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Controlling Solid-State Structure and Film Morphology in Non-Fullerene Organic Photovoltaic Devices

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Abstract

Organic solar cells (OSCs) have long promised to provide renewable energy in a scalable, cost-effective way; however, for years, their relatively low efficiency has been a significant barrier to commercialization. Recent progress on cell efficiency means that OSCs are now much more competitive with other established technologies. These key advancements have come from better understanding and controlling the molecular structure, solid-state packing, and film morphology of the light absorbing layer. This focused review will explore the different ways that the solid-state structure and film morphology of the light absorbing layer can be controlled. It will examine the key features of an efficient light absorbing layer and present guiding principles for creating efficient OSCs. The future directions and remaining research questions of this field will be briefly discussed.

Keywords

organic photovoltaics; organic solar cells; non-fullerene acceptors; film morphology; organic electronics

Introduction

Organic solar cells (OSCs) are an established technology that is recently experiencing a renaissance due to the development of new classes of materials and a deeper understanding of device physics. It took the field 20 years to break the threshold of cells with power conversion efficiencies (PCEs) of over 10%,¹⁻³ but within the past four years laboratory-scale devices with PCEs exceeding 18%⁴ and large-scale (>1 cm²) modules surpassing 10% PCE have been produced.⁵⁻⁷ These metrics now make OSCs competitive with other solar technologies.⁸ Beyond PCE, OSCs also have many competitive advantages, such as solution processability, lightweight modules, excellent low-light efficiency, flexible form-factors, semi-transparency, short energy payback times, and low toxicity.⁹⁻¹² Together, these make OSCs an attractive and *sustainable* way of extracting energy from petroleum stores.

The recent progress in OSCs has been due to two main factors: (1) the development of non-fullerene acceptor (NFA) materials; and (2) a better understanding of the microstructure of OSC active (light absorbing) layers. This focused review will provide a brief introduction to the current state of the field of OSCs, including the synthetic methodologies and engineering controls required to obtain an optimal solid-state structure and film morphology of the active layer. It will focus on non-fullerene OSCs; devices based on a polymer donor and a small-molecule acceptor are the most well-studied and will be the main focus of this review.

OSC Background

Extensive discussions on the working principles of OSCs can be found elsewhere.^{9,13,14} But in short, the active layer of the cell absorbs a photon, creating a tightly bound electron-hole pair (a Frenkel exciton). This exciton diffuses to the interface between the electron-donor and the

electron-acceptor where electron transfer occurs. The separated charge carriers then travel to the electrodes where they are collected as current.

A complication arises due to the short lifetime of excitons, which limits the distance they can diffuse before recombining (ca. 5 – 10 nm); this in turn limits the size of the donor and acceptor domains (ca. 10 – 20 nm). The absorbance coefficients of common organic semiconductors ($\epsilon \sim 10^4 - 10^6 \text{ M}^{-1} \text{ cm}^{-1}$) require film thicknesses of ca. 100 nm or more to fully absorb incident light (assuming complete reflection at a metal back-electrode). These considerations make the bulk heterojunction (Figure 1) ubiquitous in OSCs. Efficient bulk heterojunctions require both small domains of relatively phase-pure material and a bicontinuous percolation pathway for charge carriers. It is, then, crucially important to control the morphology of the donor-acceptor blend to achieve optimal device performance.

Figure 1. Schematic representation of an ideal bulk heterojunction. Purple represents donor-rich domains and green represents acceptor-rich domains. The ETL and HTL are the electron-transport layer and hole-transport layer, respectively.

Historically, the best acceptor materials were fullerene derivatives (Figure 2a).¹⁵⁻¹⁷ Fullerene derivatives have high electron mobilities, low lying LUMO energies, and a tendency

not to form excessively large crystalline domains. They primarily suffer from a poor absorption profile (requiring the donor material to contribute most of the light absorption), limited synthetic tunability (which prevents the fine-tuning of orbital energies and packing interactions), and poor scalability for large-scale production. There are numerous reviews that focus on fullerene-containing OSCs;^{13,16,18–21} however, it has become abundantly clear that NFAs often behave very differently than fullerene acceptors. These differences necessitate different device design strategies, and thus this review will focus exclusively on NFA-based OSCs.

Figure 2. Structures of (a) PC₆₁BM and (b) an early high-performance NFA: O-IDTBR.

By 2015, there were a few seminal reports^{22–25} of efficient OSCs that did not use fullerenes. The efficient NFAs shared a similar structural motif; their structures featured an electron-rich core containing one or more sp^3 -hybridized carbon atoms. This allows two side-chains to protrude orthogonally from the core, sterically protecting the electron-rich portion of the molecule. In contrast, the molecular periphery is electron-deficient and sterically accessible (Figure 2b). This motif is similar to that of calamitic liquid crystals, and these types of NFAs are sometimes referred to as calamitic or ladder-type NFAs.²⁶ The steric bulk at the core of the calamitic NFAs limits packing interactions at the core, which are more favorable electrostatically, and encourages π - π stacking of only the peripheral electron-deficient units. This provides a packing mode that mimics that of polymers (see below), allowing a linear string of

calamitic NFAs to efficiently transport charge. This leads to high electron mobilities without as much crystallization as in fullerenes.

Electronic Considerations

There has been much work on the energetic factors that contribute to efficient OSCs.^{12,14,27,28} In short, the offset between the HOMO of the donor and the LUMO of the acceptor defines the maximum open-circuit voltage (V_{oc}) of an OSC. One absorbed photon can only contribute one electron to the circuit, so absorbing the maximum *number* of photons provides the highest photocurrent; in the AM1.5G spectrum, the peak photon *flux* is between 480 and 900 nm (Figure 3a). It is generally accepted that a frontier-orbital offset of ca. 0.5 eV between the donor and acceptor (Figure 3b) provides a sufficient energetic driving force for *efficient* separation of the electron and hole.²⁹ NFAs tend to have long-lived excited states and high fluorescent quantum yields; in these cases there can be less (sometimes even negligible) HOMO-HOMO offsets, while still separating excitons generated in the acceptor.^{30–34} To maximize both the V_{oc} and the short-circuit current density (J_{sc}), there must be a trade-off between absorbing photons and maximizing photon energy. The lower bandgap material should therefore be the acceptor to minimize energy losses due to exciton separation. The donor should have a complimentary absorption profile (or congruent absorption profile if at peak photon flux),³⁵ and provide a large enough LUMO-LUMO offset to facilitate electron transfer due to absorption in the donor (to overcome the exciton binding energy).

Figure 3. (a) AM1.5G solar spectrum; (b) ideal energy level alignment between the donor and acceptor.

Morphology Effects

Although material design is the easiest way to control the V_{oc} and J_{sc} , the morphology can also significantly affect these parameters.¹⁴ If the phase domains are too large, excitons will not be able to reach a donor-acceptor interface and will recombine. In this case, fewer excitons will be converted into free charge carriers and there will be a loss of photocurrent. As an example, Ade and coworkers³⁶ showed that larger domain sizes lead to lower J_{sc} values in blends of the same chromophore backbones. Conversely, if the domains are too small, most of the excitons will separate; however, the resulting charge carriers will be confined to these small domains. This increases the probability of recombination which also leads to a decrease in photocurrent. This has been demonstrated by both our group³⁷ as well as Liang et al.³⁸ where small domain sizes lead to lower J_{sc} values. Optimally, there should be a vertical phase separation of donor and acceptor towards their respective electrodes; this provides free charge carriers a direct pathway to their respective electrodes and decreases the probability of bimolecular (non-geminate) recombination. This has been demonstrated by the Hou group,³⁹ where the vertical phase-separation induced in their blend lead to a higher FF with the appropriate device architecture.

Phase purity is also a consideration. If the domains are too mixed (i.e., they are not purely donor or acceptor) then there will be an increase in non-geminate recombination from trapped charge carriers. There will also be an increase in geminate recombination events due to poor transport pathways (similar to the effect of small domains). In addition, convoluted pathways for charge carriers will decrease the charge carrier mobility, further increasing the odds of non-geminate recombination. This manifests as an increase in the series resistance of the cell, which reduces the fill factor (FF). Conversely, if there is no mixed region and the domains are completely phase-pure, there will be a high energy interfacial boundary between the two materials; this increases the energy required to split an exciton, reducing the V_{oc} . These observations about domain purity are a common occurrence in both fullerene⁴⁰ and non-fullerene^{41–43} devices.

Energetic Disorder

Recently, there has been debate about the role that energetic disorder plays in OSCs. Seminal work^{44–48} has shown that for highly efficient solar cells, the energetic disorder should be as low as possible. Energetic disorder arises from distortions in molecular structure, such as rotations about a single bond, as well as distortions in the solid-state packing and the donor-acceptor interface. This disorder leads to an increase in the effective HOMO level of the donor and a decrease in the effective LUMO level of the acceptor (Figure 4), reducing the V_{oc} . In addition, charge carriers move more efficiently through crystalline materials, and more disorder typically leads to lower charge carrier mobilities.⁴⁹ This leads to higher rates of non-geminate recombination, resulting in lower fill factors and photocurrents.

Figure 4. Schematic representation of the V_{oc} losses due to energetic disorder in the donor and acceptor. This figure does not consider other sources of V_{oc} loss.

Control of Solid-State Structure

Influence of NFA Molecular Structure

As mentioned above, the calamitic or ladder-type design for NFAs has been remarkably successful. For more in-depth reviews, the reader is directed elsewhere.^{12,15,50–53} A problem with the formation of large crystalline domains (over-crystallization) was observed in early NFAs, particularly those based on perylene diimide. Perylene diimide is a large aromatic polycyclic molecule that forms very strong and extensive π -stacks. Calamitic NFAs employ an extended π -conjugated framework with electron-deficient peripheries flanking an electron-rich core; this increases the extinction coefficient by introducing some charge-transfer character to the π - π^* transition. As a way to discourage over-crystallization, long alkyl chains protrude orthogonally from the electron-rich core, but the electron-deficient end-groups are left accessible for π -stacking interactions (Figure 2b). This allows very strong π -stacking interactions only among the electron-deficient periphery, and leads to packing motifs that resemble one-dimensional chains. This allows a high degree of order in one (or more) dimensions without forming overly large domains. This packing motif accomplishes two other things: (1) it allows the LUMO (situated

primarily on the electron-deficient region of the molecule) to be accessible for electron transfer events, and (2) it ensures that the electron-rich region of one acceptor molecule is not in close contact with the electron-deficient portion of another acceptor, which can lead to quenching of the excited state.

The exact packing mode of calamitic NFAs is influenced by the molecular shape, how far away the steric bulk is from the electron-deficient end-group, the amount of steric bulk at the core, and the effective size of the end-group. The prototypical example is the molecule ITIC (Figure 5a); it has been derivatized extensively^{54–56} due to its early success in OSCs. In particular, ITIC displays a brick-like packing motif with an end-group above and below each alternate end-group, forming a two-dimensional network (Figure 6a).⁵⁷ Fluorination of the end-group (ITIC-4F) increases the electron density at the end of the indanedione end-group, leading to stronger π -stacking interactions and better orbital overlap at wider angles. This results in alternating herringbone and linear packing which provides a more inter-penetrating three-dimensional network (Figure 6b).⁵⁷ Different functionalizations of the end-group have been extensively explored,⁵⁶ and other directing groups can similarly change the packing modes to encourage more three-dimensional packing, particularly halogenation and/or regiospecific functionalization.^{58,59} Recently, a new family of materials based on the Y6 scaffold (Figure 5b) has set new efficiency records for OSCs.^{4,52,60} These materials have a C-shape, as opposed to the linear or S-shaped nature of ITIC derivatives. The resultant packing modes adopted by Y6 derivatives resemble the brick-like packing of ITIC, with end-groups above and below each alternate end-group; however, due to the curve in the backbone, the Y6 derivatives pack in a three-dimensional inter-penetrating structure (Figure 7).⁴¹ This is further accentuated by the helicene-like twisting of the Y6 backbone that gives it chirality; this restricts the crystalline

coherence lengths to prevent excessive crystallization while encouraging electron transport in three dimensions.⁶¹

Figure 5. Chemical structures of (a) ITIC and its tetrafluorinated analog, ITIC-4F, and (b) Y6.

Figure 6. Single crystal X-ray diffraction structures of (a) ITIC and (b) ITIC-4F. Adapted with permission.⁵⁷ Copyright 2019 American Chemical Society.

Figure 7. Single crystal X-ray diffraction structure of Y6 from (a) above and (b) the side.

Adapted with permission.⁴¹ Copyright 2020 American Chemical Society.

One important feature of high-performance NFAs is a rigid, planar chromophore backbone.^{46,62,63} Having limited flexibility in the chromophore through ring-fusion, electrostatic interactions, and/or steric restrictions reduces disorder in the NFA, and particularly in the solid-state packing. By reducing crystalline disorder through rigidifying the NFA, electron-transport is improved; this results from improved electrostatic interactions of the end-groups and an increase in preferential face-on ordering of the NFA relative to the substrate. A good example is IDT-BOC6, synthesized by the Bo group (Figure 8).⁶⁴ The authors showed that conformationally-locking the end-group to the core increased the electron mobility, lowered the absorption onset, decreased energetic disorder, and significantly improved the PCE.

Figure 8. Chemical structures and optimized geometries (B3LYP/6-31G(d)) of (a) IDT-BC6 and (b) IDT-BOC6. PCEs of devices made using PBDB-T as the donor polymer are shown in green. Adapted with permission.⁶⁴ Copyright 2017 American Chemical Society.

In terms of polymer NFAs, the most reliable method of producing high performing polymeric NFAs is to take a calamitic NFA and copolymerize it with a short spacer.^{65–69} At least one report has shown that the use of an electron-deficient spacer is beneficial.⁷⁰ Although this is a new field of study, it appears that the features that make calamitic NFAs successful are also applicable to polymeric NFAs.

Influence of Donor Molecular Structure

An excellent review on the design of donor polymers can be found elsewhere;⁷¹ however, aspects pertinent to the control of film morphology and solid-state structure are given below. In a typical OSC composed of a polymeric donor and small-molecule NFA, the donor plays multiple roles in directing the film morphology and solid-state structure. Foremost, polymers are macromolecules and tend to entangle; as such, the polymer typically defines the large-scale morphology of the active layer.^{37,38,42} It is becoming well-established that polymers can confine the small-molecule NFA over nanometer to micrometer length scales, preventing the formation

of large crystallites and defining the domain sizes of both donor and acceptor. For this reason, polymer molecular weight^{42,72} and backbone rigidity⁷³ are two important parameters that influence the morphology of the bulk heterojunction. Low molecular weight polymers are notorious for producing large domains, having poor hole mobilities, creating disorder, and producing poor efficiencies.^{71,74} This can also be said for polymers with highly flexible backbones, with more flexible backbones typically allowing the formation of larger NFA domains.⁷³ Short of ring-fusion, the most successful way to create a more rigid polymer backbone is through dipole interactions or non-classical hydrogen bonding interactions between adjacent monomer units; notable examples include S-O, S-F, or F-H interactions that enforce planarity across single bonds.^{73,75–77} These interactions rigidify the polymer backbone at room temperature in the solid state, but allow for bond rotation in solution and/or at elevated temperatures. This strategy has been extremely effective for the PBDB-T family of donor polymers. Here the various rigidifying interactions can be progressively overcome at different temperatures in solution,^{78,79} allowing different portions of the conformational free energy landscape to be accessed during the deposition process. This facilitates the controlled pre-aggregation of polymer segments in solution and leads to a mixture of crystalline and amorphous regions in the film; this in turn helps define the level of phase separation in the overall blend.

Influence of Alkyl Chains

The alkyl chains of the donor and acceptor materials were historically introduced to increase solubility and allow for easier processing. The alkyl chains, however, play a crucial role in OSC performance;⁸⁰ although it is difficult to predict exactly how they will impact device performance, there are some general trends in alkyl chain design. The alkyl chain placement affects the lamellar packing modes available, and can drastically affect the preferred orientation

of the molecule or polymer relative to the substrate.^{81–83} The alkyl chain length will affect the strength of the Van der Waals interactions, the distance between adjacent molecules, and the solubility in different solvents.^{39,84} Branched alkyl chains increase the steric bulk and introduce disorder at uncontrolled (racemic) stereogenic centers; this reduces the crystalline coherence length.⁷¹ The position of the branch point will affect where the steric bulk is presented and can drastically change packing modes, intermolecular distances, and the solubility of the molecule.^{83,85}

The side-chains of ITIC are 4-alkylphenyl groups, but when replaced with linear alkyl chains (C8-ITIC, Figure 9a) the level of disorder is reduced and the strength of the end-group interactions increases, leading to more efficient OSCs.⁸⁶ Similar trends hold for IDIC derivatives⁸⁷ and IDTBR derivatives²³ (Figure 9b,c). The newer, high performance Y6 family has branched alkyl chains that provide the steric bulk at the electron-rich core. In this system, however, the branched chains fold back around one side of the core, something allowed by the twisted core and the low inversion barrier of the amine. The length and branch point of this alkyl chain has been explored, showing that a further branch point (at the 3 position)⁸⁸ or a longer alkyl chain (2-butyloctyl)^{89,90} improves the solubility, increases the crystallinity, and decreases conformational disorder in the crystal. The Y6 family also has alkyl chains at the ends of the core, providing additional solubility to the large π -conjugated system while also acting as a conformational lock to decrease the conformational disorder at the end-group.⁴⁸ This approach was originally demonstrated with an ITIC derivative, ITC6-IC (Figure 10); it reduced disorder and improved efficiencies by increasing the FF and V_{oc} .⁹¹ A recent report by the Yan group⁹² replaced the conformationally locking alkyl chain on a Y6 derivative with an alkyl-substituted phenyl ring (Figure 11). They showed that the substitution pattern of the phenyl ring (*ortho*,

meta, or *para*) greatly affected the FF of the devices, and in particular they showed that the *meta*-substituted side-chain led to the highest FF, longest crystalline coherence length, highest electron mobility, and highest device efficiency. The more sterically demanding phenyl ring imparts a greater rotational barrier than a linear alkyl chain, and may provide lower conformational disorder in these acceptors. In addition, the authors hypothesized that the dihedral angle of the phenyl ring induces tighter packing of the indandione end-groups while simultaneously encouraging the three-dimensional packing motif known for Y6 derivatives.

Figure 9. Chemical structures of (a) ITIC and ITIC-C8, (b) IDIC-PhC6 and IDIC, and (c) EH-IDTBR and O-IDTBR. PCEs of devices made using (a,b) PBDB-T, or (c) P3HT as the donor polymer are shown in green.

Figure 10. Chemical structures of ITIC and ITC6-IC, highlighting the lack of free rotation in ITC6-IC due to the peripheral alkyl chain. Adapted with permission.⁹¹ Copyright 2018 John Wiley and Sons, Inc.

Figure 11. Calculated (B3LYP/6-31G(d,p)) structures of Y6 derivatives, with alkyl-substituted phenyl side-chains as conformational locking groups, showing front and side view. Adapted with permission.⁹² Copyright 2021 Royal Society of Chemistry.

The most popular branched alkyl chain is the 2-ethylhexyl chain, due in part to its solubilizing ability, cost effectiveness (commercial availability), and steric bulk. In particular, the 2-position is generally the most favorable branching position because it provides enough steric bulk to reduce over-crystallization, but not so much as to remove intermolecular interactions altogether.^{93,94} Effective locations and branch positions for branched alkyl chains have been well-established in the design of donor polymers,^{71,79,80,94} although much of our knowledge comes from studies using fullerene acceptors; there is relatively little research on whether branched alkyl chains are required for modern NFAs.^{39,95–97} In general, the larger monomer unit of a donor polymer contains the branched alkyl chain in order to reduce chain aggregation, while the smaller monomer unit has either a smaller, linear, or non-existent alkyl chain. But again – these design principles were developed in bulk heterojunctions with fullerene acceptors, and have not been thoroughly validated with NFAs.

The presence of branched alkyl chains can change the preferential packing mode of π -conjugated molecules. A face-on orientation of the π -system relative to the substrate is associated with increased charge carrier mobilities⁹⁸ and can reduce interfacial disorder/resistance.⁹⁹ Yet while a significant amount of research has been done on the effect of varying the alkyl chain, trial and error remains the standard method of side-chain optimization.

Control of Film Morphology

Flory-Huggins Interaction Parameter

The miscibility of a polymer and a small molecule can be described using the Flory-Huggins (FH) interaction parameter (χ), which describes the enthalpic contributions to the free energy of mixing (ΔG_{mix}). The free energy of mixing for such a two-component system is described by FH theory (equation 1):

$$\frac{\Delta G_{\text{mix}}}{k_B T} = \frac{\phi_p}{N_p} \ln \phi_p + \phi_s \ln \phi_s + \chi_{ps} \phi_p \phi_s \quad (1)$$

where ϕ_p is the volume fraction of polymer, ϕ_s is the volume fraction of the small molecule, N_p is the number of lattice segments occupied by the average polymer chain (related to the relative partial molar volumes), and χ_{ps} is the FH interaction parameter of the polymer and small molecule. If ΔG_{mix} is positive, mixing is non-spontaneous and there will be a two-phase system at equilibrium. If ΔG_{mix} is negative, the two components will mix to some degree, although there may still be a two-phase system at equilibrium (with one polymer-rich phase and one small-molecule-rich phase). Beyond thermodynamic considerations, it is also important to consider the slow movement of polymers; it is certainly possible to obtain a polymer blend where the film remains kinetically trapped in a non-equilibrium morphology with a relatively low degree of phase separation.

The Ade group has applied FH theory to OSCs, and in a seminal report¹⁰⁰ measured χ for OSC blends using a combination of SIMS (secondary ion mass spectrometry) and R-SoXS (resonant soft X-ray scattering). A simpler DSC (differential scanning calorimetry) method, developed by Kyu and coworkers,¹⁰¹ can also be used to determine χ as shown in equation 2:

$$1 - \frac{T_m}{T_m^0} = \frac{RT_m}{\Delta H_u} \chi_{ca} (1 - \phi_p) \quad (2)$$

where T_m is the melting point of the blend, T_m^0 is the melting point of the pure polymer, ΔH_u is the enthalpy of melting for the crystalline small molecule, and χ_{ca} is the interaction parameter for the amorphous polymer and crystalline small molecule. The Ade group showed¹⁰⁰ that by plotting the binodal curve for χ vs. ϕ_p (Figure 12), the relative material fractions can be correlated to the fill factor with good precision (equation 3):

$$FF \approx k \sqrt{(\phi_0 - \phi_1)(\phi_2 - \phi_0)} \quad (3)$$

where k is a scaling factor, ϕ_0 is the initial polymer volume fraction (estimated as the weight fraction before deposition), ϕ_2 and ϕ_1 are the *polymer* volume fractions of the two phases on the binodal curve. ϕ_2 and ϕ_1 correspond to the volume fractions of the polymer-rich and small-molecule-rich domains, respectively, after deposition and annealing.

Figure 12. FH phase diagrams of an OSC active layer showing (a) the binodal curve and (b) FF fit based on Equation 3. Altered with permission.¹⁰⁰ Copyright 2018 Springer Nature.

Donor-Acceptor Selection

Donor-Acceptor Interactions

The choice of what donor and acceptor to combine depends on more than just electronic factors. The two materials will have unique interactions, which means that a donor polymer may produce efficient cells with one acceptor and poor cells with another, even though both acceptors might perform similarly with a different donor. FH miscibility models (see above) can be used to accurately infer the degree of phase separation between two materials. As discussed previously, phase-pure domains with sizes on the order of the exciton diffusion length, with vertical phase separation and a defined percolation pathway, are ideal for OSCs. If the donor and acceptor are completely miscible, no phase separation will occur, resulting in extensive geminate recombination.^{102–104} If the donor and acceptor are completely immiscible, there will be no

mixed region, increasing non-geminate recombination and lowering the V_{oc} .^{97,105,106} The alkyl chains on the donor and acceptor are one of the primary contributors to their miscibility. If the alkyl chains are missing from one component, extensive phase separation will occur, whereas a similarly soluble alkyl-substituted component will be more significantly more miscible.¹⁰⁵

Molecule Shape/Functionality

Aside from through the alkyl chains, the miscibility can be controlled by the shape of the molecule, the molecular polarity, and the presence of charged functional groups. The molecular shape partially controls the way in which two materials can approach one another, affecting the possible orbital overlap and the relative strength of self- vs. cross-interactions. In particular, it appears that the donor and acceptor are more miscible when the two materials share a similar shape or structure (or adopt a similar shape upon crystallization).^{4,107} Altering the permanent dipole of a molecule by changing strongly electron-donating or withdrawing groups can also alter the miscibility of two materials. This was demonstrated by Yang et al.,¹⁰⁸ where the dicyano functional group at the terminus of common indandione-based NFAs increased their miscibility with common donor polymers; replacement with a less polar ketone functional group led to more phase separation of the donor:acceptor blend. This allowed the authors to obtain more favorable morphologies with simpler donor polymers (Figure 13). It is important to note that each donor:acceptor system is different, and so the effect of altering a functional group will depend on the other component of the blend.

Figure 13. AFM height images of (a) a P3HT:BTP-4Cl blend and (b) a P3HT:ZY-4Cl blend, with their chemical structures. Altered with permission.¹⁰⁸ Copyright 2020 Royal Society of Chemistry.

Deposition Solvent

As shown above, the miscibility of the donor and acceptor can drastically change the morphology of the active layer. This is further influenced by the choice of deposition solvent. Other reviews provide a detailed explanation of solvent:active layer interactions,²⁰ but the fundamentals are presented here. As the active layer dries, if the two components have a sufficiently high χ , phase separation will occur by either a solid precipitating out of solution (solid-liquid, S-L, phase separation) or by diffusion away from the mixed system in solution (liquid-liquid, L-L, phase separation). If χ is not sufficiently high, then phase separation will not occur and only one-phase of intimately mixed donor and acceptor will be present.²⁰ The solvent choice controls the solubility of both components, *and* can facilitate miscibility *between* the donor and acceptor, altering the probability of the three outcomes. Because of the requirement for highly crystalline, phase-pure domains, S-L phase separation is preferable as it allows for

preferential crystallization of one component until most or all of the solvent is removed. A small mixed region can then be formed around the crystallites to facilitate charge separation.

The evaporation rate of the solvent is another key factor that influences the film morphology. As polymer motion in the film is relatively slow, fast evaporation can kinetically trap the film in a non-equilibrium state. This means that low-boiling solvents spin-cast at high speeds¹⁰⁹ lead to a relatively intermixed active layer with a majority of L-L phase separation, while high boiling¹¹⁰ solvents allow more time for S-L demixing and contribute to higher levels of phase separation in the film.²⁰ This was demonstrated by Chen et al.¹¹⁰ where chloroform led to small domains and chlorobenzene led to large domains, but a mixture of the two produced optimal domain sizes. Historically, chlorobenzene has been the solvent of choice as it has a relatively high boiling point (132 °C) and preferentially solubilizes most donor polymers, thereby encouraging the S-L demixing of the small-molecule acceptor. Attempts to avoid the use of halogenated solvents (for environmental and health reasons) has shown that success can also be found with toluene, xylene derivatives, and trimethylbenzene derivatives.^{89,111} Many low-boiling solvents such as chloroform and THF require an additional post-deposition annealing step in order to further phase-separate the blend, which is discussed in more detail below.

FH theory can also be extended to include a solvent in addition to the donor and acceptor. This can help predict what type of demixing will occur and in turn help select the optimal solvent for a given donor-acceptor system. Further reading on the subject can be found elsewhere.^{18,20,112}

Solvent Additives

One important method of optimizing film morphology is the use of a secondary solvent additive (usually less than 5% by volume). An extensive review on this subject can be found elsewhere.²⁰ The solvent additive, by its nature, should be even higher boiling than the host

solvent; this allows the additive to remain in the film to encourage the solubilization of one (or both) components of the blend. Remaining in the film after the host solvent evaporates allows for prolonged S-L demixing, which encourages a higher degree of phase separation in the film. The most used solvent additive, 1,8-diiodooctane (DIO), has a very high boiling point (168 °C) and typically encourages the solubilization of the small-molecule acceptor, allowing slow crystallization of the polymer component. Solvent additives such as DIO do not leave the active layer until they are either exposed to extremely low pressures or are rinsed away with a suitable solvent, and thus they can continue to alter the morphology of the cell until they are removed. In the context of non-fullerene solar cells, however, very low loadings of solvent additives (< 1%) are generally used, and DIO is not always a good choice as it tends to produce overly large domains.^{113,114} In addition, there are concerns that halogenated solvent additives can contribute to device degradation.^{113,115,116} Diphenyl ether^{117,118} and other non-halogenated additives have successfully been used as replacements for DIO; they have been shown to lead to S-L demixing and enhanced crystallinity in the NFA. In theory, there should be no need for a solvent additive if the correct solvent system is chosen, but in practice solvent additives are simple to add and are more broadly applicable than specific solvent blends.

Popular NFAs tend to have low barriers to crystallization and thus require very little solvent additive; however, polymers are semi-crystalline at best and tend to form somewhat amorphous or poorly ordered domains as-cast. The use of solvent additives or solvent choice is therefore often focused on either increasing the crystallinity of the polymer component or quickly driving the NFA component to crystallize so that further post-processing methods can be used.

Vertical Phase Separation

Vertical phase separation of the two materials is another important aspect of efficient active layers. It is beneficial to have a donor-rich region at the hole transport layer, and an acceptor-rich region at the electron transport layer. This facilitates efficient charge transfer to the respective transport layers as well as reducing shunting by removing recombination pathways. A consequence of good vertical phase separation is higher domain-purity near each electrode, reducing the likelihood of non-geminate recombination events. Li and coworkers³⁹ demonstrated that vertical phase separation can arise from a sufficiently high χ ; in their study, the denser acceptor diffused to the bottom of the active layer, while the donor rose to the top. Therefore, by using an inverse device architecture (substrate/electrode/ETL/active layer/HTL/electrode) they were able to improve the FF as a result of vertical phase separation.

The deposition method can also control the degree of vertical phase separation. Most devices are deposited from a solution containing both the donor and acceptor; unless χ is unusually high, this typically leads to minimal vertical phase separation. In contrast, sequential deposition (also called layer-by-layer deposition) provides more control over phase separation in the vertical direction.^{119–122} By depositing the second component on top of the first, the amount of mixing that occurs at the interface can be controlled by the solubility of the first layer, the drying time, and the miscibility of the donor and the acceptor. This method is effectively a compromise between the planar heterojunction and the bulk heterojunction (Figure 14). It ensures that the donor and the acceptor are segregated at the proper electrodes, and that there is a small amount of limited mixing at the interface. Sequential deposition has the added benefit of allowing the polymer ample time to crystallize without becoming trapped in an amorphous state by the NFA crystallites; the domains formed from sequential deposition tend to be more phase-

pure as a result. Noted benefits of the sequential deposition method include improved efficiency,^{119,120} stability,^{119,122} and reproducibility.¹²²

Figure 14. Schematic representation of (a) an ideal bulk heterojunction and (b) an ideal sequential-deposition heterojunction. Purple represents donor-rich domains and green represents acceptor-rich domains.

Post-deposition Annealing

Thermal Annealing

Thermal annealing (TA) is a common post-deposition process used to promote phase separation in kinetically-trapped films. By heating the film above the glass-transition temperature of the polymer, the two components become more mobile, allowing them to achieve a more thermodynamically favorable morphology. In general, NFAs tend to have a low barrier to crystallization and thus crystallize readily. Polymer donors, on the other hand, have a much higher barrier to crystallization and thus higher temperatures are often required to achieve the necessary ordering and alignment.³⁸ TA of NFA solar cells encourages the crystallization of the donor polymer and an increase in the mixed region at the donor-acceptor interface. Overcoming the glass-transition temperature leads to cold-crystallization of the polymer and excludes the NFA from the polymer matrix, but does not necessarily crystallize the NFA.³⁸ This makes the

boundaries around the polymer-rich domains become increasingly mixed and the bulk of the polymer-rich domains more phase-pure.⁴¹ Since the FH interaction parameter decreases at high temperatures, and the entropic contribution to ΔG_{mix} also increases, the two components will also become more miscible with each other.

If a high boiling solvent or solvent additive is used, and it is not fully removed after deposition, the TA process will increase the solubility of the preferentially-solubilized component and lead to significant S-L phase separation. TA and the solvent additive work together to drive phase separation and polymer crystallization. These steps are therefore often used together to promote phase separation and allow the polymer to crystallize without increasing the mixed region.^{123,124} Köntges and coworkers even showed that combining TA and solvent additives can facilitate co-crystallization at the interface, imprinting the packing modes of the polymer onto the acceptor. This allows for more favorable charge-transfer in the mixed region.¹²³

Solvent Vapor Annealing

Solvent vapor annealing (SVA) swells the film with solvent vapor to allow the active layer components to reorganize. SVA achieves results similar to the use of solvent additives, but with more control over the solvent choice and annealing time. SVA is often done using the bell-jar method,¹²⁵ but this technique is poorly reproducible and not industrially viable; in contrast, variable pressure SVA (VP-SVA, Figure 15) allows for precise control of the solvent partial pressure, enabling much lower concentrations of solvent vapor to be used.^{37,125} Although more complex than TA, VP-SVA offers additional levels of control due to the choice of solvent, vapor pressure, and exposure time. TA and SVA can also be used together to better fine-tune the morphology of the active layer.³⁷

Figure 15. Schematic representation of a VP-SVA setup. Two mass-flow controllers separate solvent-saturated (blue) and dry (red) carrier gas to be mixed in controlled ratios before entering an annealing chamber. Altered with permission.³⁷ Copyright 2020 American Chemical Society.

SVA works by swelling the film with a solvent that is either a poor solvent for both materials, a selective solvent for one component, or a good solvent for both; this allows the film to be swollen and controls the solvation of neither, one, or both components. Simply swelling the film with a poor solvent encourages only local reordering, and the domain size is not drastically affected, although the local domain purity is generally increased (if χ is sufficiently high). There is not much recent work on SVA of NFAs with poor solvents, since it generally does not improve crystallinity or effect a drastic morphology change.¹²⁶ Most SVA is done with a selective solvent. In particular, it is more beneficial to select a solvent that preferentially solubilizes the small-molecule component, as the polymer will still be allowed to move slightly due to the film-swelling.^{20,126,127} The selective solvation of a NFA, with a low barrier for crystallization, will encourage crystallization of the NFA while (ideally) leaving the polymer relatively unaffected, save for perhaps a higher phase-purity.^{4,37,38,127} Extreme cases of SVA can lead to extensive phase separation, similar to a long exposure to a large amount of solvent additive, so precise control over both solvent concentration and annealing time is required.^{37,103,125,127} If a good solvent for both components is used, due to the slow kinetics of the polymer, the effect is often similar to that of a solvent that is selective for the small-molecule

acceptor. Small amounts of solubilization of the polymer, however, generally increase the degree of L-L demixing and do not generally contribute to an increase in the crystallinity of the polymer component. As such it is best to either avoid annealing with a solvent that solubilizes both components, or to anneal for only a short period, thereby taking advantage of the slow kinetics of the polymer.^{103,125,127}

Conclusion

Better control over OSC morphology has now led to single-junction devices with 18% PCE.^{4,128} This makes OSCs more competitive with other solar technologies, and for applications like indoor power generation, OSCs have tremendous commercial potential. But it is important to consider that PCE is only a single piece in the puzzle of commercial viability; a more holistic metric is the cost-per-Watt.^{129,130} Now that we know how to design high efficiency donor and acceptor materials, we need to begin reducing their synthetic complexity in order to improve scalability and reduce cost.^{15,27,50} Another hurdle is long-term stability; OSCs are notorious for their short shelf-life and poor photostability, so improving the lifetime of these devices will also serve to reduce both the cost-per-Watt and the waste produced by device turnover.^{27,129,131} Another focus of future research is the move towards environmentally-friendly solvents and processing techniques, which are much more significant considerations at industrial scales.^{132,133} Scalability is also a major consideration for commercial devices, and ideally devices would be solution processed using roll-to-roll methods, not evaporatively.^{130,134} Currently, state-of-the-art devices rely on extremely thin, spin-coated active layers; there must be a shift toward materials and devices that can be deposited by either blade or slot-die coating (which typically produce thicker films than spin-coating). The issue of scalability also goes hand-in-hand with the production of large area cells ($> 1 \text{ cm}^2$) and modules. But overall, it is inspiring to see how far

the field of OSCs has come, and new advances make their widespread application more feasible every day.

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