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Christoph J. Brabec, Martin Heeney, Iain McCulloch and Jenny Nelson

This tutorial review discusses the factors influencing blend microstructure and performance in bulk heterojunction organic photovoltaic cells.
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Influence of blend microstructure on bulk heterojunction organic photovoltaic performance†

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The performance of organic photovoltaic devices based upon bulk heterojunction blends of donor and acceptor materials has been shown to be highly dependent on the thin film microstructure. In this tutorial review, we discuss the factors responsible for influencing blend microstructure and how these affect device performance. In particular we discuss how various molecular design approaches can affect the thin film morphology of both the donor and acceptor components, as well as their blend microstructure. We further examine the influence of polymer molecular weight and blend composition upon device performance, and discuss how a variety of processing techniques can be used to control the blend microstructure, leading to improvements in solar cell efficiencies.

1. Introduction

Organic solar cells have recently emerged as promising low-cost alternatives to conventional inorganic photovoltaic devices. The opportunity to fabricate flexible, lightweight devices from solution by a variety of high throughput printing processes may offer significant advantages over conventional devices built from inorganic materials like silicon. However current device efficiencies and stabilities require further improvement before they can become truly competitive with their inorganic counterparts.

In this tutorial review, we start with a brief overview of the main operating principles of an organic solar cell. The simplest device structure for an organic solar cell is based upon a bilayer blend of an electron donor material and electron acceptor material sandwiched as a photoactive layer between two electrodes, one of which is transparent (Fig. 1). In such a device the absorption of a photon in the photoactive layer

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Fig. 1  (Top) Schematic of a bilayer organic solar cell illustrating the main processes occurring in the photoactive layer: (1) absorption of photon to create an exciton, (2) exciton diffusion, (3) exciton splitting at the interface between donor and acceptor, (4) diffusion and collection of charges. (Bottom) Schematic of the side-view microstructure of a bulk heterojunction donor–acceptor blend film, illustrating the ways in which non-optimum microstructure can affect device performance.

excites an electron from the HOMO (highest occupied molecular orbital) to the LUMO (lowest unoccupied molecular orbital) creating an exciton (a bound electron–hole pair). Due to the low dielectric constant of organic materials there is a strong coulombic attraction between the electron and the hole and the exciton is unable to dissociate into free charges. However if the exciton encounters a donor/acceptor interface, the difference in LUMO energy between the two materials creates a driving force whereby dissociation by rapid electron transfer from the donor to the acceptor can occur. After exciton dissociation, the free carriers created at the interface are ideally transported to their respective electrodes under the influence of the internal electric field to generate the photovoltage and photocurrent. Two possible loss mechanisms can occur to limit this. The first termed geminate recombination is that the electron–hole pair created at the interface recombines by transfer of the electron back from the LUMO of the acceptor to the HOMO of the donor. The second mechanism termed bimolecular recombination occurs when the dissociated free carriers recombine before reaching the electrodes.

For typical soluble organic materials such as polymers, the exciton diffusion length is relatively small, on the order of 10 nm or so, and if the exciton does not encounter a donor/acceptor interface during its lifetime, it can undergo non-radiative decay in a loss mechanism for the cell. For organic devices, film thicknesses on the order of 100–200 nm are typically required to absorb all of the incident light due to the high absorption coefficient of conjugated materials. Thus, for a simple bilayer device this would result in the majority of the excitons being created away from the donor/acceptor interface and they not be harvested. It should be noted that for devices based upon highly crystalline, vacuum sublimed organic semiconductors the exciton diffusion lengths are longer, resulting in good efficiencies even for bilayer devices. The solution to this problem for soluble materials was to mix the donor and acceptor in a so-called bulk heterojunction (BHJ). With appropriate control of the morphology all excitons can be created within a diffusion length of a donor/acceptor interface, and hence be harvested. Therefore control of the nanoscale morphology, or microstructure of the blend is critical to ensuring that all excitons are collected and dissociated. Once the exciton has dissociated, the free holes and electrons must then be transported through the donor and acceptor phases to their respective electrodes. Consequently continuous percolation pathways are required through each phase. In addition the transport of the hole and electron through each phase will be strongly influenced by the local order and crystallinity within each phase, with crystalline morphologies generally leading to the highest charge carrier mobilities. Accordingly microstructure can influence solar cell

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Jenny Nelson has 20 years’ experience of research into novel nanostructured and molecular photovoltaic materials. Her current research is focused on the fundamental electrical, spectroscopic and structural characterization of pi-conjugated molecular electronic materials, the multi-scale modeling of optoelectronic properties of such materials, and their application to photovoltaic energy conversion. She has published over 150 articles in peer reviewed journals, several book chapters and a book on the physics of solar cells.
performance in several ways, and these are highlighted in Fig. 1 and summarized below.

- Local molecular ordering influences the ease of exciton transport (influencing exciton dissociation efficiency) and charge transport (influencing collection).
- Domain size or intimacy of blending influences exciton dissociation and charge separation.
- Formation of percolating structures influences transport and collection.
- Vertical segregation influences electrode selectivity.

In addition to the influence on the dynamics of charges and excitons listed above, microstructure influences the optical and electrochemical properties of the organic thin films. In particular, increased crystallization or aggregation of the molecules can lead to a red shift in the absorption spectrum of the film relative to that of the same material in solution, and thus extend the spectral sensitivity further into the red. Changes in molecular structure can also influence the oxidation potential of the donor component, for example by changing the degree of backbone torsion. Both types of change are relevant for bulk heterojunction solar cells: the two most common strategies to increase organic solar cell performance are to reduce the optical gap of the donor material, so as to harvest more of the solar spectrum and to increase the potential photocurrent, and to increase the difference between the oxidation potential of the donor and the reduction potential of the acceptor, so as to increase the photovoltage. ¹ Thus, modifications in molecular structure have a wide potential impact on the performance of organic bulk heterojunction devices.

The microstructure of molecular solids, especially when solution processed, depends upon the self-organizing tendencies of the components and hence on both molecular structure and processing route, and is not easy to control. Furthermore the microstructure may not be thermodynamically stable, and may alter by diffusion or crystallization over time, particularly under device operating conditions. In this article we use “microstructure” to refer to both the local molecular packing within one phase and to the size and arrangement of domains within the binary blend film. In the remainder of the article we focus upon strategies that have been used to control and understand the microstructure of the blend. We will focus initially upon the influence of chemical structure of the donor and acceptor materials on the microstructure of the photoactive layer, and then the influence on device performance.

### 2. Control of the structure of organic photovoltaic materials through chemical design

Since the first reports of BHJ solar cells comprising blends of soluble polymer/polymer or polymer/fullerene derivatives, there has been an intensive research effort upon the development of novel materials to improve the device efficiency of such cells. In the following sections we briefly review approaches to donor and acceptor materials, with a particular emphasis on how the tuning of chemical structure can be utilized to influence microstructure and device performance.

The optoelectronic properties relevant to BHJ solar cell performance, i.e. exciton diffusion lengths, charge carrier mobilities, interfacial charge separation rates and charge recombination rates, are controlled to a large extent by the manner in which the components pack together within the active layer. Within each phase, molecular ordering and, in particular, π stacking is important for efficient exciton and charge transport, and in addition usually assists in the absorption of long wavelength light. Hence, polymers with a high tendency to crystallise are preferred, although this must be balanced by the fact that soluble polymers are required. The specific arrangement of molecules within the film is controlled by both intrinsic structural parameters, such as the molecular weight, polydispersity, backbone planarity and location and nature of the solubilising sidechains, as well as extrinsic factors influencing the processing of the film such as solvent, deposition temperature, post-deposition treatments, etc. Here we illustrate the influences of chemical structure on micro-structure, taking representative organic photovoltaic (OPV) materials as examples. We pay particular attention to thiophene polymers as a class of highly crystalline and low optical gap materials.

#### 2.1 Factors influencing microstructure of conjugated polymer films

Conjugated polymeric semiconductors are comprised of directly coupled aromatic repeat units, with delocalized π electron conjugation along the length of the backbone. In the absence of solubilising sidechains, the closely packed aromatic backbones typically exhibit high melting temperatures, and are often insoluble in most organic solvents. One approach to this problem is to use soluble precursor polymers, which following deposition from solution can be treated either thermally or photochemically to remove the solubilising groups affording intractable materials in situ. Such approaches have been reviewed recently.² Another approach has been to attach aliphatic side chains to the polymer backbone, such that they become soluble in organic solvents and can be formulated and processed. Ideally these should be incorporated in such a way as not to inhibit inter-backbone π stacking. The crystallinity of many of these conjugated aromatic semiconductors has been well studied, not only in the context of solar cells but also concerning the development of thin film organic transistors, and has been shown to be related to several molecular features that can be controlled and optimised by judicious chemical design and synthesis, as discussed below.

Thiophene based polymers have been extensively studied in the context of OPV because of their dual advantages of extended spectral sensitivity in the long wavelength part of the spectrum and their good charge carrier mobilities, which can be related to their good backbone planarity and high tendency to crystallize. This high tendency to crystallize adds to their ability to phase separate into well defined heterojunction morphology when blended with electron acceptors like [6,6]-phenyl C61-butyric acid methyl ester (PCBM).

The most investigated thiophene polymer has been regio-regular poly(3-hexylthiophene) (P3HT), partly due to its ready availability at the multi-gram scale and its relative ease of processing from solution. Efficiencies above 5% have been
reported for blends with soluble fullerene derivatives.\textsuperscript{3} Because of the widespread use and relevance of P3HT and its well understood properties, we will use P3HT as an example to discuss some of the structural parameters of conjugated polymers in the following sections.

2.1.1 Influence of molecular weight. Polymer molecular weight (MW) and polydispersity have a fundamental influence on many polymer properties influencing the chain packing, the formulation rheology, the thin film coherence and morphology. In conjugated systems the chain packing also influences the optoelectronic properties. Optimizing the polymer MW is therefore important both for processing and performance of OPV active layers.

In the case of P3HT films, increasing MW initially enhances intermolecular ordering (\(\pi\)-stacking) of the polymer, leading to more extended crystalline regions and improved charge carrier mobility, but at higher MW, chain entanglement limits the crystallinity of the film.\textsuperscript{4} In transistor studies of P3HT films over a range of MWs, it has been shown that higher MW P3HT has better quality crystallites which are more co-aligned and connected, possibly by individual polymer chains spanning between crystallites\textsuperscript{5} leading to high field effect transistor (FET) mobility. Low MW polymer exhibits reduced transistor performance, which has been explained either by grain boundary trapping effects at lower MW,\textsuperscript{4} or enhanced out-of-plane backbone twisting,\textsuperscript{6} which results in a reduction in backbone planarity and a resulting decrease in effective conjugation length and the efficiency of charge hopping. Solution studies upon higher MW P3HT have also shown that physical entanglements can initiate polymer aggregation in some solvents, which then leads to gellation.\textsuperscript{7} This can be a significant problem for some printing techniques. However it was demonstrated that increasing polydispersity through the blending of high and low molecular weight fractions could suppress the gellation kinetics whilst maintaining reasonable device performance. Low regioregularity polymer (see below) has a similar effect to high polydispersity in reducing gellation, however this can result in lower performing devices due to the poorer transport and optical absorption.\textsuperscript{8} The detailed studies on P3HT clearly demonstrate that control of polymer MW through appropriate synthetic methods is an important part of the optimisation process, and that MW effects should be considered when comparing the results between different materials.

2.1.2 Influence of regioregularity. In non-centrosymmetric polymers, regioregularity (RR) quantifies the degree of defined regiochemistry of the solubilising groups along the polymer backbone. For P3HT, RR is defined as the percentage of the side chains in the 3 position along the backbone that adopt a head-to-tail rather than a head-to-head configuration, and is typically determined by comparing the integrated peaks of the \(\alpha\)-methylene protons on the hexyl chains by NMR, which occur at \(\delta 2.78\) and \(\delta 2.54\) for head-to-tail and head-to-head, respectively (see Fig. 2). Head-to-head couplings can result in significant steric strain which causes torsional twists of the polymer backbone and prevents planarisation in the solid state. This is particularly apparent in comparing poly(3,3\textsuperscript{00}-dialkylterthiophene), which contains only tail-to-tail linkages, to poly(4,4\textsuperscript{00}-dialkylterthiophene), which is exclusively head-to-head coupled (Fig. 2).\textsuperscript{9} The tail-to-tail polymer exhibits a maximum thin film UV absorbance at 550 nm, whilst the absorbance of the head-to-head polymer is significantly blue-shifted at 438 nm as a result of the reduced conjugation length. This also manifests in the transistor performance with the head-to-head polymer having hole carrier mobility over three orders of magnitude lower than the tail-to-tail polymer.

Several synthetic polymerisation processes have been developed which efficiently afford P3HT with high regioregularities (\(>96\%\)).\textsuperscript{10} For high RR P3HT the sulfur atoms

![Fig. 2](image-url) Chemical structure of poly(3,3\textsuperscript{00}-dialkylterthiophene) containing head–head linkages and poly(4,4\textsuperscript{00}-dialkylterthiophene) containing tail–tail linkages.
on adjacent thiophenes adopt the sterically preferred “anti or s-trans” position with respect to each other, allowing the polymer main chain to extend linearly in a stiff “rigid rod” form, alternately bending slightly to accommodate the bond angle between adjacent thiophene units. The conjugated backbone is thus able to adopt a near planar configuration, facilitating intermolecular \( \pi \) stacking. This leads to the formation of highly ordered and laterally extended \( \pi \)-stacked lamellar type structures (crystalites) in the solid state, comprised of alternating layers of disordered alkyl chains and orthogonally stacked aromatic backbones.

Low RR P3HT contains a larger proportion of head-to-head linkages, which result in considerable steric strain upon planarization of the polymer backbone. As a result, decreasing the RR in pristine P3HT has been shown to both reduce FET hole mobility, and the absorbance coefficient of long wavelength absorption maxima saturates around 20 thiophene units, studies on thiophene oligomers demonstrate that the optical band gap, providing the molecular orbitals are distributed along the band gap, or the energy difference between the polymer highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) (Fig. 3). Several strategies have been developed towards low band gap polymers, for example using donor-acceptor hybridised molecular orbitals, as shown in Fig. 3(b), maximizing the delocalisation of \( \pi \) electrons along the length of the conjugated aromatic system, shown in Fig. 3(a); and maximizing interchain (\( \pi \) stacking) interactions. The latter two depend upon control of the polymer conformation through molecular design.

Increasing the number of conjugated units in the backbone increases the delocalisation, which in turn reduces the optical band gap, providing the molecular orbitals are distributed along the \( \pi \) electron system rather than localized. Optical studies on thiophene oligomers demonstrate that the absorption maxima saturates around 20 thiophene units, although small red shifts have been observed upon further increases in conjugation length. The conjugation can be reduced by inserting either cross-conjugated or fully non-conjugated units into the polymer backbone. It is also possible to reduce conjugation between adjacent aryl groups by steric effects, and therefore to affect delocalization along the changes. For example typical phenyl–phenyl links along a backbone significantly twist out of a coplanar conformation, mainly due to the steric interactions of the ortho hydrogen atoms. The energetic minimum of this bond conformation occurs at about 45°. Replacement of the 6-membered phenyl ring with a 5-membered thiophene ring reduces the unfavourable steric interaction of the ortho hydrogens. Although the torsional bond angle of 2,2'-bithiophene is still at an angle of just over 30°, the enthalpy gained in the solid phase from intermolecular \( \pi \) stacking overcomes the steric effects and acts to planarise the conformation. The thiophene–thiophene C–C bond is also shorter than a phenyl–phenyl C–C bond, which is consistent with the quinoidal form of the thiophene ring electron distribution being more favourable than the quinoidal form of the phenyl ring, i.e. the phenyl ring is more aromatic. The quinoidal resonance form of these aromatic linked polymers is also fully planar, and the combination of these effects ensures that thiophene polymers such as P3HT can have an essentially fully coplanar backbone, which is a major factor in being able to achieve a highly crystalline morphology.

Biaryl monomers such as fluorene, carbazole, dithienoanthiphene and cyclopentabithiophene fix aromatic ring coplanarity within the repeat unit through a bridging atom. This bridge creates a fused, coplanar five membered ring between the aryl groups, with a sp\(^3\) hybridised bridging atom, usually carbon, nitrogen, oxygen, silicon or sulfur. When the bridging atom valency allows, alkylation can provide both additional solubilising function and acts to potentially inhibit oxidation of the heteroatom at the bridgehead. One consequence is that any substituent groups on the sp\(^3\) bridging atoms, such as alkyl chains, will project out of plane of the coplanar backbone. Although this does not necessarily prevent crystallisation, it is often suppressed in comparison to fully coplanar backbones with alkyl chains projected in the plane of the backbone from sp\(^3\) carbons. Clearly, the polymer conformation is therefore a critical factor in controlling both the extent of \( \pi \) electron conjugation along the backbone as

Fig. 3 Controlling the molecular orbital energy levels through (a) conjugation lengths of delocalized aromatic segments or (b) hybridisation of donor–acceptor intramolecular interactions.
well as the ability for intermolecular π stacking and long range crystalline order. As a more delocalised backbone typically has the beneficial effect of red-shifting the optical absorption to longer wavelengths and increasing its intensity through increasing the oscillator strength of the electronic transition, higher currents would be expected in devices through increased photogeneration of charge carriers.

One drawback is that increased delocalization typically corresponds with an increase in highest occupied molecular orbital (HOMO) energy levels, and thus reduces the potential photovoltage available from a bulk heterojunction device since this is related to the energy offset between the donor HOMO and the acceptor LUMO.1 It is necessary therefore to compromise between these factors when optimizing the HOMO energy level of donor polymers. Reduction of the polymer band gap through stabilization of the LUMO energy level of the donor polymer is a potential approach to achieving long wavelength absorption without necessarily compromising the device photovoltage. The recently reported poly(3-hexyl)selenophene (P3HS) demonstrates such behaviour, since the replacement of the sulfur atom with selenium in the fivemembered heterocycle has a larger stabilizing effect of the LUMO than the HOMO.15

Molecular energy level hybridisation through donor–acceptor intramolecular π electron interactions results in the LUMO energy level of the molecular orbital having the character of the acceptor repeat unit. Combining the concepts of backbone coplanarity with low band-gap hybridized molecule orbital energy levels has resulted in several promising electron donor polymers. The alternating co-polymers of electron rich donors such as the biaryl monomers listed earlier with electron deficient repeat units such as benzothiadiazole have been shown to have low optical gaps. As the benzothiadiazole unit is unfunctionalised and provides no solubilising groups, the bridgehead atoms of the fused electron donors typically need to be alkylated, often with branched alkyl groups required to provide enough solubility to support the growing polymer chain on polymerization, as well as subsequent solution coating. There are many recent examples of high performing co-polymers with benzothiadiazole.16 An exemplary case is the donor polymer developed through a collaboration between UCSB and KonARKA, which is an alternating copolymer of benzothiadiazole and dialkylated cyclopentabithiophene,17 commonly known as PCPDTBT (poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b’]-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)]) as shown in Fig. 4. This polymer has a low band-gap due to the donor character of the bithiophene and the acceptor character of the benzothiadiazole, the strong π orbital overlap from the bridged bithiophene and the low torsion of the phenylthiophene link. The coplanarity ensures that the donor polymer is crystalline, even with branched dialkyl groups on the carbon bridge of the bithiophene.

Further exploring the donor–acceptor design concept, Yu in collaboration with Solarmer have recently prepared a co-polymer with sequential repeat unit of benzodithiophene and thieno[3,4-b]thiophene (PTB7) (Fig. 4).18 The benzodithiophene group substituted with dialkoxy solubilising sidechains both provides electron donating function, and also ensures that any torsional twist away from co-planarity caused by steric interaction with the co-monomers is minimized. The thieno[3,4-c]thiophene co-monomer reduces the band gap of the resulting polymer by stabilizing the quinoidal form of LUMO. The resultant polymer has a band gap of 1.6 eV, close to the optimal level. Inclusion of an electron withdrawing fluorine substituent on the thieno[3,4-c]thiophene helps to lower the HOMO level of polymer, to approximately 5.15 eV, a reduction of over 0.1 eV compared to the non-fluorinated analogue. Blends of both polymers with PC71BM achieved efficiencies over 7%.19 The best results were achieved using high boiling solvents with a diarylbutane additive. This served to control the morphology of the film, suppressing large scale phase segregation compared to the pure solvent alone.

2.3 Factors influencing the structure and performance of fullerene films

Electron acceptor materials for BHJ possess similar requirements to donor materials i.e. high exciton diffusion lengths and charge carrier mobilities, fast interfacial charge separation rates, etc. However, in contrast to donor materials, there have been far fewer high performance electron acceptors reported for BHJ devices. Although many different donor polymers have been reported with device efficiencies greater than 3%, these have all used acceptors based upon soluble fullerene derivatives. Although fullerenes do possess a number of attractive characteristics for this purpose, as discussed below, their current prevalence may also be partly attributed to their ready commercial availability. Considering the recent progress in the development of high performance organic n-type for transistor applications, it is likely that new classes of acceptor will be developed.

Fullerene based materials have been widely investigated as electroactive materials since their discovery in 1985, with particular attention focusing upon the readily available C60 and its derivatives. C60 exhibits a relatively low lying LUMO energy level that is triply degenerate and is able to accept up to 6 electrons in solution. C60 itself exhibits low solubility in common solvents, and therefore a variety of functionalisation approaches have been explored, both to improve solubility and to further tune the electronic properties. One of the first soluble derivatives to be investigated, and subsequently one of the most widely used is [6,6]-phenyl C61-butryric acid methyl ester (abbreviated as PC61BM or, more commonly, PCBM, Fig. 5). It has excellent electron transport combined with a LUMO energy (−3.7 eV) that is both high enough to support a large photovoltage, given that Voc is limited by the energy difference between donor HOMO and acceptor LUMO, but also low enough to provide ohmic contacts for electron extraction and injection from common cathode electrodes.
Like C₆₀, pristine PCBM is capable of crystallizing into well defined structures, with crystal structure that depends upon the solvent used for processing. In blend films with conjugated polymers, the tendency of the fullerene molecules to aggregate and crystallize assists phase segregation, as discussed below.

Efforts to improve upon the performance of PCBM have focussed upon three main areas, changing the electron affinity of the fullerene, improving the light absorption of the n-type and influencing the blend morphology. The HOMO and LUMO energies of fullerene derivatives can be modulated by varying the type and number of sidechains, and this can be an attractive route to increase the photovoltage from the fullerene/polymer blend. For example it has been shown that adding electron donating alkoxy substituents to the phenyl ring of PCBM derivatives decreases their electron affinity, and results in an increase in the device $V_{oc}$ of up to 86 meV.

Despite this, overall device efficiencies were lower relative to PCBM due to the comparatively low solubility of these derivatives. The reaction of a second double bond in the fullerene derivative with a solubilising group, as in the case of bis-PCBM, in which two 4-phenyl butyric methyl ester groups are attached to the core, has the effect of further decreasing the electron affinity. Devices made with blends of this fullerene with P3HT show an increase in $V_{oc}$ of 100 meV, with comparable electron mobilities and photocurrent to the P3HT device, despite the fact that bis-PCBM exists as several isomers.

Continuing the trend, tris-PCBM adducts have recently been reported as an inseparable multi-isomer blend. As expected the electron affinity is further decreased, and blend devices show an enhancement of photovoltage of 100 meV over the bisadducts. However, the electron transport of the tris-PCBM was significantly reduced, possibly due to the high disorder of the fullerene phase, and devices show low efficiencies.

Very recently indene-C₆₀ bisadducts have been reported which exhibit a further reduction in electron affinity of 70 meV compared to bisPCBM. Blends with P3HT demonstrated excellent performance and high photovoltages up to 0.84 V.

Endohedral metallofullerenes, which are fullerene derivatives with a metal cluster encapsulated within the cage, are a fascinating class of fullerene derivatives. Drees et al. have recently demonstrated that lutetium based endohedral fullerenes (Lu₂N@C₆₀) can be chemically derivatised with solubilising sidechains, and the resulting derivatives have LUMO energies up to 0.2–0.3 eV higher than PCBM. Such derivatives exist as single isomers, preserving the beneficial self-organising and transport properties of PCBM, but increasing the available photovoltage to the cell.

One drawback of C₆₀ derivatives is their poor light absorption in the visible region, which is attributed to the high symmetry of C₆₀ making the lowest-energy transitions formally dipole forbidden. This means that they do not significantly contribute to device photocurrent, limiting the Jsc available for a given active layer thickness. Soluble analogues of the less symmetrical higher fullerenes, such as C₇₀ (PC₇₁BM) and C₈₄ (PC₈₅BM), which absorb better in the visible have been developed to overcome this. The high electron affinity of PC₈₅BM results in low device $V_{oc}$, but PC₇₁BM has proven to be a highly effective material, combining similar LUMO energy, electron mobility, solubility and crystallinity to PC₆₁BM, but higher optical absorption in the visible as a result of its lower symmetry. This is particularly useful in blends where high fullerene concentrations are required in a device.

There have also been significant efforts to develop fullerene derivatives in which phase segregation from the polymer can be controlled and manipulated. For example Troshin and co-workers undertook a detailed study of the influence of the solubilising substituent of over 25 differently substituted C₆₀ and C₇₀ derivatives, and concluded that matched solubility between the donor polymer and fullerene was desired for efficient phase segregation. The attachment of perfluorinated sidechains to the PCBM has been shown to influence vertical phase segregation of the blend with P3HT. The low surface energy of this group drives it to the air interface during coating, where it acts as a buffer layer, reducing the electron injection barrier between PCBM and the aluminum anode and resulting in a significant enhancement in device performance.

The thermal stability of the device blend, particularly under operating conditions, has also been a concern since it may alter by diffusion or crystallization over time. One approach to improve thermal stability has been to derivatise the fullerene derivative with bulky aromatic groups which suppress crystallization in the blend. The resultant amorphous materials exhibited similar device efficiencies in blends with P3HT to PCBM, but importantly did not crystallize even under extended annealing conditions. This is in contrast to PCBM blends in which extended annealing results in the growth of large PCBM domains, and a resultant loss in device efficiency.

### 3. Factors influencing the microstructure of polymer:fullerene blend films

The active layer of a bulk heterojunction device is typically a composite of a conjugated hole transporting polymer and a soluble fullerene, co-deposited from solution. This composite film contains, in general, both crystalline and amorphous domains of each component and amorphous domains containing both components. The size, composition and crystallinity of these domains, as well as the structure of the interface between them, influence the efficiency of exciton transport and dissociation, the efficiency of photoinduced charge separation and the rate of charge transport (and recombination). High purity, crystalline domains are known to enhance charge separation and retard charge
recombination, albeit at the possible cost of less efficient exciton dissociation, and are a common feature of high photovoltaic performance blend films.

The microstructure of the blend film, and in particular the size and purity of segregated domains, is a function both of the self-organising tendencies of the donor and acceptor components, the interaction between them and the process parameters. Nano-scale phase separation typically begins upon film formation from solution. As polymers typically have low entropies of mixing, phase separation readily occurs, especially with higher molecular weights. Often domain formation occurs through an initial nucleation and crystallisation of the polymer phase, which grows and excludes the small molecule phase. The excluded small molecule (typically PCBM) then diffuses to form amorphous aggregates that can crystallise. Polymer crystallization and fullerene exclusion, and the subsequent fullerene crystallisation may require a thermal annealing stage. Control of substrate surface energy, as well as solubility and the rate of solvent evaporation for both components can also control microstructure and can drive vertical phase separation.

In this section we briefly review the ways in which the polymer properties influence the blend film microstructure.

3.1 Polymer molecular weight, regioregularity and end group

In the polymer crystallization and fullerene exclusion process described above, the size and purity of the polymer domains formed is a function of the ability of the polymer to crystallize, and therefore of the parameters mentioned in section 2.1, i.e. molecular weight, planarity of the conjugated backbone, and steric effects of side chains (regioregularity in the case of P3ATs).

In P3HT:PCBM blend films, increasing MW causes enhanced intermolecular ordering (π-stacking) of the P3HT phase leading to the formation of more extended crystalline regions. For MW up to ca. 40 kDa, increasing MW leads to improved charge carrier mobility and subsequently better device performance. As MW increases further, chain entanglement starts to limit the crystallinity of the film and eventually leads to reduced mobility, leading to reduced solar cell fill factor and efficiency. In another study of the influence of MW and annealing, an “ideal” morphology was reported using a blend of high and low MW P3HT with an optimum ratio (of 1:4 by weight) of high MW to low MW components. This led to the formation of highly ordered crystalline regions formed by low MW P3HT embedded and interconnected by a high MW P3HT matrix. This arrangement constrains the size of fullerene aggregates that can form and could be superior in morphology to a single MW P3HT:PCBM blend.

It has recently been reported that the nature of the end group of P3HT of medium molecular weight (Mn 15.6 kDa) can have a significant influence on morphology and performance of blends with PCBM. The authors observed that the surface energy of the polymer was influenced by the nature of the polymer end group, and that polymers with similar surface energy to PCBM afforded highly miscible blends with nanoscale phase segregation, as opposed to polymers with larger surface energy differences to PCBM which tended to result in large domain sizes and significant vertical phase separation. The blends with closely matched surface energies showed the highest efficiency devices, up to 4.5%.

Regioregularity (RR) is found to have a similar influence on the solid state morphology of P3HT as molecular weight. For P3HT:PCBM blend films, increasing P3HT regioregularity (RR) increases the crystallinity of the polymer phase within the blend, as determined from the sharpness of the X-ray diffraction features for intraplane stacking, and increases the tendency of the lamellae to orient with the plane of the conjugated backbone normal to the substrate. Kim et al. ascribed the beneficial effect of higher RR and annealing on solar cell performance to the enhanced intraplane stacking and resulting enhancements in optical absorbance and mobility. Recently Frechet and co-workers have reported that high RR is not always a prerequisite for obtaining a high solar cell performance and, moreover, that lower RR could benefit the thermal stability of the device by reducing the degree of crystallization-induced phase segregation of PCBM. In this case, low RR P3HT was synthesized by the co-polymerisation of 3-hexylthiophene with a 3,3′-dihexyl-2,2′,2-bithiophene to chemically fix the percentage of tail-to-tail couplings, whilst maintaining a similar MW to the high RR samples. Optical microscope images of P3HT:PCBM films with different degree of RR confirm the formation of many large needlelike PCBM crystals which get longer as RR increases (as shown in Fig. 6(a)). The two-dimensional grazing-incidence X-ray scattering (GIXS) patterns (Fig. 6(b)) show that the PCBM is highly crystalline in the higher RR P3HT blend film and moreover suggests that at higher RR the P3HT stacks are less oriented in the axis normal to the substrate due to the presence of large PCBM crystallites.

3.2 Side chain density

The side chain packing density has recently been shown to be another important factor which can influence the degree of phase separation between the fullerene and the polymer phase. Initial studies have focussed upon blends of PCBM with poly(2,5-Bis[3-alkyl]Thiophen-2-yl)Thieno[3,2-b]Thiophene (pBTTT), which is an alternating co-polymer of thieno[3,2-b]thiophene and 4,4-dialkyl 2,2-bithiophene repeat units. The reduced sidechain density of pBTTT compared to P3HT facilitates the formation of highly ordered thin film structures, which are driven by interdigitation of the alkyl sidechains of adjacent polymer backbone.

On the addition of PCBM to pBTTT, simple models have shown that there is sufficient space between the solubilising sidechains along the polymer backbone to incorporate a single fullerene molecule per repeat unit. This can be observed experimentally as an increase in the lamella spacing, due to the reduced interdigitation of the alkyl sidechain as a result of the fullerene intercalation. Interestingly if the sidechains are shorter than the width of the intercalated fullerene (for example hexyl), then registration by interdigitation of the chain ends with adjacent polymer backbones is not possible, and a thermally stable amorphous blend is produced. However increasing the sidechain length to decyl allows

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PCBM intercalation whilst retaining some alkyl chain interdigitation and registration, and now the blend is semi-crystalline but with an increase in the lamella spacing over the pristine polymer film (Fig. 7). The close proximity of the fullerene to the polymer backbone results in efficient exciton quenching, but the intercalated PCBM molecules are not electronically well connected and therefore do not provide an effective percolation path for electron transport, whereas the larger polymer can still transport holes without detriment. Therefore the device efficiency of the 1 : 1 blend is low. In order to ensure sufficient electron transport in this type of system, it is necessary to incorporate excess PCBM, which aggregates outside the bimolecular crystals, forming a charge carrier percolation pathway. Fullerene : polymer ratios of up to 4 : 1 by weight are required to achieve optimal performance. Other crystalline polymers which also have a wide enough alkyl spacing distance, such as poly[1,4-bis(3-alkyl-2-thienyl)phenylene] (PQT) polymers, have also been shown to require a high fullerene content to achieve optimal device efficiency, consistent with intercalation occurring also in these polymers. The use of a larger fullerene derivative, such as bisPC71BM, has been shown to suppress intercalation in pBTTT blends, and as a result the optimal device performance is observed for a 1 : 1 blend. It is also likely that intercalation of PCBM occurs with amorphous polymers such as MDMO-PPV (poly(2-methoxy-5-(30,70-dimethyloctyloxy))-1,4-phenylene vinylene). This can explain why high fullerene ratios (typically 1 : 4 polymer:PCBM) are required for optimal device performance, and also the increase in hole mobility that is observed when MDMO-PPV is blended with PCBM, since intercalation may change the structure of the polymer backbone from coil-like in the absence of PCBM to rod-like in the presence of PCBM. The rod-like polymer is able to undergo improved intermolecular interactions accounting for the higher mobility. The failure of amorphous polymers to crystallize and exclude the fullerene, so that some fullerene remains trapped within the amorphous polymer phase where it cannot contribute to charge transport, may also be a factor.

3.3 Alternative strategies to control the microstructure of donor–acceptor blends

Thus far we have considered blend films made from the co-deposition of the donor and acceptor phases, usually from a single solution. The composite films so formed rely upon the
interactions between donor and acceptor molecules to determine the microstructure. Whilst the thermodynamically preferred configuration would have complete phase segregation of donor and acceptor components, this limit is seldom reached on relevant time scales because of steric effects, low molecular mobility and the low entropy of mixing of polymers, and the binary film is more usually in some non-equilibrium, intermixed configuration. A consequence of this poor definition of the microstructure is that over time, or on exposure to heating, the phases may become less mixed with negative impact on exciton dissociation or charge transport efficiency. The problem can be partly solved by using materials of higher thermal stability. However, a more reliable solution can be found by enforcing a certain domain size, for example by using donor–acceptor block copolymers. Studies of charge generation in block copolymers of different block lengths have shown that control of the donor and acceptor segment lengths allows the efficiency of charge pair generation to be optimized, by modulating the efficiencies of exciton dissociation and charge recombination. The potential advantage of this approach is that the domain size is built-in at synthesis via the choice of block type and length, and should then be independent of processing or post-deposition sample history.

The block copolymer templating strategy has also been used to produce bicontinuous binary structures composed of a metal oxide and a conjugated polymer, by replacing the degradable organic component of the block copolymer with an electrochemically grown oxide. The use of an inorganic semiconductor as acceptor allows the construction of a rigid nanostructured acceptor phase, e.g. by solution based techniques, and the subsequent infilling of the pores of the inorganic film with an organic donor component. This provides a mechanically stable donor–acceptor structure, but there may be difficulties in achieving the ideal domain size or in inserting the organic component.

The use of a sacrificial phase directing polymer to control morphology has also been recently reported by Friend et al. They demonstrated that conjugated polymers could be cross-linked without degradation in the electrical performance by the use of a bis(azide) based deep UV photoinitiator. Upon exposure to 254 nm light, the azide photoinitiator formed a reactive singlet nitrene species in situ, which preferentially reacted at the polymer sidechains by nitrene insertion, resulting in crosslinked polymer films at low photoinitiator concentrations (around 1%). The resulting films demonstrated similar luminescence and transistor performance to uncrosslinked films. Building upon these results, they were demonstrated that blends of donor OPV polymers (polyfluorene derivatives) with low molecular weight polystyrene formed phase separated thin films upon spin coating. The polystyrene was readily removed by solvent washing, and the resulting polyfluorene film was crosslinked by UV exposure to create columnar nanostructures. These could then be backfilled with electron accepting polymers to create high aspect ratio nanostructured blends. The heterostructures exhibited a fourfold improvement in short-circuit external quantum efficiency over the simple blended structure, demonstrating the potential of this approach.

3.4 Control of microstructure in polymer:fullerene blend devices via processing

In the previous section we have addressed the influence of chemical structure on the microstructure of conjugated polymer films, molecular films, and binary polymer:small molecule blend films. However, because the intermolecular interactions in molecular solids are relatively weak, chemical structure alone does not determine the final structure adopted by a molecular film, especially when deposited from solution. Processing parameters such as choice of solvent, evaporation rate, blend composition and thermal treatment also influence the blend film microstructure, for example by controlling how close the binary comes to its equilibrium configuration. Here we address the influence of such processing and post-deposition factors on the structure of blend films and on device performance.

3.4.1 Solvent. The choice of coating solvent has been shown to have a significant influence on the film morphology and organisation for many BHJ blends, affecting as it does such factors as donor and acceptor solubility, their interaction and miscibility, along with evaporation rate and viscosity. A representative case is the blend of MDMO-PPV with PCBM. Upon changing from toluene to chlorobenzene (CB), the PV power conversion efficiency increased significantly (from 0.9% to 2.5%, with a concurrent improvement in fill factor and J Voc). Further studies using transmission electron microscopy (TEM) and atomic force microscopy (AFM) verified the strong influence of solvent on the size of the phase separated PCBM-rich domains in spin-coated MDMO-PPV:PCBM films. Fig. 8 shows that on replacing chlorobenzene with toluene, the average size of PCBM-rich domains reduces from ±100 nm to ±15 nm, increasing the probability of exciton diffusion to and dissociation at the donor–acceptor interface. This effect of solvent on phase structure is mainly attributed to the higher solubility of fullerene in chlorobenzene. Some interesting results have also been obtained using mixed solvents. For example, a study on a blend of a polyfluorene copolymer, poly(2,7-(9,9-diocetyl-fluorene)-alt-5,5-(4,7-di-2-thienyl-2′,1′,3′-benzothiadiazole)) (APFO-3) with PCBM revealed an enhancement in the photocurrent generated by devices coated from a mixture of chloroform and chlorobenzene (CFCB) relative to devices coated from neat chloroform, while devices processed from chloroform mixed...
with xylene (CFXY) or with toluene (CFTO) exhibited a reduction in photocurrent density. AFM studies show smaller domains and a smoother surface for the films based on CFCB as compared to the CF, CFXY and CFTO films.46

Time-resolved spectroscopy of the blend films indicates an influence of solvent mixture on the formation of free charge carriers, through its influence on charge mobility, and on the non-geminate charge recombination dynamics.46

Solvent additives have also been reported as an alternative method to create better order in blends of PCPDTBT:PCBM and P3HT:PCBM. It was reported that the addition of alkylthiols of different lengths,47 such as n-hexylthiol, n-octylthiol, or n-dodecylthiol, or oleic acids into P3HT:PCBM solutions led to the formation of thin films with slightly enhanced hole mobility and significantly enhanced charge carrier lifetime as a result of enlarged P3HT domains with higher crystallinity. Nevertheless, some thermal annealing was still necessary to give the highest performance. In the case of PCPDTBT:PCBM, applying alkanedithiol resulted in an increase of efficiency from 2.8% to 5.5%17 and a microstructure containing larger polymer and fullerene domains. The microstructural evolution was explained by the fact that alkanedithiol is a better solvent for the fullerene than the polymer, allowing the polymer to crystallize more slowly and exclude the fullerene more effectively. The separate phases formed during the process of liquid–liquid phase separation and drying, a fullerene–alkanethiol phase, a polymer aggregate phase, and a polymer–fullerene phase, are schematically depicted in Fig. 9.48 Similarly controlling the rate at which the solvent dries can have an important influence on the morphology of the blend films. For example in blends of P3HT:PCBM improved ordering of the polymer was observed when the solvent (1,2-dichlorobenzene) was allowed to evaporate slowly (over 20 min) at room temperature in an enclosed atmosphere, versus rapid drying (30 s) at 70 °C. The improved order was reflected in higher hole mobility,79 higher fill factors, reduced serial resistance and overall improved device efficiency.

3.4.2 Thermal annealing. A large number of studies have demonstrated improved power conversion efficiency (PCE) of some polymer–fullerene composite solar cells upon thermal treatment. A substantial improvement in the PCE of P3HT:PCBM based solar cells has been obtained by thermal annealing at around 140 °C, and the favourable influence of annealing on blend film microstructure and solar cell performance is well documented.50–53 The mechanism by which current density and PCE increase upon thermal annealing in P3HT:PCBM is not known precisely but it is believed to involve increased optical absorption and improved charge transport, both due to polymer crystallization, as well as improved charge pair separation efficiency, due to optimized phase segregation. Some of the literature is reviewed below.

Chirvase et al.50 ascribed the enhancement of the P3HT:PCBM optical absorption to the molecular diffusion of fullerene out of the polymer matrix upon annealing. The growth of the PCBM clusters leads to the formation of percolation paths and, therefore, improvement of the photocurrent. Further studies by Erb et al.51 suggest that the significant increase in optical absorption is due to the aggregation state of P3HT, from amorphous (non-annealed) to crystalline (annealed). Grazing-incidence X-ray diffraction (XRD) measurements of P3HT:PCBM films reveal an increase in sharpness of the diffraction peak pertaining to the inter-chain, intra-lamellar ordering (a-axis) of P3HT upon thermal annealing (Fig. 10(a)). The main effect of annealing can be described as redistribution of fullerene: before annealing, crystallization of P3HT chains is inhibited by the presence of PCBM molecules dispersed within the polymer, leading to a relatively amorphous character of the P3HT. Upon annealing, P3HT chains begin to crystallize, expelling isolated molecules

![Fig. 9](image-url) Schematic depiction of the role of the processing additive in the self-assembly of PCPDTBT:PCBM blend. Reproduced with permission from ref. 47.

![Fig. 10](image-url) (a) Diffractogram (grazing incidence) of P3HT:PCBM composite film deposited on glass/ITO/PEDOT-PSS. (b) Structural changes of P3HT:PCBM films upon annealing (schematic). Reproduced with permission from ref. 50.
of PCBM from the polymer phase and allowing the PCBM molecules to diffuse and combine into larger aggregates (Fig. 10(b)).

Conventional bright field TEM images of P3HT:PCBM blend films confirm the presence of fibrillar P3HT crystals even prior to thermal treatment. TEM studies show that controlled annealing increases the length of these fibers without significantly affecting the width. Comparison of TEM images and small angle electron diffraction (SAED) patterns of non- and annealed films of P3HT:PCBM blend films (as shown in Fig. 9) indicates that the longer fibrillar-like P3HT crystals enhance the formation of a P3HT network within the composite film and hinders the formation of excessively large PCBM aggregates. Therefore, in contrast to the case of MDMO-PPV:PCBM blend films, only small PCBM crystals are formed (dark domains between the P3HT fibrillar-like crystals denote the PCBM crystals). In fact, after annealing, a large interfacial area, necessary for efficient charge generation, is not hindered by the presence of long fibers since P3HT favourably tends to crystallize in one direction. A very powerful technique for probing the blend morphology is electron tomography, in which a series of TEM images are taken at different tilt angles in the beam and then reconstructed to give a three dimensional image of the thin film. It has recently been used to examine the effects of thermal annealing in P3HT/PCBM blends demonstrating directly the changes in both the domain size and crystallinity and vertical composition upon annealing. Here thermal or solvent annealing leads to vertical segregation within the film, with P3HT preferentially accumulating at the bottom hole collecting cathode, and PCBM at the top, electron collecting anode (Fig. 11).

Some authors attribute the significant increase in the current density of annealed P3HT:PCBM devices to more balanced electron and hole transport upon annealing. Whilst space charge build up due to low hole mobility limits the photocurrent in non-annealed devices, increased hole mobility and resulting balance in charge mobilities upon annealing eliminate this problem in annealed devices. However, the effect of annealing on transport is variable and the annealed and non-annealed devices can show comparable values for the majority carrier mobility-lifetime product. The efficiency gain upon annealing is therefore more commonly attributed to reduced recombination losses, resulting from the increased phase segregation and molecular ordering, and increased spectral photocurrent generation in the near-IR than to improved transport.

Savenije and co-workers reported that annealing of P3HT:PCBM composites not only changes the morphology and optical absorption but can also change the redox and photoconductive properties of the blend layer. Enhanced photoconductivity is mainly ascribed to the increase in the hole mobility. This study suggests that in the annealed P3HT:PCBM samples, after photo-induced charge separation, holes are localized on the crystalline P3HT fibrils and since these fibrils are enclosed by less ordered polymer regions, the less ordered region would act as an energetic barrier and tend to confine the holes to the more ordered domains, thus keeping them away from the interface where recombination could occur. The appearance of domains with a higher lying HOMO energy is supported by measurements of oxidation potential of the blend film before and after annealing.

Besides P3HT:PCBM, some other systems such as the blend of poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT) with PCBM have shown higher PCE after thermal annealing. Although the improvement is not as large as reported for P3HT based devices, these are all strong motivations for
further investigation of the effects of thermal treatment on the composite film microstructure. Moreover, studies of the effect of harsh thermal treatments are valuable in assessing the long term thermal stability of the film microstructure.

3.4.3 Blend composition. The blend ratio of the donor and acceptor components as well as the overall concentration of the applied solution can have an important influence on charge transport, photophysical properties and morphological organization of the system. In the case of P3HT:PCBM, the best device performance is typically reported for a P3HT:PCBM weight ratio of between 1 : 0.8 and 1 : 1 with an overall solution concentration of around 1 wt % P3HT (10 mg mL⁻¹). Time-of-flight (TOF) measurements on P3HT:PCBM blend films made using different blend ratios verified that balanced, non-dispersive electron and hole transport is found only at these ratios. AFM studies revealed that films cast from more concentrated solutions or solutions with smaller P3HT:PCBM ratios exhibited “overgrown” PCBM crystals after high-temperature annealing, leading to degradation of the morphology and poor device performance. A study using differential thermal calorimetry has shown that the P3HT:PCBM binary possesses a eutectic phase behaviour, such that the polymer:fullerene interface area is maximized and the domain size minimized at a blend composition of about 35% PCBM by weight. The higher PCBM content required for maximum efficiency is explained in terms of the need for sufficient PCBM to build up a sufficiently conducting network to achieve balanced charge mobility, in agreement with the ToF measurements cited above. In contrast to the semicrystalline P3HT:PCBM, many systems such as MEH-PPV:PCBM, MDMO-PPV:PCBM require a high fullerene content of typically 1 : 4 by weight to provide a proper nanoscale phase separation and an efficient charge transport. As discussed above, this effect has been explained in terms of the poor exclusion of fullerene from the more amorphous polymers, meaning that more fullerene is required to build up a continuous and conducting PCBM network within the blend film in addition to the possibility for the fullerene to intercalate along the polymer backbone in some instances.

Apart from influencing the efficiency of exciton dissociation via domain size and the efficiency of charge transport via percolation effects, blend composition can also influence the efficiency of charge pair separation, by influencing the intermediate states involved in charge separation. Charge separation is now commonly believed to result from a sequence of steps, involving exciton dissociation into a geminate charge pair which may then form a charge transfer state at the interface, or recombine, or separate into free charges. Recently, the existence of an intermediate charge transfer (CT) state between the exciton and the free charges in some blend systems based on polyfluorene has been reported. Understanding the nature of such an intermediate state and its dependence on blend composition is important in understanding the effect of microstructure on charge generation. As an example, Veldman et al. confirmed the existence of a charge transfer (CT) state in the blend of a fluorene copolymer (PF10TBT) “poly[2,7-(9,9-dialkylfluorene)-alt-5,5-(4′,7′-di-2-thienyl-2,1′,3′-benzothiadiazolo)] with PCBM.” The formation and decay of emissive CT excited states via electron transfer from photoexcited PF10TBT or PCBM is confirmed by photoluminescence measurements. It is shown that the CT emission peak shifts to lower energy and decreases in intensity as PCBM content increases, whilst the efficiency of charge pair generation increases. The reduction in energy of the CT state at higher PCBM content is attributed to the higher relative permittivity of PCBM (εr = 4.0) compared to that of the polymer (εr = 3.4), stabilizing the energy of CT states and of the free charge carriers. The microstructure of the PF10TBT:PCBM blend films is similar to that observed for MEH-PPV:PCBM and MDMO-PPV:PCBM blends, in that TEM measurements demonstrate the formation of PCBM domains (> 10 nm) at high fullerene concentration. SAED patterns indicate that nanocrystalline PCBM clusters are present even at low PCBM concentration and increase in size as PCBM concentration increases. These clusters with high local electron mobility appear to facilitate the efficient dissociation of short-lived CT excitons that may otherwise recombine radiatively or nonradiatively. Therefore the improved device efficiency of the PF10TBT:PCBM devices at higher PCBM content is attributed to the effect of phase separated fullerene domains on the relative energy of charge separated versus CT state, and on the separation dynamics of the bound charges at the donor–acceptor interface.

Evidence for such intermediate charge transfer states has been presented for a number of other blend systems including PCPDTBT:PCBM. The appearance of CT states is in general a function of blend composition and therefore of microstructure. In the case of PCPDTBT:PCBM, the yield of long-lived mobile carriers originating from this intermediate state is found to be sensitive to the blend ratio, with a maximum at the ratio which yields the highest PCE in devices. This supports the notion that the CT state competes with the fully charged separated state and that emissive CT states are therefore a loss pathway.

3.4.4 Surface control. The strategies mentioned above mainly concern control of the microstructure of the donor–acceptor blend film in order to achieve the optimum combination of domain size and connectivity, so as to maximize charge pair generation and current collection. However, efficient photocurrent generation in a bulk heterojunction also depends upon the existence of selective electrodes, each of which permits barrier free collection of one charge type and blocks the other, in order to direct the photocurrent. Photocurrent can also be assisted by the vertical composition profile of the photoactive layer. For example, a buffer layer of pure donor beside the anode would minimize electron leakage to the anode, while a layer of acceptor close to the cathode would block hole leakage. A vertical composition gradient would assist in driving the hole current towards the donor rich side and the electron current towards the acceptor rich side, through the associated gradient in conductivity and density of states. For evaporated molecular active layers, a vertical gradient in composition can be built in through the successive co-deposition of blend layers of different composition. This approach has been shown to improve fill factor and open circuit voltage in copper phthalocyanine:Ca heterojunctions.
For solution processed active layers, successive processing of polymer layers is difficult and requires orthogonal solvents or solid film transfer techniques. An alternative approach is to reply upon the different interaction energies between the components and the substrate or the top surface, to drive preferential segregation of the different components towards or away from either interface. Arias et al. showed that vertical phase segregation could be achieved in a blend of poly(9,9’-dioctylfluorene-co-bis-N,N’-(4-butylphenyl)-bis-N,N’-phenyl-1,4-phenylenediamine) (PFB) and poly(9,9’-dioctylfluorene-benzothiadiazole) (F8BT) when the components were cast from a high boiling point solvent, and that more complete vertical segregation could be achieved by coating the substrate with a silane based molecular monolayer to reduce its surface energy.68 Moons and co-workers have shown that choice of a high boiling point solvent increases the extent of stratification within a polyfluorene:PCBM blend film and influences device performance.69

Evidence for spontaneous vertical phase segregation has also been reported in blends of polymers with PCBM. Campoy-Quiles et al.70 showed using spectroscopic ellipsometry that P3HT tends to segregate towards the top of a 1 : 1 blend film of P3HT and PCBM and that this segregation is enhanced following thermal annealing for a blend film on silica. However, replacing the silica substrate with a lower surface energy substrate led to the opposite sense of segregation, with P3HT moving towards the substrate. This behaviour was confirmed by studies by DeLongchamp and co-workers who confirmed the different sense of segregation on high and low energy substrates (OTS and SiO₂, respectively) by probing the top and buried interfaces of a P3HT:PCBM blend film using NEXAFS on delaminated films.71,72 When applied onto a low surface energy substrate, the blend component with the lower surface energy (in this case P3HT) was shown to migrate to the interface in order to minimise the interfacial free energy, which is proportional to the difference between the surface energies of the blend and substrate. When a high energy substrate such as silicon dioxide is employed, the higher surface energy PCBM component preferentially segregates to this surface. In all cases the P3HT migrates preferentially to the air interface to create the lowest energy surface. The electron tomography results of Loos discussed above also observed a preferential segregation of P3HT at the bottom interface (in this case PEDOT:PSS).3

The authors noted that some pre-aggregation in solution prior to coating may also account for this. More recently using a combination of NEXAFS, XRD, UV-Vis and XRD, Dastoor and co-workers have suggested that a three phase morphology, with thin P3HT rich interfacial layer at both the bottom and top interfaces, sandwiching a blended phase.73 A P3HT upper layer, adjacent to the cathode would be expected to be detrimental to device performance, but the thin nature of this layer may mean that diffusion of aluminum during deposition or annealing occurs readily, allowing the good performance observed.

4. Conclusions

Over the last seven years, since the well reported observation that changing the solvent could more than double the power conversion efficiency of a polymer:fullerene blend solar cell, understanding the effect of chemical structure and processing on OPV device function has steadily increased. As we have discussed, blend film microstructure influences device performance in several ways and is itself controlled both by the chemical structure of component molecules and by the processing route used. It has been established that components with a strong tendency to self-organize are beneficial, both because of the improved charge and exciton dynamics that result from ordered molecular domains, and because of the nm–μm phase segregation that can be achieved through crystallization and improves the efficiency of charge pair generation. The degree of order and size of domains can be controlled by choice of solvent, casting conditions, annealing treatments and control of interface energies. The aggregated knowledge on control of microstructure through molecular design and processing, together with powerful and flexible modelling tools provides a basis for the design and realization of optimized blend film microstructures for a wide range of future functional organic materials, for solar cells and other applications.

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