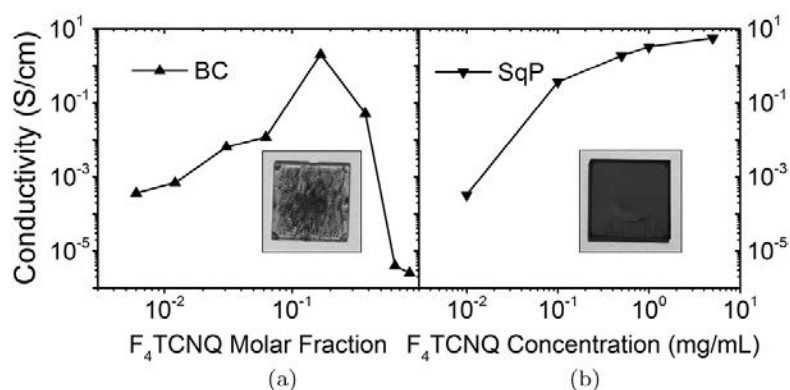


Fig. 7. Comparison of the conductivity of P3HT films doped by (a) blend casting (data from³⁸) and (b) sequential processing. The different units on the horizontal-axis result from the two distinct doping methods; for BC, doping is reported as a mole fraction of the F_4 TCNQ dopant in the blended solution, whereas for SqP, doping is reported as the F_4 TCNQ concentration (mg/mL) in the solution from the second casting step. The inset is an image of each doped film.

film quality was unchanged from the originally-cast polymer film, we were also able to quantify the carrier density and mobility via AC-field Hall Effect measurements,¹²⁴ not believed to be possible with films fabricated by BC since early 2015.¹⁵¹

1.5. Conclusions and Perspective

Sequential processing makes BHJ design a tractable and more rational process by decoupling BHJ formation into two, independently tunable steps. With SqP, one can choose the solvent in the first casting step to control the degree of polymer crystallinity. The initial film could also be molecularly doped, patterned or modified by thermal annealing if desired. Fullerene incorporation into the tailored polymer film is then precisely tuned by the selection of the appropriate solvent for the second casting step, along with the fullerene concentration. By making some very simple swelling measurements, it is straightforward to choose an optimal solvent or solvent blend for the SqP fullerene-casting step with the proper χ value to allow for fullerene intercalation without dissolution of the underlying polymer. Because SqP depends on the thermodynamics of swelling and not the kinetics of solvent evaporation, SqP is amenable to large-scale fabrication techniques, avoiding the need to re-optimize small-scale results to the large-scale processing. The SqP technique works for both polymers that are highly soluble in common solvents and those that are not, providing a rational means to create desired BHJ morphologies without need for trial-and-error. The general principles that govern BHJ formation via blend-casting are poorly understood, making SqP the processing technique of choice.

In addition, forming a BHJ in two separate steps facilitates a greater understanding of BHJ formation. In this way, SqP enabled us to argue that solvent additives act as non-evaporating polymer swelling agents, improving BHJ morphology by effectively turning BC into SqP. This also opens the possibility to use solvent additives in the first SqP casting step, pre-swelling the polymer film and allowing for a wider choice of solvents for the second step since it is no

longer necessary to optimize χ . Without the ability to independently control swelling and fullerene intercalation, solvent additives would need to be continually re-optimized through trial-and-error.

Finally, since SqP is an efficient method for inserting small molecules into conjugated polymer films, SqP is also a highly effective technique for molecular doping. By swelling, molecular dopants can be effectively inserted into conjugated polymer films, resulting in unprecedented film quality and conductivity. With both BHJ formation and molecular doping, SqP allows us to take advantage of swelling to control conjugated polymers for a wide variety of optoelectronic applications.

References

1. Aguirre, J. C., Arntsen, C., Hernandez, S., Huber, R., Nardes, A. M., Halim, M., Kilbride, D., Rubin, Y., Tolbert, S. H., Kopidakis, N., Schwartz, B. J., Neuhauser, D., Understanding Local and Macroscopic Electron Mobilities in the Fullerene Network of Conjugated Polymer-Based Solar Cells: Time-Resolved Microwave Conductivity and Theory. *Adv. Funct. Mater.*, **24** (2014) 784–792.
2. Aguirre, J. C., Ferreira, A., Ding, H., Jenekhe, S. A., Kopidakis, N., Asta, M., Pilon, L., Rubin, Y., Tolbert, S. H., Schwartz, B. J., Dunn, B., Ozolins, V., Panoramic View of Electrochemical Pseudocapacitor and Organic Solar Cell Research in Molecularly Engineered Energy Materials, *J. Phys. Chem. C*, **118** (2014) 19505–19523.
3. Aguirre, J. C., Hawks, S. A., Ferreira, A. S., Yee, P., Subramaniyan, S., Jenekhe, S. A., Tolbert, S. H., Schwartz, B. J., Sequential Processing for Organic Photovoltaics: Design Rules for Morphology Control by Tailored Semi-Orthogonal Solvent Blends. *Adv. Energy Mater.*, **5** (2015) 1402020.
4. Amb, C. M., Chen, S., Graham, K. R., Subbiah, J., Small, C. E., So, F., Reynolds, J. R., Dithienogermole As a Fused Electron Donor in Bulk Heterojunction Solar Cells. *J. Am. Chem. Soc.*, **133** (2011) 10062–10065.
5. Ayzner, A. L., Doan, S. C., Tremolet de Villers, B., Schwartz, B. J., Ultrafast Studies of Exciton Migration and Polaron Formation in Sequentially Solution-Processed Conjugated Polymer/Fullerene Quasi-Bilayer Photovoltaics. *J. Phys. Chem. Lett.*, **3** (2012) 2281–2287.

6. Ayzner, A. L., Tassone, C. J., Tolbert, S. H., Schwartz, B. J., Reappraising the Need for Bulk Heterojunctions in Polymer-Fullerene Photovoltaics: The Role of Carrier Transport in All-Solution-Processed P3HT/PCBM Bilayer Solar Cells. *J. Phys. Chem. C*, **113** (2009) 20050–20060.
7. Ayzner, A. L., Wanger, D. D., Tassone, C. J., Tolbert, S. H., Schwartz, B. J., Room to Improve Conjugated Polymer-Based Solar Cells: Understanding How Thermal Annealing Affects the Fullerene Component of a Bulk Heterojunction Photovoltaic Device. *J. Phys. Chem. C*, **112** (2008) 18711–18716.
8. Bakulin, A. A., Rao, A., Pavelyev, V. G., van Loosdrecht, P. H. M., Pshenichnikov, M. S., Niedzialek, D., Cornil, J., Beljonne, D., Friend, R. H., The Role of Driving Energy and Delocalized States for Charge Separation in Organic Semiconductors. *Science*, **335** (2012) 1340–1344.
9. Bartelt, J. A., Beiley, Z. M., Hoke, E. T., Mateker, W. R., Douglas, J. D., Collins, B. A., Tumbleston, J. R., Graham, K. R., Amassian, A., Ade, H., Fréchet, J. M. J., Toney, M. F., McGehee, M. D., The Importance of Fullerene Percolation in the Mixed Regions of Polymer-Fullerene Bulk Heterojunction Solar Cells. *Adv. Energy Mater.*, **3** (2013) 364–374.
10. Bartesaghi, D., Ye, G., Chiechi, R. C., Koster, L. J. A., Compatibility of PTB7 and [70]PCBM as a Key Factor for the Stability of PTB7:[70]PCBM Solar Cells. *Adv. Energy Mater.*, **6** (2016) 1502338.
11. Beiley, Z. M., Hoke, E. T., Noriega, R., Dacuña, J., Burkhard, G. F., Bartelt, J. A., Salleo, A., Toney, M. F., McGehee, M. D., Morphology-Dependent Trap Formation in High Performance Polymer Bulk Heterojunction Solar Cells. *Adv. Energy Mater.*, **1** (2011) 954–962.
12. Bijleveld, J. C., Gevaerts, V. S., Nuzzo, D. D., Turbiez, M., Mathijssen, S. G. J., de Leeuw, D. M., Wienk, M. M., Janssen, R. A. J., Efficient Solar Cells Based on an Easily Accessible Diketopyrrolopyrrole Polymer. *Adv. Mater.*, **2** (2010) E242–E246.
13. Blom, P. W. M., Mihailtchi, V. D., Koster, L. J. A., Markov, D. E., Device Physics of Polymer: Fullerene Bulk Heterojunction Solar Cells. *Adv. Mater.*, **19** (2007) 1551–1566.
14. Brown, H. R., Flory-Huggins-Rehner Theory and the Swelling of Semicrystalline Polymers by Organic Fluids. *J. Polym. Sci. Polym. Phys. Ed.*, **16** (1978) 1887–1889.
15. Bruggeman, V. D. A. G., Berechnung Verschiedener Physikalischer Konstanten von Heterogenen Substanzen. I. Dielektrizitätskonstanten und Leitfähigkeiten der Mischkörper aus Isotropen Substanzen. *Ann. Phys.*, **416** (1935) 665–679.

26 *World Scientific Handbook of Organic Optoelectronic Devices*

16. Campoy-Quiles, M., Alonso, M. I., Bradley, D. D. C., Richter, L. J., Advanced Ellipsometric Characterization of Conjugated Polymer Films. *Adv. Funct. Mater.*, **24** (2014) 2116–2134.
17. Cates, N. C., Gysel, R., Beiley, Z., Miller, C. E., Toney, M. F., Heeney, M., McCulloch, I., McGehee, M. D., Tuning the Properties of Polymer Bulk Heterojunction Solar Cells by Adjusting Fullerene Size to Control Intercalation. *Nano Lett.*, **12** (2009) 4153–4157.
18. Chan, K., Gleason, K. K., Initiated Chemical Vapor Deposition of Linear and Cross-Linked Poly (2-Hydroxyethyl Methacrylate) for use as Thin-Film Hydrogels. *Langmuir*, **21** (2005) 8930–8939.
19. Chang, J. F., Sun, B., Breiby, D. W., Nielsen, M. M., Sölling, T. I., Giles, M., McCulloch, I., Sirringhaus, H., Enhanced Mobility of Poly(3-hexylthiophene) Transistors by Spin-Coating from High-Boiling-Point Solvents. *Chem. Mater.*, **16** (2004) 4772–4776.
20. Chang, J.-H., Wang, H.-F., Lin, W.-C., Chiang, K.-M., Chen, K.-C., Huang, W.-C., Huang, Z.-Y., Meng, H.-F., Ho, R.-M., Lin, H.-W., Efficient Inverted Quasi-Bilayer Organic Solar Cells Fabricated by using Non-Halogenated Solvent Processes. *J. Mater. Chem. A*, **2** (2014) 13398–13406.
21. Chen, D., Liu, F., Wang, C., Nakahara, A., Russell, T. P., Bulk Heterojunction Photovoltaic Active Layers via Bilayer Interdiffusion. *Nano Lett.*, **11** (2011) 2071–2078.
22. Chen, H.-Y., Yang, H., Yang, G., Sista, S., Zadoyan, R., Li, G., Yang, Y., Fast-Grown Interpenetrating Network in Poly(3-hexylthiophene): Methanofulleres Solar Cells Processed with Additive. *J. Phys. Chem. C*, **113** (2009) 7946–7953.
23. Chen, W., Du, Z., Xiao, M., Zhang, J., Yang, C., Han, L., Bao, X., Yang, R., High-Performance Small Molecule/Polymer Ternary Organic Solar Cells Based on a Layer-By-Layer Process. *ACS Appl. Mater. Interfaces*, **7** (2015) 23190–23196.
24. Cheng, P., Li, Y., Zhan, X., A DMF-Assisted Solution Process Boosts the Efficiency in P3HT: PCBM Solar Cells. *Nanotechnology*, **24** (2013) 484008.
25. Cheng, P., Lin, Y., Zawacka, N. K., Andersen, T. R., Liu, W., Bundgaard, E., Jorgensen, M., Chen, H., Krebs, F. C., Zhan, X., Comparison of Additive Amount used in Spin-Coated and Roll-Coated Organic Solar Cells. *J. Mater. Chem. A*, **2** (2014) 19542–19549.
26. Cheng, P., Yan, C., Wu, Y., Dai, S., Ma, W., Zhan, X., Efficient and Stable Organic Solar Cells via a Sequential Process. *J. Mater. Chem. C*, **4** (2016) 8086–8093.

27. Chiang, C. K., Fincher, C. R., Park, Y. W., Heeger, A. J., Shirakawa, H., Louis, E. J., Gau, S. C., MacDiarmid, A. G., Electrical Conductivity in Doped Polyacetylene. *Phys. Rev. Lett.*, **39** (1977) 1098–1101.
28. Cho, S.-M., Bae, J.-H., Jang, E., Kim, M.-H., Lee, C., Lee, S.-D., Solvent Effect of the Fibrillar Morphology on the Power Conversion Efficiency of a Polymer Photovoltaic Cell in a Diffusive Heterojunction. *Semicond. Sci. Technol.*, **27** (2012) 125018.
29. Chu, T.-Y., Alem, S., Tsang, S.-W., Tse, S.-C., Wakim, S., Lu, J., Denmler, G., Gaudiana, R., Tao, Y., Morphology Control in Polycarbazole Based Bulk Heterojunction Solar Cells and its Impact on Device Performance. *Appl. Phys. Lett.*, **98** (2011) 253301.
30. Clarke, T. M., Durrant, J. R., Charge Photogeneration in Organic Solar Cells. *Chem. Rev.*, **110** (2010) 6736–6767.
31. Clulow, A. J., Tao, C., Lee, K. H., Velusamy, M., Mcewan, J. A., Shaw, P. E., Yamada, N. L., James, M., Burn, P. L., Gentle, I. R., Meredith, P., Time-Resolved Neutron Reflectometry and Photovoltaic Device Studies on Sequentially Deposited PCDTBT-Fullerene Layers. *Langmuir*, **30** (2014) 11474–11484.
32. Cochran, J. E., Junk, M. J. N., Glaudell, A. M., Miller, P. L., Cowart, J. S., Toney, M. F., Hawker, C. J., Chmelka, B. F., Chabynyc, M. L., Molecular Interactions and Ordering in Electrically Doped Polymers: Blends of PBTTT and F4TCNQ. *Macromolecules*, **47** (2014) 6836–6846.
33. Collins, B. A., Li, Z., Tumbleston, J. R., Gann, E., Mcneill, C. R., Ade, H., Absolute Measurement of Domain Composition and Nanoscale Size Distribution Explains Performance in PTB7:PC₇₁BM Solar Cells. *Adv. Energy Mater.*, **3** (2013) 65–74.
34. Collins, B. A., Tumbleston, J. R., Ade, H., Miscibility, Crystallinity, and Phase Development in P3HT/PCBM Solar Cells: Toward an Enlightened Understanding of Device Morphology and Stability. *J. Phys. Chem. Lett.*, **2** (2011) 3135–3145.
35. Dang, M. T., Wantz, G., Bejbouji, H., Urien, M., Dautel, O. J., Vignau, L., Hirsch, L., Polymeric Solar Cells Based on P3HT:PCBM: Role of the Casting Solvent. *Sol. Energy Mater. Sol. Cells*, **95** (2011) 3408–3418.
36. Deibel, C., Dyakonov, V., Polymer-Fullerene Bulk Heterojunction Solar Cells. *Reports Prog. Phys.*, **73** (2010) 096401.
37. Deschler, F., Riedel, D., Deák, A., Ecker, B., von Hauff, E., Da Como, E., Imaging of Morphological Changes and Phase Segregation in Doped Polymeric Semiconductors. *Synth. Met.*, **199** (2015) 381–387.

28 *World Scientific Handbook of Organic Optoelectronic Devices*

38. Duong, D. T., Wang, C., Antono, E., Toney, M. F., Salleo, A., The Chemical and Structural Origin of Efficient p-Type Doping in P3HT. *Org. Electron.*, **14** (2013) 1330–1336.
39. Elbs, H., Krausch, G., Ellipsometric Determination of Flory-Huggins Interaction Parameters in Solution. *Polymer*, **45** (2004) 7935–7942.
40. Flory, P. J., Thermodynamics of High Polymer Solutions. *J. Chem. Phys.*, **10** (1942) 51–61.
41. Flory, P. J., Statistical Thermodynamics of Liquid Mixtures. *J. Am. Chem. Soc.*, **87** (1964) 1833–1838.
42. Fontana, M. T., Kang, H., Yee, P., Fan, Z., Hawks, S. A., Schelhas, L. T., Tolbert, S. H., Schwartz, B. J., Solvent Additives Function as Polymer Swelling Agents in Bulk Heterojunction Organic Photovoltaics (*Submitted*).
43. Gadisa, A., Tumbleston, J. R., Ko, D.-H., Aryal, M., Lopez, R., Samulski, E. T., The Role of Solvent and Morphology on Miscibility of Methanofullerene and Poly(3-hexylthiophene). *Thin Solid Films*, **520** (2012) 5466–5471.
44. Gao, F., Tress, W., Wang, J., Inganäs, O., Temperature Dependence of Charge Carrier Generation in Organic Photovoltaics. *Phys. Rev. Lett.*, **114** (2015) 128701.
45. Gao, J., Niles, E. T., Grey, J. K., Aggregates Promote Efficient Charge Transfer Doping of Poly(3-hexylthiophene). *J. Phys. Chem. Lett.*, **4** (2013) 2953–2957.
46. Gao, J., Roegling, J. D., Li, Y., Guo, H., Moulé, A. J., Grey, J. K., The Effect of 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane Charge Transfer Dopants on the Conformation and Aggregation of Poly(3-hexylthiophene). *J. Mater. Chem. C*, **1** (2013) 5638–5646.
47. Gevaerts, V. S., Koster, L. J. A., Wienk, M. M., Janssen, R. A. J., Discriminating Between Bilayer and Bulk Heterojunction Polymer: Fullerene Solar Cells Using the External Quantum Efficiency. *ACS Appl. Mater. Interfaces*, **3** (2011) 3252–3255.
48. Ghasemi, M., Ye, L., Zhang, Q., Yan, L., Kim, J.-H., Awartani, O., You, W., Gadisa, A., Ade, H., Panchromatic Sequentially Cast Ternary Polymer Solar Cells. *Adv. Mater.*, **29** (2017) 1604603.
49. Ghooos, T., Malinkiewicz, O., Conings, B., Lutsen, L., Vanderzande, D. J., Bolink, J., Maes, W., Solution-Processed Bi-Layer Polythiophene-Fullerene Organic Solar Cells. *RSC Adv.*, **3** (2013) 25197–25203.
50. Glauddell, A. M., Cochran, J. E., Patel, S. N., Chabinyc, M. L., Impact of the Doping Method on Conductivity and Thermopower in Semiconducting Polythiophenes. *Adv. Energy Mater.*, **5** (2015) 1401072.

51. Graham, K. R., Wieruszewski, P. M., Stalder, R., Hartel, M. J., Mei, J., So, F., Reynolds, J. R., Improved Performance of Molecular Bulk-Heterojunction Photovoltaic Cells through Predictable Selection of Solvent Additives. *Adv. Funct. Mater.*, **22** (2012) 4801–4813.
52. Gu, Y., Wang, C., Russell, T. P., Multi-Length-Scale Morphologies in PCPDTBT/PCBM Bulk-Heterojunction Solar Cells. *Adv. Energy Mater.*, **2** (2012) 683–690.
53. Guo, X., Cui, C., Zhang, M., Huo, L., Huang, Y., Li, Y., High Efficiency Polymer Solar Cells Based on Poly(3-hexylthiophene)/Indene-C₇₀ Bisadduct with Solvent Additive. *Energy Environ. Sci.*, **5** (2012) 7943–7949.
54. Guo, X., Zhang, M., Ma, W., Ye, L., Zhang, S., Liu, S., Ade, H., Huang, F., Hou, J., Enhanced Photovoltaic Performance by Modulating Surface Composition in Bulk Heterojunction Polymer Solar Cells Based on PBDTTT-C-T/PC₇₁BM. *Adv. Mater.*, **26** (2014) 4043–4049.
55. Halls, J. J. M., Walsh, C. A., Greenham, N. C., Marseglia, E. A., Friend, R. H., Moratti, S. C., Holmes, A. B., Efficient Photodiodes from Interpenetrating Polymer Networks. *Nature*, **376** (1995) 498–500.
56. Hammond, M. R., Kline, R. J., Herzing, A. A., Richter, L. J., Germack, D. S., Ro, H.-W., Soles, C. L., Fischer, D. A., Xu, T., Yu, L., Toney, M. F., DeLongchamp, D. M., Molecular Order in High-Efficiency Polymer/Fullerene Bulk Heterojunction Solar Cells. *ACS Nano*, **5** (2011) 8248–8257.
57. Hawks, S. A., Aguirre, J. C., Schelhas, L. T., Thompson, R. J., Huber, R. C., Ferreira, A. S., Zhang, G., Herzing, A. A., Tolbert, S. H., Schwartz, B. J., Comparing Matched Polymer:Fullerene Solar Cells Made by Solution-Sequential Processing and Traditional Blend Casting: Nanoscale Structure and Device Performance. *J. Phys. Chem. C*, **118** (2014) 17413–17425.
58. He, Z., Xiao, B., Liu, F., Wu, H., Yang, Y., Xiao, S., Wang, C., Russell, T. P., Cao, Y., Single-Junction Polymer Solar Cells with High Efficiency and Photovoltage. *Nat. Photonics*, **9** (2015) 174–179.
59. Heeger, A. J., 25th Anniversary Article: Bulk Heterojunction Solar Cells: Understanding the Mechanism of Operation. *Adv. Mater.*, **26** (2014) 10–28.
60. Hoven, C. V., Dang, X.-D., Coffin, R. C., Peet, J., Nguyen, T.-Q., Bazan, G. C., Improved Performance of Polymer Bulk Heterojunction Solar Cells Through the Reduction of Phase Separation via Solvent Additives. *Adv. Energy Mater.*, **22** (2010) 63–66.

30 *World Scientific Handbook of Organic Optoelectronic Devices*

61. Howard, I. A., Hodgkiss, J. M., Zhang, X., Kirov, K. R., Bronstein, H. A., Williams, C. K., Friend, R. H., Westenhoff, S., Greenham, N. C., Charge Recombination and Exciton Annihilation Reactions in Conjugated Polymer Blends. *J. Am. Chem. Soc.*, **132** (2010) 328–335.
62. Huttner, S., Sommer, M., Chiche, A., Krausch, G., Steiner, U., Thelakkat, M., Controlled Solvent Vapour Annealing for Polymer Electronics. *Soft Matter*, **5** (2009) 4206–4211.
63. Jacobs, I. E., Aasen, E. W., Oliveira, J. L., Fonseca, T. N., Roehling, J. D., Li, J., Zhang, G., Augustine, M. P., Mascal, M., Moulé, A. J., Comparison of Solution-Mixed and Sequentially Processed P3HT:F4TCNQ Films: Effect of Doping-Induced Aggregation on Film Morphology. *J. Mater. Chem. C*, **4** (2016) 3454–3466.
64. Jhuo, H.-J., Liao, S.-H., Li, Y.-L., Yeh, P.-N., Chen, S.-A., Wu, W.-R., Su, C.-J., Lee, J.-J., Yamada, N. L., Jeng, U.-s., The Novel Additive 1-Naphthalenethiol Opens a New Processing Route to Efficiency-Enhanced Polymer Solar Cells. *Adv. Funct. Mater.*, **26** (2016) 3094–3104.
65. Jørgensen, M., Carlé, J. E., Søndergaard, R. R., Lauritzen, M., Dagnæs-Hansen, N. A., Byskov, S. L., Andersen, T. R., Larsen-Olsen, T. T., Böttiger, A. P. L., Andreasen, B., Fu, L., Zuo, L., Liu, Y., Bundgaard, E., Zhan, X., Chen, H., Krebs, F. C., The State of Organic Solar Cells — A Meta Analysis. *Sol. Energy Mater. Sol. Cells*, **119** (2013) 84–93.
66. Kan, B., Zhang, Q., Li, M., Wan, X., Ni, W., Long, G., Wang, Y., Yang, X., Feng, H., Chen, Y., Solution-Processed Organic Solar Cells Based on Dialkylthiol-Substituted Benzodithiophene Unit with Efficiency Near 10%. *J. Am. Chem. Soc.*, **136** (2014) 15529–15532.
67. Kang, K., Watanabe, S., Broch, K., Sepe, A., Brown, A., Nasrallah, I., Nikolka, M., Fei, Z., Heeney, M., Matsumoto, D., Marumoto, K., Tanaka, H., Kuroda, S.-I., Sirringhaus, H., 2D Coherent Charge Transport in Highly Ordered Conducting Polymers Doped by Solid State Diffusion. *Nat. Mater.*, **15** (2016) 896–903.
68. Kim, D. H., Mei, J., Ayzner, A. L., Schmidt, K., Giri, G., Appleton, A. L., Toney, F., Bao, Z., Sequentially Solution-Processed, Nanostructured Polymer Photovoltaics Using Selective Solvents. *Energy Environ. Sci.*, **7** (2014) 1103–1109.
69. Kline, R. J., McGehee, M. D., Morphology and Charge Transport in Conjugated Polymers. *J. Macromol. Sci. Part C Polym. Rev.*, **46** (2006) 27–45.
70. Kolesov, V. A., Fuentes-Hernandez, C., Chou, W.-F., Aizawa, N., Larrain, F. A., Wang, M., Perrotta, A., Choi, S., Graham, S.,

- Bazan, G. C., Nguyen, T.-Q., Marder, S. R., Kippelen, B., Solution-Based Electrical Doping of Semiconducting Polymer Films Over a Limited Depth. *Nat. Mater.*, **1** (2016) 1–8.
71. Kong, J., Hwang, I.-W., Lee, K., Top-Down Approach for Nanophase Reconstruction in Bulk Heterojunction Solar Cells. *Adv. Mater.*, **26** (2014) 6275–6283.
 72. Krebs, F. C., Fabrication and Processing of Polymer Solar Cells: A Review of Printing and Coating Techniques. *Sol. Energy Mater. Sol. Cells*, **93** (2009) 394–412.
 73. Kwon, S., Kang, H., Lee, J.-H., Lee, J., Hong, S., Kim, H., Lee, K., Effect of Processing Additives on Organic Photovoltaics: Recent Progress and Future Prospects. *Adv. Energy Mater.*, **7** (2016) 1601496.
 74. Kwon, S., Park, J. K., Kim, G., Kong, J., Bazan, G. C., Lee, K., Synergistic Effect of Processing Additives and Optical Spacers in Bulk-Heterojunction Solar Cells. *Adv. Energy Mater.*, **2** (2012) 1420–1424.
 75. Lang, C., Fan, J., Zhang, Y., Guo, F., Zhao, L., Utilizing Intermixing of Conjugated Polymer and Fullerene from Sequential Solution Processing for Efficient Polymer Solar Cells. *Org. Electron.*, **36** (2016) 82–88.
 76. Lee, J. K., Ma, W. L., Brabec, C. J., Yuen, J., Moon, J. S., Kim, J. Y., Lee, K., Bazan, G. C., Heeger, A. J., Processing Additives for Improved Efficiency from Bulk Heterojunction Solar Cells. *J. Am. Chem. Soc.*, **130** (2008) 3619–3623.
 77. Lee, K. H., Schwenn, P. E., Smith, A. R. G., Cavaye, H., Shaw, P. E., James, M., Krueger, K. B., Gentle, I. R., Meredith, P., Burn, P. L., Morphology of All-Solution-Processed “Bilayer” Organic Solar Cells. *Adv. Mater.*, **23** (2011) 766–770.
 78. Lee, K. H., Zhang, Y., Burn, P. L., Gentle, I. R., James, M., Nelson, A., Meredith, P., Correlation of Diffusion and Performance in Sequentially Processed P3HT/PCBM Heterojunction Films by Time-Resolved Neutron Reflectometry. *J. Mater. Chem. C*, **1**, (2013) 2593–2598.
 79. Li, B. G., Yao, Y., Yang, H., Shrotriya, V., Yang, G., Yang, Y., “Solvent Annealing” Effect in Polymer Solar Cells Based on Poly(3-hexylthiophene) and Methanofullerenes. *Adv. Funct. Mater.*, **17** (2007) 1636–1644.
 80. Li, G., Shrotriya, V., Huang, J., Yao, Y., Moriarty, T., Emery, K., Yang, Y., High-Efficiency Solution Processable Polymer Photovoltaic Cells by Self-Organization of Polymer Blends *Nat. Mater.*, **11** (2005) 864–868.

32 *World Scientific Handbook of Organic Optoelectronic Devices*

81. Li, G., Zhu, R., Yang, Y., Polymer Solar Cells. *Nat. Photonics*, **6** (2012) 153–161.
82. Li, H., Li, Y.-F., Wang, J., Optimizing Performance of Layer-by-Layer Processed Polymer Solar Cells. *Appl. Phys. Lett.*, **101** (2012) 033907.
83. Li, H., Qi, Z., Wang, J., Layer-by-Layer Processed Polymer Solar Cells with Self-Assembled Electron Buffer Layer. *Appl. Phys. Lett.*, **102** (2013) 213901.
84. Li, H., Wang, J., Layer-by-Layer Processed High-Performance Polymer Solar Cells. *Appl. Phys. Lett.*, **101** (2012) 263901.
85. Li, H., Zhang, Z.-G., Li, Y., Wang, J., Tunable Open-Circuit Voltage in Ternary Organic Solar Cells. *Appl. Phys. Lett.*, **101** (2012) 163302.
86. Liang, Y., Xu, Z., Xia, J., Tsai, S.-T., Wu, Y., Li, G., Ray, C., Yu, L., For the Bright Future - Bulk Heterojunction Polymer Solar Cells with Power Conversion Efficiency of 7.4%. *Adv. Mater.*, **22** (2010) E135–E138.
87. Liang, Y., Yu, L., A New Class of Semiconducting Polymers for Bulk Heterojunction Solar Cells with Exceptionally High Performance. *Acc. Chem. Res.*, **43** (2010) 1227–1236.
88. Liao, H.-C., Ho, C.-C., Chang, C.-Y., Jao, M.-H., Darling, S. B., Su, W.-F., Additives for Morphology Control in High-Efficiency Organic Solar Cells. *Mater. Today*, **16** (2013) 326–336.
89. Lin, Y., Ma, L., Li, Y., Liu, Y., Zhu, D., Zhan, X., Small-Molecule Solar Cells with Fill Factors up to 0.75 via a Layer-by-Layer Solution Process. *Adv. Energy Mater.*, **4** (2014) 1300626.
90. Liu, B., Png, R.-Q., Zhao, L.-H., Chua, L.-L., Friend, R. H., Ho, P. K. H., High Internal Quantum Efficiency in Fullerene Solar Cells Based on Crosslinked Polymer Donor Networks. *Nat. Commun.*, **3** (2012) 1321–1328.
91. Liu, C., Hu, X., Zhong, C., Huang, M., Wang, K., Zhang, Z., Gong, X., Cao, Y., Heeger, A. J., The Influence of Binary Processing Additives on the Performance of Polymer Solar Cells. *Nanoscale*, **6** (2014) 14297–14304.
92. Liu, F., Zhao, W., Tumbleston, J. R., Wang, C., Gu, Y., Wang, D., Briseno, A. L., Ade, H., Russell, T. P., Understanding the Morphology of PTB7: PCBM Blends in Organic Photovoltaics. *Adv. Energy Mater.*, **4** (2014) 1301377.
93. Liu, Y., Liu, F., Wang, H.-W., Nordlund, D., Sun, Z., Ferdous, S., Russell, T. P., Sequential Deposition: Optimization of Solvent Swelling for High-Performance Polymer Solar Cells. *ACS Appl. Mater. Interfaces*, **7** (2015) 653–661.
94. Liu, Y., Zhao, J., Li, Z., Mu, C., Ma, W., Hu, H., Jiang, K., Lin, H., Ade, H., Yan, H., Aggregation and Morphology Control

- Enables Multiple Cases of High-Efficiency Polymer Solar Cells. *Nat. Commun.*, **5** (2014) 5293.
95. Loiudice, A., Rizzo, A., Biasiucci, M., Gigli, G., Bulk Heterojunction versus Diffused Bilayer: The Role of Device Geometry in Solution p-Doped Polymer-Based Solar Cells. *J. Phys. Chem. Lett.*, **3** (2012) 1908–1905.
 96. Loiudice, A., Rizzo, A., Latini, G., Nobile, C., Giorgi, M. D., Gigli, G., Graded Vertical Phase Separation of Donor/Acceptor Species for Polymer Solar Cells. *Sol. Energy Mater. Sol. Cells*, **100** (2012) 147–152.
 97. Lou, S. J., Szarko, J. M., Xu, T., Yu, L., Marks, T. J., Chen, L. X., Effects of Additives on the Morphology of Solution Phase Aggregates Formed by Active Layer Components of High-Efficiency Organic Solar Cells. *J. Am. Chem. Soc.*, **133**, (2011) 20661–20663.
 98. Lu, L., Zheng, T., Wu, Q., Schneider, A. M., Zhao, D., Yu, L., Recent Advances in Bulk Heterojunction Polymer Solar Cells. *Chem. Rev.*, **115** (2015) 12666–12731.
 99. Ma, B. W., Yang, C., Gong, X., Lee, K., Heeger, A. J., Thermally Stable, Efficient Polymer Solar Cells with Nanoscale Control of the Interpenetrating Network Morphology. *Adv. Funct. Mater.*, **15** (2005) 1617–1622.
 100. Machui, F., Langner, S., Zhu, X., Abbott, S., Brabec, C. J., Determination of the P3HT:PCBM Solubility Parameters via a Binary Solvent Gradient Method: Impact of Solubility on the Photovoltaic Performance. *Sol. Energy Mater. Sol. Cells*, **100** (2012) 138–146.
 101. Mauger, S. A., Chang, L., Friedrich, S., Rochester, C. W., Huang, D. M., Wang, P., Moulé, A. J., Self-Assembly of Selective Interfaces in Organic Photovoltaics. *Adv. Funct. Mater.*, **23** (2013) 1935–1946.
 102. Mayer, A. C., Toney, M. F., Scully, S. R., Rivnay, J., Brabec, C. J., Scharber, M., Koppe, M., Heeney, M., McCulloch, I., McGehee, M. D., Bimolecular Crystals of Fullerenes in Conjugated Polymers and the Implications of Molecular Mixing for Solar Cells. *Adv. Funct. Mater.*, **8** (2009) 1173–1179.
 103. Moon, J. S., Takacs, C. J., Cho, S., Coffin, R. C., Kim, H., Bazan, G. C., Heeger, A. J., Effect of Processing Additive on the Nanomorphology of a Bulk Heterojunction Material. *Nano Lett.*, **10** (2010) 4005–4008.
 104. Morteani, A. C., Sreearunothai, P., Herz, L. M., Friend, R. H., Silva, C., Exciton Regeneration at Polymeric Semiconductor Heterojunctions. *Phys. Rev. Lett.*, **92** (2004) 247402.
 105. Müller, L., Nanova, D., Glaser, T., Beck, S., Pucci, A., Kast, A. K., Schröder, R. R., Mankel, E., Pingel, P., Neher, D., Kowalsky, W.,

34 *World Scientific Handbook of Organic Optoelectronic Devices*

- Lovrincic, R., Charge-Transfer-Solvent Interaction Predefines Doping Efficiency in p-Doped P3HT Films. *Chem. Mater.*, **28** (2016) 4432–4439.
106. Nardes, A. M., Ayzner, A. L., Hammond, S. R., Ferguson, A. J., Schwartz, B. J., Kopidakis, N., Photoinduced Charge Carrier Generation and Decay in Sequentially Deposited Polymer/Fullerene Layers: Bulk Heterojunction vs Planar Interface. *J. Phys. Chem. C*, **116** (2012) 7293–7305.
107. Ng, A., Li, C. H., Fung, M. K., Djurišić, A. B., Zapien, J. A., Chan, W. K., Cheung, K. Y., Wong, W.-Y., Accurate Determination of the Index of Refraction of Polymer Blend Films by Spectroscopic Ellipsometry. *J. Phys. Chem. C*, **114** (2010) 15094–15101.
108. Noriega, R., Rivnay, J., Vandewal, K., Koch, F. P. V., Stingelin, N., Smith, P., Toney, M. F., Salleo, A., A General Relationship Between Disorder, Aggregation and Charge Transport in Conjugated Polymers. *Nat. Mater.*, **12** (2013) 1038–1044.
109. Ogieglo, W., van der Werf, H., Tempelman, K., Wormeester, H., Wessling, M., Nijmeijer, A., Benes, N. E., n-Hexane Induced Swelling of Thin PDMS Films Under Non-Equilibrium Nanofiltration Permeation Conditions, Resolved by Spectroscopic Ellipsometry. *J. Memb. Sci.*, **431** (2013) 233–243.
110. Oh, J. Y., Lee, T. I., Jang, W. S., Chae, S. S., Park, J. H., Myoung, J.-M., Baik, H. K., Mass Production of a 3D Non-Woven Nanofabric with Crystalline P3HT Nanofibrils for Organic Solar Cells. *Energy Environ. Sci.*, **6** (2013) 910–917.
111. Papanu, J. S., Hess, D. W., Bell, A. T., S, S. D., In Situ Ellipsometry to Monitor Swelling and Dissolution of Thin Polymer Films. *J. Electrochem. Soc.*, **136** (1989) 1195–1200.
112. Park, H. J., Lee, J. Y., Lee, T., Guo, L. J., Heterojunction Structure of Polymer Photovoltaic Cell Generating High Photocurrent with Internal Quantum Efficiency Approaching 100%. *Adv. Energy Mater.*, **3** (2013) 1135–1142.
113. Park, S. H., Roy, A., Beaupré, S., Cho, S., Coates, N., Moon, J. S., Moses, D., Leclerc, M., Lee, K., Heeger, A. J., Bulk Heterojunction Solar Cells with Internal Quantum Efficiency Approaching 100%. *Nat. Photonics*, **3** (2009) 297–303.
114. Peet, J., Kim, J. Y., Coates, N. E., Ma, W. L., Moses, D., Heeger, A. J., Bazan, G. C., Efficiency Enhancement in Low-Bandgap Polymer Solar Cells by Processing with Alkane Dithiols. *Nat. Mater.*, **6** (2007) 497–500.
115. Peet, J., Soci, C., Coffin, R. C., Nguyen, T. Q., Mikhailovsky, A., Moses, D., Bazan, G. C., Method for Increasing the Photoconductive

- Response in Conjugated Polymer/Fullerene Composites. *Appl. Phys. Lett.* **89** (2006) 252105.
116. Pingel, P., Neher, D., Comprehensive Picture of p-Type Doping of P3HT with the Molecular Acceptor F4TCNQ. *Phys. Rev. B*, **87** (2013) 115209.
 117. Pivrikas, A., Stadler, P., Neugebauer, H., Sariciftci, N. S., Substituting the Postproduction Treatment for Bulk-Heterojunction Solar Cells Using Chemical Additives. *Organic Electronics*, **9** (2008) 775–782.
 118. Richter, L. J., Delongchamp, D. M., Bokel, F. A., Engmann, S., Chou, K. W., Amassian, A., Schaible, E., Hexemer, A., In Situ Morphology Studies of the Mechanism for Solution Additive Effects on the Formation of Bulk Heterojunction Films. *Adv. Energy Mater.*, **5** (2015) 1400975.
 119. Ro, H. W., Downing, J. M., Engmann, S., Herzing, A. A., Delongchamp, D. M., Richter, L. J., Mukherjee, S., Ade, H., Abdelsamie, M., Jagadamma, L. K., Amassian, A., Liu, Y., Yan, H., Morphology Changes Upon Scaling a High-Efficiency, Solution-Processed Solar Cell. *Energy Environ. Sci.*, **9** (2016) 2835–2846.
 120. Rochester, C. W., Mauger, S. A., Moulé, A. J., Investigating the Morphology of Polymer/Fullerene Layers Coated Using Orthogonal Solvents. *J. Phys. Chem. C*, **116** (2012) 7287–7292.
 121. Rogers, C. E., Stannett, V., Szwarc, M., The Sorption of Organic Vapors by Polyethylene. *J. Phys. Chem.*, **63** (1959) 1406–1413.
 122. Salleo, A., Kline, R. J., DeLongchamp, D. M., Chabinc, M. L., Microstructural Characterization and Charge Transport in Thin Films of Conjugated Polymers. *Adv. Mater.*, **22** (2010) 3812–3838.
 123. Salzmann, I., Heimel, G., Toward a Comprehensive Understanding of Molecular Doping Organic Semiconductors (Review). *J. Electron Spectros. Relat. Phenomena*, **204** (2015) 208–222.
 124. Scholes, D. T., Hawks, S. A., Yee, P. Y., Wu, H., Lindemuth, J. R., Tolbert, S. H., Schwartz, B. J., Overcoming Film Quality Issues for Conjugated Polymers Doped with F4TCNQ by Solution Sequential Processing: Hall Effect, Structural, and Optical Measurements. *J. Phys. Chem. Lett.*, **6** (2015) 4786–4793.
 125. Scholes, D. T., Yee, P. Y., Lindemuth, J. R., Kang, H., Onorato, J., Ghosh, R., Luscombe, C. K., Spano, F. C., Tolbert, S. H., Schwartz, B. J., The Effects of Crystallinity on Charge Transport and the Structure of Sequentially Processed F₄TCNQ-Doped Conjugated Polymer Films. *Adv. Funct. Mater.*, (2017) 1702654.
 126. Seok, J., Shin, T. J., Park, S., Cho, C., Lee, J.-Y., Ryu, D. Y., Kim, M. H., Kim, K., Efficient Organic Photovoltaics Utilizing Nanoscale

36 *World Scientific Handbook of Organic Optoelectronic Devices*

- Heterojunctions in Sequentially Deposited Polymer/Fullerene Bilayer. *Sci. Rep.*, **5** (2015) 8373.
127. Shaheen, S. E., Brabec, C. J., Sariciftci, N. S., Padinger, F., Fromherz, T., Hummelen J. C., 2.5% Efficient Organic Plastic Solar Cells. *Appl. Phys. Lett.*, **78** (2001) 841–843.
 128. Shin, N., Richter, L. J., Herzing, A. A., Kline, R. J., Delongchamp, D. M., Effect of Processing Additives on the Solidification of Blade-Coated Polymer/Fullerene Blend Films via In-Situ Structure Measurements. *Adv. Energy Mater.*, **3** (2013) 938–948.
 129. Sirringhaus, H., Brown, P. J., Friend, R. H., Nielsen, M. M., Bechgaard, K., Langeveld-Voss, B. M. W., Spiering, A. J. H., Janssen, R. A. J., Meijer, E. W., Herwig, P., de Leeuw, D. M., Two-Dimensional Charge Transport in Self-Organized, High-Mobility Conjugated Polymers. *Nature*, **401** (1999) 685–688.
 130. Spaeth, K., Kraus, G., Gauglitz, G., In-Situ Characterization of Thin Polymer Films for Applications in Chemical Sensing of Volatile Organic Compounds by Spectroscopic Ellipsometry. *Fresenius. J. Anal. Chem.*, **357** (1997) 292–296.
 131. Su, M.-S., Kuo, C.-Y., Yuan, M.-C., Jeng, U.-S., Su, C.-J., Wei, K.-H., Improving Device Efficiency of Polymer/Fullerene Bulk Heterojunction Solar Cells Through Enhanced Crystallinity and Reduced Grain Boundaries Induced by Solvent Additives. *Adv. Mater.*, **23** (2011) 3315–3319.
 132. Subramanian, S., Xin, H., Kim, F. S., Jenekhe, S. A., New Thiazolothiazole Copolymer Semiconductors for Highly Efficient Solar Cells. *Macromolecules*, **44** (2011) 6245–6248.
 133. Sun, Y., Welch, G. C., Leong, W. L., Takacs, C. J., Bazan, G. C., Heeger, A. J., Solution-Processed Small-Molecule Solar Cells with 6.7% Efficiency. *Nat. Mater.*, **11** (2011) 44–48.
 134. Tao, C., Aljada, M., Shaw, P. E., Lee, K. H., Cavaye, H., Balfour, M. N., Borthwick, R. J., James, M., Burn, P. L., Gentle, I. R., Meredith, P., Controlling Hierarchy in Solution-Processed Polymer Solar Cells Based on Crosslinked P3HT. *Adv. Energy Mater.*, **3** (2013) 105–112.
 135. Tassone, C. J., Ayzner, A. L., Kennedy, R. D., Halim, M., So, M., Rubin, Y., Tolbert, S. H., Schwartz, B. J., Using Pentaarylfullerenes to Understand Network Formation in Conjugated Polymer-Based Bulk-Heterojunction Solar Cells. *J. Phys. Chem. C*, **115**, (2011) 22563–22571.
 136. Thompson, B. C., Fréchet, J. M. J., Polymer Fullerene Composite Solar Cells Angewandte. *Angewandte Chemie*, **47** (2008) 58–77.

137. Thummalakunta, L. N. S. A., Yong, C. H., Ananthanarayanan, K., Luther, J., P3HT Based Solution-Processed Pseudo Bi-Layer Organic Solar Cell with Enhanced Performance. *Organic Electronics*, **13** (2012) 2008–2016.
138. Tournebize, A., Rivaton, A., Peisert, H., Chassé, T., The Crucial Role of Confined Residual Additives on the Photostability of P3HT:PCBM Active Layers. *J. Phys. Chem. C*, **119** (2015) 9142–9148.
139. Treat, N. D., Brady, M. A., Smith, G., Toney, M. F., Kramer, E. J., Hawker, C. J., Chabinye, M. L., Interdiffusion of PCBM and P3HT Reveals Miscibility in a Photovoltaically Active Blend. *Adv. Energy Mater.*, **1** (2011) 82–89.
140. Tremolet de Villers, B. J., Hara, K. A. O., Ostrowski, D. P., Biddle, P. H., Shaheen, S. E., Chabinye, M. L., Olson, D. C., Kopidakis, N., Removal of Residual Diiodooctane Improves Photostability of High-Performance Organic Solar Cell Polymers. *Chem. Mater.*, **28** (2016) 876–884.
141. Vakhshouri, K., Smith, B. H., Chan, E. P., Wang, C., Salleo, A., Wang, C., Hexemer, A., Gomez, E. D., Signatures of Intracrystallite and Intercrystallite Limitations of Charge Transport in Polythiophenes. *Macromolecules*, **49** (2016) 7359–7369.
142. van Bavel, S. S., Sourty, E., With, G. D., Loos, J., Three-Dimensional Nanoscale Organization of Bulk Heterojunction Polymer Solar Cells. *Nano Lett.*, **9** (2009) 507–513.
143. Vandewal, K., Albrecht, S., Hoke, E. T., Graham, K. R., Widmer, J., Douglas, J. D., Schubert, M., Mateker, W. R., Bloking, J. T., Burkhard, G. F., Sellinger, A., Fréchet, J. M. J., Amassian, A., Riede, M. K., McGehee, M. D., Neher, D., Salleo, A., Efficient Charge Generation by Relaxed Charge-Transfer States at Organic Interfaces. *Nat. Mater.*, **13** (2014) 63–68.
144. van Franeker, J. J., Kouijzer, S., Lou, X., Turbiez, M., Wienk, M. M., Janssen, R. A. J., Depositing Fullerenes in Swollen Polymer Layers via Sequential Processing of Organic Solar Cells. *Adv. Energy Mater.*, **5** (2015) 1500464.
145. Venkatesan, S., Adhikari, N., Chen, J., Ngo, E. C., Dubey, A., Galipeau, D. W., Qiao, Q., Interplay of Nanoscale Domain Purity on Charge Transport and Recombination Dynamics in Polymer Solar Cells. *Nanoscale*, **6** (2014) 1011–1019.
146. Vohra, V., Arrighetti, G., Barba, L., Higashimine, K., Porzio, W., Murata, H., Enhanced Vertical Concentration Gradient in Rubbed P3HT:PCBM Graded Bilayer Solar Cells. *J. Phys. Chem. Lett.*, **3** (2012) 1820–1823.

38 *World Scientific Handbook of Organic Optoelectronic Devices*

147. Vohra, V., Dorling, B., Higashimine, K., Murata, H., Investigating the Effect of Solvent Boiling Temperature on the Morphology of P3HT:PCBM Diffusive Bilayer Solar Cells. *Appl. Phys. Express*, **9** (2016) 0112301.
148. Vohra, V., Higashimine, K., Murakami, T., Murata, H., Addition of Regiorandom Poly(3-hexylthiophene) to Solution Processed Graded Bilayers to Tune the Vertical Concentration Gradient. *Appl. Phys. Lett.*, **101** (2012) 173301.
149. Vohra, V., Higashimine, K., Tsuzaki, S., Ohdaira, K., Murata, H., Formation of Vertical Concentration Gradients in Poly(3-hexylthiophene-2,5-diyl): Phenyl-C₆₁-Butyric Acid Methyl Ester-Graded Bilayer Solar Cells. *Thin Solid Films*, **554** (2014) 41–45.
150. Walker, B., Tamayo, A., Duong, D. T., Dang, X.-D., Kim, C., Granstrom, J., Nguyen, T.-Q., A Systematic Approach to Solvent Selection Based on Cohesive Energy Densities in a Molecular Bulk Heterojunction System. *Adv. Energy Mater.*, **1** (2011) 221–229.
151. Wang, C., Duong, D. T., Vandewal, K., Rivnay, J., Salleo, A., Optical Measurement of Doping Efficiency in Poly(3-hexylthiophene) Solutions and Thin Films. *Phys. Rev. B*, **91** (2015) 085205.
152. Wang, D. H., Kim, J. K., Park, O. O., Park, J. H., Analysis of Surface Morphological Changes in Organic Photovoltaic Devices: Bilayer versus Bulk-Heterojunction. *Energy Environ. Sci.*, **4** (2011) 1434–1439.
153. Wang, D. H., Lee, H. K., Choi, D.-G., Park, J. H., Park, O. O., Solution-Processable Polymer Solar Cells from a Poly(3-hexylthiophene)/[6,6]-Phenyl C₆₁-Butyric Acid Methyl Ester Concentration Graded Bilayers. *Appl. Phys. Lett.*, **95** 043505.
154. Wang, D. H., Moon, J. S., Seifert, J., Jo, J., Park, J. H., Park, O. O., Heeger, A. J., Sequential Processing: Control of Nanomorphology in Bulk Heterojunction Solar Cells. *Nano Lett.*, **11** (2011) 3163–3168.
155. Wang, T., Pearson, A. J., Dunbar, A. D. F., Staniec, P. A., Watters, D. C., Yi, H., Ryan, A. J., Jones, R. A. L., Iraqi, A., Lidzey, D. G., Correlating Structure with Function in Thermally Annealed PCDTBT:PC₇₀BM Photovoltaic Blends. *Adv. Funct. Mater.*, **22** (2012) 1399–1408.
156. Xiao, Z., Yuan, Y., Yang, B., Vanderslice, J., Chen, J., Dyck, O., Universal Formation of Compositionally Graded Bulk Heterojunction for Efficiency Enhancement in Organic Photovoltaics. *Adv. Mater.*, **26** (2014) 3068–3075.
157. Xie, L., Lee, J. S., Jang, Y., Ahn, H., Kim, Y.-H., Kim, K., Organic Photovoltaics Utilizing a Polymer Nanofiber/Fullerene Interdigitated

- Bilayer Prepared by Sequential Solution Deposition. *J. Phys. Chem. C*, **120** (2016) 12933–12940.
158. Xu, Z., Chen, L.-M., Yang, G., Huang, C.-H., Hou, J., Wu, Y., Li, G., Hsu, C.-S., Yang, Y., Vertical Phase Separation in Poly(3-hexylthiophene): Fullerene Derivative Blends and its Advantage for Inverted Structure Solar Cells. *Adv. Funct. Mater.*, **19** (2009) 1227–1234.
 159. Yang, B., Yuan, Y., Huang, J., Reduced Bimolecular Charge Recombination Loss in Thermally Annealed Bilayer Heterojunction Photovoltaic Devices with Large External Quantum Efficiency and Fill Factor. *J. Phys. Chem. C*, **118** (2014) 5196–5202.
 160. Yang, H., Shin, T. J., Yang, L., Cho, K., Ryu, C. Y., Bao, Z., Effect of Mesoscale Crystalline Structure on the Field-Effect Mobility of Regioregular Poly(3-hexyl thiophene) in Thin-Film Transistors. *Adv. Funct. Mater.*, **15** (2005) 671–676.
 161. Yang, H. Y., Kang, N. S., Hong, J.-M., Song, Y.-W., Kim, T. W., Lim, J. A., Efficient Bilayer Heterojunction Polymer Solar Cells with Bumpy Donor-Acceptor Interface Formed by Facile Polymer Blend. *Org. Electron.*, **13** (2012) 2688–2695.
 162. Yao, K., Intemann, J. J., Yip, H.-L., Liang, P.-W., Chang, C.-Y., Efficient All Polymer Solar Cells from Layer-Evolved Processing of a Bilayer Inverted Structure. *J. Mater. Chem. C*, **2** (2014) 416–420.
 163. Yao, Y., Hou, J., Xu, Z., Li, G., Yang, Y., Effects of Solvent Mixtures on the Nanoscale Phase Separation in Polymer Solar Cells. *Adv. Funct. Mater.*, **18** (2008) 1783–1789.
 164. Ye, L., Jing, Y., Guo, X., Sun, H., Zhang, S., Zhang, M., Huo, L., Hou, J., Remove the Residual Additives toward Enhanced Efficiency with Higher Reproducibility in Polymer Solar Cells. *J. Phys. Chem. C*, **117** (2013) 14920–14928.
 165. Yim, K.-H., Whiting, G. L., Murphy, C. E., Halls, J. J. M., Burroughes, J. H., Friend, R. H., Kim, J.-S., Controlling Electrical Properties of Conjugated Polymers via a Solution-Based p-Type Doping. *Adv. Mater.*, **20** (2012) 3319–3324.
 166. Yu, G., Gao, J., Hummelen, J. C., F., W., Heeger, A. J., Polymer Photovoltaic Cells: Enhanced Efficiencies via a Network of Internal Donor-Acceptor Heterojunctions. *Science*, **270** (1995) 1789–1791.
 167. Zhang, G., Huber, R. C., Ferreira, A. S., Boyd, S. D., Luscombe, C. K., Tolbert, S. H., Schwartz, B. J., Crystallinity Effects in Sequentially Processed and Blend-Cast Bulk-Heterojunction Polymer/Fullerene Photovoltaics. *J. Phys. Chem. C*, **118** (2014) 18424–18435.

40 *World Scientific Handbook of Organic Optoelectronic Devices*

168. Zhang, S., Ye, L., Zhao, W., Yang, B., Wang, Q., Hou, J., Realizing Over 10% Efficiency in Polymer Solar Cell by Device Optimization. *Sci. China Chem.*, **58** (2015) 248–256.
169. Zhang, Y., de Boer, B., Blom, P. W. M., Controllable Molecular Doping and Charge Transport in Solution-Processed Polymer Semiconducting Layers. *Adv. Funct. Mater.*, **19** (2009) 1901–1905.
170. Zhang, Y., Li, Z., Wakim, S., Alem, S., Tsang, S.-W., Lu, J., Ding, J., Tao, Y., Bulk Heterojunction Solar Cells Based on a New Low-Band-Gap Polymer: Morphology and Performance. *Org. Electron.*, **12** (2011) 1211–1215.
171. Zhao, J., Li, Y., Yang, G., Jiang, K., Lin, H., Ade, H., Wei, M., Yan, H., Efficient Organic Solar Cells Processed from Hydrocarbon Solvents. *Nat. Energy*, **1** 15027 (2016).
172. Zhao, Y., Xie, Z., Qu, Y., Geng, Y., Wang, L., Zhao, Y., Xie, Z., Qu, Y., Geng, Y., Wang, L., Solvent-Vapor Treatment Induced Performance Enhancement of Poly(3-hexylthiophene): Methanofullerene Bulk-Heterojunction Photovoltaic Cells. *Appl. Phys. Lett.*, **90** (2007) 043504.
173. Zhokhavets, U., Erb, T., Hoppe, H., Gobsch, G., Sariciftci, N. S., Effect of Annealing Poly(3-hexylthiophene)/Fullerene Bulk Heterojunction Composites on Structural and Optical Properties. *Thin Solid Films*, **496** (2006) 679–682.
174. Zhu, R., Kumar, A., Yang, Y., Polarizing Organic Photovoltaics. *Adv. Mater.*, **23**, (2011) 4193–4198.
175. Zusan, A., Zerson, M., Dyakonov, V., Magerle, R., The Effect of Diiodooctane on the Charge Carrier Generation in Organic Solar Cells Based on the Copolymer PBDTTT-C. *Sci. Rep.*, **5** (2015) 8286.