ABSTRACT


Organic Photovoltaic (OPV), as one of the most promising energy alternatives, attracts huge amount of interests. The performance has manifested rapid improvement toward commercial thresholds in the last two decades largely thanks to progressive understanding of the photoactive layer morphology and its correlation with the device performance. A constructive combination of several important morphology characterization tools makes it possible to provide the detailed and comprehensive morphological pictures about photoactive layers. A great amount of emphasis is given to the soft X-ray based scattering and imaging tools, which are capable of providing highly quantitative information about the photoactive layer morphology. Resonant soft X-ray scattering (R-SoXS) and scanning transmission X-ray microscopy (STXM) utilize the complex index of refraction, \( n=1-\delta+i\beta \), of organic materials which varies rapidly as a function of photo energy around the carbon absorption edge. The highly quantitative morphological information given by R-SoXS and STXM largely help to construct morphology - property - performance correlation. Furthermore, a novel analytical method based on the combination of optical microscopy and absorption is developed to evaluate temperature dependent miscibility and effective molecular interaction parameters of organic material blends with the purpose of predicting the morphology development at certain processing conditions.
Morphological Characterization of Organic Photovoltaic Devices and Prediction of Photoactive Layer Morphology

by
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DEDICATION

This thesis is dedicated to my family and all of my friends.
BIOGRAPHY

Xuechen Jiao was born on December 7th, 1987, in Baoding, China. His father, as a police officer and his mother, as a physician put all of their love and raised him in a happy family. He received his Bachelor of Science degree in Department of Physics from Liaoning University in July 2009. In the same year, he joined Prof. Jiahua Zhang group in Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Science. He then obtained the Master of Science degree in December 2011. Later on, he started his PhD study in the Department of Physics at North Carolina State University under the direction of Prof. Harald Ade.
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Chapter 1

Introduction

1.1 Bulk heterojunction organic solar cells

Solar energy is one of the best options for sustainable alternative energy sources in the 21st century. Various photovoltaic techniques that convert solar energy to electricity exist, such as crystalline silicon solar cells,[1] inorganic compound solar cells,[2] dye-sensitized solar cells,[3] quantum dot solar cells,[4] organic solar cells[5] and hybrid perovskite solar cells.[6] Among these technologies, organic solar cells (OSCs) attract much attention due to the potential of providing low-cost energy solution,[7] mechanical flexibility[8] and the nature of readily deployable thin film configuration. Depending on the architecture of the active layers and the deposition techniques, OSCs can be mainly divided into planer-heterojunction (PHJ) cells[9] or bulk-heterojunction (BHJ) cells[10] and vacuum deposited cells[11] or solution deposited cells. Among these combinations, solution processable bulk-heterojunction OSCs receive the most attention and interests. Whereas PHJ cells have to be made by successively depositing several layers, the components of photoactive layers in BHJ cells can be deposited by a common solvent in the same time, which largely simplify the manufacturing process.[12,13] Also, the ability of being solution processable offers the great potential of being low cost.[14] While the inorganic counterparts already approach the theoretical maximum limits, the current state-of-the-art OSCs are still below half of the theoretical maximum
The continuous optimization of OSCs necessitates a better understanding and comprehension of the working mechanisms for bulk heterojunction (BHJ) OSCs.\textsuperscript{[20-22]}

OSC\textsubscript{s} are made of π-conjugated organic donor molecule and acceptor molecule. The π-conjugation system is formed when the carbon atoms covalently bond with alternating single bonds and double bonds.\textsuperscript{[23]} The electrons on the $p_z$ atomic orbital delocalize and form π bonding orbitals and π* anti-bonding orbitals.\textsuperscript{[24]} The delocalized π orbital is the highest occupied molecular orbital (HOMO), and the π* orbital is the lowest unoccupied molecular orbital (LUMO). The HOMO in organic semiconductors takes the role of the valence band in inorganic semiconductors, while the LUMO serves as the conduction band. The energy difference between HOMO and LUMO is considered the band gap of the organic semiconductor materials, with whose existence the photoabsorption with well-defined spectrum range become possible.\textsuperscript{[25]} The π conjugation also means that the charge carriers, either generated electrically or optically, are weakly bound and free to travel along the molecules or between them.\textsuperscript{[26]} Unlike the inorganic materials, where the constitute atoms are capable of arranging in a highly ordered behavior, the π-conjugated organic materials, as the building block of OSC photoactive layers, organize themselves in a much more complicated manner.\textsuperscript{[27]} Due to the weak non-covalent interaction between donor and acceptor, the π-conjugated organic molecules usually form complex multi-phase morphology, including ordered crystallites, relatively pure donor and acceptor aggregates and molecularly mixed amorphous phase.\textsuperscript{[28-30]}
1.2 Device working mechanism

The figure of merit for OSCs is power conversion efficiency (PCE), defined as

\[ PCE = \frac{J_{sc} \times FF \times V_{oc}}{P_{in}} \]

where \( J_{sc} \) is the short circuit current density, FF is the fill factor, \( V_{oc} \) is the open circuit voltage and \( P_{in} \) is the incident power density (Figure 1.1). When a photon is absorbed by an organic semiconductor material, a neutral excited state or exciton consisting of bound electron and hole is generated, which is located on a single molecule within a volume of a few nm\(^3\). The strong spatial confinement as well as the low dielectric constants of organic semiconductors leads to strong binding energy (\( \sim 1 \) eV) compared to the thermal energy of \( k_B T \). In comparison, the binding energy of the exciton in inorganic materials is 1 order of magnitude lower (\( \sim 0.1 \) eV) and comparable to the thermal energy in room temperature. As a result, the primary product of photoabsorption in organic materials is exciton with limited diffusion length of 10 nm - 20 nm, instead of free charge carriers.\(^{[31]}\)

Accordingly, photovoltaic process in OSCs involves photon absorption, exciton generation and diffusion, exciton dissociation and charge transfer (CT) state generation, charge carrier transport and recombination.\(^{[32]}\) In order for efficient photocurrent generation, the following requirements must been fulfilled: 1) Strong and wide enough photoabsorption within the spectral range of solar illumination for high exciton generation rate; 2) Large area of D/A heterointerface and properly aligned LUMO-LUMO energy level between donor and acceptor for efficient exciton dissociation; 3) Interpenetrating donor-rich and acceptor-rich domains with purity above percolation threshold for efficient charge carrier transport.\(^{[33,34]}\)
The functional OPV devices are build upon layered architectures. Depending on the polarity of the commonly used transparent substrate (usually ITO coated glass), the layered architecture can adopt traditional or inverted architectures, as shown in Figure 1.1a.[35] In the traditional architecture of glass/indium tin oxide (ITO)/polyethylenedioxythiophene:polystyrene sulphonate (PEDOT:PSS)/photoactive layer/cathode, the doped conducting polymer PEDOT:PSS is used as anode to collect holes due to the high work function, while the low work function cathode, such as Ca or LiF/Al is used to collect electrons. On the other hand, the inverted architecture of glass/ITO/metal oxide/photoactive layer/metal oxide/Ag is also widely used, where the low work function of metal oxide, such as TiO$_2$ or ZnO serves as cathode, while the Ag with high work function serves as anode. Despite OSCs with traditional architecture are relatively easier to fabricate, it suffers from low stability with the indium contaminating PEDOT:PSS and thus degrading...
device performance. In contrast, the air-stable high work function metals, such as Ag or Au, are used as anode and ITO is used as cathode in inverted OSCs. The elimination of PEDOT:PSS in inverted devices largely improves the long term stability.

1.3 Molecular design

Molecular design is one major pathway to enhance efficiency of OSCs. One limitation of OSCs is the low $J_{sc}$ resulting from the intrinsic narrow absorption range of $\pi$-conjugated organic semiconductors. Thereby, novel molecules with low optical band gaps are highly desirable due to the possibility of broadening photoresponse and thus raise $J_{sc}$. Besides, molecular design is one of the few ways to effectively manipulate molecular energy levels. To this regard, donor molecules with higher ionization potential and acceptor molecules with lower electron affinity can be paired together and potentially provide high $V_{oc}$. Plus, reduced LUMO-LUMO difference between donor molecules and acceptor molecules enables reducing the energy loss associated with the charge separation procedure. Molecular structure also plays a vital role of determining the molecular packing behaviors. For example, by moving the alkyl side chain branching position of PDPPTTT polymers, the PDPPTTT:PCBM blends deposited using identical processing condition exhibit considerably different crystallinity. Higher crystallinity usually results in higher charge carrier mobility, which in turn brings higher photocurrent and fill factor.
1.4 Importance of photoactive layer morphology

Although molecular design is capable of effectively aligning molecular levels, which enables to increase $V_{oc}$ and extend absorption range, the $J_{sc}$ as well as FF do not manifest improvement in many blends. Fill factor is largely determined by the interplay between photocurrent generation and charge carrier recombination. Recombination process is usually categorized into geminate recombination and non-geminate recombination. Geminate recombination refers to the recombination between the electron and hole generated from the same exciton, which often happens within the time scale of ~100 ns. It is a specific issue for OPVs owing to the difficulty of exciton dissociation resulting from the large exciton binding energy. Non-geminate recombination refers to the recombination between electron and hole originated from different excitons. It is a prevalent obstacle in OPVs because that the intrinsic low charge carrier mobility and interpenetrating feature of donor-rich and acceptor-rich domains within photoactive layers lead to high probability for separated charge carriers to encounter each other during transport.

For a given pair of electron-donating material and electron-accepting material, the effective way of optimizing OSCs relies on enhancing FF and $J_{sc}$. As mentioned above, FF is dependent on the interplay between charge carrier photogeneration and recombination, both of which are highly sensitive to photoactive layer morphology. For instance, domains with low purity tends to induce stronger non-geminate recombination during charge carrier transport. In comparison, charge carriers moving in domains with higher purity involves less non-geminate recombination resulting from the fact that there is less chance for a charge
carrier to meet the opposite charge carrier. On the other hand, molecular orientation with respect to donor/acceptor (D/A) heterointerface plays a vital role of governing the charge carrier generation.\cite{60,61} Often the face-on molecular orientation promotes charge carrier generation because of the stronger π-π orbital overlaps between donor molecule and acceptor molecule. Another important morphological parameter is domain spacing, which directly controls the amount of interfacial area density. Since that the typical exciton diffusion length is ~ 10 - 20 nm in organic semiconductor materials, reducing domain spacing down to 10 - 20 nm usually enhance $J_{sc}$ given that other morphological parameters, such as domain purity and crystallinity do not change significantly.

As introduced above, OSCs are highly complex systems. The photovoltaic process involves multiple steps from photon harvesting, though exciton generation and dissociation, to charge carrier transport and extraction. These events occur over 4 order of magnitude of length scales, spanning from molecular-scale through nanoscale, mesoscale to device-scale. The opto-electrical properties at all length scales collectively influence and determine the ultimate PCE of solar cells. My PhD work is mainly focused to quantitatively characterize photoactive layer morphology and construct morphology - property - performance correlation in order to promote the further optimization of OPV devices.
1.5 Morphology characterization tools of organic solar cells

1.5.1 Imaging techniques in real space

a) Optical Microscopy

Optical microscopy (OM) refers to the microscopy operated at the range of visible light wavelength. [62] Thereby, visible light microscopy (VLM) is often used in the exchangeable way. OM can operate at two modes - transmission and reflection with the former providing the bulk information and the latter providing the surface information. Thanks to the modest cost and average physical volume, OM can be readily installed within gloveboxes for in-situ and variable environmental investigation. OM finds wide usage in the study of OPVs. Figure 1.2 exemplifies the OM images taken from TS1:PC$_{71}$BM (40 wt%) blends isothermally annealed at different temperatures. The crystallization behaviors of polymer blends can be conveniently investigated by this characterization technique. Besides, the macroscopic phase separation owing to the impurity and thickness variation can also be easily detected by OM.
b) Atomic force microscopy

Atomic force microscopy (AFM) is a specialized scanning probe microscopy (SPM) utilizing the atomistic interaction between the samples surface and the AFM tip. The usage of extremely sharp AFM tips enables to provide topographical information with high resolution down to several nm. Besides of the most commonly measured properties, such as height and phase images, many other properties, including Young's modulus, surface potential and photocurrent can also be measured with proper accessories. [64,65] Optimal operation of AFM requires close proximity between sample surface and probing tips, which in turn requires flat enough surfaces (usually with roughness less than 100 nm average deviation). Due to the wide accessibility, AFM is usually the first step to gain useful information on lateral mesoscale morphology in OPV research. Figure 1.3 demonstrates several AFM height images and phase images.
Figure 1.3. Atomic force microscopy (AFM) topological images on DRCN5T:PCBM blends. (a) is height image and (b) is phase image.

c) Transmission electron microscopy

Transmission electron microscopy (TEM), as a powerful and versatile tool, is capable of providing morphological information within the bulk of photoactive layers with the spatial resolution as high as AFM. In imaging mode, the electron beam passes through the samples and the transmitted intensity is recorded. The most common operation mode in OPV study is bright-field transmission electron microscopy (BF-TEM), where the transmitted electron beam with attenuated intensity is recorded to present composition variation. Aside from imaging, TEM can also record spectroscopy, which is called electron-energy loss spectroscopy (EELS). EELS grants TEM the ability of resolving chemical species. Combination of imaging mode and spectroscopy mode enables one to obtain quantitative compositional information of photoactive layers. Besides, despite of popular usage of diffraction mode in inorganic materials, electron diffraction finds little application in OPV
materials owing to the low crystallinity in most organic materials. With the strengths of TEM, such as capable of providing intuitive images with high resolution in real space, we have to recognize the weaknesses in the meantime, such as strong electron beam damage,[66] low material contrast and small sampling area with little statistics.

1.5.2 Scattering techniques in reciprocal space

a) Small angle X-ray scattering technique

Conventional small angle X-ray scattering (SAXS) is a scattering measurement usually conducted in hard X-ray regime, where the electron density variation is probed on the length scales from several nm up to several hundred nm.[20,67] SAXS possesses the advantages of good statistics, non-destructive and usually requires minimum of sample preparation. Conventional SAXS has been widely used in cements, colloids, biomaterials and block copolymers.[68] Several important morphological parameters, such as domain size, domain shape and domain interface can be extracted from the scattering profiles.[20] However, SAXS found itself less usage in OPVs due to the fact that the component materials used in high performing OPVs are usually similar in composition. A simplified schematic of SAXS experiment is demonstrated in Figure 1.4. As shown in the schematic, the measurement can be carried out in either transmission geometry or grazing incident geometry by changing the angle $\alpha$ and $\beta$. Transmission SAXS provides the convenience of easily setting up and relatively straightforward analysis. Yet this mode suffers from low signal-to-noise issue due to the intrinsically low scattering cross section of organic materials at hard X-ray energies and thin film thickness. Conversely, grazing incident geometry can provide better signal-to-
noise response from the maximized scattering volume under grazing incident.\textsuperscript{[69,70]} Meanwhile, grazing incident measurement delivers surface/interface sensitivity.\textsuperscript{[71]} A highly collimated and energy tunable X-ray from synchrotron impinges on samples. Subsequently, the scattered intensity is recorded by a 2D CCD detector, where the raw data is recorded as \((q_x,q_y)\) basis. Similar with AFM and TEM, the conventional SAXS utilizes mass-thickness contrast (or vacuum contrast), which predominantly describes electron density variation. This sometimes brings up confusions in the description of OPV morphology due to the similar electron densities among component materials. This is more severe in non-fullerene based OPVs where the electron densities of the component materials are almost same and the scattering mainly comes from the surface roughness or void within the bulk. If the compositional domain size is smaller than the film thickness, the SAXS may not provide the relevant morphological information.
Figure 1.4. Simplified scheme of small angle X-ray scattering (SAXS) setup. The transmission mode or grazing incident mode can be switched by changing the sample tilting angle $\beta$ and incident angle $\alpha$.

b) Resonant soft X-ray scattering technique

Resonant soft X-ray scattering (R-SoXS) adopts the same configuration with SAXS except for the utilization of soft X-ray. Figure 1.5 displays a representative 2D R-SoXS pattern recorded in transmission geometry. The magnitude and direction of scattering momentum transfer $q = q_f - q_i$ are recorded and represented as $q$ and $\omega$, where

$$ q = \sqrt{(q_x^2 + q_y^2)} \cdot \frac{4\pi \sin(\theta)}{\lambda} $$

and

$$ \omega = \sin^{-1}\left(\frac{q_x}{q}\right). $$

The technical details of the R-SoXS setup can be found in literatures.$^{[72]}$ Morphological information such as domain spacing, domain purity and orientational distribution can be extracted by reducing the 2D scattering patterns into 1D profiles.$^{[73]}$ For instance, Figure 1.6a demonstrates the 1D angular line-cut profile at constant
\( q \sim 0.04 \text{ nm}^{-1}. \) The sinusoidal distribution of scattering intensity along with angle \( \omega \) indicates anisotropic scattering pattern. Meanwhile, a line-cut profile at constant \( \omega = 45^\circ \) is plotted in Figure 1.6b. The scattering intensity distribution along with momentum transfer \( q \) provides information regarding domain spacing and domain purity. The details regarding each morphological information will be given in the latter sections.

**Figure 1.5.** Typical 2D R-SoXS patterns at transmission mode. The magnitude and direction of scattering momentum transfer \( \mathbf{q} = \mathbf{q}_f - \mathbf{q}_i \) are recorded and represented as \( q \) and \( \omega \), where

\[
q = \sqrt{(q_x^2 + q_y^2)} = \frac{4\pi \sin(\theta)}{\lambda} \quad \text{and} \quad \omega = \sin^{-1}\left(\frac{q_x}{q}\right).
\]
Figure 1.6. (a) 1D angular line-cut profile at constant $q \sim 0.04$ nm$^{-1}$. The blue curve is the sinusoidal fit. (b) 1D radial line-cut profile at constant $\omega=45^\circ$.

While R-SoXS shares many characteristics with SAXS such as good statistics from large probing area, capability of probing morphology from several um down to several nm and flexibility of deploying various geometry to obtain morphological information in 3-dimention,\textsuperscript{74} it possesses its unique advantages over the conventional SAXS techniques. Unlike SAXS, which operates at hard X-ray regime, where the scattering contrast for organic materials relies on variation of electron density, R-SoXS is performed at soft X-ray regime, where the scattering contrast can be enhanced remarkably due to the resonance between incident soft X-ray and organic molecules.\textsuperscript{75,76} In R-SoXS measurement, the scattering intensity at resonant energies can be several orders of magnitude higher than non-resonant condition, making it possible to measure ultra thin organic films in transmission geometry with very short time duration, largely reducing the chance of sample damage.\textsuperscript{77} Operating
at soft X-ray regime gives R-SoXS considerable flexibility to tune contrast mechanism. Quantitative analysis and comprehensive interpretation of soft X-ray scattering data requires the detailed knowledge of scattering contrast function. Fully understanding of contrast mechanism employed in R-SoXS requires the knowledge of near edge X-Ray absorption fine structure (NEXAFS) measurement, which will be deliberately explained in the next section.

c) Wide angle X-ray scattering

Wide angle X-ray scattering (WAXS) is one of the most employed X-ray techniques to qualitatively describe the ordered fraction of organic thin films. The experimental setup of WAXS is similar with SAXS, with the sample - detector distance reduced in WAXS compared with SAXS. Lattice spacing, grain size, paracrystallinity and preferential orientation distribution can be readily extracted from WAXS measurements.\(^{[20,78]}\) In the real experiment, the samples is scanned by the goniometer and the scattering pattern with maximized intensity is chosen at the critical angle. Due to that WAXS is usually operated at hard X-ray regime, which is far away from the absorption edge of any organic materials, WAXS is considered as a non-destructive method.

d) Vertical depth profiles analysis

Whereas most of the techniques outlined above are used for lateral morphology characterization, the vertical morphology information is as important in OPV devices given that the charge transport is dominantly along vertical direction. Critical parameters along vertical direction includes surface and interface properties and vertical composition gradient
of each component.\textsuperscript{[79]} Dynamic secondary ion mass spectrometry (D-SIMS) is an effective technique for answering these questions. During D-SIMS measurements, a focused primary ion beam is used as sputtering source to remove the surface of a sample, followed by the bombardment and collection of secondary ion, which is used as the representative of each component. Figure 1.7 illustrates the simplified scheme of time-of-flight secondary ion mass spectrometer. D-SIMS is sensitive to chemical composition with the depth resolution of 1 - 2nm.

![Figure 1.7. Simplified scheme of time-of-flight secondary ion mass spectrometer.](image)

Another surface-sensitive quantitative spectroscopic technique sensitive to the elemental composition is X-ray photoelectron spectroscopy (XPS). XPS spectra can be obtained by irradiating a material with a focused beam of X-rays and subsequently measure the kinetic energy and number of electrons that escape from the surface of the samples under high vacuum.
The thesis is structured into four major parts: 1) Introduction to morphology characterization tools useful for OPV devices; 2) Morphology investigation on several OPV systems, including small molecule:fullerene system, polymer:fullerene system and all-polymer system with different degree of complex in terms of photoactive layer morphology; 3) Prediction of phase behaviors and morphology development. 4) The conclusion and outlook on OPVs.
Chapter 2

Morphological parameters extracted from resonant soft X-ray scattering techniques

2.1 Introduction

Among all of the morphology characterization techniques mentioned in chapter 1, R-SoXS is the most emerging technique. Although the comprehensive understanding of photoactive layer morphology is not possible without the collaborative combination of various techniques altogether, large amount of efforts has been devoted to the comprehension and application of R-SoXS. The ability of probing domain information across 3 orders of magnitude spanning form several nm to um, the flexibility of tuning contrast mechanism and the plentiful morphological parameters can be extracted, such as domain spacing, domain purity and molecular orientation make R-SoXS as one of the most powerful and promising innovative techniques useful in organic electronics. This chapter is divided into four parts: 1) Understanding of the optical constants determined by NEXAFS; 2) Domain spacing and domain purity; 3) Molecular orientational ordering; 4) Molecular orientation relative to D/A interface.
2.2 Determination of optical constants of organic materials near the carbon 1s absorption edge

Operating at soft X-ray regime gives R-SoXS considerable flexibility to tune contrast mechanism in the application of characterizing organic materials. Quantitative analysis and comprehensive interpretation of soft X-ray scattering data requires the detailed knowledge of scattering contrast function, which is based on Near edge X-ray absorption fine structure (NEXAFS) measurement. NEXAFS spectroscopy is a versatile absorption-based technique, where the core electrons of the atoms are promoted to the unoccupied frontier molecular orbital after photo-ionization.[76] Since the light absorption process involves the excitation of the core electrons to the unoccupied anti-bonding molecular orbitals, NEXAFS produces element specific spectral features related to the specific binding energies of core electrons in different atoms. In other words, the distinct x-ray absorption edges of different elements give the NEXAFS measurement the capability of distinguishing different elements. Additionally, NEXAFS is also sensitive to the molecular bonding environment of the absorbing atoms, which renders different electronic structures of unoccupied frontier molecular orbitals in different molecules. The sensitivity toward bonding environment enables NEXAFS to unravel considerably fine electronic structures above each elemental absorption edge.[80] Given the richness of the electronic and bonding structures in organic molecules, the NEXAFS measurement becomes an ideal approach to spectrally resolve different chemical moieties in organic systems with high energy accuracy. Besides, the NEXAFS measurements are usually carried out in the state-of-the-art scanning transmission x-ray microscopy
(STXM) stations, which operates at diffraction limit. This grants NEXAFS measurement with high spatial accuracy. By using the STXM station located at beamline 5.3.2 advanced light source (ALS), the NEXAFS measurement can be conducted with high spatial resolution up to 30 nm and high energy resolution up to 50 meV.\[81]\n
NEXAFS is the prerequisite for determining the complex index of refraction (optical constants) of the constitute material, which is defined as \( n(E)=1-\delta(E)+i\beta(E) \). The imaginary part of the complex index of refraction (or absorptive optical constant) \( \beta(E) \) is related with the mass absorption coefficient \( \mu(E) \) as \( \beta(E) = \frac{\rho E}{4\pi hc} \mu(E) \), where \( \rho \) is mass density, \( E \) is incident X-ray energy, \( h \) is Plank constant and \( c \) is speed of light. The mass absorption coefficient can be determined in transmission mode NEXAFS by \( \mu = \ln(I_0/I)/\alpha \), where \( \alpha \) is the areal mass density of the materials \( I_0 \) and \( I \) are incident X-ray intensity and transmitted X-ray intensity in NEXAFS measurement. The corresponding real part \( \delta \) (dispersive optical constant) can then be calculated through Kramer-Kronigs equation following

\[ \delta(E) = -\frac{2}{\pi} \int_0^\infty \frac{\beta(E')E'}{E'^2-E^2} dE' \].

To exemplify the NEXAFS measurement of organic materials, the mass absorption coefficient of a DPP-based low band gap polymer is plotted in Figure 2.1a and c. The bare atom mass absorption coefficient is calculated based on the total population of constitute atoms in DPP monomer without considering the bonding structures. As shown in Figure 2.1a, the bare atom mass absorption coefficient of DPP monomer exhibits sharp enhancement at C-, N- and O- absorption edges related to the corresponding binding energies. From Figure 2.1c, the experimentally measured mass absorption coefficient
of DPP is revealed more abundant features around C absorption edge due to the existence of molecular bonding environments.

The knowledge of optical constants of constitute materials provides the basis for quantitative analysis and comprehensive interpretation of soft X-ray based scattering and reflectivity measurements. After determination of the optical constants across C absorption edge, it is feasible to calculate different contrast functions, including donor:acceptor material contrast originating from compositional variation, vacuum contrast originating from surface roughness or void in the bulk and orientational contrast from the orientational ordering variation.

The contrast function is defined as

\[ C(E) = E^4 \Delta n^2 = E^4 (\Delta \delta^2 + \Delta \beta^2) \]

where the E is the incident photon energy, \( \Delta \delta \) and \( \Delta \beta \) are the difference of real part and imaginary part of the complex refractive index of materials. Near the absorption edge, the scattering intensity is strongly modulated by photon energy due to the strong energy dependence of \( \delta \) and \( \beta \). Thus, even in the absence of significant differences of the electron densities between components, the large differences in \( \delta \) and \( \beta \) around absorption edge can still provide large scattering contrast. This feature is significantly valuable in the characterization of non-fullerene BHJs, where the component materials almost possess identical electron densities.

To exemplify the calculation of contrast function, the material contrast and vacuum contrast of DPP and PCBM have been calculated based on the experimentally measured optical constants of DPP and PCBM. As illustrated in Figure 2.1b, vacuum contrasts are
dominant across all energy range, except around C absorption edge. In the extended view of Figure 2.1d, both material contrast and vacuum contrast display widely variation with energy. The widely varying contrast function around C absorption edge originates from that the mass absorption coefficients of constitute materials varying considerably with energy. By choosing incident energy around C absorption edge, it enables to enhance material contrast and suppress vacuum contrast.
Figure 2.1. (a) Bare atom mass absorption coefficient of a low bandgap polymer DPP over a large range of photon energy across C-, N- and O- absorption edges, overplotted with the experimentally measured mass absorption coefficient around carbon K-edge ; (b) The material contrast of DPP:PCBM and vacuum contrast of DPP:vacuum and PCBM:vacuum across the same energy range as shown in (a); (c) Expended view of bare atom mass absorption coefficient and experimentally measured mass absorption coefficient of DPP; (d) Expended view of contrast functions around carbon K-edge.

2.3 Domain spacing and domain purity

Traditionally, the BHJ photoactive layer was viewed as interpenetrating network of pure donor domains and acceptor domains with discrete interfaces. In this traditional paradigm,
the photogenerated excitons diffuse to the discrete interfaces, followed by exciton
dissociation and charge generation. Afterward, the photogenerated charge carriers transport
through the interpenetrating networks formed by pure donor domains and acceptor domains
without consideration of domain purity. In 2010, Brian et al. reported the discovery of partial
molecular miscibility, which proposes that pure amorphous phases do not exist in BHJs.[82] It
points out that in BHJs comprised of semicrystalline or amorphous materials, at least three
phases - including relatively pure donor aggregates, acceptor aggregates and molecularly
mixed amorphous domains - have to be considered to adequately describe and understand the
morphology. More recent works suggest the existence of considerable miscibility between
donor and acceptor molecules and the presence of molecularly mixed region with certain
volume fraction in BHJs are beneficial for the exciton dissociation and charge
generation.[33,82-88]

According to the Fraunhofer approximation of kinematic scattering theory, the
scattering signal represents the 3-dimentional Fourier transform of the real-space electron
density distribution of a sample in the reciprocal space.[89] If transmission geometry is used,
the 2D detector mainly record the 2D Fourier transform of the overlap of the in-plane
electron density distribution across the whole thickness of the active layer. In transmission
mode, the lateral morphology is predominantly probed. After data acquisition, the 2D
scattering patterns need to be reduced into 1D scattering profiles in order for quantitative
analysis. Lorentz correction is usually implemented, by which the 1D I(q) vs q plots are
transferred to I(q)q^2 vs q plots. This is because the samples without special directional
treatments such as stretching or shearing are globally isotropic, where the 2D scattering
patterns do not change with the rotation of the samples. Under this condition, at a given $q$ in the reciprocal space, the whole reciprocal sphere with the given $q$ value is sampled equally. In the cases where strong asymmetry exists, Lorentz correction may bring artifacts. For instance, in stretched samples or for domains with size larger than the film thickness.

The integrated scattering intensity (ISI) is (also called Porod's invariant when infinite range of lengthscale are probed) defined as $ISI = \int_{q_{\text{min}}}^{q_{\text{max}}} I(q) q^2 dq = 2\pi^2 V \sum_{i \neq j} \Delta \rho_i^2 \phi_i \phi_j$ where $\Delta \rho$ is the difference of electron density, $\phi_i$ is the volume fraction of $i$th phase.$^{[90,91]}$ Note that $\Delta \rho^2$ is proportional to the difference of optical contrast of $\Delta n^2$ and we can define $\Delta c$ as the parameter describing the average composition variation. Then the ISI expression can be rewritten as $ISI = \int_{q_{\text{min}}}^{q_{\text{max}}} I(q) q^2 dq \propto 2\pi^2 V \sum_{i \neq j} \Delta c^2$. This is independent on the assumed model due to that different shape and different domain spacing produce scattering at different $q$, which can be all included in the integral.

The most straightforward morphological information can be extracted is domain spacing, which describes the characteristic length scale of average composition variation. According to thermal dynamics, phase separation is determined by the interplay between entropy and enthalpy of mixing.$^{[92]}$ During the thin film morphology formation, composition fluctuation occurs by either spinodal decomposition or nucleation and growth. Both of the morphology formation mechanisms induce periodic modulation of composition. The average length scale of the periodic modulation is usually called domain spacing. Domain spacing can be represented by the characteristic mode length scale or characteristic median length scale. The characteristic mode length scale is defined as $d_{\text{mode}} = 2\pi / q_{\text{peak}}$, where $q_{\text{peak}}$ is the
peak location of the scattering maximum. The characteristic median length scale is defined as 
\[ d_{1/2} = \frac{2\pi}{q_{1/2}} \], where \( q_{1/2} \) is the location of the half maximum of ISI. In some cases, large part of scattering signals can also originate from orientational correlation, instead of compositional correlation. Compositional domain spacing and orientational domain spacing should be used to distinguish them in these cases. Extended discussion on orientational correlation will be given in the latter section.

Previously, domain spacing and domain size have been interchangeably used frequently. It should be emphasized that these two terms are conceptually different. Domain spacing originates from the periodic modulation of composition and does not depend on the shape of the domain. According to Babinet’s principle, the scattering cannot identify the relative arrangement of different domains. For example, the scattering cannot distinguish which component is matrix or dispersion in matrix-dispersion paradigm. On the other hand, domain size can be calculated based on the model and shape assumed. For instance, in a 2D geometry of circular dispersion with a hexagonal close-packed structure in a matrix, the diameter of the circular dispersion can be calculated by 
\[ d = D \sqrt{\frac{2\sqrt{3}}{\pi}} v \], where \( D \) is domain spacing and \( v \) is the volume fraction of the dispersion phase and defined by 
\[ v = \frac{R \rho_r (1 - x_{f2}) - x_{f2}}{(R \rho_r + 1)(x_{f1} - x_{f2})} \]. The overall blend mass ratio \( R \), the relative mass density ratio \( \rho_r = \frac{\rho_b}{\rho_a} \) can be known beforehand and the fractional composition in each phase \( x \) can be measured by STXM.\[^{93}\]
Another frequently extracted morphological parameter is relative average composition variation, also called relative average *domain purity*. Based on previous Monte Carlo modeling, \(^{[94]}\) domain purity is a crucial morphological parameters to impact charge separation and transport. As mentioned above, the relative average composition variation is proportional to the square root of ISI across the q range probed. The relative average composition variation is equivalent to relative domain purity in 2-phase model. In the more complicated cases where three phase morphology is needed to be considered, the relative domain purity becomes complicated. If calibration is used, absolute average composition variation can be determined. In OPVs, average composition variation is usually observed to be correlated with FF due to the fact that higher domain purity induces less geminate and nongeminate recombination given the phase separation does not change a lot.

Here we continue to use DPP:PCBM BHJ to exemplify the determination of domain spacing and domain purity. Lorentz corrected 1D R-SoXS profiles at varying energies are plotted in **Figure 2.2a**. All profiles except for 270 eV display a well-defined single peak around 0.14 nm\(^{-1}\). At 270 eV, besides of the peak around 0.14 nm\(^{-1}\), a tail at low q can be readily observed, indicating a strong scattering peak located at q<0.1 nm\(^{-1}\). It should be noted that at resonant energy (284.2 eV), compositional contrast is dominant, while at non-resonant energy (270 eV), vacuum contrast is dominant. Although the R-SoXS profiles at 270 eV and 284.2 eV show peaks with same q location, the origins are never the same. The same peak location of 270 eV and 284.2 eV implies that the compositional inhomogeneity correlates with electron density inhomogeneity. To verify the scattering profiles represent the material contrast instead of vacuum contrast, the total ISI of each profiles have been calculated and
plot with energy as shown in Figure 2.2b. It is clear that the ISI trend follows with the simulated material contrast of DPP:PCBM.

Figure 2.2. (a) Lorentz-corrected R-SoXS profiles of DPP:PCBM at various energies. (b) integrated scattering intensity (ISI) plot along with magnitude of momentum transfer $q$. (c) Energy dependent ISI plot with simulated material contrast DPP:PCBM. (d) Lorentz-corrected R-SoXS profile of TPD:PCBM at resonant energy, overplotted with component log-normal fit peaks.
2.4 Molecular orientational ordering

In R-SoXS measurements, the material contrast originating from compositional variation is utilized and the scattering is highly sensitive to the chemical moieties. The incident light polarization dependence of the transition dipole moment (TDM) of organic materials is not yet utilized and the orientational contrast is neglected. If polarized soft X-ray is used, the orientational contrast can be probed and the R-SoXS measurements are preferentially called P-SoXS as abbreviation of polarized soft X-ray scattering. The highly polarized soft X-ray generated in modern synchrotrons provides P-SoXS unique opportunities of extracting morphological parameters which are hardly probed by other conventional methods. Among them, molecular orientational ordering can be resolved based on careful modeling of contrast functions.

Before the advent of P-SoXS, the investigation of molecular orientational ordering is mainly restricted to highly crystalline materials, which produce strong diffraction. Due to the sensitivity of soft X-ray to anisotropic molecular bonding, P-SoXS is capable of probing the molecular orientational ordering in crystalline domains, as well as amorphous domains. The average spatial modulation length scale of molecular orientational ordering is called orientational correlation length (OCL), which represents the characteristic length scale across which the molecular orientational ordering is reserved. OCL was named to be the counterpart of compositional correlation length (CCL), which describes the average spatial modulation length scale of compositional variation. An example will be given in chapter 6 regarding how to determine OCL from P-SoXS scattering profiles.
2.5 Molecular orientation relative to the donor/acceptor interface

In P-SoXS measurements, anisotropic 2D scattering patterns sometimes can be observed on the organic thin films without overall in-plane directional ordering.\textsuperscript{[95,96]} This phenomenon is fundamentally different from the anisotropic scattering pattern of thin films with global directional ordering. The polarization dependent anisotropic 2D scattering patterns observed in P-SoXS occur at resonant energy and rotate with the polarization of incident soft X-ray, rather than the overall film orientation.\textsuperscript{[97]} π-conjugated organic molecules are often anisotropic due to the existence of the ring structure. When mixing multiple organic molecules together, the molecules usually stack along C\textsubscript{1s-π*} transition dipole moment (TDM) direction. At the D/A interface, the molecular alignment is face-on if the TDM is orthogonal to the interface and edge-on if the TDM is along with the interface. In recent work from Eliot Gann et al., 2D P-SoXS scattering patterns of different molecular alignments relative to the D/A interface have been simulated. The corresponding experimentally measured 2D scattering patterns have also been demonstrated. For conceptual simplicity, P3HT with uniaxial symmetry along backbone and PC\textsubscript{61}BM with isotropic symmetry were used as models. Different compositional arrangements and molecular alignments relative to the D/A interfaces, along with simulated as well as measured 2D scattering patterns are presented in that work.\textsuperscript{[97]} It is clear that the scattering patterns become anisotropic only at resonant energies. Moreover, the anisotropic direction flips at different energies, depending on whether π* or σ* transition is excited.

The degree of molecular orientation (DMO) is used as the parameter to quantify the direction and extent/magnitude of molecular orientation with respect to the D/A interface.
Exceptional correlation between DMO and device performance, such as FF and $J_{sc}$ has been established.[95] Anisotropic optical constants of constitute materials are the prerequisite for the determination of DMO, of which many have been well-documented in the literature.[80] To quantify the molecular orientation relative to the D/A interface, we define a phenomenological morphological parameter - anisotropy ratio $A(E)$ as

$$
A(E) = \frac{\langle ISI_{\parallel} - ISI_{\perp} \rangle}{\langle ISI_{\parallel} + ISI_{\perp} \rangle}
$$

The accurate determination of anisotropy ratio of a given system can be fulfilled by multiplying a fraction constant between -1 and 1 to make the experimentally measured anisotropy ratio matches with the extreme anisotropy ratio. In real experiments, the acquisition of high quality anisotropic optical constants of a given material may be not feasible. If so, high-quality and well-documented anisotropic optical constants can be used given that the ratio of aromatic to aliphatic carbon atoms is close for the two materials.

It is worth to stress that OCL and DMO extracted from P-SoXS technique are completely different concepts. There have been confusions about these two concepts. Polarization dependent anisotropic X-ray scattering (PAXS) is generated by local molecular orientation composition correlation (MOCC). It is generated by the correlation between local molecular alignment and spatial compositional changes. On the other hand, OCL describes the characteristic modulation length scale of orientational ordering. The scattering of OCL can be generated by molecular alignment itself and the corresponding 2D patterns can be anisotropic or isotropic.
Chapter 3

Control of mesoscale morphology and photovoltaic performance in Diketopyrrolopyrrole-based small band gap terpolymers

3.1 Preface

Morphology control is one of the key strategies in optimizing the performance of organic photovoltaic devices, particularly for devices made from diketopyrrolopyrrole (DPP)-based donor polymers. The design of DPP-based polymers that provide high power conversion efficiency (PCE) presents a significant challenge that requires optimization of both energetics and morphology. Herein, we report a series of high performance, small band gap DPP-based terpolymers via two-step side chain engineering, namely introducing alternating short and long alkyls for reducing the domain spacing and inserting alkylthio for modulating the energy levels. The new DPP-based terpolymers are compared to delineate how the side chain impacts the mesoscale morphology. By employing the resulting polymer PBDPP-TS, the new polymer solar cell (PSC) device realized a good balance of a high $V_{oc}$ of 0.77 V and a high $J_{sc}$ over 15 mA/cm$^2$, and thus realized desirable PCE in excess of 8% and 9.5% in single junction and tandem PSC devices, respectively. Our study indicates that dual side chain engineering is a useful strategy to manipulate the morphological characteristics of conjugated terpolymers, and thereby greatly optimize their photovoltaic performance.
This work has been published in Advanced Energy Materials (Adv. Energy Mater. DOI: 10.1002/aenm.201601138). This is a collaborative work between NCSU and Chinese Academy of Sciences (CAS). Jianhui Hou group from CAS synthesized the materials and fabricated the devices. Harald Ade group in NCSU conducted X-ray based morphology characterization and helped construct the morphology - performance correlation. I am the co-first author in this paper.

3.2 Introduction

The morphological characteristics of DPP-based polymer:phenyl-C$_{71}$-butyric acid methyl ester (PC$_{71}$BM) blends at the mesoscale have been recently recognized as critical factors in determining the photovoltaic parameters of PSCs.$^{[98]}$ That is to say, high performance DPP-based polymers can only be achievable with a mesoscale morphology that has a length scale close to the exciton diffusion length. Molecular design is a feasible tool to achieve this goal. For instance, Janssen’s group found the fiber width of DPP-based polymers can be reduced by shortening the length of alkyl chains, which afforded considerably enhanced EQE and $J_{sc}$ accordingly.$^{[99]}$ Recently, Kim et al.$^{[100]}$ found that the crystallinity, mobility and photovoltaic performance of DPP-based polymers could be optimized by a terpolymer approach based on three monomers, including DPP, selenophene and thiophene. The resulting DPP-based polymers in both cases exhibited excellent PCE values over 7%. In addition, terpolymer design strategy is a feasible strategy used to create other kinds of semiconducting polymers with tailored energy levels and optical band gaps, and optimal crystalline behaviors.$^{[101-104]}$ Applying alkyl engineering and terpolymer strategies
simultaneously may lead to highly tunable morphological properties and thus greatly enhanced device performances.

In this work, we show that the mesoscale morphology of DPP-based polymers can be finely manipulated by a two-step molecular design strategy, i.e., a series of novel PBDPP terpolymers, by stepwise modulation of the side chains appended to the donor and acceptor units. First, the crystallinity and mesoscale morphology of the PBDPP terpolymers can be systematically controlled by tuning the ratio between short and long alkyls of DPP units. Second, optimizing the open-circuit voltage without sacrificing the other parameters by introducing alkylthio side chains in the BDT-T units. On the basis of quantum-chemical calculations, alkylthio-substituted BDT-T (BDT-TS) was expected to obtain a theoretical HOMO level ~0.24 eV lower than the BDT-T (Figure 3.1). In this regard, we may increase the $V_{oc}$ of PBDPP polymer by sulfur substitution of BDT-T, which lowered HOMO level without sacrificing the high current density ($J_{sc}$) of the original and well-defined backbone. The impact of stepwise side chain engineering on the band gaps, the molecular energy levels, the mesoscale morphologies of the DPP-based terpolymers was investigated by means of 2D-grazing incidence wide-angle X-ray scattering (GIWAXS) and resonant soft X-ray scattering (R-SoXS) and correlated well with their photovoltaic properties. More importantly, our work establishes excellent and direct correlations between morphological parameters (long period, domain purity variations) and device parameters ($J_{sc}$, $FF$) in new terpolymer materials for the first time.
Figure 3.1. Molecular design of DPP-based terpolymers with two-step side chain engineering starting from PBDPP copolymer, and the evolution of HOMO levels of BDT-T unit by inserting sulfur atom.

3.3 Results and Discussion

3.3.1 Basic properties of DPP based terpolymers

All of the PBDPP terpolymers are composed of identical backbones, but have different composition and distribution of the alkyl chains, i.e., 2-ethylhexyl (EH) and 2-octyldodecyl (OD) in DPP unit. The molecular weight of these terpolymers were determined by high temperature gel permeation chromatography (GPC) using 1, 3, 5-trichlorobenzene (TCB) as eluent at 140 °C. The resulting number-averaged molecular weights are $M_n = 81$ kg/mol for
PBDPP-T1, $M_n=100$ kg/mol for PBDPP-T2, and $M_n=131$ kg/mol for PBDPP-T3, with similar polydispersity (PDI) values around 4. A copolymer PBDPP-OD ($M_n=114$ kg/mol, PDI=3.6) was also synthesized as control. The terpolymers exhibited moderate solubility (4~8 mg/ml) in chlorobenzene and chloroform. As observed from thermogravimetric (TGA) curves, all PBDPP polymers showed a decomposition temperature over 400 °C. The UV-vis absorption spectra of the PBDPP-Tx terpolymers were measured both in solution and thin film, as shown in Figure 3.2b and c. Compared to the PBDPP-OD, these terpolymers exhibit a slightly red-shifted absorption maximum and absorption onset by approximately 5 nm in both film and dilute solution forms. The optical band gaps ($E_{g \text{opt}}$) of terpolymers are approximately 1.41 eV. Cyclic voltammetry (CV) measurements were used to estimate HOMO energy levels of these terpolymers by using the onset of oxidation potential and lowest unoccupied molecular orbital (LUMO) energy levels were deduced by addition of $E_{g \text{opt}}$ to the HOMO energies. Compared with PBDPP copolymer, all of the terpolymers exhibited an identical HOMO level of -5.27 eV.
Figure 3.2. Basic properties of PBDPP polymers: (a) TGA curves; (b) absorption spectra in CF solution and (c) thin film; (d) energy levels.

In many cases, polymer crystallinity and crystallite preferential orientation have been shown to impact charge transport within active layers\footnote{105,106}. Here, grazing-incidence wide-angle X-ray scattering (GIWAXS) was used to study the molecular packing of the pure polymer films to reveal the impact of different side chains on the overall crystallinity. The in-plane and out-of-plane $15^\circ$ sector averages of pure polymer are displayed in Figure 3.3a. From the GIWAXS profiles, all five DPP-based polymers exhibit a defined π-π stacking (010) peak along out-of-plane direction, mirrored with lamellar stacking (100) peak along in-plane
direction. It indicates that the beneficial face-on preferential orientation relative to the substrate remains irrespective of the side-chain engineering. The 2D GIWAXS patterns as shown in Figure 3.2b and c further verify the face-on preferential orientation of polymer crystallites. Additionally, the π-π stacking distances of all pure polymers in the out of plane direction are approximately \( 3.8 \ \text{Å}^{-1} \) (Table 3.1), indicative of similar charger transport property. However, the broad (100) and (010) peaks and weak higher order (i00) peaks imply that the side chain engineering employed in this study does not improve the relatively low crystallinity and low molecular ordering exhibited by PBDPP-OD.
Figure 3.3. (a) Out-of-plane and in-plane 15° sector average GIWAXS profiles of pure terpolymer films. The profiles of different films are offset vertically for clarity. (b) and (c) are the representative 2D GIWAXS patterns for DPP-T1 and DPP-T3.

Table 3.1. Optical properties and molecular energy levels of the PBDPP terpolymers and PDPP-OD.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\lambda_{\text{peak}}/\lambda_{\text{edge}}$ solution[nm]</th>
<th>$\lambda_{\text{peak}}/\lambda_{\text{edge}}$ film [nm]</th>
<th>$E_g$ [eV]</th>
<th>HOMO [eV]</th>
<th>LUMO [eV]</th>
<th>$d_{010}$ [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBDPP-OD</td>
<td>765/810</td>
<td>770/880</td>
<td>1.41</td>
<td>-5.27</td>
<td>-3.86</td>
<td>3.79</td>
</tr>
<tr>
<td>PBDPP-T1</td>
<td>770/830</td>
<td>775/880</td>
<td>1.41</td>
<td>-5.27</td>
<td>-3.86</td>
<td>3.80</td>
</tr>
<tr>
<td>PBDPP-T2</td>
<td>770/830</td>
<td>775/880</td>
<td>1.41</td>
<td>-5.27</td>
<td>-3.86</td>
<td>3.82</td>
</tr>
<tr>
<td>PBDPP-T3</td>
<td>770/830</td>
<td>775/880</td>
<td>1.41</td>
<td>-5.27</td>
<td>-3.86</td>
<td>3.81</td>
</tr>
<tr>
<td>PBDPP-TS</td>
<td>775/835</td>
<td>775/885</td>
<td>1.40</td>
<td>-5.34</td>
<td>-3.94</td>
<td>3.80</td>
</tr>
</tbody>
</table>
3.3.2 Photovoltaic performance and mesoscale morphology

Single junction PSCs with a conventional device structure of ITO/PEDOT:PSS/PBDPP-Tx:PC$_{71}$BM/Mg/Al were fabricated by spin-coating of a 1:2 terpolymer:PC$_{71}$BM mixture from a chlorobenzene/1,8-diiodooctane (97/3) solvent mixture. The corresponding device performance parameters (Table 3.2) were measured under AM 1.5G 100 mW/cm$^2$ condition with the combination of Class AAA solar simulator and a KG3 filtered silicon reference cell. The difference between the $J_{sc}$ values from $J$-$V$ and $EQE$ tests (Figure 3.4) is below 5%. Compared to the poor performance of PBDPP-OD, PBDPP-Tx terpolymers-based PSCs showed high $J_{sc}$ values with 2-3 fold enhancement (see Figure 3.4a). The device performance of PBDPP-OD:PC$_{71}$BM is rather poor, which indicate that better molecular ordering doesn’t necessarily leads to good device performance. We note that the overall shape of $EQE$ curve does not always follow the same trend with that of UV-vis absorption spectra of terpolymers, which means the relative photo-response from PDPP3T or PCBM is highly morphology dependent, mirroring similar previous observations in PDPP3T.

![Figure 3.4](image)

**Figure 3.4.** (a) $J$-$V$ and (b) $EQE$ curves of the DPP-based polymers.
Table 3.2. Photovoltaic parameters of the conventional PSCs based on the blends of PBDPP-based polymer:PC$_{71}$BM.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$V_{oc}$ [V]</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>$FF$</th>
<th>$PCE_{max(ave)}$ [%]</th>
<th>Long Period [nm]</th>
<th>Domain Purity [%] [±0.01]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBDPP-OD</td>
<td>0.74</td>
<td>4.3 (4.0)</td>
<td>0.67</td>
<td>2.13 (1.9)</td>
<td>128.0</td>
<td>1.00</td>
</tr>
<tr>
<td>PBDPP-T1</td>
<td>0.71</td>
<td>12.6 (12.5)</td>
<td>0.64</td>
<td>5.82 (5.6)</td>
<td>63.4</td>
<td>0.95</td>
</tr>
<tr>
<td>PBDPP-T2</td>
<td>0.71</td>
<td>15.5 (15.8)</td>
<td>0.65</td>
<td>7.19 (7.0)</td>
<td>43.7</td>
<td>0.94</td>
</tr>
<tr>
<td>PBDPP-T3</td>
<td>0.71</td>
<td>17.3 (17.3)</td>
<td>0.58</td>
<td>7.03 (6.8)</td>
<td>26.8</td>
<td>0.79</td>
</tr>
<tr>
<td>PBDPP-TS</td>
<td>0.77</td>
<td>15.7 (16.0)</td>
<td>0.64</td>
<td>8.04 (7.8)</td>
<td>35.7</td>
<td>0.93</td>
</tr>
</tbody>
</table>

Atomic force microscopy (AFM) is used to study the surface morphology of these blend films (Figure 3.5) and the corresponding surface roughness values are also indicated. PBDPP-OD:PCBM showed a rougher surface and larger length scale of phase separation from the phase image compared to the terpolymer:PCBM blends. However, there exists quite limited differences between those terpolymers with a surface roughness of 1~2 nm though PBDPP-T1:PC$_{71}$BM film exhibits a slightly coarser feature of aggregates. To probe the bulk, the high spatial resolution from a few nanometers to several microns and contrast tunability from material contrast to mass-thickness contrast make R-SoXS one of the most quantitative tools to probe the compositional domain structure of polymer composites, particularly polymer:fullerene blends. To gain insight into the impact of alkyl chains on the bulk morphology of DPP-based terpolymers, R-SoXS was employed in a transmission geometry. R-SoXS profiles of all blends (Figure 3.6a) show well-defined peaks, corresponding to domain spacing with a long period $d=2\pi/q$, where $q$ is the mode of the spatial frequency distribution, of 128.0, 63.4, 43.7, and 26.8 nm for the PBDPP-OD, PBDPP-T1, PBDPP-T2, and PBDPP-T3-based blend films, respectively. In comparison with the PBDPP copolymer PBDPP-OD blend, the blend films based on PBDPP-Tx terpolymers exhibits substantially
reduced long periods. This observation is also verified by the TEM images shown in Figure 3.6b. In addition, the average composition variation (relative purity variations) can be extracted via the integration of R-SoXS profiles over the \( q \) range probed. For the BHJ systems with a straightforward morphology, the relative domain purity variation is proportional to the square root of the integrated scattering intensity (ISI), where 
\[
\text{ISI} = \int I(q)q^2dq.
\]
Here, the relative purity variations of all blend films are normalized to the highest relative purity, assigned a value of 1. The long period and relative domain purity are tabulated in Table 3.2. With the increase of molar ratio of short chain (x), the long period (domain spacing) and relative domain purity are reduced in PBDPP-Tx terpolymers gradually. As is well known, a small long period is beneficial for maximizing the D/A interface area and improving charge generation and thus \( J_{sc} \) when the length scale of phase separation is much higher than the typical exciton diffusion length (20 nm), while a low relative domain purity leads to a detrimental increased charge recombination and thus poor \( FF \). Specifically, the PBDPP-T3:PCBM blend has on average more impure domain than PBDDP-OD:PCBM blend yet a very small long period of 26.8 nm, which is approaching the optimum length scale on the order of the exciton diffusion length, consistent with its enhanced EQE (Figure 3.4b). Accordingly, a highest \( J_{sc} \) and lowest \( FF \) are observed in PBDPP-T3-based PSC. In contrast, a highest \( FF \) and lowest \( J_{sc} \) are recorded in PSC based on PBDPP-T1. Owing to the optimized trade-off between \( J_{sc} \) and \( FF \), PBDPP-T2 with a monomer ratio of 2:1 is the highest performing one in the above-mentioned PBDPP-Tx terpolymers.
Figure 3.5. AFM images of blend films of various PBDPP polymer:PCBM and the corresponding surface roughness values are also indicated.

3.3.3 Direct Correlation of morphological and device parameters

In order to further quantify the relationship between device performance and morphological parameters extracted from R-SoXS, plots of $J_{sc}$ vs. dominant domain spacing and FF vs. relative domain purity are displayed in Figure 3.6c and 3.6d, respectively. Remarkably, linear correlations are found in both plots, i.e., purer domain contributes to higher FF and smaller domain results in higher $J_{sc}$ in this class of PBDPP polymers. The precise reason for such linearity are currently not known and require additional study to understand. FF generally depends on a number of factors, such as mobility and bimolecular recombination coefficient, which in turn depends on the square of the current density and domain purity. Regarding $J_{sc}$ and considering round fibrils, the interfacial area is proportional to the diameter. If $J_{sc}$ is limited by exiton harvesting, indeed $J_{sc}$ should show a linear relation with long period if the spacing of the fibrils scales with its diameter. Indeed, the $J_{sc}$-long period correlation in our study is consistent with the previous trend that smaller fibrillar
width leads to higher EQE and $J_{sc}$ in other DPP-based copolymers as observed by Janssen and co-workers using TEM.

The results presented above established that the mesoscale morphology can be highly manipulated by side chain engineering in a new class of PBDPP terpolymers. Considering that the long period changes considerably and anti-correlates with $J_{sc}$ without much deviation from linearity, higher $J_{sc}$ over 20 mA/cm$^2$ may be possible if the long period decrease to 20 nm or below. Simultaneous control over purity would further improve the performance. It is noteworthy that all of the R-SoXS profiles are completely dominated by a single log-normal distribution and this is the first time that such strong correlations have been reported for $J_{sc}$ and $FF$. Our PBDPP terpolymer might be a superb and simple model system to understand the morphology creation and its impact. Clearly, these PBDPP terpolymers with different alkyl chains have different Hansen solubility parameters$^{[107]}$ and thus exhibit likely different miscibility with the fullerene, similar to the differences observed for PSBTBT-08:fullerenes$^{[108]}$. The molecular interactions of donor:acceptor pairs may be the fundamental factor dominating the phase purity and thus morphology and performance.
Figure 3.6. (a) Thickness normalized and Lorentz corrected R-SoXS profiles of various blend films of PBDPP-OD and PBDPP terpolymers; (b) TEM image of PBDPP-TS:PC$_{71}$BM blend film; (c) Plot of the $J_{sc}$ of PSCs for DPP-based polymers versus the respective average long period obtained from R-SoXS; (d) Plot of FFs of PSCs for DPP-based polymers versus the respective domain purities obtained from R-SoXS. The correlation coefficients ($R^2$-squared) of both plots are also indicated. The dashed lines in Figure 3c are added to estimate the long period for a higher $J_{sc}$ above 20 mA/cm$^2$.

3.4 Conclusions

In summary, we demonstrate a two-step side chain engineering strategy to significantly improve the mesoscale morphology and device performance of PBDPP copolymers. A series of new PBDPP terpolymers were designed, synthesized and characterized. We found that domain purity correlates positively with the device FF. In contrast, $J_{sc}$ has a reciprocal relationship with long period in this class of terpolymers. Remarkably, an alkylthio-
substituted terpolymer PBDPP-TS afforded a high \textit{PCE} of \(\sim 8\%\) and \(\sim 9.5\%\) in single and double junction respectively, which is seldom achieved in the copolymer analog for such a low band gap of \(1.4\ \text{eV}\). The exceptional photovoltaic performance of PBDPP-TS are ascribed to the relatively small characteristic domain spacing and high average relative domain purity as evidenced by R-SoXS characterizations. We also speculate that better control of purity will greatly improve performance toward \(10\%\) efficiency. Although the stepwise side chain engineering has been exemplified with PBDPP copolymers, its utility can be easily expanded to other kinds of well-defined copolymers and trigger efficiency breakthroughs in novel terpolymers for photovoltaic and related applications.
Chapter 4

Morphology evolution of small molecule bulk-heterojunction solar cells during solvent vapor annealing

4.1 Preface

Along with the development of polymer:fullerene solar cells, small molecule:fullerene bulk-heterojunction organic solar cells (SM-OSCs) have also shown rapid and continuous progresses in the last two decades. Compared with polymer-based solar cells, SM-OSCs possess extra advantages, such as well-defined molecular structure, high reproducibility in synthesis as well as feasibility of solution processability and vacuum processability. Aside from novel molecular design of small molecule donor, better understanding and control of active layer morphology is the other primary factor contributing to the remarkable progresses in power conversion efficiency (PCE) of SM-OSCs. In this collaborative project, the active layer morphology evolution of a high-performing small molecule BHJ based on UU07:PC$_7_1$BM during solvent vapor annealing have been systematically investigated and correlated with photophysical properties as well as device performances.

This is a collaborative work between Christoph Brabec group from Friedrich-Alexander-University Erlangen-Nuremberg (FAU) and Harald Ade group from NCSU. Christoph Brabec group fabricated the devices and conducted the device physics study, including mobility measurement, charge carrier density measurement and light intensity
dependent J-V measurement. Harald Ade group conducted the morphology investigation, including R-SoXS, GIWAXS and specular XRD. I am a co-first author in this project. This work has been published in Advanced Energy Materials (Adv. Energy Mater. DOI: 10.1002/aenm.201502579).

4.2 Introduction

Small molecule organic solar cells (SM-OSCs) have attracted extensive attention due to their well-defined molecular structures, high reproducibility, easy purification as well as low fabrication costs achievable via solution-processing methods. The dynamic development in solution-processed SM-OSCs with the most promising bulk heterojunction (BHJ) configuration has recently led to high power conversion efficiencies (PCEs) of over 9%, primarily due to improved molecular design and enhanced morphological control. Apart from a smart molecular design, microstructure engineering is one of the key strategies to achieve well-ordered and crystalline domains, allowing to further improve device performance. Generally, BHJ composites consists of a donor (D) and an acceptor (A) that are arranged in multiple phases, among them a crystalline donor and aggregated acceptor phase as well as a mixed amorphous or disordered regime resulting from partial miscibility of the components. This remarkable interpenetrating network with domain sizes on the ≈ 10 nm length scale as well as a suitable D/A interfacial area is beneficial to enhanced exciton dissociation and improved charge transport, and thus yields enhanced device efficiency. Besides, a well-connected acceptor network in the amorphous mixed regions can promote effectively geminate pair splitting, and thus result in near unity internal quantum efficiency.
for a device.\cite{116} However, phase separation is a complex process often resulting in metastable morphologies due to rapid solvent evaporation, unbalanced solubilities or unmatched surface energies between the components, the ink and the substrate.\cite{117} Beyond the design and selection of suitable materials several strategies to effectively influence and modify the nanoscale morphology were demonstrated for small molecular systems, including additives, thermal and solvent vapor annealing (SVA),\cite{118,119} and postadditive soaking,\cite{120} etc. These morphological modifications directly impact the optical and electronic properties of the BHJ layer and also influence the competition between carrier extraction and recombination.\cite{121,122} In order to direct these efforts to design new photovoltaic materials and thin film nanoscale architectures, an in-depth understanding of BHJ microstructure and its kinetic evolution as a function of post treatment is critical.

Among these high performance SMOSCs with PCEs of over 9%,\cite{123} some systems applied SVA to controlling the blend morphology and thus improving short circuit current density ($J_{sc}$) and fill factor (FF) in devices. This widely used strategy effectively improve donor crystallinity, enhance fullerene aggregation and improve both, domain size and phase purity. For instance, Sun et al. demonstrated that a higher efficiency of 9.3%, as compared to that without SVA treatment (5.2%) was achieved for benzodithiophene terthiophene rhodanine (BTR) based blends. More recently, Kan et al. applied SVA treatment combined with thermal annealing (TA) to achieve a recorded PCE of 10.1% in devices based on DRCN5T as a donor. Although the device efficiencies subject to the SVA treatments are promising, the kinetics of morphology evolution during SVA is not investigated in detail. Thus, understanding the time dynamic effects of SVA on the morphology evolution plays a
vital role in facilitating the applications of SVA treatment and developing SVA free material systems.

**Scheme 4.1.** Molecular structure of the investigated UU07.

In this manuscript we explore the correlation between photovoltaic performance and morphology evolution as a function of SVA time. The subject of this study is the small molecular donor 2,2′-[5′,5′′-(N-(2-hexylnonyl)-dithieno[3,2-b:2′,3′-d]pyrrole-2,6-diyl)-bis(3,4′-dihexyl-2,2′-bithien-5,5′-diyl)]-bis(methane-1-yl-1-ylidine) dimalononitrile (UU07, see **Scheme 4.1**), blended with [6]-phenyl-C61-butyric acid methyl ester (PCBM) as acceptor. The performance of UU07:PCBM is extremely sensitive to the SVA process using chloroform as solvent, and the optimized blend exhibits a hugely improved PCE up to 6.1% with very high FFs of over 70% as compared to untreated device
with a PCE of app. 1.1%. Prior investigations directed toward understanding the morphology of UU07:PCBM blend films by morphological characterizations highlighted the enhanced donor crystallinity and increased fullerene segregation for active layers processed with optimized SVA condition. Our previous work studying the optimized SVA time for a series of oligomers also confirmed this general trend. Hence, we further delineate the causative relations between blend morphology, charge generation, transport properties and device performance of UU07:PCBM blends as a function of annealing time. We find that the photovoltaic and charge transport parameters follow a nonmonotonic behavior with SVA time which is implying that the composite undergoes a plurality of microstructure modifications. These microstructure modifications were further investigated by optical microscopy, atomic force microscopy (AFM), grazing incidence wide angle X-ray scattering (GIWAXS), X-ray diffraction (XRD) and resonant soft X-ray scattering (R-SoXS). Moreover, the various microstructures were categorized according to their electro-optical properties. Our aim is to provide a schematic summary insight into the time-dependent morphological evolution and its relation to charge transport, carrier recombination kinetics and the observed trade-offs in J<sub>sc</sub> and FF in device performance.
4.3 Results and discussion

4.3.1 Device performance

Figure 4.1. (a) short-circuit current density ($J_{sc}$) and photogenerated current density ($J_{ph}$) at reverse bias of -3 V as a function of SVA times; (b) FF at standard and low illumination conditions; (c) $V_{oc}$ at standard illumination condition; (d) PCE at standard illumination conditions as a function of SVA times.
A conventional device structure, ITO/PEDOT:PSS/UU07:PCBM (1:2, wt%)/Ca/Al, was used in this work. SVA was varied between 0 – 240 s, allowing to control and improve the nanoscale microstructure with respect to device performance. The resulting photovoltaic parameters, including open circuit voltage ($V_{oc}$), $J_{sc}$, fill factor and PCE were measured under AM 1.5 solar illumination and are shown in Figure 4.1. As the SVA time increases from 0 to 90 s, all of the device parameters, especially $J_{sc}$ and FF undergo a monotonic improvement. The maximum PCE is found at 90 s of SVA with over 6%. In addition, extending the SVA time from 90 to 240 s, the $J_{sc}$ and FF values as well as the PCEs decreased gradually. Note that the same trend holds for the external quantum efficiency (EQE) data (Figure 4.2), being consistent with the $J_{sc}$ values (see Figure 4.1a). Figure 4.1a again shows the trend for the reverse bias photocurrent measured at −3V ($J_{ph}$ (−3V)), with the reverse photocurrent ($J_{ph} = J_L$)
being defined as the difference between the dark ($J_D$) and light current density ($J_L$) under one sun. At large reverse voltage ($−3V$), the photocurrent is expected to saturate and all free carriers are effectively extracted due to the strong internal field in devices. The $J_{ph}$ at $−3V$ bias again shows the same nonmonotonic behavior. The device at 90 s SVA exhibits the highest value $J_{ph}$ of app. 11 mA cm$^{-2}$. Besides, the $J_{ph}$ of devices without (0 s) and with long (180 and 240 s) SVA treatment yield a significantly lower saturated photocurrent. These data indicate that device at 90 s SVA shows only negligible voltage-dependent geminate recombination losses, whereas the photocurrent of devices without and with unsuitable SVA treatments was limited by a combination of voltage-dependent geminate recombination and nongeminate recombination. Overall, the good correlation between $J_{sc}$ and $J_{ph}$ ($−3V$) and their quite comparable magnitudes highlight that the devices were already quite well optimized with respect to thickness. Not surprisingly, these results are consistent with the time-dependent optical absorption of UU07:PCBM blends after SVA treatment. The different optical absorption as a function of varying SVA times reflects the modified microstructure and phase purity and is expected to directly impact the charge generation profiles. Apart from the $J_{ph}$ data, we also measured the current density–voltage ($J$–$V$) curves of devices at an illumination intensity of only 0.1 sun in order to gain more insight into the different recombination mechanisms. For all annealing times we find that the FF measured at 0.1 sun is higher than the one at 1 sun (see Figure 4.1b). The relative decrease in FF from 0.1 to 1 sun is smallest for 90 s SVA, which confirms that these processing conditions provide the more suitable blend morphology, ensuring efficient charge carrier extraction and thus minimizing bimolecular recombination losses. The FF for longer or shorter SVA times result
in a significantly larger variation with light intensity from 0.1 to 1 sun, primarily indicating enhanced recombination losses resulting from the nonoptimum distribution of domain compositions as discussed below.\textsuperscript{[124,125]}

**Figure 4.3.** Optical microscopy images of the UU07:PCBM blends films without and with SVA treatments as a function of time.
Figure 4.4. AFM topography images of UU07:PCBM blend films as a function of annealing time, including (a) wo SVA, (b) 30s SVA, (c) 60s SVA, (d) 90s SVA, (e) 120s SVA, (f) 150s SVA, (g) 180s SVA, (h) 240s SVA. The bottom side also shows the corresponding phase for each blend film. The scanning area is $5 \times 5 \mu m^2$ for all images.

Before discussing morphological characterizations, we again refer to the optical absorption spectra of the blends prepared on glass substrates as well as their corresponding EQE spectra for different SVA periods. A proper SVA treatment is able to gain back molecular ordering and results in an enhanced absorption coefficient. The same trend holds for the EQE data and confirms that SVA indeed facilitates reordering. In addition, a digital photo of the relevant blends (see Figure 4.3) indicates that the longer SVA time damages the optimized BHJ morphology required for a high photovoltaic performance. The results are also consistent with the absorption spectra of these blends. In order to directly determine the morphological characteristics and further understand the fundamentals of SVA kinetics, we
applied optical microscopy, AFM, GIWAXS, XRD and R-SoXS. Optical microscopy images of the UU07:PCBM blended films without and with SVA treatments as a function of time are shown in Figure 4.3. These data showed that the films with SVA treatments from 0 to 90 s are homogenous without any obvious large crystallites, probably suggesting that all the oligomers are homogeneously dispersed in the blends. However, further extending SVA time (from 90 to 240 s) results in more rough films with significant phase separation and large domain size. Similarly, the AFM images of the various composites as a function of annealing time (see Figure 4.4) showed strong support and account for the optical absorption and microscopy data. SVA treatment significantly influences the film quality with enhanced nanoscale phase separation and bi-continuous network formation upon shorter SVA treatment (see Figure 4.4b–d), and the formation of large domain features at longer SVA periods (see Figure 4.4e–h). Note that the large domain sizes on the length scale of hundred nanometers in blends processed with longer SVA time cause the poor charge separation process, resulting from the longer distance for exciton diffusions.
4.3.2 Molecular packing and mesoscale morphology

Figure 4.5. 2D GIWAXS patterns of UU07:PCBM blends at different SVA times.
UU07:PCBM blends treated with different SVA times were further examined via GIWAXS to clarify the molecular packing and preferential orientation distribution. 2D GIWAXS patterns of the relevant UU07:PCBM blends are presented in Figure 4.5. All images except for the blend with 240 s SVA show clear out-of-plane (OOP) diffraction peaks (100) (200) (300) originating from UU07 lamellar stacking (Figure 4.6), mirrored with an in-plane (IP) $\pi$–$\pi$ stacking diffraction peak (010). This implies that UU07 preferentially adopts an edge-on orientation. It is noteworthy that after 90 s SVA, the observable intensity of higher order lamellar peaks decreases. This is because longer SVA induces extremely oriented UU07 molecules, which hide the lamellar peaks inside the missing wedge. In order to resolve the real OOP lamellar information at longer SVA times, specular XRD was utilized and the results are shown in Figure 4.7. Figure 4.7 plots the specular XRD results of UU07:PCBM blends with 0, 90, and 240 s SVA times. It reveals that along SVA times, the
OOP (100) peak becomes sharper, indicating enhanced coherence length for donor molecule at longer SVA times. Besides, higher order lamellar peaks clearly manifest themselves at 240 s SVA, while negligible higher order signal is observed at 90 s SVA and no higher order signal is recorded at 0 s SVA. Together, the specular XRD and GIWAXS results confirm that the crystallinity of UU07 monotonically increases with SVA time, which is also in good agreement with the AFM images.

![Specular XRD results of UU07:PCBM blends processed by 0 s, 90 s and 240 s SVA times.](image)

**Figure 4.7.** Specular XRD results of UU07:PCBM blends processed by 0 s, 90 s and 240 s SVA times.

Finally, R-SoXS was utilized to study the lateral morphology of UU07:PCBM blends. 284.2 eV was used as resonant energy to maximize inter-domain composition contrast
relative to vacuum contrast, in the meantime eliminating the fluorescence. **Figure 4.8** summarizes the Lorentz-corrected R-SoXS profiles at 284.2 eV. The domain spacing is represented by characteristic mode length scale by \( d=2\pi/q_{\text{peak}} \), where \( q_{\text{peak}} \) is the peak position in the R-SoXS profiles. As plotted in **Figure 4.9a**, the domain spacing of UU07:PCBM monotonically increases with SVA time. The domain spacing reaches 100 nm at 90s SVA, followed by more rapid enlargement at longer SVA times. In addition, the total ISI as a function of SVA time is also plotted in Figure 4.9b. The relative average domain purity, which is proportional to square root of total ISI if the volume fractions of the domains are constant, improves quickly after only 30s SVA and then stays rather constant until 90s. After that, the relative phase purity scattering intensity drops down quickly and becomes even lower than the blend without SVA. However, at longer annealing times were we have large crystals deplete the small molecule volume fraction in the remainder of the film (see optical analysis), the scattering is reduced to this geometric factor (ISI proportional to \( \varphi(1- \varphi) \)), where \( \varphi \) is the volume fraction) and likely the dominant mechanism by which the ISI is reduced at long SVA times. The high domain purity for the 90s SVA blend with domain spacing of app. 100 nm is important to prevent geminate and non-geminate recombination losses, being underlined by the \( J_{sc} \) and FF analysis. Combined with the rapid reduction of ISI and large crystallite size at longer SVA time, we speculate that the fast growing donor crystallite at longer SVA time changes the effective donor/acceptor ratio in the mixed domain, which reduce the interfacial area between donor and acceptor.
Figure 4.8. Lorentz-corrected R-SoXS profiles for UU07:PCBM at different SVA times from 0 to 240 s. All data were taken under 284.2 eV, which maximizes inter-domain scattering and eliminates fluorescence background.

Figure 4.9. (a) Domain spacing represented by characteristic median length scale extracted from R-SoXS as a function of SVA time. (b) Total ISI as a function of SVA time.
4.3.3 Device physics

In order to further understand the relationship between charge transport and composite microstructure we determined the hole and electron only device mobility from space charge limited current (SCLC) measurements on representative thin film devices. Figure 4.10 summarizes the hole and electron only mobility as a function of annealing time by fitting the current voltage response of single carrier diodes to the Mott-Gurney law for SCLC. The hole mobility rises sharply from 0s to 90s SVA treatment and then reduces for longer SVA periods up to 180s. The electron mobility follows a similar trend and only drops significantly as the SVA is prolonged to 180s. 90s SVA treated composites exhibit the highest and most balanced hole and electron mobility in the order of \(10^{-4} \text{cm}^2\text{V}^{-1}\text{s}^{-1}\), and, as a consequence, corresponding devices reach FF of up to 70%. This result confirms previous studies reporting that hole and electron mobility in a blend must be at least \(10^{-4} \text{cm}^2\text{V}^{-1}\text{s}^{-1}\) or higher to prevent recombination limited FF losses. We also find quite well balanced hole and electron mobility for composites after 150s SVA, but the related devices exhibit FF of only 60% due to the too low absolute mobility value of app. \(3 \times 10^{-5} \text{cm}^2\text{V}^{-1}\text{s}^{-1}\). This can be understood by considering that the charge carrier sweep out time is proportional to the mobility. If the mobility is lower, the average charge carrier density will be higher and bimolecular recombination losses will be more expressed. Note that the SCLC mobility in the device treated with 240s SVA cannot be investigated due to the severely damaged blend morphology. Although the blends with longer SVA time exhibited the obvious phase separation and increased donor crystallite size, the poor mixed domains as well as larger domain spacing can impact the charge separation
processes, which probably resulted in the poor charge transport properties. In addition, the poor charge generation attributed to the large donor domain size in BHJ films as a result of over-aggregation of UU07 phase can also impact the charge separation process.

Figure 4.10. Hole and electron only mobility as a function of SVA time measured in single carrier diodes. Measurements were made on five devices of each type, and the error bars represent plus or minus 1 standard deviation from the mean.
Figure 4.11. Measured (a) $V_{oc}$ and (b) $J_{sc}$ of devices with different SVA times plotted against light intensity on a logarithmic scale. Fitting a power law (solid lines) to these data yields $\alpha$. (c) Extracted carrier density as a function of delay time (symbols) and the corresponding fits (lines). (d) 2nd order recombination coefficient (left) and transient time (right) calculated from time delayed collection field photo-CELIV data as a function of SVA time.

The mobility measurements give great insight into the transport properties, but a comprehensive understanding of the device performance requires the acquisition of both, the recombination dynamics as well as the transport dynamics.\cite{126} We first studied the relative recombination losses, as a function of light intensity as shown in Figure 4.11. The light intensity dependence of $V_{oc}$ and $J_{sc}$ of UU07:PCBM devices without and with 90s and 240s SVA treatments under illumination intensities ranging from 100 to 1 mW cm$^{-2}$ are plotted in
Figure 4.9a and 4.9b, respectively. The slope of $V_{oc}$ versus light intensity for the device with 90s SVA treatment is 1.07 $kT/q$, implying that the trap-assisted recombination losses are negligible. The other two systems without and with 240s SVA treatment show a strong dependence of $V_{oc}$ on light intensity. At low light intensities a slope of 2.18 $kT/q$ and 2.97 $kT/q$ are observed respectively which is reduced to 1.26 $kT/q$ and 1.80 $kT/q$ at higher light intensities. Defect assisted recombination dominates at low light intensities and the device performance strongly depends on bias and light intensity.\textsuperscript{1127} We further looked into the recombination kinetics at short circuit for these three types of devices, as shown in Figure 4.9b. The fitting of the data yield $\alpha = 0.84$ for device without treatment and $\alpha = 0.78$ for device with 240s SVA treatment, reflecting significant contributions from 2\textsuperscript{nd} order recombination. For 90s SVA treatment, the related devices in contrast show a slope of 1.01, obviously benefitting from the optimized BHJ microstructure possessing a homogenous nanocrystalline films with small grains sizes. We conclude that SVA efficiently quenches recombination from microstructure related devices, which most probably arise in the disordered amorphous phase.

To finally understand the recombination dynamics of the different microstructures, CELIV measurements with delayed collection fields were employed. Here, the time-dependence of the charge carrier density was studied in order to investigate the recombination dynamics (see Figure 4.9c). The initial density of photogenerated carriers ($n(0)$) and the effective 2\textsuperscript{nd} order recombination coefficient ($\tau_B$) are calculated by fitting the corresponding time-dependence of the charge carrier density (Equation: $n(t) = \frac{n(0)}{1+(t/\tau_B)^\gamma}$).
where \( \gamma \) is the time-independent parameter) and are further summarized in Figure 7d. In addition, we calculated the transient time \( (t_{tr}) \) by using a formula \( (t_{tr} = d^2/\mu V) \), where \( d \) is the film thickness (see Figure 7d). The deepest insight is gained by analyzing \( \tau_B \) in parallel to \( t_{tr} \), as these two material parameters are independent from each other. We find that SVA in parallel reduces 2nd order recombination as well as enhances ambipolar charge carrier extraction. This only can be explained by a well ordered two phase microstructure with little relevance of the amorphous regimes.

### 4.4. Conclusion

In summary, solvent vapor annealing was demonstrated to very efficiently improve the photovoltaic performance of UU07:PCBM based solar cells by optimizing the composite’s microstructure with respect to charge generation and charge extraction in parallel. Films treated with chloroform vapor for 90s showed optimum performance with a PCE of over 6.0%. Irrespective of device performance parameters, a plurality of experimental results all prove the same trend: absorption spectroscopy, unipolar mobility measurements, analysis of the light intensity dependence of \( J-V \) curves, determination of the recombination kinetics via photo-CELIV data, – they all confirm a non-monotonic trend as a function of SVA duration and uniquely proof that a plurality of microstructures is generated during SVA. Two distinct microstructure regimes were identified for UU07:PCBM as a function of annealing time. From 0s to 90s SVA, the average coherence lengths of the donor molecule, the domain spacing and the domain purity of UU07:PCBM is increased, which is consistent with enhanced phase separation and donor ordering. The increased structural order and phase
separation leads to high and balanced hole and electron only mobilities, which in turn significantly improve FF and $J_{sc}$. Light intensity dependent $J-V$ analysis and photo-CELIV analysis that defect assisted as well as bimolecular recombination are reduced upon increasing phase purity and structural order. Consequently, the relative device parameters, charge transport properties, carrier density and lifetime were all found to peak at 90s SVA. After further extending the SVA time from 90s to 240s, we found that the domain spacing with the length scale of hundred nanometers are becoming significantly increased, verified by the specular XRD and AFM results. This part of morphological evolution was monitored by a reduced absorption coefficient, reduced mobility and enhanced recombination. Both, $J_{sc}$ and FF drop dramatically as the consequence. Thus, the two regimes are assigned to separate processes: during the first phase (0 – 90 seconds), chloroform vapor “mobilizes” either of the components and the subsequent vapor assisted diffusion creates a more phase separated microstructure. Extending SVA beyond 90 starts the second stage, and we found that the phase separation are more clear in the solid film, exhibiting too large domain size and a few large donor crystallites. Our work suggests that SVA is following a very generic mechanism allowing to straighten up too intermixed, disordered donor–acceptor microstructures. More detailed insight into SVA may lead to improved material specifications for the corresponding SVA solvents and to better process control for organic solar cells and other organic electronic devices.
Chapter 5

Highly complex multi-length scale morphology in OPV and its correlation with charge creation and recombination

5.1 Preface

While the extremes in organic photovoltaic bulk heterojunction morphology (finely mixed or large pure domains) are easily understood and known to be unfavorable, efficient devices often exhibit a complex multi-length scale, multi-phase morphology. The impact of such multiple length scales and their respective purities and volume fractions on device performance remains unclear. Here, the average spatial composition variations, i.e., volume-average purities, are quantified at multiple size scales to elucidate their effect on charge creation and recombination in a complex, multi-length scale polymer:fullerene system (PBDTTPD:PC$_{71}$BM). The apparent domain size as observed in TEM is not a causative parameter. Instead, a linear relationship is found between average purity at length scales <50 nm and device fill-factor. Our findings show that a high volume fraction of pure phases at the smallest length scales is required in multi-length scale systems to aid charge creation and diminish recombination in polymer:fullerene solar cells.
This work is proposed and implemented entirely by Harald Ade group. Both Subhrangsu Mukherjee and Xuechen Jiao involved in collecting and analyzing R-SoXS and STXM data. Subhrangsu Mukherjee deduced the detailed quantitative correlation between device performance and morphology. Xuechen Jiao took the TEM images and conducted the FFT analysis of the direct images. This work has been published in Advance Energy Materials (Adv. Energy Mater. DOI: 10.1002/aenm.201600699).

5.2 Introduction

In a three-phase morphology, the aggregated fullerene and particularly the crystalline donor polymer domains are likely discontinuous and charge transport across an active layer likely involves charges traversing mixed domains multiple times. Reports on polymer:fullerene blends have shown the existence of a critical threshold for the average domain purity of the mixed phase in some systems. Mixed regions having fullerene content below the threshold value results in loss of percolation leading to decreased performance. Thus, as shown in Figure 5.1, while charges generated due to splitting of excitons in the mixed regions migrate to the aggregated domains due to a favorable energy cascade, these charges do not necessarily have a continuous electronic “highway” to the electrodes but must likely reenter the mixed domains during extraction in spite of the unfavorable electronic landscape and lower mobility in the mixed domain. Similarly, charges created in the pure domains also must likely traverse mixed domains on the way to the electrodes. This scenario results in the possible recombination of charge-carriers in the mixed regions or at the interfaces of the aggregated domains. While we have recently shown a
correlation between FF and average domain purity in a small molecule system with relatively simple morphology,\textsuperscript{[29]} a quantitative understanding of the domain size distribution, and domain composition/volume fractions, as well as their net effect on the geminate and bimolecular recombination in a complex, multi-phase, multi-length scale morphology is still unclear.

\textbf{Figure 5.1.} Multi-phase morphology simplified to a three-phase polymer–fullerene BHJ morphology. Schematic (left) illustrating composition variations that lead to an energetic landscape (right) with difference in energy levels for pure donor (PBDTTTPD), acceptor (PCBM), and mixed amorphous phases. Recombination of trapped charges (electron—e and hole—h) under the action of an external electric field occurs in the mixed regions or at the interface of poorly connected aggregates. [\textit{E}_{\text{vac}}: \text{Vacuum reference level}; \text{EA}: \text{Electron affinity}; \text{IP}: \text{Ionization potential}].
Previous studies have shown that, in general, increasing the molecular weight often leads to higher efficiency devices due to favorable phase separation in the active layer that provides efficient charge generation and collection for polymer solar cells.\textsuperscript{[129]} More recent investigation\textsuperscript{[130]} has shown that increasing the molecular weight beyond a certain value leads to sub-optimum device performance indicating the requirement of an intermediate molecular weight for optimized device performance. Recent studies using different number-average molecular weights (M\textsubscript{n}) of the D-A polymer poly(di(2-ethylhexyloxy)benzo[1,2-b:4,5-b′]dithiophene-co-octylthieno[3,4-c]pyrrole-4,6-dione) (PBDTTPD) blended with PC\textsubscript{71}BM acceptor have shown the monotonic variation of phase separation as well as internal quantum efficiency (IQE) with the polymer M\textsubscript{n} and thus offer a good model system.\textsuperscript{[131]} The highest M\textsubscript{n} device was shown to attain efficiencies over 7% with fill-factor (FF) > 0.7 and an open-circuit voltage (V\textsubscript{oc}) close to 1 V. The IQE measurements and presence of large fullerene-rich macrophases observed in transmission electron microscopy (TEM) for low M\textsubscript{n} devices have led to the hypothesis that the increased recombination loss is caused by the potential decrease of the amount of fullerene in the amorphous, mixed regions owing to extensive phase separation in these BHJs.\textsuperscript{[131]}

Our study puts to test prior hypotheses on the composition of multiple phases and their relation to recombination losses. We show an effect and impact corollary to the case of excessive purity, with decreased performance due to loss of percolation, in the same polymer:fullerene system used previously: if the composition variation at length scales <50 nm is too low, corresponding to small volume fraction of pure domains or low purity, poor
charge generation and/or extraction lowers the short-circuit current density. Based on recently developed methodology to elucidate small molecule donor:fullerene as well as polymer:fullerene systems, we use multi-peak lognormal distributions to fit resonant soft X-ray scattering (R-SoXS) profiles to obtain quantitative information on the composition and volume fraction of the multiple phases present in the polymer:fullerene blends prepared using different Mₙ PBDTTDP polymer donors and PC₇₁BM as acceptor. Because these samples will have similar values for the overall average composition variation and degree of molecular orientation relative to the D/A heterojunction, they allow us to rule out effects due to these parameters in our analysis of the relevant structure-property relationships. Notwithstanding the differences in apparent length scales observed from TEM, the results reveal that all samples show presence of the same set of five length scales, and size-scale alone is not the determining factor for device performance. Rather the volume fraction or purity of a given length scale matters. We find a direct correlation of the volume fraction of pure domains at the smallest length scales with device photocurrent and FF. This indicates that a high volume fraction of small and pure domains is required in these BHJs for optimal charge extraction as well as reduced recombination losses and improved device quantum efficiency.
5.3 Results and Discussion

5.3.1 Device performance

A set of photoactive films with the polymer donor PBDTTPD with four different $M_n$ (viz., 23, 29, 36 and 39 kDa) and similar polydispersity indexes (PDIs), and PC$_{71}$BM as acceptor, and identically prepared as in a previous study were studied. The chemical structures of the donor and acceptor materials are shown in Figure 5.2.

![Chemical structures of PBDTTPD (donor) and PC$_{71}$BM (acceptor).](image)

**Figure 5.2.** Chemical structures of PBDTTPD (donor) and PC$_{71}$BM (acceptor).

All devices were made with PBDTTPD and PC$_{71}$BM in a 1:1.5 weight ratio, and were spun-cast from chlorobenzene (CB) on PEDOT:PSS/ITO substrates. The active layer nominal thicknesses were 100 nm. The average device performance parameters
(photocurrents, FF, Voc, and PCE) for the devices fabricated using polymer of different $M_n$ are displayed in **Figure 5.3**.

Figure 5.3a shows the trend of the photocurrent measured at bias voltage $-3$ V ($J_{ph}(-3$ V)) alongside the short-circuit current ($J_{sc}$). A prominent difference between the performance of lower and higher $M_n$ devices is the dependence of the current density on the bias voltage. Recent studies on the dependence of device performance on the polymer $M_n$ showed that the performance of low $M_n$ PBDTTPD devices is affected by charge-carrier recombination rather than optical or excitonic losses. The lower $M_n$ PBDTTPD devices suffered from significant amounts of both light-intensity-dependent and electric bias-dependent charge-carrier recombination. The estimated amount of bimolecular recombination was found to decrease with increasing $M_n$. The bias-dependent current density (Figure 5.3a) suggests that while geminate recombination losses may contribute to the poor performance of low $M_n$ PBDTTPD devices, charge extraction in low $M_n$ PBDTTPD devices could be assisted with a moderate electric field, indicating that morphological traps may hinder charge-carrier extraction. Likewise the FF exhibited a steady rise with the polymer $M_n$ as shown in Figure 5.3b. Notwithstanding the nearly constant $V_{oc}$ (Figure 5.3c) for all the samples (except for a modest decrease for higher $M_n$ samples), the PCE showed a monotonic dependence on $M_n$, as shown in Figure 5.3d.
Figure 5.3. Average device performance (at 1 Sun illumination) parameters for the PBDTTPD:PC$_{71}$BM solar cells as function of polymer M$_n$: a) device photocurrent at −3 V ($J_{ph}(-3\, V)$) (open symbols) and $J_{sc}$, (solid symbols), b) FF, c) $V_{oc}$, and d) PCE.

5.3.2 Multiple Length Scales and Composition Variation

Bright-field transmission electron microscopy was utilized to elucidate the real-space morphology of the PBDTTPD:PC$_{71}$BM blends. The morphology evolution with polymer M$_n$ as observed from TEM is shown in Figure 5.4. All samples exhibit a multi-length scale morphology that is progressively evolving as function of M$_n$. For the 23 kDa M$_n$ sample,
large dark-colored PC$_{71}$BM-rich regions reminiscent of liquid–liquid phase-separation\textsuperscript{[133]} are clearly observed. The significant internal structure is likely due to a second-phase separation occurring at a slightly later stage in the casting and solidification process. Likewise the scanning transmission X-ray microscopy (STXM) images acquired at PC$_{71}$BM absorption resonance of 284.4 eV (Figure 5.5) also show that the size of the domains with the highest contrast is found to decrease progressively with increasing polymer M$_n$. At high M$_n$, the large-scale domains are almost completely absent and only a fibrillar network is observed. The high- molecular-weight polymer is less soluble than PC$_{71}$BM and separates out of the solution during casting before a liquid–liquid phase separation can occur. Due to the lower solubility of the high M$_n$ PBDTTPD, the polymer forms a fibrillar network that acts as a template and defines the size scales for the PC$_{71}$BM-rich domains. The data for the 36 kDa system show the cross-over between these two regimes.
Figure 5.4. Bright-field transmission electron microscopy (TEM) of PBDTTPD:PC$_{71}$BM with (a) 23 kDa, b) 29 kDa, c) 36 kDa, and (d) 39 kDa. All TEM images were taken with similar resolution and exposure times.
Figure 5.5. STXM images of PBDTTPD:PC$_{71}$BM blends prepared with different M$_n$ polymers (a) 23 kDa, (b) 29 kDa, (c) 36 kDa, (d) 39 kDa acquired at 284.4 eV. Owing to the strong absorption of PC$_{71}$BM at 284.4 eV, the dark irregular spherical domains are assigned as PC$_{71}$BM-rich domains. The size of the PC$_{71}$BM-rich domains is observed to decrease with higher M$_n$.

In order to obtain further insights into the morphology and particularly to analyze any internal structures of the larger domains present in the samples, power spectral density profiles were calculated by Fourier transform of the TEM images. The multiple spatial frequencies present in the system could be obtained by deconvolution of the PSD profiles by multi-peak fitting as shown in Figure 5.6. Excellent fits to all the PSD profiles could be obtained using multiple log-normal peaks. The reality of these multiple spatial features will be discussed below in the context of the reciprocal space X-ray data. Here we note that the TEM images are a projection of the 3D morphology onto a 2D plane. Moreover, the
technique being sensitive to electron density variations a quantitative analysis of the intensities of the different peaks might not relate well to the actual domain composition variations in the samples.

**Figure 5.6.** Multipeak fit to PSD profiles calculated from the TEM images for 29 kDa sample. The profiles were fitted by multiple log-normal peaks. Artifact in PSD corresponding to intrinsic feature in a TEM image was characterized by fitting a single log-normal peak to the PSD profile calculated from the TEM image of a blank sample or “open space”. An identical peak (indicated with broken line) with position and width held constant to values corresponding to “open space” feature was then used to the PSD profiles for the different samples to eliminate the effects of such features from our analysis.

In order to assess the relations of device performance and recombination with morphological features, the in plane spatial composition variations and degree of molecular orientation relative to the D/A heterointerface were determined with resonant soft X-ray scattering (R-SoXS). Generally R-SoXS profiles arise from composition correlations
weighted by the scattering contrast and volume fractions of these correlations. The scattering intensity is proportional to the variations of average composition. Completely mixed domains result in negligible scatter over the q-range probed. A two-phase morphology with pure phases will produce maximum scattering whereas a three-phase morphology having molecularly mixed as well as aggregated phases will yield intermediate scattering intensity. Multi-peak fits to the scattering profiles provide further details concerning phase separation at various length scales. Unlike previously studied systems the current PBDTTPD:PC71BM case is unique in that a larger number of log-normal peaks are needed to achieve good fits to the circular and sector-averaged (parallel and perpendicular to the incident X-ray polarization) scattering profiles. Notably, the circular as well as the different sector-averaged profiles can only be simultaneously fitted if five peaks are used. The multipeak fits are shown in **Figure 5.7.** We will further validate this procedure below from comparisons with the PSD calculated from TEM images.
Figure 5.7. Multi-peak fits to Lorentz corrected and absorption normalized R-SoXS profiles obtained at 284.2 eV (circular average (Circ), and sections perpendicular (Perp) and parallel (Para) to the polarization of the incident X-rays) with five log-normal peaks for (a) 23 kDa, (b) 29 kDa, (c) 36 kDa, (d) 39 kDa samples. Peak labels and length scale indicators are shown in (a). All five peaks were ascertained to originate from donor-fullerene material contrast and relate to phase separations at multiple length scales. Scattering in the direction perpendicular to the polarization was found to be higher for all the peaks and for all samples implying a “face-on” orientation at the D/A heterointerface. Shaded area for each component peak indicates the difference between scattered intensity in the perpendicular and parallel sectors.

In the Fraunhofer approximation of kinematic scattering theory the scattered intensity I(q) is related to the real-space electron density distribution in a sample ρ(r) by a 3D Fourier
For a two-phase system with uniform composition within a phase, the integrated R-SoXS intensity (ISI) is defined as:

\[
\text{ISI} = \int_{q_a}^{q_b} I(q)q^2 dq = 2\pi^2 V \Delta\rho_{12}^2 \phi_1 \phi_2
\]  

(1)

where \( e \Delta\rho_{12}^2 \) is proportional to the optical contrast between phases (domains) 1 and 2 and, \( \phi_1 \) and \( \phi_2 = 1 - \phi_1 \) are the volume fractions of the two phases respectively. Therefore, the ISI is affected by the domain contrast as well as volume fraction of each phase (as shown in Figure 5.8). For a multiphase system, the delineation of the effects of volume fractions and domain contrast becomes more difficult. The above equation (1) can be generalized and extended for a multiphase system by summing over all phases and the ISI can be written as

\[
\text{ISI} = \int_{q_a}^{q_b} I(q)q^2 dq = 2\pi^2 V \sum_{i \neq j} \Delta\rho_{ij}^2 \phi_i \phi_j
\]  

(2)

We shall define the square of the “average composition variation” (\( \Delta c \)) to be the quantity expressed as the summation in equation (2) above in analogy with our earlier definition of domain purity for a two-phase system.

\[
\text{ISI} = \int_{q_a}^{q_b} I(q)q^2 dq \propto V \sum_{i \neq j} \Delta c_{ij}^2
\]  

(3)
Figure 5.8. Variations of normalized integrated scattering intensity (ISI) due to change in the volume fraction term (φ(1−φ)) or composition variation (Δρ) in a two-phase system. The dashed vertical line indicates the maximum volume fraction contribution at 50:50 volume ratio.

Figure 5.9. Contrast followed by the five fitted peaks shown in Figure 5.7 for the 23 KDa and 39 KDa blends.
The intensities of the five peaks comprising the broader envelope in the circular as well as the sector-averaged profiles exhibit a distinct and defining energy dependence as well as a unique scattering anisotropy. By integrating the scattering profiles and ensuring that scattering originates from materials and not mass-thickness contrast, the scattering intensity of each peak component henceforth abbreviated as the component scattering intensity (CSI) reveals the relative average composition variations $\Delta c$ ($\text{CSI} \propto \Delta c^2$) between the samples over the length scales corresponding to the different peaks. Scattering between mixed domains or low volume fraction of the corresponding morphological feature would result in lower CSI. The energy dependence of the CSI of all the five peaks were found to follow the PBDTTPD:PC71BM materials contrast as a function of energy (Figure 5.9), demonstrating that the peaks measure the composition variations at the respective five length scales rather than mass-thickness variations or molecular orientation correlations. The peak intensities between the samples exhibit a monotonic and rational evolution as progressively larger intensities at higher $q$ values are observed with increasing $M_n$. The three lower-$q$ peaks 1-3 correspond to length scales greater that the film thickness ($\approx 100$ nm) originate due to the large PC$_{71}$BM-rich domains and the intensities provide a measure of the degree of large-scale phase separation in the samples. The combined intensity of these three lower-$q$ peaks is observed to be maximum for 23 kDa and decreases progressively with increasing polymer $M_n$ with and minimum for 39 kDa sample (not shown). The long periods extracted from the fitted peaks in Figure 5.7 are given in Table 5.1. The corresponding long periods are found to be similar for all samples, with the 36 kDa sample exhibiting slightly lower values. The apparent changes observed in the TEM are therefore not so much changes on length scales
per se, but changes of the composition variation, i.e. purity and volume fraction, at a given length scale.

**Table 5.1.** Long periods extracted from the fitted peaks in Figure 5 that follow the material contrast for the different $M_n$ samples.

<table>
<thead>
<tr>
<th>$M_n$ (kDa)</th>
<th>Peak 1</th>
<th>Peak 2</th>
<th>Peak 3</th>
<th>Peak 4</th>
<th>Peak 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>479</td>
<td>320</td>
<td>183</td>
<td>95</td>
<td>47</td>
</tr>
<tr>
<td>29</td>
<td>398</td>
<td>294</td>
<td>170</td>
<td>94</td>
<td>48</td>
</tr>
<tr>
<td>36</td>
<td>324</td>
<td>227</td>
<td>125</td>
<td>73</td>
<td>39</td>
</tr>
<tr>
<td>39</td>
<td>389</td>
<td>247</td>
<td>144</td>
<td>91</td>
<td>45</td>
</tr>
</tbody>
</table>

Since R-SoXS takes advantage of the contrast function specific to the materials, the scattering at energies well below the absorption edge of both materials will be dominated by mass-thickness contrast. The scattering profiles acquired at 270 eV (low material contrast) were analyzed similarly using multiple peaks. Apart from the five material contrast peaks a distinct peak at extreme low-q corresponding to large (≈μm) length scales was required to obtain excellent fits to the data. Since that particular low-q peak was only observed at certain energies at which the scattering is dominated by mass-thickness contrast it could be linked to the presence of large mass-thickness features in the samples. The correlation between long periods obtained from multipeak fits to the high material contrast (284.2 eV) and high mass-thickness (270 eV) R-SoXS data were compared with the length scales obtained from the
TEM PSD analysis and shown in Figure 5.10. Notwithstanding the superficial dissimilarities between the PSD and R-SoXS profiles a striking similarity between the three datasets emerges. Two distinct regimes—a linearly correlated and an uncorrelated set of data points—could be identified in the size-scale plot as indicated by the dashed boxes in the figure. Within the range of length scales revealed by the material contrast peaks (Table 1) the length scales obtained from the three datasets are very similar and scale linearly. Larger length scales that lack any correlation arise from mass-thickness features and occur only in the TEM and 270 eV R-SoXS data.
Figure 5.10. Plot of length scales obtained from multipeak fits to the R-SoXS high material contrast (284.2 eV) (hollow squares), high mass-thickness contrast (270 eV) (hollow triangles) and PSD profiles (calculated by taking the FFT of TEM images) (solid circles). Dashed line through the datapoints is drawn to guide the eye. $Z_n$ and $Z_{n+1}$ are length scales corresponding to nth and (n+1)th peaks, respectively. Dashed boxes indicate the two distinct regimes observed in the dataset—linear correlation for entire range of length scales corresponding to material-contrast peaks and larger uncorrelated length scales related to mass thickness.

The linear correlation indicates a fixed length scale ratio or similar spatial correlations for all the samples. The similar individual peak positions and the fixed ratio between the different peak positions indicate that the microscopic length scales are similar for all samples and likely have the same physical origin. We note here that the relative degree of aggregation of the polymer-rich regions obtained from $\pi-\pi$ stacking peak in grazing incidence wide angle scattering (GIWAXS) data for different $M_n$ samples is low and does not change significantly between different samples. This indicates a similar aggregation of polymer fibrillar structure.
irrespective of molecular weight. The similar aggregation properties of the polymer when combined with the following facts—(i) peak intensities in R-SoXS track the material contrast (i.e., originate from polymer:fullerene phase separations), (ii) similar spatial correlations, and (iii) intensities (composition variations) of the multiple peaks (phase separations at multiple length scales), suggest that hierarchical fine structures exist in the large fullerene-rich domains in the low $M_n$ samples. Notably, the presence of fine structure in fullerene-rich regions has also been observed in PTB7:PC$_{71}$BM systems prepared without DIO additive exhibiting a double peak in R-SoXS.

### 5.3.3 Correlation between domain purity and FF

Having determined that the multiple peaks arise from contrast between polymer-rich regions and internal structures inside the fullerene-rich macrophase regions, we shall focus on understanding the effect of composition variations at the different length scales. As the device current is normal to the substrate plane, morphological features that are smaller than the film thickness should dominate the average extraction and average recombination across all large domains. We shall henceforth focus our attention on the length scales $\leq$100 nm, which would relate to peaks 4 and 5. The average composition variation of all peaks, and the scattering anisotropy and composition variation corresponding to peaks 4 and 5 for the different PBDTTTPD samples are shown in Figure 5.11. The differences observed from R-SoXS could be further understood by considering the strong variations in device performance and the relative invariance of all other parameters (average composition variation and anisotropy). Moreover, as inferred from PL quenching studies, exciton diffusion and CT
creation is not a factor. Therefore charge separation and recombination are likely to be the most important factors in determining the device performance and possibly determined by the smallest observable length scales (peak 5). The monotonic trends of the relative composition variation over these length scales with the FF, $J_{sc}$, and total recombination current ($J_{recombination}$) are shown in Figure 5.12. For thermodynamic reasons, we note that the aggregated donor and the aggregated PCBM domains observed at the smallest length scales are essentially pure. As the CSI is a product of the phase purity and volume fraction of the respective phases (see Equation (2)) and the fact that aggregated domains are nearly pure for thermodynamic reasons, CSI$_5$ ($\Delta c_5$) is effectively equivalent to the volume fraction of pure domains at the smallest length scales. It is observed that the FF (Figure 5.12a) as well as $J_{sc}$ (Figure 5.12b) exhibits a monotonic correlation with $\Delta c_5$. In both plots the 36 kDa sample exhibits a lower composition variation than would be expected from a strictly linear correlation. Referring back to Table 1, we note that the 36 kDa sample also exhibited slightly smaller length scales so it is very possible that this deviation could be due to a faster quenching during the film casting and/or drying stages. An excellent linear fit ($r^2 \approx 0.98$) to the monotonic variation of the FF is obtained if the 36 kDa samples is treated as an outlier (Figure 5.12a). While mixed phases might be favorable for charge separation due to formation of an energy cascade, presence of impure phases negatively affect local mobilities leading lower charge extraction as well as increased bimolecular recombination. Moreover high average composition variation over all length scales or high volume fraction of pure phases has been shown to assist geminate splitting and promote charge generation. Therefore a high volume fraction of small and pure domains help to decrease geminate as well as
bimolecular recombination and assist charge generation. The steady decrease of $J_{\text{recombination}}$ with $\Delta c_5$ as observed in Figure 5.12c is in line with these aforementioned arguments.

**Figure 5.11.** (a) Average composition variation for peaks 4 and 5 (as indicated in Figure 5.7) that originate from size scales $\lesssim$ film thickness ($\approx 100$ nm) for the different PBDTTTPD devices normalized to the average composition variation for all peaks (1-5) for the 39 kDa sample. The average composition variation calculated from all peaks 1-5 for the different samples is also shown for comparison; (b) scattering anisotropy for peaks 4 and 5.
Figure 5.12. (a) Linear increase of FF with the average composition variation of smallest length scales ($\Delta c_5$) observed in R-SoXS with linear fits to all datapoints (solid line) as well as with 36 kDa sample treated as an outlier (dashed line); (b) increase of $J_{sc}$ with $\Delta c_5$; (c) decrease of recombination current ($J_{\text{recombination}}$) with $\Delta c_5$. $J_{\text{recombination}}$ for the different devices were estimated from the difference between the photocurrent at $-3$ V bias and maximum power condition.

5.4 Conclusion

We have quantified phase separations at multiple length scales and elucidated their role in charge creation and recombination in an efficient polymer:fullerene blend system (PBDTTPD:PC$_{71}$BM). The relative composition at each of these length scales varied with the polymer $M_n$, but were otherwise surprisingly similar. The trends of FF and $J_{sc}$ can be comprehended and related to the active layer morphology. Direct correlations of these parameters were found with the morphology at the smallest length scales. Similar to an efficient small-molecule system with much simpler morphology, a strong linear (monotonic) correlation between the composition variation of the smallest length scales and device FF and $J_{sc}$ alongside a steady reduction of the recombination current were observed. The similarity of these monotonic trends imply that regardless of the complexity of the morphology a general
relation exists between the FF, photocurrent and average composition variation of pure phases at length scales that are smaller than the device thickness. Neither the existence of a multi-length scale morphology nor the length-scale with the largest contrast controlled performance. The results therefore underline the importance of achieving a high volume fraction of pure phases at the smallest length scales to optimize charge extraction and minimize charge recombination. The optimal volume fraction of the mixed domains in which the charge recombination likely occurs remains to be determined.
Chapter 6

Manipulating Aggregation and Molecular Orientation in All-Polymer Photovoltaic Cells

6.1 Preface

The charge separation process, in which the photogenerated hole–electron pairs bound by Coulomb interaction (known as excitons) are split into free charge carriers at the heterojunction formed by the electron donor and acceptor materials, is one of the key steps for realizing high power conversion efficiency (PCE) of an organic photovoltaic cell (OPV). To pursue more efficient charge separation, the bulk heterojunction (BHJ) structure has been successfully applied in OPVs to reduce the recombinination of excitons prior to the charge separation process by dramatically enlarging the D/A interface area. Due to the beneficial BHJ structures, over 10% efficiencies have been realized in single junction OPV devices. As is well known, organic semiconductors often possess low dielectric constants and in the charge separation process, charges must migrate from the donor to the acceptor or vice versa. The relatively unscreened Coulomb interaction hampers the charge separation process and for this reason, the alignment of molecular energy levels of the donor and acceptor materials must be carefully tuned to afford sufficient driving force. Conversely, since the Coulomb force is inversely proportional to the square of the distance between charges, reduction of the distance of the π-orbits of donor and acceptor will be more efficient to facilitate the charge
separation process. Thus, to control and optimize the π–π interaction between the donor and acceptor materials is of great importance to developing efficient OPV device. It has also been argued that the mobility of the aggregate phases is critical for charge creation, which again is strongly influenced by π–π interactions.

Manipulating molecular orientation at the donor/acceptor interface is the key to boosting charge separation properties and efficiencies of anisotropic-materials-based organic photovoltaics (OPVs). By replacing the polymeric donor PBDTBDD with its 2D-conjugated polymer PBDTBDD-T, the power conversion efficiency of OPVs featuring the anisotropic polymer acceptor PNDI is drastically boosted from 2.4% up to 5.8%. This is a collaborative work between Jianhui Hou group from Chinese Academy of Sciences and Harald Ade group from NCSU. Jianhui Hou group synthesized the materials and fabricated the devices. I conducted the morphology characterization and construct the morphology - performance correlation. This work has been published in Advanced Materials (Adv. Mater. DOI: 10.1002/adma.201503218). I am the co-first author.

6.2 Introduction

Fullerenes have nearly isotropic conjugated cages and their derivatives have been widely used as acceptor materials in OPVs. Obviously, when a ball-like small molecular fullerene derivative such as (6,6)-phenyl-C61-butyric acid methyl ester (PCBM) is blended with a conjugated polymer donor, the interaction between their respective π-orbits can be comparatively easily formed (see Figure 6.1a), which might be the main reason why
fullerenes are still the predominant acceptor material in OPVs. The above speculation can be partially supported by recent progresses in nonfullerene acceptors, i.e., when small molecular nonfullerene compounds are used as acceptors in BHJ OPVs, the molecules with weakly anisotropic π-orbits (highly twisted conjugated moieties) often showed better photovoltaic properties than their counterparts with highly anisotropic π-orbits (planar conjugated skeletons).\textsuperscript{[136,137]} That is to say, if both the donor and acceptor materials in a BHJ layer have highly anisotropic conjugated chemical structure, the charge separation process will dependent on the molecular/segmental orientations of the donor and acceptor at the D/A interface. Although the molecular orientation at or relative to the D/A interface is correlated to device performance in a few cases of polymer:PCBM photovoltaic systems, it is more challenging to correlate the anisotropic morphologies at or relative to D/A interfaces to charge separation processes and thus photovoltaic performance of all-anisotropic materials-based OPVs.\textsuperscript{[138]} Moreover, manipulating the potentially critical parameter, i.e., molecular orientation at the D/A interface in the anisotropic materials-based OPVs through materials design efforts has not yet been reported.
Figure 6.1. (a) Schematic representation of the almost isotropic material (PCBM) and anisotropic polymer. (b) Molecular structures of the polymer donors (PBDTBDD, PBDTBDD-T) and the polymer acceptor PNDI and the corresponding molecular conformations and π electronic structures.

Here, one pair of donor polymers namely poly{1-(5-(4,8-bis((2-ethylhexyl)oxy)-6-methylbenzo[1,2-b:4,5-b′]dithiophen-2-yl)thiophen-2-yl)-5,7-bis(2-ethylhexyl)-3-(5-methylthiophen-2-yl)benzo[1,2-c:4,5-c′]dithiophene-4,8-dione} (PBDTBDD) and poly{1-(5-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-6-methylbenzo[1,2-b:4,5-b′]dithiophen-2-yl)thiophen-2-yl)-5,7-bis(2-ethylhexyl)-3-(5-methylthiophen-2-yl)benzo[1,2-c:4,5-c′]dithiophene-4,8-dione} (PBDTBDD-T) were selected to respectively blend with an anisotropic polymer acceptor poly((N,N′-bis(2-octyldodecyl)-1,4,5,8-naphthalenedicarboximide-2,6-diyl)-alt-5,5′-(2,2′-bithiophene)) (PNDI2OD-T2)\textsuperscript{139} also known as ActivInk N2200 (abbreviated to PNDI hereafter, see Figure 1b) in OPV devices.
As illustrated in Figure 1b, the backbones of both donor polymers are highly anisotropic and a slight difference exists in their side chains, i.e., the alkoxy group of PBDTBDD is replaced by alkylthienyl moiety in PBDTBDD-T. Interestingly, although a small change exists in chemical structure, the molecular orientation relative to the D/A and electrode interfaces are distinct for PBDTBDD:PNDI and PBDTBDD-T:PNDI-based OPVs as revealed by soft X-ray scattering anisotropy and X-ray diffraction. Therefore, the photovoltaic systems based on the donor and acceptor polymers in this study will be an excellent model for revealing the correlations among the molecular structures of donor polymers, the molecular orientations with respect to the D/A interface, the domain population distributions in bulk morphology and photovoltaic performance of anisotropic materials-based OPVs.

6.3 Results and Discussion

6.3.1 Device performance

The BHJ OPV device performances of PBDTBDD:PNDI and PBDTBDD-T:PNDI blends were evaluated in a conventional device geometry of indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS)/polymer blend/Mg/Al (Figure 6.2a). Variation of the weight ratio of PBDTBDD/PBDTBDD-T and PNDI revealed the optimum D/A ratio to be 1:1. All of the polymer blends were processed by chlorobenzene and no further treatment was utilized. As depicted in Table 6.1 and Figure 2b, the optimized OPV based on PBDTBDD:PNDI yielded a PCE of 2.4% with an open-circuit voltage ($V_{oc}$) of 0.82 V, a short-circuit current density ($J_{sc}$) of 6.8 mA cm$^{-2}$ and fill factor (FF) of 43.0%. In
comparison, PBDTBDD-T:PNDI-based OPV exhibited a more than twofold PCE of up to 5.8% (certificated as 5.39%, see Figure 2c), along with a \( V_{oc} \) of 0.87 V, \( J_{sc} \) of 11.7 mA cm\(^{-2}\) and FF of 57.4%. Notably, these results were obtained without resorting to any special treatments such as thermal annealing or processing additives.

Table 6.1. Photovoltaic parameters of BHJ OPVs employing various polymer blends.

<table>
<thead>
<tr>
<th>Polymer blends</th>
<th>( V_{oc} ) [V]</th>
<th>( J_{sc} ) [mA/cm(^2)]</th>
<th>FF [%]</th>
<th>PCE(^{[a]}) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBDTBDD:PNDI</td>
<td>0.82</td>
<td>6.8</td>
<td>43.0</td>
<td>2.4 (2.3)</td>
</tr>
<tr>
<td>PBDTBDD-T:PNDI</td>
<td>0.87</td>
<td>11.7</td>
<td>57.5</td>
<td>5.8 (5.6)</td>
</tr>
</tbody>
</table>

[a] Average results of 15 devices were provided in the parentheses.

Figure 6.2d presents the external quantum efficiency (EQE) curves of PBDTBDD:PNDI and PBDTBDD-T:PNDI-based OPVs. PBDTBDD-T:PNDI device exhibited broad photoresponse coverage from 300 to 850 nm with relatively high absorption (Figure 6.3) of PBDTBDD-T (≈600 nm) and PNDI (≈720 nm), indicating charge carrier could be efficiently generated from both polymer donor and polymer acceptor. Although the PBDTBDD:PNDI device also exhibited similar photoresponse, its EQE values are much lower than that of the PBDTBDD-T:PNDI device over the whole wavelength range. In the following, a combination of characterizations covering morphological, photophysical, device physical and computational aspects was explored to understand the underlying differences of PBDTBDD:PNDI and PBDTBDD-T:PNDI photovoltaic systems.
Figure 6.2. (a) Device diagram of BHJ OPV. (b) J–V curves of the OPVs based on PBDTBDD:PNDI and PBDTBDD-T:PNDI blend. (c) The J–V certification of PBDTBDD-T:PNDI-based OPV device from the National Institute of Metrology. (d) EQE curves of PBDTBDD:PNDI and PBDTBDD-T:PNDI-based OPVs.

Figure 6.3. UV-vis absorption spectrum of PBDTBDD, PBDTBDD-T and PNDI films.
6.3.2 Molecular packing and texture

The nanoscale packing and texture of the films of PBDTBDD, PBDTBDD-T, PNDI, PBDTBDD:PNDI, and PBDTBDD-T:PNDI are examined by synchrotron-based X-ray characterizations. As shown in Figure 6.4, the orientation tendency of each component relative to the electrodes can be determined from the 2D grazing incidence wide angle X-ray scattering (GIWAXS) patterns. As observed from the patterns of PNDI (Figure 6.4a), a well defined (010) reflection from π–π stacking is observed out-of-plane (OOP). A corresponding (100) reflection from lamellar stacking is located in-plane (IP), without a diffuse ring. This mirrored reflection between (100) and (010) suggests that the ordered fraction of PNDI tends to be exclusively face-on relative to the substrate. A most noteworthy difference is observed between the two polymer donors. In Figure 6.4b, no (010) reflection is observed, but a weak lamellar stacking (100) peak manifests itself out-of-plane, indicating edge-on tendency for PBDTBDD with poor π–π stacking. In contrast, PBDTBDD-T (see Figure 6.4c) gives rise to a well defined (010) reflection in the out-of-plane direction. Yet a (100) diffuse ring with strong OOP intensity is observed instead of in-plane (100) peak. Furthermore, a (001) rod is observed which indicates strong in-plane orientation of the backbone. This implies that the PBDTBDD-T signal in the lamellar and π–π staking direction resemble a 2D “powder” with one axis locked in-plane. Locking one axis in-plane shifts the apparent orientation distribution so that the other two axes appear (due to small Ewald's sphere interception of the in-plane population) to be more likely to be out-of-plane even though they are mostly randomly oriented in-plane. Such a distribution would be the result of a morphology
dominated by in-plane fibrils. As shown in Figure 6.4d,e, blending PBDTBDD or PBDTBDD-T with PNDI does not alter the overall orientation distribution, i.e., texture/mosaicity, of each component very much. However, the ordered population, which is proportional to the corresponding diffraction peak intensity, reveals considerable difference when the materials are blended. The OOP (010) peak area for each component are shown in Figure 6.4f. The population of ordered, face-on PNDI in PBDTBDD-T:PNDI is much higher than that in PBDTBDD:PNDI blend. The considerable enhancement for PNDI face-on population in PBDTBDD-T:PNDI, even beyond that of the pure PNDI control, is likely due to the preferential in-plane PBDTBDD-T fibrils and a favorable π–π interaction between PBDTBDD-T and PNDI, facilitating PNDI enhanced crystallite formation in face-on orientation when blending them together. In contrast, PBDTBDD manifests edge-on orientation preference, disturbing PNDI face-on orientation and π–π ordering in the blend. No matter what the backbone orientation distribution, the π–π stacking in the out-of-plane is strongly enhanced for PBDTBDD-T. Clearly, the intermolecular π–π interaction of the PBDTBDD with itself and possibly with the PNDI is significantly enhanced by introducing conjugated side group.
Figure 6.4. 2D GIWAXS patterns of thin films of (a) PNDI, (b) PBDTBDD, (c) PBDTBDD-T, (d) PBDTBDD:PNDI, and (e) PBDTBDD-T:PNDI blend. (f) (010) π−π stacking diffraction intensity (without correction for missing wedge) for each component, red dashed line indicates the PNDI (010) diffraction intensity in homo-PNDI. GIWAXS data are without missing wedge correction and q_z is an approximation only. Vertical and horizontal artifacts arise from a segmented detector.

6.3.3 Mesoscale morphology

To gain in-depth insight into the in-plane morphology, transmission resonant soft X-ray scattering (R-SoXS) experiments were performed to provide quantitative information regarding spatial frequency distribution, relative average domain purity, and molecular orientation correlations of the polymer blends (see Figure 6.5). The scattering intensity can arise from three contributions: mass-thickness differences (referred to as vacuum contrast), compositions variations (referred to as material contrast) and molecular orientation
correlations (referred to as orientation contrast). Each has a specific energy dependence and can thus be identified. **Figure 6.6a,b** plot Lorentz corrected R-SoXS profiles against spatial frequency for PBDTBDD:PNDI and PBDTBDD-T:PNDI, respectively, at a photon energy of 284.2 eV, which minimizes vacuum contrast relative to material and orientation contrast (see Figure 6.5). The peak position represents characteristic length scale at \( d = 2\pi/q_{\text{peak}} \). The PBDTBDD:PNDI blend film exhibits a single mode distribution with a peak near 100 nm and scattering anisotropy with a single signature, i.e., scattering parallel to the polarization is larger than perpendicular, for all \( q \). In contrast, PBDTBDD-T:PNDI exhibits a single mode signal with tails toward high \( q \) and a unique anisotropy signal with a change in sign and two maxima in amplitude corresponding to characteristic lengths of \( \approx 200 \) and \( \approx 60 \) nm.

**Figure 6.5.** (a) 2D R-SoXS pattern of PBDTBDD-T:PNDI at 284.2 eV, where blue wedge represents the perpendicular sector and green wedge represents the horizontal sector, x-ray polarization is indicated as the arrow. (b) Simulated material contrast of PBDTBDD-T:PNDI and orientation contrast for PNDI and P3HT (a proxy for PBDTBDD-T due to lack of good aligned PBDTBDD-T NEXAFS spectra), overplotted with experimental ISI of low-\( q \) and high-\( q \) peaks for PBDTBDD-T:PNDI.
Figure 6.6. Circular integrated R-SoXS profiles at 284.2 eV, as well as integrated sectors parallel and perpendicular to the polarization, for (a) PBDTBDD:PNDI and (b) PBDTBDD-T:PNDI compared to R-SoXS at 270 eV and the PSD from AFM height and phase images shown.

In order to deduce the origin of the features and interpret the scattering anisotropy, the integrated scattering intensity (ISI) of the main features were extracted. The resulting energy dependence (see Figure 6.5b) indicates only small differences between the low-q and high-q features in PBDTBDD-T:PNDI. Overall, the low-q feature might originate from PBDTBDD-T orientation contrast and not from PNDI orientation contrast or materials contrast, whereas the high-q feature in PBDTBDD-T:PNDI and the scattering in PBDTBDD:PNDI are clearly
dominated by composition/materials contrast arising from scattering between PNDI-rich and PBDTBDD-rich or PBDTBDD-T domains, respectively (see Figure 6.5b). However, the differences are not very large, and the modeling of the energy dependence of orientation contrast is currently very limited (see below) and thus impacting the orientation contrast predictions. Given that the GIWAXS analysis indicates that the overall orientation distributions are rather different, with PBDTBDD-T having a larger in-plane orientation, the dipole transition moment (TDM) distributions that impact materials contrast are also different and impact composition contrast. Qualitatively, one would expect reduced contrast for the 2D distribution. Since, the ISI ratio analysis of the features dominated by materials contrast reveals an increase of 15% in scattering for PBDTBDD-T:PNDI over PBDTBDD:PNDI, this indicating an increase in average domain purity for PBDTBDD-T:PNDI. A quantitative measurement would require a full resolution of the orientation population distributions of the TDM.

A comparison to the power spectral density (PSD, see Figure 6.6) of the AFM height and phase images is also instructive. Overall, there is strong correlation of the height images with the low-q feature in the scattering data at 270 eV, which is sensitive to mass-thickness contrast. The phase images are less well correlated to the R-SoXS data, which likely indicates that the surface morphology is different from the bulk morphology. Interestingly, the q ≈ 0.04 nm⁻¹ features in PBDTBDD-T:PNDI for 284.2 eV, 270 eV and the height image map out the same morphological aspect that is dominated by PBDTBDD-T orientation-contrast with reverse scattering anisotropy compare to the high q feature. This correspondence is not present in PBDTBDD:PNDI, which furthermore shows no anisotropy
reversal for different q-ranges. PBDTBDD-T:PNDI also shows more fibrillar texture in the height and even phase image compared to PBDTBDD:PNDI. Collectively, this divergent R-SoXS and AFM data, in conjunction with the GIWAXS, indicates that the two materials systems have very different in-plane bulk morphologies and molecular orientation correlations.

The scattering anisotropy signature of the two samples is fundamentally different and deserves further consideration. The phenomenological anisotropy \((\text{ISI}_\perp - \text{ISI}_\parallel)/(\text{ISI}_\perp + \text{ISI}_\parallel)\) at 284.3 eV is 0.45 for the high q-peak of PBDTBDD-T:PNDI and 0.27 for PBDTBDD:PNDI. The low-q peak of PBDTBDD-T:PNDI has a small anisotropy ratio of opposite sign. We assume for now that this peak is not related to composition variations. Due to the dipole selection rules and use of linear polarization in the R-SoXS measurements, it is only the orientation distribution of the molecular segments with an effective edge-on orientation relative to the electrodes that gives rise to scattering anisotropy. Since both materials have strongly anisotropic optical constant when oriented and can have amorphous populations of edge-on segments with respect to the substrate, the complete analysis of the anisotropic scattering is more complex than for devices based on nearly optically symmetric fullerene as one component. Complete quantitative analysis requires detailed knowledge of the optical constants of both materials and has not yet been achieved for any polymer–polymer system. It is thus outside the scope of this Communication. We will instead construct a qualitative argument to achieve further insights. Using optical anisotropy data from poly(3-hexylthiophene) (P3HT), see Figure 6.5, as a proxy for PBDTBDD and PBDTBDD-T, models of pairwise combinations of ordered (P3HT or PNDI) versus amorphous (P3HT, or
PNDI) regions show amorphous PNDI versus ordered, face-on P3HT exhibits an energy dependence of the scattering anisotropy that resembles the data most closely. This is consistent with the following conceptual argument: Given that PNDI is the materials common to both sets of devices and exhibits increased face-on orientation relative to the electrodes as observe in GIWAXS for PBDTBDD-T and this face-on population cannot contribute to scattering anisotropy and would thus reduce the anisotropy amplitude, yet the orientation contrast contributions to the R-SoXS signal changes significantly with the chemical modification of the PBDTBDD, it is reasonable to conclude that the anisotropic scattering is dominated by the molecular segments of the PBDTBDD-based materials that are preferentially edge-on relative to the substrate and thus capable of creating an R-SoXS anisotropy signal. The increased anisotropy in PBDTBDD-T-based devices for the high q-peak corresponds thus to an increased face-on orientation of the PBDTBDD-T with respect to in-plane D/A interfaces. Such face-on orientation has been previously correlated to improved device performance with the more isotropic fullerenes as acceptor.

An alternative interpretation of the low q R-SoXS anisotropy signature in PBDTBDD-T:PNDI blends tentatively assigned above to be originating from PBDTBDD-T orientation contrast would be that all the R-SoXS scattering relates to materials contrast. In that case, the anisotropy of opposite sign must arise from an edge-on PBDTBDD-T population with respect to the D/A interface. Consider now samples with fibrils whose backbone is preferentially oriented in-plane (see GIWAXS) and with face-on internal ordering relative to the fibril axis. Such fibril organization would yield face-on R-SoXS signal relative to the interface along the fibril axis and edge-on R-SoXS signal relative to the ends of the fibrils,
just as observed. The scattering might thus arise of elongated fibrils with a length that corresponds to the low q peak and a width that corresponds to the high q peak. Either interpretation indicates much stronger molecular ordering of the PBDTBDD-T.

Exciton quenching is a good complementary indicator about the morphology and proximity of the donor and acceptor as an integral measurement of average purity and molecular proximity. We observe high photoluminescence (PL) quenching efficiency of ≈80% and ≈90% for PBDTBDD:PNDI and PBDTBDD-T:PNDI (Figure 6.7), respectively, clearly indicating that even though the average domains are larger than the exciton diffusion length in both samples, the domains are impure enough to have sufficient distributed D/A interfaces to yield very high and comparable efficiency of charge transfer (CT) state generation. We thus will have to invoke mechanism other than domain size and CT state formation by charge transfer to explain the relative large difference in performance, particularly in $J_{sc}$. 
Figure 6.7. PL quenching spectrum of PBDTBDD:PNDI and PBDTBDD-T:PNDI blend films. Steady state photoluminescence (PL) quenching was performed to evaluate the CT state PBDTBDD or PBDTBDD-T are detected in the neat film, the ratio in the corresponding blend films can be easily qualified. As observed from the typical PL spectra in Figure S7, it is clear that the PL (~650 nm) of PBDTBDD-T is almost quenched completely in blend film while there still exists approximately 20% in the PBDTBDD:PNDI blend film.

The following aspects about the morphology can be inferred. The dominant composition variations are at length scales larger than the canonical exciton diffusion length of ≈10 nm, yet the domains are impure enough to have good molecular proximity that leads to very good exciton quenching at the distributed D/A interfaces with quenching of 80% and 90% respectively. The PBDTBDD-T has improved in-plane and out-of-plane molecular ordering at the molecular level as well as at the length scales of the domain size, with a preferential face-on molecular orientation relative of the average in-plane D/A interface. Furthermore, at the
average molecular level, the GIWAXS shows also increased π–π stacking face-on with respect to the electrode for both polymers in the PBDTBDD-T based devices. This increased face-to-face orientation might occur at distributed D/A interfaces in the impure domains or at more discrete D/A interfaces in the out-of-plane direction for domains that are smaller than the film thickness. In both the in-plane and out-of-plane directions, the different orientation correlations impact the device performance, with the observed increased π–π interactions and overall increase orientational order correlating to better performance.

By examining all performance parameters (V_{oc}, J_{sc}, FF) of OPVs based on the pair of donor polymers, it can be concluded that the improved efficiency of PBDTBDD-T:PNDI device is mainly contributed by J_{sc}. Basically, the J_{sc} is determined by several device processes including light absorption, exciton quenching via CT state creation, CT state dissociation, geminate, and bimolecular recombination which are both impacted by charge transport properties in the presence of extraction field, and collection at the electrodes. In view of the fact that the PL quenching, energy levels and absorption ranges of PBDTBDD and PBDTBDD-T are quite similar, the main contribution factors to the large differences in J_{sc} need to be probed by photophysical and charge extraction analysis. As observed from the absorption spectrum in Figure 6.8a, the magnitude of absorption coefficients for two blend films is 105 cm⁻¹. Clearly, the light absorption difference contributes a minor fraction to the high J_{sc} in PBDTBDD-T:PNDI. The J–V characteristics over a large bias range indicates that (Figure 6.8b) PBDTBDD-T:PNDI device exhibit reduced bimolecular recombination and lower field-dependence of charge carrier generation than PBDTBDD devices. This is also confirmed by simple light intensity studies where low light conditions create much lower
charge carrier densities and thus significantly reduce the bimolecular recombination. The relative change in FF from 0.034 to 1 Sun in PBDTBDD-T:PNDI device is much smaller than that of PBDTBDD:PNDI device.

Figure 6.8. (a) Absorption spectra; (b) biased J–V characteristics, (c) photocurrent analysis, and (d) J^{0.5}–V plots of hole-only diodes of PBDTBDD:PNDI and PBDTBDD-T:PNDI blend films.

We have discussed above already that exciton quenching is comparable, nearly complete, and differs only by about 10%. In contrast, the photocurrent (J_{ph}, the difference of light and dark current density) to effective voltage (V_{eff}, defined as V_0–V_a, where V0 is the voltage at J_{ph} = zero and V_a is the applied voltage) plots (Figure 6.8c) revealed that CT-state
dissociation at the D/A heterojunction is quite efficient (≈87%) in PBDTBDD-T:PNDI device while the dissociation efficiency (≈58%) is rather poor in PBDTBDD:PNDI-based OPV at the short-circuit condition, and thus a major contributor to the low J_{sc}. Note that for CT-state dissociation efficiency calculations, J_{ph} at high V_{eff} region (≈10 V) is selected as the saturation value of J_{ph}. Regarding charge extraction, the hole mobilities of PBDTBDD and PBDTBDD-T were respectively determined to be 6.5 \times 10^{-4} and 1.1 \times 10^{-3} \text{ cm}^{2} \text{ V}^{-1} \text{ s}^{-1}, by applying the space-charge limited current (SCLC) model to the dark J–V measurements of the hole-only devices (as illustrated in Figure 6.8d). This indicates that charge transport characteristic is also improved for PBDTBDD-T:PNDI devices.

**6.3.4 Molecular simulation**

From a standpoint of molecular structure, the insertion of conjugated side moiety (thiophene) most probably leads to variations of some intrinsic features of PBDTBDD-T. To verify the presumption, the unimers of PBDTBDD and PBDTBDD-T were examined by density functional theory (DFT) calculations. Both of the donor polymers adopt planar conformations and no significant difference was observed in energy levels. A slightly improved J-type aggregation is observed for PBDTBDD-T. Compared with PBDTBDD, the \pi electrons could delocalize within two dimensions in PBDTBDD-T (Figure 6.1b), which contributes to enhance the \pi–\pi interaction of donor and acceptor. The 2D GIWAXS patterns confirmed that PBDTBDD-T exhibits better crystallinity than PBDTBDD in both neat and blend films, which is also in accordance with the increased hole mobility of PBDTBDD-T. The R-SoXS and PL analysis revealed that the average purity of the domain in the
PBDTBDD:PNDI film is slightly less than that in PBDTBDD-T:PNDI film and that overall excitons are efficiently quenched due to impure domains that provide sufficient D/A interfacial area. This eliminates average domain or domain size distribution of a major factor in explaining performance. Give the overall similarity in PL quenching, these differences are not critical though to the overall device performance, yet inform about critical differences that relate to molecular interactions. The differences in charge extraction were also explored and improved hole mobilities were observed for PBDTBDD-T:PNDI. The impact of the improved mobility on charge density was counter-balanced by a similar increase in CT-state dissociation efficiency, i.e., free carrier generation, resulting in comparable charge densities in the two devices. Consequently, the improved FF for PBDTBDD-T:PNDI due to reduced bimolecular recombination must be either due to differences in the recombination site density (i.e., purity) or an asymmetry in the molecular interactions. Since the domain purities are rather similar, we ascribe the majority of the improvement in FF to favorable differences in D/A molecular interactions that reflect the molecular orientation correlations observed with R-SoXS and GIWAXS. The biggest difference in performance between the blends resulted from differences in geminate recombination and CT-state dissociation, which we attribute to a more favorable segmental orientation distribution for PBDTBDD-T:PNDI and improved π–π interaction. As a result, the overall Jsc is dramatically improved from 6.8 to 11.7 mA cm$^{-2}$. Compared to PBDTBDD:PNDI devices, the underlying origins of excellent device performances of PBDTBDD-T:PNDI systems were mainly ascribed to the extended π electron overlap, which leads to beneficial molecular orientation relative to the D/A interface and relative to the electrode interface, in turn leading to efficient CT dissociation, charge
transport, and reduced bimolecular recombination. Considering all of the data, the correlation of chemical structural features, device morphology and device performance is found to be very clear in the cases of OPVs presented here, i.e., the insertion of conjugated side group on the polymer donor results in stronger molecular interaction, and thereby the molecular orientation at the distributed and concrete D/A interface and relative to the electrodes are highly tuned, facilitating charge separation and transport and ultimately leading to PCE improvements. In addition, this work provides comprehensive and detailed insights into the superiority of 2D-conjugated polymers, which could help explain the results of multiple cases of efficient OPVs employing other 2D-conjugated photovoltaic polymers.

6.4 Conclusion

In summary, we highlighted for the first time the importance of donor/acceptor molecular interactions and orientation correlations in governing the device performance of OPVs based exclusively on anisotropic polymeric materials and successfully constructed an efficient all-polymeric OPV by replacing the anisotropic polymeric donor PBDTBDD with its 2D-conjugated version PBDTBDD-T. The efficiency of OPV devices featuring the anisotropic polymer acceptor PNDI was drastically boosted to 5.8%. More fundamentally, our results indicate that manipulation of aggregation and molecular orientation of photovoltaic polymers via molecular design will stimulate the advances of OPVs based on anisotropic materials. This study opens up a new frontier in understanding the critical structure-morphology-function relationship of anisotropic photovoltaic materials and devices.
Chapter 7

Manipulation of Domain Purity and Orientational Ordering in High Performance All-Polymer Solar Cells

7.1 Preface

All-polymer solar cells (All-PSCs) are of great interest as a renewable and economically viable energy technology, which has shown potential advantages in practical photovoltaic applications due to the highly tunable optical, electronic, and mechanical properties. A quantitative understanding of the domain composition variations and orientational ordering of all-polymeric films affected by solvent additives had been unattainable until now. This study demonstrates how the use of trace amount solvent additive can indeed manipulate domain purity and molecular orientational ordering as revealed by polarized soft X-ray scattering (P-SoXS). Additionally, the BDDT/PNDI all-polymeric blend exhibits enhanced average domain purity with the use of a trace amount of solvent additive and thus improved charge mobility, device fill factor and power conversion efficiency. A high power conversion efficiency of ~7.1% was obtained in the All-PSC mainly contributed by this morphology control strategy. Manipulation of domain purity and orientation ordering, both of which are impacted by the aggregation kinetics, may be a key to further boost the efficiency of new fullerene-free solar cells and all-anisotropic materials-based devices.
This is a follow-up work from the "Manipulating Aggregation and Molecular Orientation in All-Polymer Photovoltaic Cells. Advanced Materials". Jianhui Hou group from Chinese Academy of Sciences synthesized materials and fabricated the devices and Harald Ade group from NCSU conducted the morphology characterization and constructed the morphology - performance correlation. This work has been published in Chemistry of Materials (Chem. Mater. DOI: 10.1021/acs.chemmater.6b02222). I am a co-first author.

7.2 Introduction

Owing to advantages such as potentially low cost, light weight, rapid energy payback time, and easy large-scale fabrication, research efforts have commenced and much progress has been made in the development of bulk heterojunction (BHJ) polymer:fullerene solar cells since their invention in 1995. Over 11.5% power conversion efficiencies (PCEs) were recently achieved in polymer:fullerene solar cell using binary hydrocarbon solvents. To achieve these inspiring devices, nanomorphology manipulation and characterization play a vital role in guiding the formation of nearly ideal interpenetrating networks of conjugated polymer donors and fullerene derivatives. With the advances of new conjugated polymers, polymer solar cells (PSC) featuring polymers in the active layer formulations, that is, all polymer solar cell (All-PSC) is emerging as an alternative to the polymer:fullerene solar cell due to the excellent morphological and chemical stability as well as superior mechanical properties. Although All-PSC was invented in the same year as fullerene-based BHJ devices, the PCEs of All-PSCs are lagging behind even when using high mobility PNDI2OD-T2 (abbreviated to PNDI hereafter), a benchmark electron acceptor polymer comprising
naphthalene diimide and bithiophene alternating building units. When the results from the best performing All-PSCs are considered, the key factor limiting PCEs of the state-of-the-art All-PSCs is the fill factor (FF), which is typically below 55%.

In comparison with polymer:phenyl-C71-butyric acid methyl ester (PCBM) system, all polymeric blend films are conjectured to be inferior in forming favorable molecular orientation at or relative to donor/acceptor heterojunction due to chain entanglements, high molecular weights, and limited π orbital overlap of polymer materials. Additionally, all-polymeric blends inherently lack high electron density contrast between constituent donor and acceptor polymers, which limits the ability to quantify the domain details and molecular orientation by utilizing conventional morphological characterization methods such as atomic force microscopy (AFM) and transmission electron microscopy (TEM). These intrinsic features make it extremely difficult to understand the morphological details, understand the true nature of the performance limitations, and guide morphology–performance optimization of all-polymeric systems.

Incorporating of a relatively large volume amount (2–5%) of a high boiling-point solvent additive such as 1,8-diiodooctane (DIO) or 1-chloronaphthalene (CN) in host solvents is rather useful in polymer:fullerene solar cells due to the preferential solubility for fullerenes,(37) but these additives do not always show an efficiency improvement in All-PSCs. Adding a large volume amount of DIO can in fact induce unfavorable FF and poor reproducibility in polymer solar cells. On the other hand, several groups demonstrated high PCEs over 4% in additive-free All-PSCs. This progress has been largely by “trial and error”
and the morphology is far from finely tuned or understood. As a result, there is a pressing need for in-depth understanding of the role of solvent additive in All-PSCs informed by the usage of advanced tools.

Here, utilizing polarized soft X-ray scattering (P-SoXS) featuring high sensitivity and quantitative nature, we reveal the effect of a trace amount (0.5 vol %) of DIO on a high-efficiency all-polymeric material system, in which a crystalline donor polymer poly{1-(5-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-6-methylbenzo[1,2-b:4,5-b’]dithiophen-2-yl)thiophen-2-yl)-5,7-bis(2-ethylhexyl)-3-(5-methylthiophen-2-yl)benzo[1,2-c:4,5-c’]dithiophene-4,8-dione}{40} (PBDTBD-D, abbreviated to BDDT hereafter) pairs with the established acceptor polymer PNDI (Figure 7.1a). Compared with the All-PSCs without DIO or with a large amount (5 vol %) of DIO, incorporating 0.5% DIO leads to higher average domain purity and distinctively different inter-BDDT orientational ordering without altering the face-on molecular orientation relative to the donor/acceptor (D/A) interfaces in the polymeric blends as evidenced by P-SoXS profiles, collectively contributing to a ~ 20% enhancement in FF (66.8% vs 56.5%) and PCE (6.53% vs 5.53%) in the All-PSC devices. More encouragingly, a higher PCE up to 7.1% was realized in BDDT:PNDI based All-PSC by using a trace amount of additive (0.5% DIO) coupled with a new cathode interlayer NDIO.
Figure 7.1. (a) Schematic illustration of the device configuration and the polymer donor BDDT and the polymer acceptor PNDI. (b) Current density versus voltage ($J-V$) curves and the corresponding external quantum efficiency (EQE) spectra (c) of the BDDT:PNDI solar cells with different DIO concentrations.

7.3 Results and discussion

7.3.1 Device performance

All-PSCs employing the BDDT:PNDI blends with a trace amount (0.5%) of DIO and without DIO were fabricated by using chlorobenzene as primary processing solvent and an identical device configuration of ITO/PEDOT:PSS/BDDT:PNDI/Mg/Al. Current density vs
voltage ($J$–$V$) curves of the resulting All-PSC devices are presented in Figure 7.1b and the corresponding photovoltaic parameters are listed in Table 7.1. Without adding any DIO, the BDDT:PNDI-based devices exhibited a PCE of 5.53% and a moderate FF of 55%, which are quite consistent with that in a previous report. Incorporating the trace amount (0.5%) DIO exhibited considerably higher PCE of 6.53% and FF of $\sim$67%, while $V_{oc}$ and $J_{sc}$ did not change much. Conversely, a large amount (5%) of DIO lead to a dramatic decrease in PCE and a poor FF of $\sim$52%. The main difference of the device with 0.5% DIO and without DIO is the FF. It is important to keep in mind that FF of a solar cell depends on multiple physical parameters including charge carrier mobility, recombination, and film morphology.

Table 7.1. Photovoltaic properties of BDDT/PNDI-based All-PSCs with different amounts of DIO under AM1.5G 100 mA/cm$^2$.

<table>
<thead>
<tr>
<th>DIO Amount (%)</th>
<th>$V_{oc}$ [V]</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>FF [%]</th>
<th>PCE$_{max}$ [%]</th>
<th>PCE$^{[a]}$ [%]</th>
<th>$\mu_h$ [cm$^2$/V$\cdot$s]</th>
<th>$\mu_e$ [cm$^2$/V$\cdot$s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.874</td>
<td>11.20</td>
<td>56.51</td>
<td>5.53</td>
<td>5.24±0.25</td>
<td>1.19×10$^{-3}$</td>
<td>2.36×10$^{-4}$</td>
</tr>
<tr>
<td>0.50</td>
<td>0.885</td>
<td>11.05</td>
<td>66.76</td>
<td>6.53</td>
<td>6.30±0.21</td>
<td>4.45×10$^{-3}$</td>
<td>1.17×10$^{-3}$</td>
</tr>
<tr>
<td>5</td>
<td>0.893</td>
<td>7.70</td>
<td>52.43</td>
<td>3.61</td>
<td>3.18±0.35</td>
<td>2.86×10$^{-3}$</td>
<td>1.03×10$^{-4}$</td>
</tr>
<tr>
<td>0.50$^{[b]}$</td>
<td>0.897</td>
<td>12.72</td>
<td>61.99</td>
<td>7.07</td>
<td>6.90±0.27</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

[a] Average values are obtained from ten devices.

7.3.2 Molecular packing

To probe the charge transport between these blends, space-charge-limited-current (SCLC) mobilities were measured via the hole-only and electron-only diodes. Results shown
in Table 7.1 revealed that the hole mobility of blend film with 0.5% (hereafter DIO-0.5) is three times higher than that without DIO (hereafter DIO-0). Molecular packing is frequently correlated with charge transport and device performance in BHJ solar cells. To assess the impact of molecular packing on device performance, grazing incidence wide angle X-ray scattering (GIWAXS) was employed to probe crystallinity and crystallite orientation relative to electrodes with trace amount DIO and without DIO. From the 2D GIWAXS patterns and 1D line-cut profiles shown in Figure 7.2, there is no obvious difference between DIO-0.5 and DIO-0 film. Both BDDT and PNDI adopt face-on orientation with respect to electrode across all two films. Trace amount DIO does not impact crystallites orientation with respect to electrode.

7.3.3 Mesoscale morphology and molecular orientation

Recent soft X-ray-based studies further revealed that molecular orientation at the D/A interface can be vital for governing device performance of all-polymeric blends, and manipulating the molecular orientation is an effective way to boost the efficiency of All-PSCs. Therefore, the in-plane morphology was investigated by transmission P-SoXS (see Figure 7.3a and 3b), which is capable of providing quantitative information regarding domain spatial frequency distribution, relative average domain purity and molecular orientation correlation. The scattering intensity originates from three contributions: mass-thickness variation (referred to as vacuum contrast), composition variation (referred to as compositional/material contrast) and molecular orientation correlation (referred to as orientational contrast). Each contribution follows unique energy dependence and thus can be
identified. The characteristic length scale $d$ is represented by the peak position (mode) with $d=2\pi/q_{\text{peak}}$, and the relative average domain purity is proportional to the square root of integrated scattering intensity (ISI) if the whole domain distribution is sampled.

Figure 7.2. 2D GIWAXS patterns (left) and 1D line-cut profiles (right) of BDDT:PNDI-based blends films without DIO and with 0.5% DIO.

Figure 7.3a and 7.3b display Lorentz corrected and thickness normalized P-SoXS profiles against spatial frequency for DIO-0 and with DIO-0.5 films at photon energy of 284.2 eV, where vacuum contrast is minimized over material contrast and orientational
contrast. The P-SoXS profiles from both DIO-0 and DIO-0.5 films show two populations or signals, separated by vastly different scattering anisotropy, i.e. an asymmetry that describes preferential scattering parallel or perpendicular to the polarization of the photons. For better depiction, multi-peak fitting was implemented to the circular profiles and the fit peaks are plotted underneath the 1D P-SoXS profiles. In order to identify the origin of each scattering population, the ISI of each peak was extracted as a function of energy and compared with simulated contrast functions (Figure 7.4). The resulting energy dependence across the absorption edge unambiguously indicates that the low-\(q\) peak follows \(\text{BDDT}_\perp:\text{BDDT}_\parallel\) orientational contrast, while the high-\(q\) peak follows \(\text{BDDT}:\text{PNDI}\) material/compositional contrast. Both DIO-0 and DIO-0.5 exhibit high-\(q\) peak located at \(\sim60\) nm, indicating similar compositional domain spacing. Scattering anisotropy was previously investigated and interpreted as originated from local molecular orientation correlations relative to donor/acceptor interface. The molecular orientation correlation was found to be well correlated with charge separation in several polymer:fullerene and all-polymer solar cell systems. So it is worth to investigate the scattering anisotropy observed for the high-\(q\) peak. It should be noted that only polymer segments with effective edge-on orientation relative to the electrodes can give rise to scattering anisotropy. Since the crystalline populations of edge-on orientation relative to electrodes are essentially the same in both blends from GIWAXS results, it is plausible to assume the overall edge-on populations relative to the electrodes are similar in DIO-0 and DIO-0.5.
Figure 7.3. Lorentz corrected P-SoXS profiles for BDDT:PNDI films without DIO (a) and with 0.5% DIO (b) under 284.2 eV, where vacuum contrast is suppressed relative to material contrast and orientational contrast. The lower panel displays the fit peaks from circular average P-SoXS profiles.

Figure 7.4. Simulated orientational contrast, material contrast and vacuum contrast, overplotted with ISI for high-q and low-q peaks in DIO-0.
The extent of molecular orientation can be quantified by the scattering anisotropy ratio
A(E) which is defined as follows:

\[ A(E) = \frac{(ISI_{\perp} - ISI_{\parallel})}{(ISI_{\perp} + ISI_{\parallel})} \]

Where ISI_{\perp} and ISI_{\parallel} are respectively corresponding to the ISI of Lorentz-corrected sector perpendicular and parallel to the X-ray electric-field polarization, and \( ISI_{\perp||} = \int I_{\text{ave,||}} q^2 dq \).

The phenomenological anisotropy of the high-\( q \) peak at 284.2 eV is calculated to be around 0.4 in both blends. In order to determine the molecular orientation relative to the compositional interface (i.e. amorphous BDDT with aligned PNDI or amorphous PNDI with aligned BDDT), the energy dependence of scattering anisotropy of high-\( q \) peak was extracted and compared with simulations (Figure 7.5). Due to the lack of preferentially aligned BDDT as a reference, available anisotropic optical constants of P3HT were used as a proxy for BDDT. The validity of this approach can be confirmed by comparison of the real part of the index of refraction between BDDT and P3HT (Figure 7.6), which are found to be very similar.

The overall energy dependence of the anisotropy (Figure 7.5) follows most closely the modeling of amorphous P3HT with face-on PNDI and not amorphous PNDI with face-on P3HT, nor amorphous P3HT with edge-on PNDI or amorphous PNDI with edge-on P3HT. This reveals that in both DIO-0 blend and DIO-0.5 blend, the PNDI-rich domain adopt face-on orientation relative to BDDT/PNDI compositional interface. In the high \( q \) range, the similar compositional domain spacing and molecular orientation relative to D/A interface altogether lead to similar charge generation, which is consistent with the devices exhibiting almost the same \( J_{sc} \) as shown in Table 7.1. Furthermore, the ISI ratio of \( ISI_{\text{DIO-0.5}}/ISI_{\text{DIO-0}} \)
amounts to 2.04:1. This suggests that the relative average domain purity of DIO-0.5 blend is 
~1.4 times higher than DIO-0 blend given that relative average domain purity is proportional
to square root of ISI. This difference in purity is likely the causative factor for the mobility
and $FF$ data shown in Table 7.1.

\[ \frac{\text{Amorphous BDDT (P3HT)}}{\text{with face-on PNDI}} \]

\[ \frac{\text{Amorphous PNDI with face-}}{\text{on BDDT (P3HT)}} \]

Figure 7.5. Simulated anisotropy $(\text{ISI}_\perp - \text{ISI}_\parallel)/(\text{ISI}_\perp + \text{ISI}_\parallel)$ as a function of photon energy for
(a) amorphous BDDT with face-on PNDI and (b) amorphous PNDI with face-on BDDT, 
overplotted with high-q anisotropy extracted from DIO-0.
Figure 7.6. The comparison of the real part of index of refraction between random P3HT and random BDDT. The similarity confirms that P3HT is a good proxy for BDDT.

Interestingly, DIO-0 and DIO-0.5 reveal distinctively different low-\(q\) peaks around \(q = 0.05\) nm\(^{-1}\). Based on the modeling of contrast functions (Figure 7.4), the low-\(q\) peak originates from inter-BDDT orientational contrast and not from inter-PNDI orientational contrast or material/compositional contrast. The existence of BDDT orientational domains implies that the BDDT-rich domains adopt high level of alignment within each BDDT domain with a predominant single orientation as one would expect from a short fibril. The spacing corresponding to the low \(q\)-peak suggests that the inter-domain correlations correspond to a length scale about 4 times larger than the compositional spacing. Thereafter, the ISI ratio of low-\(q\) peak over high-\(q\) peak as represented by \(\text{ISI}_{\text{orientation}}/\text{ISI}_{\text{material}}\) is extracted to represent the tendency of inter-domain molecular orientation correlations of BDDT-rich domains. Remarkably, a much higher \(\text{ISI}_{\text{orientation}}/\text{ISI}_{\text{material}}\) of 0.75 in DIO-0 film than 0.26 in DIO-0.5 film implies BDDT-rich domains in DIO-0 exhibits higher tendency of inter-domain molecular orientation correlation than in DIO-0.5. Considering that charge
transport predominantly occurs within the same type of material, the stronger tendency of molecular orientation correlation of BDDT-rich domains in DIO-0 blend may be detrimental to the charge transport and reduce charge carrier mobility transverse to the active layer. Molecular orientation correlation optimized by trace amount additive may also show positive effects to the charge transport and recombination of all-polymer solar cells.

Figure 7.7. DSC heat-only traces of neat PNDI and BDDT:PNDI blend (1:1 weight ratio). Melting point depression was observed for this polymer/polymer blend systems, indicative of partial miscibility.

7.3.4 Recombination mechanism

Light intensity \((I)\) dependent \(J-V\) characteristics were examined to further understand the impact of molecular orientation and domain purity on charge recombination, and the relationship between \(J_{sc}\) and \(I\) can be represented by a power law equation: \(J_{sc}=aI^{\alpha}\), where \(\alpha\) is
the recombination factor (see Figure 7.8). Since $\alpha=1$ indicates a minimum in bimolecular recombination, the bimolecular recombination ($\alpha=0.998$) in the DIO-0.5 blend is more suppressed compared to that in DIO-0 blend ($\alpha=0.941$). Utilizing the demonstrated optimized molecular orientation and domain purity in the active layer, the BDDT:PNDI-based All-PSC processed with trace amount of DIO could be further improved to a $PCE$ of 7.07% using a small molecular cathode interlayer instead of Mg under AM 1.5G 100 mW/cm$^2$ simulated solar light (see Figure 7.7 and Table 7.1).

Figure 7.8. Light intensity dependent $J$-$V$ measurements of BDDT:PNDI devices processed with 0.5% DIO and without DIO.

7.3.5 Impact of solvent additive on film formation

Aiming to better understand the effect of DIO on the kinetics of morphology formation during the film casting, we determine the solubility of both BDDT and PNDI in
DIO solution based on a well-established solubility test procedure by Yang et al. The solubility of PNDI in DIO is ~0.02 mg/ml, while the solubility of BDDT is much lower (< 0.001 mg/ml). During the process of film formation, trace amount of DIO crashes out BDDT more quickly from the solution due to the poor solubility, thus improving the domain purity and suppressing the inter-domain molecular orientation. This mirrors the generally observed mechanism by which additives help improve fullerene-based devices.

![Figure 7.9](image)

**Figure 7.9.** (a) J-V and (b) EQE curves of BDDT:PNDI solar cells with 0.5% DIO and a small molecule NDIO as cathode buffer layer.

Additionally, the understanding of poor performance in BDDT:PNDI blend with large amount (5% vol) DIO (DIO-5 for short) is straightforward, originating from the much stronger aggregation and larger interdomain spacing (as shown in **Figure 5.9**). Upon incorporating large amount of DIO into blend solution, the BDDT aggregates too early during casting into large aggregates which remain preserved in the device. Additionally, the films remain wet longer with some mobility that might lead to further phase separation.
Therefore, when processing All-PSCs with additive-containing solutions, it is imperative to use appropriate volume amounts to achieve relatively pure, yet small enough domains and eliminated orientational correlation.

7.4 Conclusion

To conclude, we revealed the impact of trace amount solvent additive in governing the scattering anisotropy, domain purity, and device performance of OPVs based on a high-efficiency all-polymeric blend. Upon adding trace amount (0.5%) of DIO, a dramatic increase was achieved in $FF$ and $PCE$ of All-PSC device employing BDDT:PNDI as active layer. The improved FF is primarily attributed to the enhanced average domain purity induced by trace amount solvent additive, which on account of differential solubility for the two polymers likely modifies the timing and kinetics of aggregation during casting. Furthermore, polarized soft X-ray scattering (P-SoXS) has been used to quantitatively characterize the molecular orientation correlation relative to the D/A interface and the tendency of molecular orientation correlation of inter-BDDT domains in the high-efficiency all-polymer solar cells. Manipulation of domain purity and orientation ordering, both of which are impacted by the aggregation kinetics, may be a key to further boost the efficiency of All-PSCs.
Chapter 8

Counterintuitive design rules of ternary bulk heterojunction solar cells with high fill factor

8.1 Preface

In conventional polymer:fullerene BHJs, one of the drawbacks is the intrinsically narrow absorption range of constituent materials. The narrow absorption hampers the further enhancement of short circuit current density ($J_{sc}$) and thus power conversion efficiency (PCE). In order to overcome this absorption limitation, several strategies have been developed, such as synthesis of novel materials with broader absorption and utilization of tandem multi-junction device architecture. However, those methods either largely increase the cost or impose difficulty of device fabrication. In the contrast, the concept of ternary blend BHJs makes use of already existent constituent materials in single junction device architecture, providing a cost efficient means to broadening absorption without sophisticating device fabrication. Ternary blends often consists of two donor materials with complementary absorption profiles and one acceptor materials or one donor materials with two acceptor materials with complementary absorption profiles. By casting from a common solvent, ternary blend thin films with significant increase of absorption can be readily made. Despite of the increased absorption, the ternary blend solar cells usually suffer from deteriorated FF due to the fact that the addition of the third constituent material into the host binary blend
often disturb the originally optimized binary blend morphology. In this project, several ternary blend solar cells with superior FF have been achieved. By carrying out systematic morphological investigation on these ternary blends, a design rule regarding ternary blend solar cells with reduced recombination and high FF has been proposed.

This work has been published as follows,

### 8.2 Introduction

One limitation of many state-of-the-art high-performing OSCs is the intrinsic narrow absorption range of the constitute materials. In order to overcome this drawback, several strategies have been developed, including synthesis of novel materials with broader absorption, tandem device architecture utilizing materials with complementary bandgaps and ternary blend solar cells with incorporation of a third component as sensitizer. Among them, ternary blend cells possess many unique advantages over others which includes 1) maintains the low cost by using already existent materials; 2) simultaneous casting of all constitute materials from a comment solvent without sophisticated device architectures.

In canonical paradigm of ternary solar cells, the third component/sensitizer is often chosen from the materials with complementary absorption characteristics and with proper HOMO-LUMO energy levels capable of forming cascade energy levels facilitating photogenerated electrons and holes. Despite that the enhancement of $J_{sc}$ can be achieved after
incorporation of sensitizer thanks to the broadened overall absorption, the FF of the ternary cells usually deteriorates due to that the incorporation of the third component disturbs the originally optimized morphology in binary reference cells.

This project goes beyond the traditional sensitization concept and proposes a novel design rule for high-performing ternary blends with high FF. A high-performing binary solar cell based on PTB7:PC$_{71}$BM was chosen as the reference binary cell with the highly ordered polymer Si-PCPDTBT chosen as the sensitizer. Unlike the canonical paradigm, the HOMO and LUMO levels of Si-PCPDTBT are slightly higher than the respective HOMO and LUMO levels of PTB7 and no cascade energy are formed. By the incorporation of proper amount of Si-PCPDTBT, the ternary solar cells with unprecedented high FF of $77\%$ can be achieved. Comprehensive investigation regarding morphology, transport behavior, recombination dynamics and device physics have been performed by advanced X-ray characterization, SIMS, TEM, light dependent current-voltage measurement and photo-CELIV.
8.3 Results and discussion

8.3.1 Photovoltaic performance and device physics

**Figure 8.1.** (a) Schematic of the device architecture used in this study. (b) Chemical structures of PTB7, Si-PCPDTBT and PC$_{71}$BM. (c) Thin film absorption spectra of the reference binary blends and ternary blends with varying content of Si-PCPDTBT sensitizer. (d) Energy diagram of PTB7, Si-PCPDTBT and PC$_{71}$BM.

We fabricated bulk heterojunction (BHJ) solar cells in an inverted configuration (**Figure 8.1a**), keeping the polymer to PC$_{70}$BM ratio constant at 1:1.5. Figure 1b,c shows the chemical structures of PTB7, Si-PCPDTBT and PC70BM and the contribution of the guest
polymer Si-PCPDTBT in the absorption spectra of the ternary systems, respectively. Si-PCPDTBT shows a clear ultraviolet-visible (UV-Vis) signature in the near-infrared (NIR) from 700–750 nm to 850 nm, and gradually increases when increasing the guest content. Simultaneously, the host donor absorption decreases slightly from 450 nm to 700 nm. Indeed, the complementary absorption characteristics and verified compatibility of the two polymers, in a preferred face-on orientation, make them good choices for ternary solar cells. Figure 8.2a shows the typical current density versus voltage (J–V) characteristics of the control devices and ternary systems under simulated AM 1.5 G solar irradiation (100 mW cm$^{-2}$).
Figure 8.2. (a) J–V characteristics of PTB7:Si-PCPDTBT:PC\textsubscript{70}BM ternary BHJ solar cells under solar simulator illumination (100 mW cm\textsuperscript{-2}). (b) EQE curves of the corresponding devices shown in (a) (c) V\textsubscript{oc} versus light intensity for the binary reference and 15 and 25 wt% Si-PCPDTBT ternary devices. The dashed lines represent linear fits of the data. (d) Charge collection probability (P(E, T)) versus voltage of the binary reference and 15 and 25 wt% Si-PCPDTBT ternary devices.
Table 8.1. Photovoltaic device parameters of binary and ternary inverted solar cells under 1 sun illumination.

<table>
<thead>
<tr>
<th>PTB7:Si-PCPDTBT:PCBM</th>
<th>$V_{oc}$ [V]</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:0:1.5</td>
<td>0.73</td>
<td>15.01</td>
<td>68.47</td>
<td>7.52</td>
</tr>
<tr>
<td>0.9:0.1:1.5</td>
<td>0.71</td>
<td>15.80</td>
<td>70.20</td>
<td>7.85</td>
</tr>
<tr>
<td>0.85:0.15:1.5</td>
<td>0.70</td>
<td>15.94</td>
<td>77.10</td>
<td>8.60</td>
</tr>
<tr>
<td>0.75:0.25:1.5</td>
<td>0.60</td>
<td>15.39</td>
<td>55.58</td>
<td>5.13</td>
</tr>
<tr>
<td>0.5:0.5:1.5</td>
<td>0.55</td>
<td>15.08</td>
<td>52.51</td>
<td>4.36</td>
</tr>
<tr>
<td>0:1:1.5</td>
<td>0.55</td>
<td>12.65</td>
<td>54.65</td>
<td>3.82</td>
</tr>
</tbody>
</table>

Table 8.1 summarizes the photovoltaics parameters for the devices. We achieved power conversion efficiencies of 7.5% and 3.8% for PTB7:PC70BM and Si-PCDTBT:PC70BM reference blends, respectively, which are in line with the current state of the art for solar cells using these polymers in an inverted architecture. Notably, with the incorporation of 15% of Si-PCPDTBT into the host blend, not only the $J_{sc}$ increased by around 6% (from 15.01 to 15.94 mA cm$^{-2}$), but more importantly we reached a high FF of 77%, leading to a PCE of 8.6%, which is 12.5% higher than the corresponding PTB7:PC$_{70}$BM binary blends. To date, the FF of 77.1% represents the highest FF for ternary BHJ solar cells. An average FF and PCE of 76.67% and 8.43%, respectively, was obtained for 20 devices. Meanwhile, loading a higher amount (25–50%) of sensitizer into the ternary system reduced the overall PCE, mainly due to a lowered FF. Generally, $V_{oc}$ is determined by the difference between the HOMO energy levels of the donor and the lowest unoccupied molecular orbital (LUMO) energy level of PC$_{70}$BM. As shown in Fig. 1d, the HOMO energy levels of the two donor
materials are $-5.15\ eV$ and $-5.05\ eV$, for PTB7 and Si-PCPDTBT, respectively. According to previous reports, $^{[142]}$ $V_{oc}$ of the ternary systems is often tuned continuously between the open-circuit voltage values of reference binary devices. This is in line with the observed gradual reduction of $V_{oc}$ from 0.72 in the reference device to 0.55 V for the 0.50:0.50:1.5 PTB7:Si-PCPDTBT:PC70BM ternary device.

To study the contribution of the two polymers to $J_{sc}$, we measured the external quantum efficiency (EQE) (Figure 8.2b). We note that the integrated EQE for these devices matches the measured $J_{sc}$ with a margin of less than 5%. Unlike the trend observed in the UV-Vis spectra, ternary solar cells with 10–15% of sensitizer content showed increased EQE values in the 600–750 nm region, where mainly PTB7 absorbs. This current gain from the host material suggests that addition of the sensitizer significantly improved charge separation and/or charge transport. Interestingly, the improvement of charge collection from the host represents the major contribution for the increased $J_{sc}$ in the ternary cells with 10–15% sensitizer, while absorption and EQE in the 700–850 nm region are still low. For the devices with 20–50% of Si-PCPDTBT content, a significant current contribution from absorption in the sensitizer is seen from the increased EQE in the 700–850 nm region, consistent with the absorption spectra of the ternary systems. In contrast to Lu et al., $^{[143]}$ where an enhancement in the fullerene region EQE (400–550 nm) upon the introduction of a sensitizer is reported, here for 10% and 15% Si-PCPDTBT concentrations the EQE values were improved mainly in the PTB7 absorption region (550–700 nm). However, loading higher amount of sensitizer reduces the EQE values in the PTB7:PC$_{70}$BM absorption region, leading to a lower overall $J_{sc}$ despite the significant contribution of Si-PCPDTBT in the NIR region. This decrease of
current collection for high sensitizer contents is caused by the formation of a Si-PCPDTBT wetting layer near the cathode that blocks electrons, as will be discussed later. If the enhanced EQE in the 600–750 nm region at low sensitizer concentrations is facilitated by enhanced charge collection due to the sensitizer, hole transfer from the host to the sensitizer is expected. To test this hypothesis, which is contrary to the operating principles of most ternary solar cells, we fabricated bilayer hole-only devices in an inverted configuration (Figure 8.3a). We found that a hole transfer occurs from PTB7 to Si-PCPDTBT, and not from Si-PCPDTBT to PTB7, which is also expected from the compound’s energy level diagram. This already suggests that charge transfer from the host polymer to the Si-PCPDTBT sensitizer may facilitate charge dissociation and further improve the charge extraction of the host system. To prove the efficient hole injection from MoOx into PTB7 and from PEDOT:PSS into Si-PCPDTBT, we fabricated hole-only pristine polymer devices. Supplementary Figure 2b,c shows a symmetric injection from the contacts into the polymers, without the presence of any energetic barriers.
Figure 8.3. Hole-only devices (a) Bilayer hole-only devices and proposed charge transfer / transport mechanism. The fabrication of the hole-only bilayer devices is made by first coating Si-PCPDTBT from a 20 mg/ml solution in chlorobenzene and then depositing PTB7 from a 10 mg/ml solution in toluene. Hole-only pristine Si-PCPDTBT (b) and PTB7 (c) devices.

The improved charge transport characteristics in ternary solar cells further allows fabricating devices with thick active layers that maintain a high FF (Figure 8.4). At 150 nm active layer thickness, the FF of the PTB7:PC$_{70}$BM solar cell has already dropped to 59%, as compared to 68% in the optimized device (100 nm). The ternary solar cell with 15%
sensitizer features an FF of 72% at a thickness of 150 nm that is higher than the FF of the optimized PTB7:PC70BM device despite a 50% increase of the layer thickness.

![J-V characteristics for thick devices](image)

**Figure 8.4.** J-V characteristics for thick devices. Current density-voltage characteristics of PTB7:PC70BM, PTB7:Si-PCPDTBT:PC70BM (0.85:0.15:1.5) with 150 nm active layer thickness.

The high FF in the ternary devices must have origin in a novel counterintuitive mechanism to manipulate and fine tune the recombination dynamics in organic BHJ composites. Thus, to get a deeper insight into the recombination and transport mechanisms, we measured the J–V curves as a function of illumination intensity for three different devices, PTB7:PC70BM, PTB7:Si-PCPDTBT:PC70BM (0.85:0.15:1.5) and PTB7:Si-PCPDTBT:PC70BM (0.75:0.25:1.5). At Voc conditions, all of the photogenerated charge carriers recombine within the carrier diffusion length inside the bulk. Thus, the
recombination mechanisms can be extracted by studying Voc as a function of generation rate. For bimolecular recombination, a slope of kT/q (thermal voltage at 300 K) in the plot of Voc versus the natural logarithm of the light intensity is expected. Instead, a signature of monomolecular or trap-assisted recombination is observed with an enhanced dependence of the open circuit on the light intensity (2kT/q).[144] As shown in Figure 8.2c, slopes of 1.22, 1.09 and 1.33kT/q were obtained for the PTB7:PC$_{70}$BM, PTB7:Si-PCPDTBT:PC$_{70}$BM (0.85:0.15:1.5) and PTB7:Si-PCPDTBT: PC$_{70}$BM (0.75:0.25:1.5) cells, respectively. Indeed, trap-assisted monomolecular recombination is weaker in the device with 15% guest compared to the PTB7:PC$_{70}$BM device. On the other hand, increasing the sensitizer content (25%) indicates that the bimolecular process evolves to trap-assisted recombination. As reported elsewhere, PTB7:PC$_{70}$BM solar cells suffer from trap states.[145] Therefore, our first analysis already suggests that the introduction of a small amount of sensitizer Si-PCPDTBT (15%) effectively deactivates traps in the host matrix and consequentially decreases monomolecular recombination.

To further understand the influence of Si-PCPDTBT on the charge dynamics of the host system, we measured the photocurrent density ($J_{\text{ph}}$) as a function of the effective voltage ($V_{\text{eff}}$), as shown in Figure 8.5. The measured photocurrent is defined as $J_{\text{ph}} = J_{l} - J_{d}$, where $J_{l}$ and $J_{d}$ are the current density under illumination at 100 mW cm$^{-2}$ and in the dark, respectively. $V_{\text{eff}}$ is given by $V_{\text{eff}} = V_{0} - V$, where $V_{0}$ is the compensation voltage defined as $J_{\text{ph}}(V_{0}) = 0$, and V is the applied voltage. The J–V plots indicate that $J_{\text{ph}}$ quickly saturates for $V_{\text{eff}} > 1$V, although the PTB7:Si-PCPDTBT:PC$_{70}$BM (0.75:0.25:1.5) ternary characteristics still show a slightly field-dependent extraction even at negative bias. Anyhow, in this
condition, we assume that all generated electron–hole pairs are dissociated and collected at the electrodes, and the saturation current ($J_{\text{sat}}$) is limited just by the total amount of absorbed incident photons. The $J_{\text{sat}}$ values for PTB7:PC$_{70}$BM, PTB7:Si-PCPDTBT:PC$_{70}$BM (0.85:0.15:1.5) and PTB7:Si-PCPDTBT:PC$_{70}$BM (0.75:0.25:1.5) BHJ cells were 152 A m$^{-2}$, 163 A m$^{-2}$ and 157 A m$^{-2}$, respectively, in line with the $J_{\text{sc}}$ values measured. To understand the different FF values, Figure 2d shows the charge collection probability $P(E, T)$ versus the applied voltage.\cite{146} $P(E, T)$ is determined by normalizing $J_{\text{ph}}$ with respect to $J_{\text{sat}}$ ($J_{\text{ph}}/J_{\text{sat}}$). Interestingly, the $P(E, T)$ values under short-circuit conditions for the three devices were 90%, 97% and 93%, respectively, consistent with the $J_{\text{sc}}$ values (Table 1), while $P(E, T)$ at the maximum power point ($M_{\text{pp}}$) decreases dramatically from the ternary system with 15% Si-PCPDTBT (88%) to the control PTB7:PC$_{70}$BM (77%) and PTB7:Si-PCPDTBT:PC$_{70}$BM (0.75:0.25:1.5) (68%) devices. The results suggest again that the incorporation of 15% of sensitizer facilitated charge dissociation and extraction in the $M_{\text{pp}}$ condition, leading to an excellent FF of more than 77% for the ternary organic solar cells.
Figure 8.5. Photocurrent density as a function of the effective voltage. Photocurrent density of PTB7:PC$_{70}$BM, PTB7:Si-PCPDTBT:PC$_{70}$BM (0.85:0.15:1.5) and PTB7:Si-PCPDTBT:PC$_{70}$BM (0.75:0.25:1.5) solar cells as a function of the effective voltage under 1 sun illumination.

Therefore, we next analyzed the transport behavior of ternary blend devices. First, we investigated the charge carrier mobility $\mu$ of the devices by employing the technique of photoinduced charge carrier extraction by linearly increasing voltage (photo-CELIV). [147]

Figure 8.6a shows the photo-CELIV measurements carried out on PTB7:PC$_{70}$BM, PTB7:Si-PCPDTBT:PC$_{70}$BM (0.85:0.15:1.5) and PTB7:Si-PCPDTBT:PC$_{70}$BM (0.75:0.25:1.5) ternary devices. We calculated a 28% improvement in mobility for the PTB7:Si-PCPDTBT:PC$_{70}$BM (0.85:0.15:1.5) system ($3.50 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$) compared to the reference PTB7:PC$_{70}$BM cells with a mobility of $2.57 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$. The higher mobility accounted for the enhancement of the EQE values in the 600–700 nm region, the
higher FF and the higher P(E, T) of the 15% guest content compared to the binary devices. Introducing a higher amount of Si-PCPDTBT led to a stronger decrease in the transport properties of the ternary blend, with a mobility of $7.90 \times 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$, in line with the poorer performance obtained. In parallel, we investigated the recombination mechanisms of the ternary systems in more detail. For this purpose, we studied the charge carrier lifetime ($\tau$) and charge carrier density ($n$) using transient photovoltage (TPV) and charge extraction (CE) measurements, respectively.$^{[148]}$ For both techniques, all samples were operated at $V_{oc}$, but under different background illumination intensity (from 0.2 to 4 suns). Combining these two powerful techniques, we were able to determine the charge carrier density in relation to the carrier lifetime, using the equation $\tau = \tau_0 (n_0/n)^{\lambda}$, where $\tau_0$ and $n_0$ are constants and $\lambda$ is the so-called recombination exponent.
Figure 8.6. (a) Photo-CELIV curves of PTB7:PC$_{70}$BM, PTB7:Si-PCPDTBT:PC$_{70}$BM (0.85:0.15:1.5) and PTB7:Si-PCPDTBT:PC$_{70}$BM (0.85:0.15:1.5) with laser excitation ($\lambda = 780\, \text{nm}$). All the transient measurements were recorded by applying a 2 V/60 s linearly increasing reverse bias pulse and a delay time (td) of 1 $\mu$s. (b) Charge carrier lifetime $\tau$, obtained from TPV, as a function of charge density $n$, calculated from CE measurements under $V_{oc}$ conditions (from 0.2 to 4 suns). The inset table presents the recombination order (R) of the studied systems. The dashed lines represent linear fits of the data. (c) and (d) Schematics of a three-phase morphology engineered by adding a more ordered polymer (green) into an amorphous solar cell (red and black depict the amorphous polymer and fullerene derivative, respectively). The ordered polymer provides efficient charge transport in the system with a narrow density of states. The energetic offset between the mixed amorphous and the crystalline material allows a spatial separation of electrons and holes. The density of states (DOS) is predicted by charge extraction measurements (c).

Figure 8.6b depicts $\tau$ versus $n$ for the ternary systems as well as the reference PTB7:PC$_{70}$BM binary cells. We found that the addition of 15% of Si-PCPDTBT enhances
the carrier lifetime ($\tau = 3.45 \mu s$) compared to PTB7:PC$_{70}$BM devices ($\tau = 2.61 \mu s$), while PTB7:Si-PCPDTBTPC$_{70}$BM (0.75:0.25:1.5) shows the lowest $\tau$ of 1.26 $\mu s$ under 1 sun illumination. The higher $J_{sc}$ obtained for PTB7:Si-PCPDTBTPC$_{70}$BM (0.85:0.15:1.5) also agrees with the charge carrier density values, where $n$ under 1 sun illumination decreases continuously from the 15% guest ternary with $n = 1.85 \times 10^{16} \text{ cm}^{-3}$ to the control PTB7:PC$_{70}$BM blend and the 25% guest devices with $n = 1.66 \times 10^{16} \text{ cm}^{-3}$ and $1.24 \times 10^{16} \text{ cm}^{-3}$, respectively. Further, the recombination exponent $\lambda$ shows the same trend as $\tau$ and $n$. A recombination order $R = \lambda + 1$ equal to 2 indicates almost perfect bimolecular recombination at open-circuit voltage conditions. We found $R = 2.09$ for the PTB7:Si-PCPDTBTPC$_{70}$BM (0.85:0.15:1.5) ternary solar cells, suggesting a mechanism close to an ideal bimolecular recombination, justified by the FF of 77%. On the other hand, a recombination order higher than two is attributed to the effect of trapping and release in energetic traps, as well as morphological traps.$^{[149]}$ We obtained $R = 2.22$ for the PTB7:PC$_{70}$BM reference, which confirms the aforementioned trapping effects for this system. This proves our hypothesis that charge transfer to the sensitizer (as observed in the measurements on bilayer devices) provides spatial separation of electrons and holes, as well as transport in ordered Si-PCPDTBTPC$_{70}$BM phases that have a lower degree of energetic disorder (Figure 8.6 c,d). Finally, we calculated a recombination order higher than 3 for the PTB7:Si-PCPDTBTPC$_{70}$BM (0.75:0.25:1.5) ternary system. Such high recombination orders have previously been correlated to spatial inhomogeneous charge carrier distributions within the active layer of organic solar. Considering the formation of a Si-PCPDTBTPC$_{70}$BM wetting layer at the cathode (Figure 8.7), an accumulation of electrons at this electron blocking layer can be
expected. This accumulation of electrons results in a highly inhomogeneous charge carrier distribution and the high recombination order, consistent with the decreased FF and inferior performance.

**Figure 8.7.** (a) and (b) 2D GIWAXS patterns for PTB7:Si-PCPDTBT:PC$_{70}$BM (0.85:0.15:1.5) (a) and PTB7:Si-PCPDTBT:PC$_{70}$BM (0.75:0.25:1.5) (b). (c) and (d) Plots of the component mass against SIMS sputtering time, which is normalized to the maximum sputtering time, for PTB7:Si-PCPDTBT:PC$_{70}$BM (0.85:0.15:1.5) (c) and PTB7:Si-PCPDTBT:PC$_{70}$BM (0.75:0.25:1.5) (d). The red dashed line is an indicator for the bottom interface between active layer and cathode. (e) Lorentz-corrected and normalized R-SoXS profiles for PTB7:PC$_{70}$BM, PTB7:Si-PCPDTBT:PC$_{70}$BM (0.85:0.15:1.5), PTB7:Si-PCPDTBT:PC$_{70}$BM (0.75:0.25:1.5) and Si-PCPDTBT:PC$_{70}$BM films under 284.2 eV.
8.3.2 Lateral morphology and molecular packing

To correlate the optoelectronic properties of ternary devices with the structural information, we first carried out resonant soft X-ray scattering (R-SoXS) to examine the lateral domain distribution within the active layer quantitatively and with high spatial resolution. The scattering profiles for PTB7:PC$_{70}$BM and Si-PCPDTBT:PC$_{70}$BM reveal a significant difference, indicating a distinctively different lateral morphology between these two binary blends (Figure 8.7e). However, the profiles for PTB7:PC$_{70}$BM, PTB7:Si-PCPDTBT:PC$_{70}$BM (0.85:0.15:1.5) and PTB7:Si-PCPDTBT:PC$_{70}$BM (0.75:0.25:1.5) are very similar to each other. The characteristic median length scale, calculated using $d = 2\pi q_{1/2}$, where $q_{1/2}$ is the half point of the integral of $\int Iq^2dq$, is around 23 nm for PTB7:PC$_{70}$BM, PTB7:Si-PCPDTBT:PC$_{70}$BM (0.85:0.15:1.5) and PTB7:Si-PCPDTBT:PC$_{70}$BM (0.75:0.25:1.5). Furthermore, the relative average composition variation, which is proportional to the square root of the integrated scattering intensity (ISI), is also comparable among blends with different amounts of Si-PCPDTBT (Figure 8.8).
Thus, blending Si-PCPDTBT into PTB7:PC$_{70}$BM binary film in different amounts does not cause any noticeable changes in the compositional domain size on a length scale of 10–20 nm, even though larger fullerene-dominated regions are observed in ternary blends (Figure 8.8b). We assume that the smaller domains dominate the transport/recombination properties of the bulk, as the larger domains are beyond the thickness of the active layer and the common diffusion length of organic materials (10–20 nm).

It is well known that crystallinity is frequently correlated with device performance in various material systems. Therefore, we used grazing-incidence wide-angle X-ray scattering (GIWAXS) to assess the evolution of crystallinity in ternary blends with different amounts of Si-PCPDTBT. From the two-dimensional (2D) pattern shown in Figure 8.7 a,b, both PTB7 and Si-PCPDTBT adopt a face-on orientation with respect to the substrate in both PTB7:Si-
PCPDTBT:PC$_{70}$BM (0.85:0.15:1.5) and PTB7:Si-PCPDTBT:PC$_{70}$BM (0.75:0.25:1.5) blends. The normalized one-dimensional (1D) profiles (shown in Figure 8.9) also demonstrate very similar diffraction intensities along circular, vertical and horizontal sectors in both blends. Again, the negligible variation of crystallinity in these two blends is not sufficient to explain the FF enhancement.

![Figure 8.9](image)

**Figure 8.9.** Normalized 1D GIWAXS profiles. Normalized 1D profiles along circular, horizontal and vertical sectors for PTB7:Si-PCPDTBT:PC$_{70}$BM (0.85:0.15:1.5) and PTB7:Si-PCPDTBT:PC$_{70}$BM (0.75:0.25:1.5).

### 8.3.3 Vertical segregation

Secondary ion mass spectrometry (SIMS), as a highly chemical sensitive technique, was utilized to provide the depth profiles of each component across the whole thickness of the active layers. As shown in Figure 8.7c,d, the depth distribution of each component is distinctly different in the PTB7:Si-PCPDTBT:PC$_{70}$BM (0.85:0.15:1.5) and PTB7:Si-
PCPDTBT:PC$_{70}$BM (0.75:0.25:1.5) blends. To be more precise, the mass fraction at the interface between the active layer and the cathode electrode was calculated. In the PTB7:Si-PCPDTBT:PC$_{70}$BM (0.85:0.15:1.5) blend, the mass ratio of Si-PCPDTBT:PTB7 is 0.65, while in the PTB7:Si-PCPDTBT:PC$_{70}$BM (0.75:0.25:1.5) film, the value becomes 2.64. We then postulate that an incomplete Si-PCPDTBT wetting layer is formed close to the cathode interface in the PTB7:Si-PCPDTBT:PC$_{70}$BM (0.85:0.15:1.5) blend, which collects the holes from host PTB7 and acts as a pathway for the holes generated in PTB7. However, in the PTB7:Si-PCPDTBT:PC$_{70}$BM (0.75:0.25:1.5) blend a complete Si-PCPDTBT wetting layer is formed due to the overwhelmingly higher concentration of Si-PCPDTBT than PTB7 at the bottom. Rather than promoting hole transport, this complete Si-PCPDTBT wetting layer behaves as a blocking layer for electrons near the cathode. Moreover, the mass fraction of PC$_{70}$BM in the PTB7:Si-PCPDTBT:PC$_{70}$BM (0.85:0.15:1.5) blend is 67%, compared with only 60% in the PTB7:Si-PCPDTBT:PC$_{70}$BM (0.75:0.25:1.5) film at the bottom. This enrichment of PC$_{70}$BM near the cathode in cells with 15% Si-PCPDTBT also contributes to the higher FF, due to more efficient charge extraction for electrons and the absence of parasitic recombination.

### 8.4 Conclusion

In summary, we successfully demonstrated that ternary composites with a distinct microstructure offer remarkable opportunities in device engineering which goes beyond the classical light harvesting approach. We carefully selected and incorporated a ternary sensitizer with energetic levels that allowed the transfer of charges from the trap-limited host
system into the highly ordered sensitizer. The efficient defect passivation of the PTB7 matrix is demonstrated by an almost perfect bimolecular recombination order (R = 2.09) and enhanced charge carrier mobility and lifetime. As a result, a high FF of 77% was achieved, surpassing the recombination limitations of the PTB7:PC_{70}BM reference cell. Furthermore, morphological analysis revealed that the introduction of Si-PCPDTBT into the host PTB7:PC_{70}BM has no significant impact on the host system microstructure, but improves performance by optimizing the electrical properties of the system. In view of obtaining similar results for further ternary composites, based on PTB7-th:Si-PCPDTBT:PC_{70}BM, our results suggest that ternary sensitization indeed has the potential to suppress recombination losses in other similarly affected binary systems. Moreover, this design rule creates an opportunity to reconsider low-FF materials providing efficient charge generation as host materials in the design of advanced composites for high-efficiency applications.
Chapter 9

Determination of Temperature-dependent Miscibility and Prediction of Phase Behaviors of Polymer Solar Cell Blends Using Optical Microspectroscopy

9.1 Preface

The morphology of bulk-heterojunction polymer solar cells (PSC) is highly dependent on processing conditions and the intrinsic properties of donor and acceptor materials. Thus a method of predicting the morphology is highly desirable. From the perspective of thermodynamics, miscibility between donor molecule and acceptor molecule provides the driving force for morphology formation. Herein, we developed a convenient and widely accessible method to assess miscibility between polymer and fullerene at various temperatures based on a combination of visible light microscopy (VLM) and UV-Vis absorption spectroscopy. Through prolonged isothermal annealing of certain polymer:fullerene blend, the polymer volume fraction $\phi$ in the mixed region under local thermodynamic equilibrium can be evaluated using the widely accessible UV-Vis absorption measurement, where absorption spectra of donor:acceptor blends are recorded and fit into component spectra. The reliability of this UV-Vis method is further verified by the well-established scanning transmission X-ray microscopy (STXM) method. More importantly, the quantitative measurement of temperature-dependent miscibility enables us to determine
phase behaviors and also effective molecular interaction parameters of PSC blends at certain temperature.

This work has been put into manuscript. Jianhui Hou group provided the materials. Harald Ade group conceived the idea. I made the thin films and conducted the VLM and UV-Vis absorption measurement. The simulation code was provided by Enrique D. Gomez.

9.2 Introduction

Molecular miscibility plays an important role in determining the physical and mechanical properties of any blend system. Conceptually, miscibility is the capability for a certain polymeric blend to form a homogeneous mixture over a range of temperature (T) and composition, whose absence provides the driving force to form a phase-separated morphology. Due to the existence of partial miscibility between components in polymer solar cell (PSC) blends, considering only discrete interfaces between phase-separated components and domains without consideration of purity are unrealistic. Recently, three-phase morphology including relatively pure aggregates from each component and amorphous intermixed phase has been widely observed and well recognized. Furthermore, definitive relations between the average purity of domains and device performance have been established. Therefore, miscibility is the key factor to provide a fundamental understanding on structure-performance relationships of any blend systems.

Polymers blended with small molecules as active layers have been seen steady and rapid progress in the field of polymer solar cells (PSCs) thanks to the large amount of new materials synthesized and novel processing condition employed. One of the key factors
contributing to the rapid progress is the manipulation and optimization of photoactive layer morphology, which impacts exciton dissociation, charge generation and charge recombination. Thus, in-depth understanding and accurate measurement of miscibility is imperative for further rational improvement of device performance. Previously, miscibility has been successfully observed by several methods, such as scanning transmission X-ray microscopy (STXM),\cite{108} dynamic secondary ion mass spectrometry (SIMS)\cite{84} and energy filtered transmission electron microscopy (EFTEM).\cite{150} However, these methods either highly rely on synchrotron facility or require high level of expertise and cost, which dramatically hinder the universality and accessibility of these methods to wider scope. Fundamentally, the miscibility is determined by molecular interaction parameter between donor molecule and acceptor molecule.\cite{150} Recently, effective $\chi$ parameter ($\chi_e$) at processing temperature can be potentially used as a metric to predict device performance by using temperature dependent miscibility acquired from synchrotron-based STXM. Therefore, quantitative measurement of miscibility with a feasible method is essential to the fundamental understanding of polymeric materials and rational optimization of PSC morphology and device.

Here, we developed an easy and widely accessible method based on the combination of visible light microscopy (VLM) and UV-Vis absorption spectroscopy. By isothermally annealing the blends at different temperatures, blends can reach thermodynamic equilibrium, which can be confirmed by the appearance of fullerene crystals and featureless mixed region from VLM images. The residual fullerene volume fraction within the mixed region can be evaluated by fitting the blend UV-Vis spectra to component UV-Vis reference spectra.
Subsequently, the binodal composition can be obtained with the consideration of the polymer degree of crystallinity in the mixed region. By implementing isothermal annealing at different temperatures, a wide range of temperature dependent binodal composition can be readily obtained. Furthermore, the effective molecular interaction parameter $\chi_e$ at different temperatures can be extracted from the simulated molecular interaction parameter - polymer volume fraction ($\chi_e$-$\phi$) phase diagram by following the binodal curve (the boundary between phase separated mixture and homogeneous mixture in $\chi_e$-$\phi$ phase diagram). Finally, the validity of this method is cross-checked by the well established STXM method. We believe this is an effective approach to predict the best process route and suitability of certain material combinations, which will speed up the optimization of complex morphology.

9.3 Results and Discussion

9.3.1 Crystallization induced by Isothermal annealing

First, we choose a high-efficiency PTB7-based analogue PBDT-TS1 as the model polymer due to its excellent photovoltaic device performance up to 10% efficiency and good solubility/processability under widely used halogenated or halogen-free solvents. Long-term isothermal annealing at various temperatures up to 3 days has been implemented to PBDT-TS1:PC$_{71}$BM (40 wt% PCBM loading) blends in order to reach thermodynamic equilibrium. **Figure 9.1** demonstrates the typical reflection visible light microscopy (VLM) images of PBDT-TS1:PC$_{71}$BM blends annealed at various temperatures. All blend films exhibit discrete PC$_{71}$BM crystals/aggregates with irregular shape and varying size. The density of crystals
decreases with annealing temperature, implying different binodal compositions between PBDT-TS1 and PC$_{71}$BM at different temperatures. Between those discrete PC$_{71}$BM crystals is the mixed region, of which the D/A composition (or amorphous polymer volume fraction) follows the binodal curve in the $\chi_c$-$\phi$ phase diagram.

![Figure 9.1](image)

**Figure 9.1.** Reflection VLM images of PBDT-TS1:PC$_{71}$BM blends under thermodynamic equilibrium by isothermally annealed at various temperatures up to 3 days. The chemical structure of PBDT-TS1:PC$_{71}$BM is shown to the right.
9.3.2 UV-Vis absorption measurements

In order to estimate the amorphous polymer volume fraction $\phi$ in the mixed region, we start with measuring the UV-Vis absorption spectra of pure PBDT-TS1 and pure PC$_{71}$BM, which are later used as reference for fitting the UV-Vis absorption spectra of PBDT-TS1:PC$_{71}$BM blends. Figure 9.2a plots the thickness normalized UV-Vis absorption spectra of pure PBDT-TS1 and pure PC$_{71}$BM. The differential absorption spectrum between pure PBDT-TS1 and pure PC$_{71}$BM, defined as $\Delta \text{O.D.}=\text{O.D.}_{\text{PBDT-TS1}}-\text{O.D.}_{\text{PCBM}}$, is plotted in Figure 2b. The well defined differential features, especially in the range of 600 nm - 800 nm indicates that the PBDT-TS1:PC$_{71}$BM blend is a suitable model system to implement robust UV-Vis spectra decomposition. Figure 9.2c and 2d exemplify the UV-Vis absorption spectra of PBDT-TS1:PC$_{71}$BM blends annealed at 160 °C and 240 °C. The UV-Vis absorption spectra are measured at three different locations in each film. The identical shapes across different locations confirm that the films are even and the impact from location variation is minimized. Note that the total intensity of UV-Vis absorption across different locations in each film exhibit certain variation. This is due to the slightly different film thickness from spin casting during sample preparation. The amorphous polymer volume fraction $\phi$ in the mixed region can be subsequently estimated by fitting the blend UV-Vis spectra into the component UV-Vis spectra. The comparisons between fitted blend UV-Vis spectra and measured blend UV-Vis spectra are summarized. It is noteworthy that the spectra fitting procedure is done without the correction of PC$_{71}$BM crystal absorption due to the small area
fraction of PC$_{71}$BM crystal (~5%) and large optical density difference between PC$_{71}$BM crystal and the mixed region.

**Figure 9.2.** (a) Thickness normalized UV-Vis absorption spectra of pure PBDT-TS1 and PC$_{71}$BM. (b) Differential UV-Vis absorption spectrum between PBDT-TS1 and PC$_{71}$BM. UV-Vis absorption spectra of PBDT-TS1:PC$_{71}$BM blends isothermally annealed at 160 °C (c) and 240 °C (d) across three different location of thin films. Optical density (O.D.) is defined as O.D.=\log(I_0/I), where I$_0$ is the incident light intensity and I is the transmitted light intensity.
9.3.3 Scanning transmission X-ray microscopy measurements

The results from UV-Vis absorption spectroscopy are further verified by the previously well established scanning transmission X-ray microscopy (STXM) method. **Figure 9.3a** displays the 2D STXM image of PBDT-TS1:PC$_{71}$BM blend annealed at 200 °C. The STXM image was acquired at 320 eV, where the vacuum contrast is maximized to emphasize the PC$_{71}$BM crystals, which are rendered as the dark region. The shape and size of PC$_{71}$BM crystal in the STXM image match well with the corresponding VLM image as demonstrated in Figure 9.1. **Figure 9.3b** illustrates the fitting procedure used in STXM measurements. The STXM line scan is implemented across the PC$_{71}$BM-depleted region around PC$_{71}$BM crystal as indicated as the red arrow in Figure 9.3a to record the Near Edge X-Ray Absorption Fine Structure (NEXAFS) spectra of the mixed region. The polymer composition in the mix region can be obtained by fitting the measured NEXAFS spectrum with the component spectra of pure PBDT-TS1 and pure PC$_{71}$BM.
Figure 9.3. (a) 2D STXM image of PBDT-TS1:PC$_{71}$BM blend annealed at 200 °C for 3 days and (b) fitting procedure of STXM line scan of that data acquired in PC$_{71}$BM-depleted region. The red arrow in (a) indicates the location and direction of STXM line scan. The orange and blue curves in (b) represent the component spectra of PBDT-TS1 and PC$_{71}$BM, respectively. Note: TS1 is short for PBDT-TS1 in (b) to save space.

9.3.4 Temperature dependence of effective molecular interaction parameters

The resultant PBDT-TS1 volume fraction $\phi$ within the mixed region between the PC$_{71}$BM crystals measured from STXM experiment at different temperatures are overplotted with the results from the UV-Vis absorption spectroscopy in Figure 9.4a. It is apparent that the UV-Vis absorption results and the STXM results are very consistent with each other within the error bars. This consistency confirms the validity of the UV-Vis absorption method.
Figure 9.4. (a) Plot of PBDT-TS1 volume fraction $\phi$ in the mixed region at different temperatures determined by the UV-Vis absorption method, overplotted with the value determined by STXM method. (b) Plot of $\chi_e$ at different temperatures, assuming polymer crystallinity of 20%. The solid line is the fitting function of $\chi_e = A + B/T + C/T^2$, with the fit parameters $A$, $B$ and $C$ shown in the inset. For comparison, $\chi_e$ values assuming 0% polymer crystallinity and 30% polymer crystallinity are shown in (c) and (d), respectively.

After obtaining the PBDT-TS1 volume fraction $\phi$ in the mixed region at different temperatures, the effective molecular interaction parameter $\chi_e$ at corresponding temperatures
can be extracted from the binodal curve in the simulated $\chi_e$-$\phi$ phase diagram as plotted in Figure 9.5 by correcting the assumed degree of crystallinity of PBDT-TS1 and assuming that the effective molecular weight is the actually molecular weight of the PBDT-TS1. It is noteworthy that the quantitative determination of polymer crystallinity in the mixed region requires the knowledge of the crystallization enthalpy of perfect PBDT-TS1 crystal, which has not yet been achieved and is thus outside the scope of this work. We note though that no melting peak can be observed in DSC thermogram of neat PBDT-TS1 (see Figure 9.6), possibly indicating that the crystallinity might be very low, consistent with the high degree of paracrystalline disordered observed in GIWAXS. Thereafter, the $\chi_e$-T phase diagram with varying assumed polymer crystallinity from 0% to 30% are constructed and plotted in Figure 4b, c and d. It is apparent that the assumed polymer degree of crystallinity only impact the absolute value of $\chi_e$, without changing the trend of $\chi_e$ with temperature. It is also noteworthy that the amorphous phase diagram shown in Figure 9.5 is simulated based on the assumption that ignores the chemical potential of the polymer crystals and the PCBM crystals.
Figure 9.5. Simulated $\chi_\phi$ phase diagram. Red curve is the binodal curve, which is the boundary between phase-separated mixture and homogeneous mixture. Black curve is spinodal curve, which divides the phase separation region into metastable region and unstable region. The simulation is carried out by assuming the number-averaged molecular weight of PBDT-TS1 $M_n=29$ KDa and polydispersity PDI=2.2. The simulation is based on the assumption that the chemical potentials of polymer crystallites and PCBM crystallites do not impact the phase diagram.
Figure 9.6. Differential scanning calorimetry (DSC) thermograms for pure PBDT-TS1.

Following the Flory-Huggins solution theory and thermodynamically self-consistent theory by Kyu and coworkers, the tendency of mixing for a certain polymer:fullerene blend is governed by the free energy of mixing in Equation 1 as follows:

\[
\Delta F_{\text{mix}} = kT \left[ \frac{\phi}{N} \ln \phi + (1 - \phi) \ln(1 - \phi) + \chi_e \phi(1 - \phi) \right]
\]

(Equation 1)

where, \( k \) is Boltzmann constant, \( T \) is absolute temperature (Unit: K), \( \phi \) is the volume fraction of polymer, \( N \) is the polymerization of the polymer and \( \chi_e \) is the effective molecular interaction parameter. Note that effective molecular interaction parameter accounts for the amorphous - amorphous interaction and amorphous - crystallite interaction and follows the Equation 2:

\[
\chi = \chi_{\text{ac}} \cdot \text{DoC}_{\text{fullerene}} + \chi_{\text{aa}} \cdot (1 - \text{DoC}_{\text{fullerene}})
\]

(Equation 2)
The first and second terms in Equation 1 represent the combinatorial entropy of mixing, which is always favorable of mixing. The third term represents the enthalpy of mixing, which can promote demixing (positive $\chi_e$) or mixing (negative $\chi_e$). Regarding the correlation between morphology and $\chi_e$ parameter, a higher $\chi_e$ leads to purer domain due to the higher tendency of demixing, reflected by the higher free energy of mixing $\Delta F_{\text{mix}}$. In many cases, the temperature dependence of $\chi_e$ is revealed to monotonically increase (phase behavior exhibiting lower critical solution temperature or LCST) or decrease (phase behavior exhibiting higher critical solution temperature or UCST) within certain temperature range. Accordingly, the phenomenological temperature dependence of $\chi_e$ can be described by Equation 3 as below

$$\chi_e = A + \frac{B}{T} \tag{Equation 3}$$

where $A$ and $B$ are temperature independent constants and $T$ is the absolute temperature. It is intriguing that in the case of PBDT-TS1:PC$_{71}$BM blend, the $\chi_e$ exhibits complex behavior within the temperature range from 140 °C to 240 °C as shown in Figure 9.4b. In particular, the $\chi_e$ increases with temperature until certain point, followed by gradual reduction at higher temperature. This indicates the coexistence of UCST and LCST phase behaviors in this system. Therefore, the simple $\chi_e$-T relation of $\chi_e$=A+B/T is not applicable here to obtain the temperature dependence of $\chi_e$. A more complex $\chi_e$-T relation as shown in Equation 4 has to be used to sufficiently describe the observed complex phase behaviors.$^{[32]}$

$$\chi_e = A + \frac{B}{T} + \frac{C}{T^2} \tag{Equation 4}$$
where $A$, $B$ and $C$ are temperature independent constants and $T$ is absolute temperature. The curve fitting of Equation 3 was applied to the $\chi_e$-$T$ plot in Figure 9.4b-d and the temperature independent constants $A$, $B$ and $C$ are fitted and listed as inset in Figure 9.4b-d.

### 9.3.5 Universality of the UV-Vis method

In order to verify the applicability of the UV-Vis method, another material system (PDPP3T:PC$_{61}$BM) is investigated. The UV-Vis absorption measurement is implemented for the PDPP3T:PC$_{61}$BM (40 wt% PCBM loading) blend thin films in the same manner as for PBDT-TS1:PC$_{71}$BM. The resultant PDPP3T polymer volume fractions in the mixed region under thermodynamic equilibrium at various temperatures are plotted in **Figure 9.7**. It is clear that the UV-Vis measurement and STXM measurement provide consistent results at 200 °C and 215 °C. However, a slight discrepancy between UV-Vis method and STXM method occurs at 165 °C with a difference just outside the error bars.
Figure 9.7. Plot of PDPP3T volume fraction $\phi$ in the mixed region at different temperatures determined by the UV-Vis absorption method, overplotted with the value determined by STXM method. The corrected UV-Vis result at 165 °C is also indicated as the green solid triangle.

The total area fractions of PC$_{61}$BM crystals are calculated to be 21.8%, 4.9% and 4.8% for PDPP3T:PC$_{61}$BM annealed at 165 °C, 200 °C and 215 °C, respectively. The apparently higher total area fraction of PC$_{61}$BM crystals at 165 °C is the principal reason for the underestimated PDPP3T volume fraction. In this case, absorption correction has to be done following the procedure described in the supporting information. The corrected UV-Vis spectra provide satisfactorily meaningful fitting results as convinced by the STXM measurements. Conversely, the UV-Vis measurements at higher temperatures provide consistent results with STXM method due to the small enough total area fraction of PC$_{61}$BM crystals, which leads to negligible absorption contributed from PC$_{61}$BM crystals. Another method of mitigating the underestimated results at high total area fraction of PCBMM crystals
is to reduce the size and density of crystals by manipulating the nucleation and growth process during isothermal annealing. The effort of minimizing the area covered by PCBM crystals is under way.

### 9.4 Conclusion

In summary, a novel and widely accessible method based on the combination of VLM and UV-Vis spectroscopy is established with the ultimate goal to quantify the temperature dependence of polymer:fullerene miscibility. The amorphous polymer volume fractions in the mixed region under thermodynamic equilibrium were measured in two different conjugated polymers blended with PC$_{71}$BM and PC$_{61}$BM, followed by the verification of the well-established STXM method. The results from UV-Vis method and STXM method are consistent given that the total area fraction of PCBM crystals is under certain threshold. Furthermore, the methodology provided here enables us to determine the phase behaviors of polymeric materials and Flory-Huggins interaction parameters at a wide range of temperatures. By fitting the phenomenological $\chi_e$-T relation, one can correlate the temperature dependent $\chi$ parameters to the morphology formation and evolution, which potentially enables to explain and predict device performance of PSC and related electronics.
Chapter 10

Conclusions and Outlooks

OPVs have been making rapid progresses over the last decade thanks to the innovative synthesis of high-performing materials and more complete and comprehensive morphology - property - performance correlations. The charge carrier generation and transport within the photoactive layer involves a large multiplicity of photoabsorption, exciton generation, CT state dissociation, geminate recombination and bimolecular recombination, of which the relevant length scales span from several Å to hundreds of nm. No single technique is capable of providing meaningful morphological information across the whole relevant length scales with equal importance and accuracy. In order to obtain the most comprehensive pictures about photoactive layer morphology, it is necessary to systematically and judiciously combine various characterization tools, such as TEM, AFM, GIWAXS, R-SoXS, STXM and D-SIMS.

Among all of the techniques mentioned above, R-SoXS stands out thanks to its unique power of providing highly quantitative and statistical morphological information spanning wide spatial range from several nm to several hundred nm. Several critical aspects of morphology, such as domain spacing, domain purity and molecular orientation, were perceived as rather difficult to characterize before the advent of R-SoXS. The unprecedented information with high chemical sensitivity and high spatial resolution delivered by R-SoXS renders the quantification of domain spacing and domain purity easy to achieve. Besides, the
molecular orientation relative to the D/A heterojunction interface, which involves both crystalline fraction and amorphous fraction, can also be determined in a quantitative way. All of these achievements realized by R-SoXS earns its critical position in morphology investigation of organic materials.

At present, we have established the quantitative correlation between several aspects of morphology with other physical properties, including charge carrier mobility, UV-Vis absorption and charge carrier recombination. Especially, the phase separation at multiple length scales have been quantified and its role in charge creation and recombination in efficient organic solar cells have been elucidated for the first time. Besides, the previously untouched morphological aspect, namely the molecular orientation relative to D/A interface within non-fullerene BHJ blends, have been successfully resolved by R-SoXS and correlated with device performance.

Along with the rapidly increasing number of donor and acceptor materials synthesized every year, extensive work has to be put into finding suitable processing conditions for each new donor/acceptor combination by trial and error, guided only by some heuristic principles, which costs large amount of effort and energy. Therefore a method of predicting the best processing route and the suitability of a certain D/A is highly desirable. To this regard, we have made initial successes in developing a new method based on the widely accessible UV-Vis absorption measurement and optical microscopy to assess the effective molecular interaction parameter, which in turn controls the phase separation behaviors of organic blends. The phase separation behaviors predicted by the effective molecular interaction, in conjunction with the already established morphology - property - performance correlation,
will provide invaluable guidelines for further optimization of OPV devices toward ultimate commercialization.

Until now, most of the morphological aspects relevant to device performance have been resolved quantitatively by the combination of the above mentioned morphology characterization tools. Furthermore, the prediction of morphology has also been seen to make the first step successfully. Considering that the BHJ solar cells have only been studied and investigated in scientific community for less than 30 years and the maximum PCE of BHJ solar cells is still below half of the theoretical maximum, we believe that the OPVs will still make rapid and steady progress in the near future with the aid of more comprehensive understanding of morphology and its role in determining device physics.
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