Poly(3-hexylthiophene) nanofibers for organic photovoltaic applications

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NANYANG
TECHNOLOGICAL
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**POLY(3-HEXYLTHIOPHENE) NANOFIBERS FOR
ORGANIC PHOTOVOLTAIC APPLICATIONS**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING
2012

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ORGANIC PHOTOVOLTAIC APPLICATIONS**

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PHOTOVOLTAIC APPLICATIONS

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Abstract

Dwindling non-renewable energy resources, as well as global warming and air pollution, have forced human beings to seek for alternative resources. Solar energy is one of the most attractive candidates to replace fossil fuels in years to come. Therefore, the research into improving the efficiency, the lifetime and the cost of solar cells has gained momentum worldwide in recent years. Organic solar cells are highly viable as cheaper options for energy harvesting. At present, the best power conversion efficiency (PCE) of close to 10% has been demonstrated although further development is still required to push the efficiency beyond the limit required for commercialization. The application of one-dimensional organic nanostructures based on conjugated polymers for organic solar cells has gained some interest recently. These nanostructures enable highly efficient solar cell devices, through improved photon harvesting and enhanced charge transport. In particular, solar cell devices based on the nanostructures of poly(3-alkylthiophene) derivatives have exhibited PCEs in the range of 3 – 4%. Nevertheless, the performance of organic nanostructure devices generally falls below those that undergo the conventional thermal annealing. The work presented in this thesis focuses on poly(3-hexylthiophene) (P3HT) nanofibers and their applications for organic solar cells, and is expected to drive the research of other organic nanostructures with high aspect ratios. The optical, electrical and morphological characterizations of the P3HT nanofiber blends reveal the potential as well as the limitations of the organic nanostructure system. It was found that the morphology of the blends of P3HT nanofibers and fullerene molecules should be optimized to reduce holes recombination prior to extraction to external electrodes. The poorer device performance could be attributed to the poor interconnectivity between the nanofibers. Subsequently, with the application of solvent additives with high boiling points and with the suitable interaction energies with the active materials, improvement in the morphology results in a better-connected nanofiber blend. The benefit of organic nanostructures is more pronounced in an all-polymer blend system, which may suffer either a more severe phase separation or intermixing. It is shown that the pre-formed P3HT nanofibers could maintain their crystallinity in the all-polymer blend, thus enabling improved blend absorption, exciton dissociation and charge transport. Besides all-polymer blends, in terms of morphological stability, organic nanostructures also have an edge for ternary blend systems. The negative impact of the dopant molecules on the original blends is moderated when the active materials are transformed into the more morphologically stable organic nanostructures.

CHAPTER ONE

Introduction

1.1 Background

The ever-increasing global energy demand is mainly driven by the growth in world population and the rise in income. According to the *Statistical Review of World Energy* and the *Energy Outlook 2030* published by BP in 2011, the world consumption of the primary energy, which encompasses both tradable renewable and non-renewable resources, was 12 billion TOE (or 504 EJ) in 2010.^{1,2} As compared to the consumption in the previous year, there was a record growth of 5.6%, the highest in the past four decades. The world primary energy consumption was projected to still increase by 39% over the next 20 years (Fig. 1.1), of which more than 80% would come from fossil fuels. In the long run, however, the market share of these fuels, oil in particular, will decline for the following reasons: (1) steady increase in world oil prices due to incessant oil depletion, (2) volatility of world oil prices because of political instability (for instance, the recent “Arab Spring”) and (3) implementation of greenhouse gas control policies that restrict the burning of fossil fuels as part of the climate change and air pollution mitigation measures. On the other hand, the aftermath of the 2011 Fukushima nuclear disaster has also sparked a myriad of debates on the future prospects of nuclear energy. Therefore, the market share of low-emission renewable resources is expected to have a more accelerated growth in the long term.

Fig. 1.1 Projection of world primary energy consumption until 2030.²

There is potentially an inexhaustible supply of energy resources to sustain the worldwide demand, ranging from solar, wind, hydroelectric, geothermal, ocean and biomass (Table 1.1). To illustrate this abundance, the approximate annual solar radiation received by the earth after reflection by the upper atmosphere is 3,850,000 EJ. This means that simply by

harnessing the solar energy efficiently for a day, it is more than sufficient to fulfill global energy consumption for the whole of the next decade. This bright outlook on solar energy is also substantiated in a recent publication by International Energy Agency (IEA), the *Solar Energy Perspectives*, which presents an optimistic yet realistic projection of solar energy to contribute approximately one-third of the global energy demand after 2060.³ The solar energy has to be converted into the more practical forms of energy; such as electricity *via* photovoltaics (PV) and thermal energy *via* concentrated solar thermal power (CSP) or solar water heating (SWH) technologies. According to the *Renewables Global Status Report 2011* published by REN21, the worldwide PV capacity alone has grown by 72% in 2010 as compared to the year before, with 75% of the installation done in Europe (44% in Germany).⁴ The other dominating PV markets are Japan, the United States, South Korea and China, and it is expected that other countries in the Middle East, Southeast Asia and Africa will also join as key players in the near future.

Table 1.1 The renewable resources in EJ (1 EJ = 10^{18} J).⁵

Renewable Sources	Theoretical Potential Energy
	(EJ/year)
Solar energy	3,850,000
Wind energy	590
Hydropower	150
Geothermal energy	137,900,000
Ocean energy	7,300
Biomass energy	2,860

The history of PV dates back to the early 19th century with the discovery of the photovoltaic effect by Becquerel.⁶ However, this fascinating material property, which enables current or voltage generation in a material upon light exposure, was only considered to have great potential when Chapin, Fuller and Pearson from Bell Laboratories unveiled their silicon *p-n* junction solar cell with a remarkable power conversion efficiency (PCE) of 6%.⁷ Ever since, the silicon solar cell has progressed tremendously in terms of performance with the best-reported PCE of 25% based on monocrystalline silicon (*m*-Si).⁸ Two main issues based on the single-junction *m*-Si devices are: (1) high production cost of the highly pure single crystal Si and (2) the necessity to use thicker absorber layer due to the indirect bandgap of Si. The alternatives to *m*-Si are polycrystalline (*poly*-Si) and amorphous silicon (*a*-Si), which are less

costly in terms of processing though they have compromised performance (best PCEs of 20.4% and 12.4%, respectively).⁸ The *a*-Si, which has better absorption properties than *m*-Si and can be directly deposited onto substrates without intricate processing, also makes up a portion of the market for thin film solar cells, together with cadmium telluride (CdTe) and gallium arsenide (GaAs). Due to their direct bandgaps, CdTe and GaAs have efficient light absorption, enabling thin film devices with PCEs as high as 16.7% and 28.1%, respectively.⁸ The toxicity issue of both CdTe and GaAs has also prompted the development of thin film solar cells based on materials with lower health risks, such as copper indium gallium selenide (CIGS) with best reported PCE of 19.6%.⁸ To enhance the performance of the solar cells, it is possible to use the multijunction cells in tandem configuration, which allows the capture of a wider spectrum of sunlight, coupled with a total spectrum solar concentrator. To date, the best solar cell reported that is NREL certified is from Solar Junction using GaInP/GaAs/GaInNAs multijunction cell with a solar concentrator (418 suns) with a PCE of 43.5%.⁸ Despite the high efficiency, the material limitations in terms of availability, processing and toxicity pose a crucial challenge for these inorganic solar cells.

Fig. 1.2 Global PV capacity in 2010.⁴

1.2 Organic solar cells

Organic solar cells based on either conjugated polymers or small molecules, or their mixtures, are progressively becoming more attractive.⁹⁻¹⁶ Their advantage over inorganic thin film solar cells arises from the possibility of the devices to be fabricated at low cost, using simple and easy-to-scale-up solution processes (roll-to-roll techniques). These devices also offer additional benefits of being lightweight, mechanically flexible as well as having the ability to tailor both

optoelectronic properties of the active components through synthesis and processing. All of these interesting features are also found in organic light emitting diodes (OLED), which are now commercially viable. Although much effort has been directed to its development, as compared to the inorganic counterpart, the organic solar cell is still below par in terms of device efficiency. Improvement in device efficiency and lifetime are prerequisites to produce commercially viable organic solar cells.

The first practical organic solar cell was demonstrated by Tang in 1986 using a bilayer configuration consisting of phthalocyanine (*p*-type) and a perylene derivative (*n*-type) with PCE of 1%.¹⁷ The performance of the small molecular bilayer device, also known as double heterojunction, could be improved by substituting the *n*-type (acceptor) material with fullerene (C₆₀) and incorporation of blocking layers. With active layer thickness optimization of ITO/PEDOT:PSS/CuPc/C₆₀/BCP/Ag device, Xue *et al.* demonstrated PCE of 4.2% more than a decade after Tang's discovery.¹⁸ Nowadays, the performance of small molecular multilayered organic solar cells has increased tremendously through the use of tandem architecture with the world record PCE of 9.8% unveiled by Heliatek GmbH.¹⁹ The multilayered organic solar cell has an inherent shortcoming in that it requires precise control of the active layer thickness and the material deposition is primarily done using costly low vacuum evaporation.

Fig. 1.3 Typical device structure of a bulk heterojunction organic solar cell device.

Bulk heterojunction configuration offers feasible solutions to the limitations of multilayered devices. The typical structure of such devices is shown in Fig. 1.3. The concept was first presented by Yu *et al.* by using a well-mixed blend of phenylene vinylene polymer (MEH-PPV) and C₆₀.²⁰ The donor polymer and fullerene acceptor form a bicontinuous network

with efficient charge generation. This solution-processed single layered device exhibited an efficiency of 2.9% under 0.2 sun illumination. Following this success, the blends of other donor polymers, such as MDMO-PPV and poly(3-hexylthiophene) (P3HT), with fullerene derivative, *i.e.* [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM), also yielded efficient solar cell devices with PCE of 3.3%²¹ and 5%²² under 1 sun illumination. The solvent-soluble derivatives of poly(phenylene vinylene) and polythiophene, which constitute the second generation π -conjugated polymers, have been widely investigated for solar cell applications. In recent years, there has been great interest to extend the functionalities of semiconducting polymers through the incorporation of novel structural units. The so-called third generation π -conjugated polymers typically have more intricate structures, as shown in a few reviews.²³⁻²⁷ Most of the current work is directed towards the development of novel materials that can harvest sunlight over a wider wavelength range with maximum photovoltage. At present, remarkable efficiencies have been obtained for blend systems based on the new polymers, such as poly[*N*-9''-heptadecanyl-2,7-carbazole-*alt*-5,5-(4',7'-*di*-2-thienyl-2',1',3'-benzothiadiazole) (PCDTBT)²⁸ and copolymer of thieno-[3,4-*b*]thiophene and benzodithiophene (PTB7)^{29,30} with PC₇₁BM result in PCEs of 6.1% and 8.4%, respectively. The solution processibility feature of bulk heterojunction has also been extended for all-small molecular solar cells. For instance, the PC₇₁BM blends with 3,6-*bis*(5-(benzofuran-2-yl)thiophen-2-yl)-2,5-*bis*(2-ethylhexyl)-pyrrolo[3,4-*c*]pyrrole-1,4-dione (DPP(TBFu)₂)³¹, squaraine (SQ)³² and 5,5'-*bis*{4-(7-hexylthiophen-2-yl)thiophene-2-yl}-[1,2,5]-thiadiazolo[3,4-*c*]pyridine-3,3'-*di*-2-ethyl-hexylsilylene-2,2'-bithiophene (DTS(PTTH₂)₂)³³ give solution-processible solar cells with PCEs of 4.4%, 5.5% and 6.7%, respectively.

Table 1.2 Device characteristics of solution-processible organic solar cell devices with record efficiencies.

Blend System	PCE	J_{sc}	V_{oc}	FF	Ref.
	%	(mA/cm ²)	(V)		
PCDTBT:PC ₇₁ BM (1:4)	6.1	10.6	0.88	0.66	[28]
PTB7:PC ₇₁ BM (1:1.5)	8.4	15.8	0.76	0.70	[30]
DPP(TBFu) ₂ :PC ₇₁ BM (3:2)	4.4	10.0	0.92	0.48	[31]
SQ:PC ₇₁ BM (1:6)	5.5	12.0	0.92	0.50	[32]
DTS(PTTH ₂) ₂ :PC ₇₁ BM (7:3)	6.7	14.4	0.78	0.59	[33]

Fig. 1.4 Chemical structures of donor materials with record efficiencies: (a) PCDTBT, (b) PTB7, (c) DPP(TBFu)₂, (d) SQ and (e) DTS(PTTH₂)₂.

In order to understand the origin of the device efficiencies and to devise methods to improve them, it is necessary to understand the typical optoelectronic processes occurring at molecular level in an organic solar cell device as shown in Fig. 1.5. Brédas *et al.* have provided an elaborate overview of the molecular processes.³⁴ In principle, there are four fundamental steps involved in the conversion of light energy to electrical energy in an organic solar cell device:

(1) *Light absorption and exciton formation.* A few conjugated organic semiconductors, either polymers or small molecules, have excellent absorption properties, which are characterized by high absorption coefficients and tunable absorption wavelengths. The former property enables these materials to harvest light efficiently even with a thin absorber layer (*i.e.* less than 0.3 μm). When the donor absorbs light, or photon, electrons are excited from the highest-occupied molecular orbital (HOMO) to the lowest-unoccupied molecular orbital (LUMO) forming electron-hole bond pairs, or excitons. Due to the low dielectric constant in organic materials, electrons and holes tend to have strong coulombic interactions. Therefore, in contrast to the inorganic solar cell, there is no instantaneous formation of free charge-carriers upon photoabsorption.

(2) *Exciton diffusion.* In order to generate holes and electrons, excitons have to diffuse to the interfaces between donor and acceptor (D/A) phases. Nevertheless, these excitons, also termed singlet excitons, are short-lived with lifetime in the nanosecond (ns) range. The singlet excitons diffuse *via* long-range Förster resonant energy transfer (FRET), and have typical diffusion length of less than 20 nm.^{35,36} The other type of excitons, *i.e.* triplet excitons, which are the minority excitons formed, has longer lifetime in the microsecond (μ s) range despite their low diffusivity as they diffuse *via* short-range Dexter energy transfer. The exciton diffusion length, in particular that of the singlet exciton, sets the requirement on the active layer thickness in bilayer heterojunction cell, as well as the dimension of the donor or acceptor domains in bulk heterojunction. To ensure efficient exciton diffusion to the interfaces, the ideal domain size has to be within 20 nm.

Fig. 1.5 Schematic diagram of typical processes involved in an organic solar cell device. D denotes the donor, while A denotes the acceptor.

(3) *Exciton dissociation and charge transfer.* Due to the internal electric field at D/A interfaces, singlet excitons that manage to reach the interfaces before decaying can be dissociated into charges. The exciton dissociation generally occurs in two steps. Firstly, the excitons convert themselves into the charge transfer (CT) states. These states can either recombine to the ground states or evolve into charge-separated (CS) states, depending on both energetics and kinetics of the separation. If the CS states are more thermodynamically stable and kinetically favorable, the excitons can be separated into holes, which stay in the donors, and electrons, which get transferred into the acceptors. In order to increase the efficiency of exciton dissociation, the amount of D/A interfaces has to be maximized.

(4) *Charge transport and collection at the electrodes.* Upon separation, the holes are transported to the anode, while the electrons go to the cathode. The two types of charges move in the opposite direction due to the build-in potential attributed to the difference in the work functions of both electrodes. Charge mobility, which has great dependency on the degree of order in the donor or acceptor phase, can be used to characterize the efficiency of charge transport within the active layer. Typically, amorphous organic semiconductor with low degree of order has low charge mobility ranging from 10^{-6} to 10^{-3} cm^2/Vs , while highly crystalline material exhibit higher mobility by a few orders of magnitude.³⁷⁻³⁹ In a bulk heterojunction device, donor and acceptor phases are intimately yet randomly mixed with each other. Therefore, it is crucial to engineer percolation pathways for both holes and electrons to ensure efficient charge transport to the respective electrodes.

Apart from the selection of compatible active materials with suitable optoelectronic properties, the blend morphology of the bulk heterojunction, *i.e.* how the donor and acceptor are distributed in the blend, is also very important to consider in obtaining high efficiency organic solar cells. To have efficient exciton dissociation, maximum amount of D/A interfaces is required, while undisturbed charge transport can only be realized with continuous domains with minimum amount of interfaces. Nevertheless, with appropriate morphological control, it is possible to have optimum exciton dissociation and charge transport, leading to maximum photocurrent generation. The blend morphology is strongly dependent on the properties of the active materials, such as molecular weight, polymer regioregularity, polymer end groups and side groups.⁴⁰ The blend composition and the choice of solvent used to deposit the blends also have significant influence on the nanoscale morphology. Additionally, there are various processing techniques to optimize the blend morphology, such as thermal annealing, solvent annealing, solvent additive and the use pre-formed organic nanostructures, which have been elaborated in a few review articles.⁴¹⁻⁴⁴

By extending the thermodynamic framework developed by Shockley and Queisser,⁴⁵ Giebink *et al.* demonstrated that the maximum efficiency achievable for the single-junction organic solar cells is 22%.⁴⁶ In an independent semi-empirical calculation, Lunt *et al.* showed that the efficiency limit is around 17% after taking optical losses and other possible electrical losses into consideration.¹² For a two-cell tandem solar cell, the efficiency limit increases to 24%, a 40% increase attributed to both improved photocurrent and photovoltage. Comparing to these efficiency limits, there is still room for the current state-of-the-art efficiencies (8–9%) to

improve and it is expected that the research into ways to improve the efficiencies of organic solar cells will still expand in the next few years. Furthermore, if the lifetime of organic solar cells can be improved to more than a decade, either by using active materials with better stability or by applying better encapsulation, the commercialization of organic solar cells will soon come into realization.

1.3 Device characteristics

Fig. 1.6 shows the typical current density-voltage (J - V) characteristics of a solar cell device. The short-circuit current (J_{SC}) and the open-circuit voltage (V_{OC}) are characterized by the curve intersections with the y - and x -axes, respectively. The maximum power point (MPP) is defined as the point along the J - V curve with the highest power product per area (*i.e.* $J_{mpp} \times V_{mpp}$), while the fill-factor (FF) is defined as

$$FF = \frac{J_{mpp} \times V_{mpp}}{J_{SC} \times V_{OC}} \quad (1.1)$$

As shown in Fig. 1.6, the FF is the ratio between the areas of the shaded rectangle to the light blue region. At certain illumination intensity (P_{in}), the power conversion efficiency (PCE) of a device can be calculated using the following relationship

$$PCE = \frac{J_{SC} \times V_{OC} \times FF}{P_{in}} \quad (1.2)$$

Fig. 1.6 Current density-voltage (J - V) characteristics of a solar cell device.

1.4 Organic nanostructured solar cells

Organic nanostructures based on π -conjugated semiconductors (small molecules, oligomers

and polymers) form another division of molecular building blocks for micro- and nano-electronic and optoelectronic applications. Out of this array of building blocks, one-dimensional (1-D) nanostructures have attracted a great deal of interest in recent years.⁴⁷⁻⁵² In terms of optical properties, 1-D organic nanostructures may exhibit anisotropic excitonic confinement effect along the long axes of the nanostructures. In addition, amplification of fluorescence quenching may be observed due to the enhanced exciton diffusion within the highly ordered nanostructures. Charge transport properties are also expected to improve in the 1-D organic nanostructures compared to the amorphous bulk organic films. The 1-D nanostructures with various morphologies, ranging from nanowires, nanowhiskers, nanorods, nanoribbons to nanotubes, can be synthesized using different approaches: template-assisted synthesis, electrospinning, nanolithography, layer-by-layer (LBL) deposition, physical vapor deposition and supramolecular self-assembly.⁴⁷⁻⁵² There are two types of templates used for the growth of the nanostructures: (1) hard templates (*e.g.* particle track-etched membranes (PTM) and anodic aluminum oxide (AAO) membranes) and (2) soft templates using block copolymers, surfactants, liquid crystals and other organic nanostructures.⁴⁹⁻⁵¹ By growing new structures onto the pre-existing ones, it is feasible to generate hybrid nanostructures. Supramolecular self-assembly of π -conjugated systems, which can be done either in bulk solution or at the interfaces or surfaces, depends largely on the intermolecular interactions among the molecules or between the molecules and substrates. There are different types of forces contributing to the formation of organic nanostructures: π - π interaction, dipole-dipole, van der Waals, hydrogen bonding, hydrophobic and electrostatic interaction. Several forces may also be involved simultaneously during the self-assembly process. Since these interactions are non-covalent in nature, the self-assembled entities are susceptible to their environments, such as temperature and solvent. Nevertheless, as pointed by Kim *et al.*,⁴⁹ the supramolecular self-assembly is still a preferred technique as it has the following virtues: (1) simplicity of the approach, (2) large-scale synthesis of the nanostructures, (3) fine-tuning of the nanostructure dimensions, (4) possibility to obtain hybridized nanostructures and (5) high reproducibility. In this thesis, we will focus on the solution-phase self-assembly of the 1-D organic nanostructures because of its versatility in generating reproducible structures independent of substrates.

Poly(3-alkylthiophene) (P3AT) derivatives are a group of donor materials ubiquitously used to generate 1-D organic nanostructures, such as nanofibers or nanowires,

for solar cell applications. After the discovery of P3AT crystallization in solution in the form of nanowhiskers by Ihn *et al.* in 1993,⁵³ there have been numerous studies on how to control self-assembly of the polymer analogues. In-situ studies on the self-assembly of P3AT in a marginal solvent using techniques such as differential scanning calorimeter (DSC), temperature-dependent rheological and UV-Vis absorption measurements, small-angle X-ray scattering (SAXS), small-angle neutron scattering (SANS) and ultra small-angle neutron scattering (USANS), have revealed how the polymer chains transform into organic nanostructures.⁵⁴⁻⁵⁷ In principle, there are two steps involved: (1) “coil-to-rod” transformation or the aggregation of the polymer chains into 1-D fiber-like structures and (2) formation of thermoreversible network, or gelation, from the crystalline nanofibers. On top of these investigations, the crystal structures of the different P3ATs also have been systematically studied using complementary X-ray and electron diffraction techniques.⁵⁸

Table 1.3 Device characteristics of representative solar cell devices using polymer nanostructures as donors. The values shown are based on 1 sun (100 mW/cm²) illumination.

Donor	Acceptor	Ratio	Solvent	Annealing	PCE	J_{sc}	V_{oc}	FF	Ref.
					%	(mA/cm ²)	(V)		
1	PC ₆₁ BM	1:1.1	<i>p</i> -xylene	n/a	3.40	9.90	0.59	0.58	[59]
	PC ₆₁ BM	1:1	DCM	n/a	3.23	9.51	0.59	0.58	[60]
	PC ₆₁ BM	1:1	CB/acetone	140 °C, 3 min	3.60	9.58	0.62	0.61	[61]
	PC ₆₁ BM	1:1	CB/cyclohexanone	100 °C, 10 min	4.04	10.9	0.60	0.62	[62]
	PC ₆₁ BM	1:1	CB/acetonitrile	100 °C, 15 min	4.09	10.4	0.61	0.64	[63]
2	PC ₇₁ BM	1:1	<i>o</i> -DCB	160 °C, 10 min	3.33	9.81	0.54	0.63	[64]
3	PC ₇₁ BM	1:1	<i>o</i> -DCB	110 °C, 10 min	3.00	8.43	0.60	0.59	[65]
4	PC ₇₁ BM	1:0.5	<i>o</i> -DCB	150 °C, 10 min	4.15	9.15	0.72	0.63	[66]
5	PC ₇₁ BM	1:0.75	<i>o</i> -DCB	140 °C, 20 min	4.02	10.3	0.63	0.62	[67]
6	PC ₇₁ BM	1:1	<i>o</i> -DCB	110 °C, 5 min	3.38	9.85	0.53	0.65	[68]
7	PC ₇₁ BM	1:4	<i>o</i> -DCB	n/a	1.76	5.55	0.57	0.55	[69]

Table 1.3 summarizes the device parameters of a few representative organic nanostructured solar cells in the literatures. The corresponding chemical structures of the polymers, which are mostly based on P3AT and copolymers of P3AT, are shown in Fig. 1.7. The following are the potential merits of the solar cells based on 1-D organic nanostructures: (1) better control of morphology for blends with phase separation issues, (2) typical width of the nanostructure is within the exciton diffusion length, (3) enhanced exciton diffusivity as

they migrate within the crystalline regions of the nanostructure, (4) excellent pathways for hole transport with high carrier mobilities, (5) thermal-free approach, compatible with flexible plastic substrates and (6) enhanced morphological stability. Berson *et al.* have successfully demonstrated for the first time that the application of P3HT nanofibers grown in *p*-xylene resulted in efficient solar cell devices with PCE of 3.4%.⁵⁹ The high performance is believed to originate from the improvement in optical absorption and charge transport properties. This observation is common for most of the nanofiber devices. They have also attributed the role of amorphous non-fiber P3HT, *i.e.* the remaining portion of the polymers that do not undergo self-assembly, as the “glue” interconnecting the nanofibers. Consequently, the ratio of the fiber-to-non fiber P3HT in the blends strongly affects the device performance. Besides *p*-xylene, the other marginal solvent that has been demonstrated to generate 1-D P3HT nanostructures used for solar cells is dichloromethane (DCM). Kim *et al.* blended the pre-formed P3HT nanowires prepared in DCM with PCBM molecules, which yielded a PCE of 3.23%.⁶⁰ The device PCE is dependent on the ageing time, as the aged nanowires tend to have enhanced π -conjugation length and crystallinity. As a result, the device J_{sc} increases with prolonged ageing and reaches its maximum after 3 days. To improve the PCE, Kim *et al.* also inserted a P3HT buffer layer between the PEDOT:PSS and active layers, creating a concentration gradient.⁶⁰ Both J_{sc} and FF of the device increase upon insertion of the P3HT buffer layer, giving best PCE of 3.94%, owing to the reduced surface recombination.

Fig. 1.7 Chemical structures of donor materials that can self-assemble into 1-D nanostructures.

The other method to grow P3AT fibers is the mixed-solvent approach. By using a mixture of “good” and “bad” (or “poor”) solvent, it is possible to drive the self-assembly of the π -conjugated materials. In principle, the material is first dissolved in “good” solvent, in which it is highly soluble. Afterwards, a small quantity of the “poor” solvent is added to induce more favorable interactions among the materials. For instance, P3HT nanowires can be obtained in the mixtures of chlorobenzene (CB) with either acetone,⁶¹ cyclohexanone⁶² or acetonitrile.⁶³ The former solvent is the “good” solvent, while the latter ones are the “poor” solvents. To promote the growth of the nanowires, the mixtures are either stirred or ultrasonicated. There are a few factors affecting the nanowire crystallinity, such as the amount and the type of “poor” solvent added. Generally, the higher the concentration of the “poor” solvent, the more crystalline the nanowires become.^{61,62} Since different solvent molecules are expected to induce different strength of intermolecular interactions with the active components, the concentration of the “poor” solvent required to generate optimally performing solar cells may also be different, *e.g.* 2.5%,⁶¹ 10%⁶³ and 33%V/V⁶² for acetone, acetonitrile and cyclohexanone, respectively. Although the nanowire devices perform better than the pristine non-fiber devices, generally they are still worse than the thermally annealed non-fiber devices. Post-fabrication heat treatment on the nanofiber devices can increase the performance by 30 – 56%, giving PCEs ranging from 3.6 to 4%.

Wu *et al.* and Xin *et al.* extended the nanostructure approach for the other P3AT analogs, by applying the blends of PC₇₁BM and nanowires of poly(3-pentylthiophene) (P3PT/2)⁶⁴ and poly(3-butylthiophene) (P3BT/3)⁶⁵, respectively. The solubility of π -conjugated polymers, including P3ATs, is dependent on the length of the alkyl side groups.⁷⁰ Longer alkyl groups facilitates stronger interactions with the solvent molecules, hence better solubility. Thus, polymers **2** and **3** are expected to self-assemble more readily than P3HT. It was also demonstrated that P3PT and P3BT nanowires could be isolated in 1,2-dichlorobenzene (*o*-DCB). On the other hand, due to the high solubility of P3HT in *o*-DCB, the nanowire formation is highly unfavorable. Wu *et al.* showed that despite the better absorption characteristics of the annealed nanowire P3PT:PC₇₁BM blend as compared to the annealed non-wire P3PT:PC₇₁BM, the device PCE of the former system was only 3.3%, while the latter one could reach 3.7%.⁶⁴ The other P3AT derivative, P3BT, has even poorer solubility in organic solvents and tends to suffer from severe phase separation when blended with acceptor molecules. As such, the device performance is much limited by the suboptimal blend

morphology. By using pre-formed nanowires of P3BT, Xin *et al.* showed that nanowire device of P3BT:PCBM could give efficiencies that are more than double the annealed device.⁶⁵ The interconnectivity between the nanowires prevents excessive phase separation in the blend, improving both J_{sc} and FF. This results in a rather efficient solar cell device with PCE of 3%. Due to the poor solubility of P3BT, it is also possible to grow the polymer nanowires in the presence of the acceptor molecules.

Chen *et al.* applied theoretical calculations based on dissipative particle dynamics (DPD) approach to predict the self-assembly behavior of π -conjugated polymers with different types of side groups, *i.e.* linear *vs* branched structures.⁶⁶ They discovered that the morphology of the nanostructures was dependent on the side groups. Based on the simulation data, polymers with linear side groups form multilayered football-like aggregates, while the ones with branched side groups evolve into fiber-like structures. Due to the bulkiness of the branched side groups, which have poorer solvophilic interactions, it is expected that the polymer backbone will aggregate at the center of the fibers, while the side groups stay at the outer part of the fibers; akin to micellar structure. Consistent with the simulation results, poly(3-2-methylbutylthiophene) (P3MBT/4), a P3AT derivative with branched side groups, spontaneously self-assemble into nanowires in *o*-DCB at room temperature. On the other hand, the less soluble P3PT and P3BT need to be first heated and then cooled, to promote the nanowire formation. In terms of device performance, blends of polymer 4:PC₇₁BM result in optimized PCE of 4.15%, with a superior photovoltage V_{oc} of 0.72 V, *i.e.* one of the highest for highly performing solar cells based on P3AT derivatives.

Organic nanostructures can also be obtained from the block copolymers of P3ATs. Typically, the P3AT selected as the co-monomers have complementary properties, in terms of the solvent solubility (longer alkyl group) and self-assembly capability (shorter alkyl group). He *et al.* applied the diblock copolymers based on P3BT and P3HT (P3BT-*b*-P3HT/5) for organic solar cells and achieved PCE of 4.02%.⁶⁷ The P3BT blocks assist a better packing, while the P3HT blocks allows a better phase separation with PC₇₁BM molecules. This combination also solves the morphological issue of P3BT mentioned earlier. The performance of copolymer 5: PC₇₁BM is also more superior to those of the constituting homopolymers. The ratio between the two blocks (m/n), *i.e.* the block composition, also strongly affects the device performance. Furthermore, in mixed-solvent environment, *e.g.* anisole (“poor” solvent) and chloroform (“good” solvent), copolymer 5 forms two distinct nanostructures: nanowires and nanorings in

chloroform-rich and anisole-rich environments, respectively.⁷¹ In the “poor” solvent-rich environment, the less soluble P3BT blocks tend to aggregate at the inner part nanostructures, leaving the more soluble P3HT blocks at the outer part of the structures interfacing with the solvent molecules. The concentration of the “poor” solvent also affects the rate of self-assembly of the copolymer chains. The other type of diblock copolymers based on P3BT and P3OT (P3BT-*b*-P3OT/**6**) exhibit a variation in the nanowire aspect ratio, depending on the ratio of P3BT to P3OT blocks (m/n).⁶⁸ Although the widths of the nanowires synthesized from the copolymers **6** with different values of m/n are quite comparable, the lengths differ quite substantially. As the P3BT blocks in the copolymers are increased from 50%, 76% to 90%, the aspect ratios vary from 48, 27 to 263, while the PCEs increase from 2.86%, 2.99% and 3.38%. The results clearly indicate a strong dependency of the device performance on the aspect ratio of the nanowires.

Kim *et al.* showed that the polymers with vinylene and bithiophene units (PVT/7) could also be pre-assembled into nanofibers in *o*-DCB.⁶⁹ Similar to the P3AT nanostructures, the nanofibers of polymer **7** also demonstrate enhanced crystallinity and optical properties. The application of the nanofibers also reduces the phase separation issue in the blends of polymer **7**: PC₇₁BM, resulting in PCE of 1.76%, around 21% higher than the annealed device. In addition, the photovoltage (V_{oc}) of the nanofiber device is also higher, indicating that its degree of polymer aggregation is less severe than the annealed system.

The organic nanostructures presented so far are generally prone to disintegrate upon heat application in solution state. One of the methods to improve the stability is to introduce crosslinking units. Hammer *et al.* synthesized diblock copolymers based on P3AT with 2 different functional groups: hydroxyl and amine (copolymers **8**).⁷² In mixed solvent of chloroform and DCM, each copolymer can self-assemble into fibrillar structures. By mixing both copolymers in the presence of “poor” solvent, the more thermally and chemically stable crosslinked nanofibers are formed. The other demonstration of the more advanced organic nanostructures is by using fullerene-P3HT dyads (polymer **9**).⁷³ The hybrid structure, which consists of fullerene as the end group of P3HT, is expected to act as compatibilizer between P3HT and fullerene units. Upon slow solvent evaporation in *o*-DCB, the dyads form fiber-like structures, which has to be driven by the interactions of the P3HT units. The hybrid structure also shows possibility of extending the self-assembly approach to other molecules with additional functionalities.

Besides nanofibers and nanowires, P3HT can also self-assemble into other nanostructures, such as 2-D nanoribbons,⁷⁴ nanosheets⁷⁵ and branched nanostructures.⁷⁶ Through proper control of the nucleation and growth processes, the versatility of P3HT to adopt various morphologies can be realized. The formation of P3HT nanoribbons is possible when low molecular weight ($M_n < 10$ kDa) P3HT is used.⁷⁴ In the mixed-solvent of anisole and *N,N*-dimethylformamide (DMF), the relatively short P3HT chains first self-assemble into fiber-like nuclei *via* π - π interactions at the early stage of the transformation. Afterwards the stacking occurs width-wise *via* alkyl side-group interactions, forming the ribbon-like entities. Based on this mechanism, the height of the nanoribbons correlates well with the length of the P3HT chains (or M_n). Yu *et al.* also demonstrated the formation of highly crystalline P3HT nanosheets through proper control of solvent evaporation of P3HT solution in THF and methanol.⁷⁵ P3HT nuclei first form in the mixed solvents, induced by the “poor” solvent methanol. Afterwards, upon gradual solvent evaporation on substrates, the self-assembly of P3HT nuclei extends along the P3HT chain axis, which eventually leads to the formation of 2-D nanosheets. Similar concept of nucleation and growth can also be applied to generate branched nanostructures, as shown by Yan *et al.*⁷⁶ In the solvent mixture of *o*-DCB and triethanolamine (TEA), homogeneous nucleation and growth promote formation of P3HT nanowires. Upon slow solvent evaporation, a new set of P3HT aggregates nucleate heterogeneously on the previously formed nanowires, resulting in branched nanostructures.

Fig. 1.8 Various nanomorphologies of P3HT: (a) nanoribbons,⁷⁴ (b) nanosheets⁷⁵ and (c) branched nanostructures.⁷⁶

To summarize the recent development of organic nanostructures, there have been a few successful demonstrations of highly efficient organic nanostructured solar cells. The approach is potentially attractive as it also provides the platforms for hybridized

nanostructures, such as block copolymers, and is not only limited to one structural dimensionality. Nevertheless, most of the nanostructure-based solar cells are still inferior to the conventionally annealed non-structured devices. The corresponding heat treatment can also be applied for the organic nanostructured devices, although this compromises the inherent thermal-free feature of the organic nanostructure approach.

1.5 Scope and objectives

The research described in this thesis focuses on the self-assembly of poly(3-hexylthiophene) (P3HT) nanofibers and their applications for organic solar cells. P3HT nanofiber, as one of the archetypal organic nanostructures, were thoroughly investigated. The objectives of the research are: (1) to investigate the optical and electrical characteristics of P3HT nanofiber-based blend films and to correlate them with the solar cells device performance, (2) to understand the solvent-dependent growth of the P3HT nanofibers, (3) to develop thermal-free strategies to improve the performance of nanofiber-based devices and (4) to extend the nanofiber approach to the other morphologically limited blend systems.

In terms of scientific contributions, the research helps to gain more insights into the factors limiting the performance of organic nanostructured solar cells, in particular ones based on P3HT nanofibers, as well as to strategize techniques to overcome such limitations. Using both “steady-state” and “time-resolved” characterization techniques, it was found that bimolecular recombination might have been the major limitation of the poorer performance observed in P3HT nanofiber-based devices. As this type of charge recombination strongly depends on the blend morphology, the results indicate that the morphology of nanofiber blend is not fully optimized. The interconnectivity between the P3HT nanofibers can be improved by crystallizing the amorphous P3HT phase that helps to hold the nanofiber together, by using “solvent-additive” approach. The high boiling point additive molecules preferentially induce some organization on the disordered P3HT regions. Furthermore, the research also emphasizes the potential and practicality of the nanostructure approach as morphology stabilizers in blends of organic materials. This is shown from the study of all-polymer blends, which suffers from the severely unoptimized blend morphology. The application of pre-formed P3HT nanofibers in the all-polymer blends, first demonstration ever in the literature, maintains the structural integrity of the nanofibers, hence providing a good platform to circumvent the morphological issue. Similarly, the morphology of a ternary blend

consisting of donor, acceptor and dopant molecules can also be stabilized when the donor polymers are converted into polymer nanostructures. It is demonstrated that the triplet-sensitization could be observed in the P3HT nanofiber-based devices, while the non-fiber device experiences device degradation due to the aggregation of the dopant molecules.

1.6 Thesis outline

The thesis consists of 6 chapters. The introduction chapter provides an overview and the motivation behind the research. A brief history of solar cells is provided, followed by the current state-of-the-art research in organic solar cells. Very importantly, the recent development of organic nanostructures for solar cell applications is also provided, highlighting the prospects and imperfections of the approach.

In Chapter 2, an exhaustive investigation on the nature and characteristics of the nanofiber solar cells is given. The polymer blends treated with conventional heat treatment are also included in the comparative studies. Both “steady-state” and “time-resolved” techniques applied on the different blends are elaborated; the results of which are correlated with the device characteristics. Furthermore, the dependency of the nanofiber growth on the solvent choice and mixed solvents is also discussed. A proper control of the nanostructure quantity and dimension is shown to result in improved device performance.

Solvent additive approach has recently gained significant interest within the organic solar cell community as a simple approach to optimize the blend morphology. In Chapter 3, it is demonstrated that solvent additive can further improve the morphology of the nanofiber blends, which is earlier suspected to be the major factor affecting the device performance. Additionally, the selection criteria of the additive molecules are also reconsidered.

Chapter 4 emphasizes the role of the polymer nanofibers as morphology stabilizers. The all-polymer blend, in which the phase separation issue between the donor and acceptor materials can be challenging, may result in underperforming solar cell devices. In this chapter, it is found that P3HT and the other copolymer interact very intimately with minimum amount of phase separation. The application of the pre-formed nanofibers prevents the excessive intermixing between the two polymers. In terms of device performance, the nanofiber blends show greater potential, which has also been observed for other systems with severe morphological issues, such as P3BT and PVTT.

To improve the device characteristics, additive molecules can be incorporated into the

blends, forming ternary blend systems. The addition of such molecules tends to affect the blend morphology significantly. In Chapter 5, triplet sensitizers are used to enhance the lifetime of the excitons and are expected to promote a more efficient charge generation. In this work, it is found that the type of polymers, whether amorphous or semicrystalline, responds differently towards the addition of the sensitizers. Molecular aggregation is more pronounced in the semicrystalline blend, while sensitizers (triplet molecules) can be dispersed homogeneously in the amorphous blend. As a result, device degrades in the former case, while improvement is observed for the latter system. The use of polymer nanofiber overcomes this morphology limitation, as the semicrystalline polymer is transformed into the more stable nanostructures.

In the last chapter, the summaries and the outlook of the studies are provided.

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Organic Solar Cells Based on Poly(3-hexylthiophene) Nanofibers: Growth Control and Device Characteristics

Summary. One-dimensional (1-D) nanostructures of conjugated polymers, such as nanofibers, offer the possibility of directed charge transport and improved absorption due to better chain packing. Furthermore, the nanofiber approach provides flexibility in manipulating dimension and morphology of the ordered regions by careful control of the nucleation and growth processes. In this chapter, the characteristics of the devices based on self-assembled poly(3-hexylthiophene) (P3HT) nanofibers are investigated in detail. In principle, the devices with pre-formed fibers possess high crystallinity, with enhancement in their optical absorption and charge transport properties. Therefore, the nanofiber approach has a huge potential to yield high device performance without undergoing any heat treatment. However, the conventionally annealed devices still surpass the nanofiber device in terms of the power conversion efficiency (PCE). It is demonstrated that in the nanofiber system, the photocurrent generation is slightly affected by the bimolecular recombination processes, indicating that the morphology of the nanofiber blend is still suboptimal. It is also postulated that the present self-assembly technique lacks the assurance to yield a more interconnected fibers. However this can be overcome through proper control of the growth parameters. It would be possible to manipulate the fiber morphology either by choosing a suitable solvent or by using mixed solvents. Although the modified fiber morphologies using these methods have not been shown to surpass the annealed device in terms of the performance, it is believed that the key to achieving high PCE is through novel and tactical self-assembly approach in order to generate the network-like nanostructures.

2.1 Background

Self-assembled organic nanostructures provide an interesting platform to achieve highly efficient organic solar cells. Although the application of polymer nanostructures (nanofiber, for instance) have often been reported by various groups to give remarkable performance, most of them are still unable to surpass the devices treated with the more orthodox annealing methods. This chapter presents the properties of nanofiber solar cell, with emphasis on the key merits, along with the pristine and annealed devices as bases for comparison. As the device performance correlates strongly with the fiber morphology, methods to control the growth are also discussed. The nanofiber systems are subsequently thoroughly characterized, using both “steady-state” and “transient” techniques, in order to give insights into the possible mechanisms behind the performance loss and hence the ways that improvement can be made in the future.

2.2 Introduction

Regioregular poly(3-alkylthiophene)s (P3ATs), particularly poly(3-hexylthiophene) (P3HT), is one of the most widely studied donor materials for organic solar cells due to their favorable optoelectrical properties, good processibility and good self-organization capability. OPV devices based on bulk heterojunctions (BHJ) that consist of binary blends of regioregular P3HT donor and fullerene derivative acceptor such as [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) have been reported to demonstrate promising power conversion efficiency (PCE) as high as 5%.^{1,2}

To achieve such high PCE, the devices require additional annealing treatment such as thermal annealing or solvent vapor annealing. Without annealing, the device performance can be seriously limited by the low hole mobility in P3HT due to the low degree of crystallinity induced during the deposition of P3HT:PCBM blend solution by spin coating.³ An optimized annealing condition can lead to improved P3HT:PCBM blend morphology with nanoscale phase separation in the BHJ as well as bi-continuous networks of donor and acceptors. However, the blend morphology is highly sensitive to the annealing conditions; as such, a good control of annealing conditions is critical. Furthermore, thermal annealing may not be compatible with flexible plastic substrates with low glass transition temperature (T_g) such as polyethylene terephthalate (PET).

One of the annealing-free methods to achieve improved degree of order in the polymer-fullerene blend is by blending acceptor molecules with self-assembled P3AT nanofibers.^{4,7} Several approaches have been developed so far to enhance the organization of P3AT into one-dimensional nanostructures, such as the marginal solvent method,⁸ the “poor” solvent-induced aggregation method⁹ and the use of crystallizable solvent.¹⁰ The application of these highly crystalline P3AT nanofibers in organic solar cells by blending them with acceptors such as PCBM yielded highly efficient devices with PCE around 3%.^{4,7,11-14} The high device performance suggests that P3AT nanofibers, as opposed to the amorphous P3AT, possess higher carrier mobility and may also facilitate a more efficient charge separation because the width of the fibers (10 – 20 nm) is compatible with the exciton diffusion length. In the blend with PCBM, the interconnected fibrillar network further enhanced the charge transport. Nevertheless, optimization of the device fabrication through adjustment of nanofiber-amorphous polymer ratio, variation of acceptor content or by choosing a more strongly absorbing acceptor, such as PC₇₁BM, is a definite prerequisite to achieve high PCE devices without any annealing. The nanofiber content in the blend, for instance, which can be adjusted through proper selection of the marginal solvent and the temperature of pre-cast solution, shows a huge influence on the device open-circuit voltage (V_{OC}), short-circuit current (J_{SC}) and hence the PCE.¹¹ Thus it is necessary to understand and to control the P3AT interchain interactions in the fiber formation, which determine the quantity and the dimensions of the nanofibers.

There are two common approaches for P3AT nanofiber assembly: (1) marginal solvent method and (2) mixed-solvent method. In the marginal solvent method, Ihn *et al.* first demonstrated the formation of crystalline P3AT whiskers due to the supercooling of a solution of dissolved polymer solution in the marginal solvent.⁸ These pure whiskers were isolated from the remaining amorphous content by centrifugation and filtration. The field-effect transistor (FET) measurement of the P3HT single fibers exhibits relatively high hole mobility of up to 0.06 cm²/Vs rendering them suitable candidates for organic electronic applications.¹⁵⁻¹⁷ A few preliminary studies have suggested that the fiber morphology depends on a few parameters such as solvent choice, solution concentration, cooling rate, P3AT regioregularity and molecular weight, and even external interference such as ultrasonication.¹⁸⁻²² The combination of these factors affects the degree of polymer-solvent interaction; hence rendering the morphology control of P3AT nanofibers a challenging proposition.

In the mixed-solvent method, a combination of poor and good solvent is used to drive organic nanofiber self-assembly. Based on most of the reported methods, the organic molecules are first dissolved in a good solvent, after which a small quantity of poor solvent is added into the main solution.^{5,9,23} The idea is to utilize the unfavorable interactions between the polymer chains and poor solvent molecules to drive self-assembly of the polymer molecules. Therefore, the degree of crystallization achievable is dependent on the amount of poor solvent in the mixed-solvent system.

In this chapter, the characteristics of nanofiber OPV device are discussed and contrasted with the thermal-annealed device. The nanofiber devices exhibit remarkable crystallinity, yet they are less efficient than expected. Various characterization techniques (structural, optoelectrical and morphological), including the “steady-state” and “time-resolved” methods, were used to unveil the root cause of the issue. As shown later, the current nanofiber approach results in a sub-optimized morphology. Consequently, charge recombination becomes more prevalent, which in turn affects the device performance. The problem with the fiber morphology is that a few of the fibers are isolated from each other, which means that the holes will have to hop from one fiber to another. The holes generated within these fibers could recombine before they can be extracted to the external electrodes.

Fortunately, these “fiber” issues also come with their own remedies. It is possible to manipulate the dimensions and morphologies of the fibers through proper control of the fiber growth conditions. Such feasibility is also demonstrated in this chapter. In this work, the approach is based on mixed-solvent method, *i.e.* P3HT was dissolved in a large quantity of marginal solvent and a small amount of good solvent was used to control the self-assembly of the P3HT fibers. The addition of a good solvent, such as chlorobenzene (CB) into the P3HT/anisole solution induced a morphological change and contrary to intuition, the crystallinity of the P3HT in the blend film increased. The improvement in crystallinity is counter-intuitive since P3HT tends to dissolve better in CB. Nevertheless, the change in crystallinity was accompanied by a change in the fiber dimension. Application of these modified fibers in the organic solar cells resulted in enhanced device performance. Based on the synchrotron SAXS study, a growth mechanism of the P3HT nanofiber in anisole with CB addition is proposed. In brief, by controlling the self-assembly of the fibers, it is possible to obtain the desirable morphology, which could eventually result in enhanced device performance.

2.3 Results and discussion

2.3.1 Growth of P3HT nanofiber

P3HT self-assembles to form nanofibers through gradual cooling of the well-dissolved warm P3HT solution (*ca.* 80 °C) to room temperature as its interaction with the solvent molecules changes from solvophilic to solvophobic. One distinct physical change that can be observed as P3HT undergoes this transition is the color change from bright orange to dark brownish-purple color.²⁴ The fiber formation is also accompanied by an increase in solution viscosity. Both changes in the color, which is related to its optical absorption, and the viscosity correlate with the amount of non-dissolved nanofiber in the solution. Solution absorption, in particular, is a direct indication of the extent of π - π interchain interaction, which is the essential force that drives the nanofiber formation. A more intense and red-shifted absorption suggests a more extended conjugation length, which will result in better charge transport.

Absorption spectroscopy To verify the formation of well-organized P3HT nanofibers, the optical absorption spectra of P3HT in *p*-xylene were measured as a function of ageing time at room temperature. As the extent of the π -conjugation of polymers changes, there is a corresponding change in the absorption of the system. Fig. 2.1 shows the change in absorption spectra over a period of 48 h. At first, P3HT exhibits a featureless absorption characteristic, suggesting well-dissolved polymeric chains in *p*-xylene. After 1 h, the solution starts to show weak vibronic features at 610 nm. The relative intensity of this “shoulder” peak with respect to the main absorption peak at 460 nm is the direct evidence of the degree of order in regioregular P3HT and can be correlated to the extent of nanofiber formation.²⁵ The second vibronic peak at 560 nm starts to appear after 6 h. The relative intensity of both peaks increases with ageing time before saturating at 38 h. Furthermore, an obvious transformation from well-dissolved polymeric chains to their aggregated forms could be observed as indicated by the clear isosbestic point at 475 nm. After 48 h, the increase in the amount of P3HT nanofiber becomes much retarded and its absorption profile shows the coexistence of both nanofiber and amorphous non-fiber P3HT in the suspension.

By assuming that the absorption intensity of the 610 nm vibronic “shoulder” to be directly proportional to the degree of order of P3HT during the self-assembly process, the relative crystallinity of the formed nanofiber (x_c) at a given ageing time t_a can be calculated using the following relationship²⁶

Fig. 2.1 Evolution of optical absorption spectra of P3HT in *p*-xylene (7 mg/ml) monitored at (a) 0, (b) 1, (c) 6, (d) 10, (e) 16, (f) 20, (g) 28, (h) 38 and (i) 48 h after cooling process. The cooling rate was kept at 10 °C/h.

$$x_c(t) = \frac{A_{610}(t_a) - A_{610}(0)}{A_{610}(\infty) - A_{610}(0)} \quad (2.1)$$

where $A_{610}(0)$ and $A_{610}(\infty)$ correspond to the initial and saturated absorption intensity at 610 nm, respectively. The points in $x_c(t)$ vs t_a plot (Fig. 2.2) fit well with the exponential function

$$x_c(t_a) = 1 - \exp(-kt_a^n) \quad (2.2)$$

The function itself also represents the Avrami equation, which illustrates the time-dependent phase transformation at a constant temperature.²⁷ Eq. 2.2 can be rearranged into the following expression

$$\ln \ln \frac{1}{1 - x_c(t_a)} = \ln k + n \ln t_a \quad (2.3)$$

Fig. 2.2 Evolution of the relative crystallinity of P3HT nanofiber as a function of ageing time.

The exponent n in the Avrami equation, typically an integer with a value between 1 and 4, reflects the nature of the transformation. The data fitting in Fig. 2.2 (dotted curve) results in n value close to 1 ($n = 1.08$), suggesting a pure anisotropic one-dimensional (1-D) growth of the polymeric crystals. The observation of the growth kinetics agrees with the formation of nanostructures with high aspect ratio, such as nanofibers.

Nanofiber morphology The evolution of the P3HT nanofibers as they undergo the ageing process is depicted in Fig. 2.3. The fiber suspensions aged for different time period were diluted to the same extent (dilution factor of 10) and then spin-cast for imaging. At the early growth stage (2 h), only short fibers are formed with length varying from $0.5 - 3 \mu\text{m}$, as pointed by the red arrows in Fig. 2.3(a). The width of the fibers is around $10 - 20 \text{ nm}$. Most of the P3HT is still in the form of amorphous non-fiber. More fibers are observed after 6 h of ageing, with typical length of $1 - 5 \mu\text{m}$ (Fig. 2.3(b)). At 12 h, longer fibers ($5 - 10 \mu\text{m}$) start to appear (Fig. 2.3(c)); and by 24 h the amount of these long fibers has increased substantially (Fig. 2.3(d)). From this series of images, it can be seen that the nanofiber growth is quite uniform in terms of dimensions. The exponential growth of the “vibronic” shoulder intensity at 610 nm (Fig. 2.1) is a consequence of the increase in both the nanofiber length and the nanofiber density. The width and height of the fibers remain constant throughout the growth, suggesting that the self-assembly of the polymer chains mainly occurs along the length of the fibers.

Fig. 2.3 AFM images of P3HT nanofibers aged for (a) 2, (b) 6, (c) 12 and (d) 24 h. The samples were prepared by spincoating P3HT solution (7 mg/mL), previously diluted by 10 times in *p*-xylene.

Crystal structure In marginal solvents, most P3ATs self-assemble into monoclinic crystal structure as shown in Fig. 2.4. The proposed structure is confirmed by the data collected from diffraction measurements performed by various research groups.^{16,21,28} The π - π stacking of the polymer chains occurs along the b -direction or fiber axis, while the P3AT backbones are aligned along the c -direction, which is orthogonal to the fiber axis. The alkyl side groups point along the a -direction; thus, the crystal dimension along a -axis has linear relationship with the alkyl length. The fiber formation can be visualized, first, as the stacking of the polymer molecules induced by the π - π interactions along the b -axis. Afterwards, due to the alkyl group interactions, the “layers” of polymers stack on each other along the a -axis. The notations used for assigning the crystal structure are to be applied in the subsequent discussions on X-ray diffractions.

Fig. 2.4 Structural model of P3HT nanofiber. The $d_{(100)}$ derived from the X-ray diffractogram corresponds to alkyl group spacing along a -direction.

2.3.2 Characteristics of P3HT nanofiber blend

This section presents the main features of the blends of P3HT nanofibers (NF) with PCBM. Comparatively, the corresponding characteristics of both as-cast (NA) and optimally annealed (TA) non-fiber P3HT:PCBM blends are also demonstrated.

Absorption spectroscopy Fig. 2.5 shows the typical solid-state optical absorption spectra of the P3HT:PCBM (10:8 wt%) blends – as-cast, annealed and nanofiber blends. The absorption characteristics of neat P3HT film are also presented. The films have comparable

thicknesses (90 ± 10 nm) and their absorption spectra are normalized at PCBM absorption peak ($\lambda = 330$ nm). The maximum absorption peak (λ_{max}) is at 520 nm and the two vibronic “shoulders” are at 560 and 610 nm. These features are typical of P3HT. The peak at λ_{max} indicates the π - π^* intrachain transition, while the “shoulder” features are related to the strength of π - π stacking. The features are similar to those observed in the nanofiber suspension in *p*-xylene. In a blend system, the positions of the maximum absorption peak and the “shoulders” can shift depending on various factors, *e.g.* regioregularity, molecular weight, PCBM amount and post-deposition treatment.

Fig 2.5 UV-Vis absorption spectra of P3HT:PCBM blend films with different morphologies. The spectra of P3HT are included for reference. The spectra of the blends are normalized at 330 nm.

The blending of P3HT with PCBM introduces molecular disruption, reducing the planarity of P3HT groups. Therefore, there is a significant blue-shift in the absorption of the as-cast (NA) blend as compared to pure P3HT films. This is accompanied by remarkable reduction in the P3HT absorption intensity. Thermal annealing (150 °C for 20 min) activates thermal diffusion of the molecules, resulting in the reorganization of both P3HT and PCBM molecules. The λ_{max} is red-shifted by *ca.* 3 nm and the vibronic “shoulders” look more obvious in the TA blend, in particular the 610 nm “shoulder”. These are the manifestations of the increase in the π -conjugation length with stronger intermolecular interactions among P3HT chains. The nanofiber (NF) blend displays a more appreciable red-shift in λ_{max} of *ca.* 11 nm, and the “shoulder” at 610 nm appears to be even more pronounced. Other than the PCBM absorption, the NF blend exhibits absorption characteristics very similar to those of a neat P3HT film. This finding suggests that the degree of order is the highest in NF out of the three

blends. The relative blend crystallinity, estimated from the intensity ratio of the vibronic “shoulder” at 610 nm, reveals that the NF blend is 2.5 times more crystalline than the as-cast NA blend, while the TA blend is only 1.7 times higher. This suggests that the fullerene molecules are not able to disrupt the order in P3HT nanofibers due to the strong interchain interactions between the P3HT molecules; hence, only inducing minimal disruption in the order of P3HT molecules. The NF blend also has a stronger absorption, which is an indication of its efficient photon harvesting. Compared to the NA blend, there is an enhancement in the relative absorption by *ca.* 23% and 31% in the TA and NF blends, respectively.

Grazing-incidence X-ray diffraction To confirm the blend crystallinity, X-ray diffraction measurement was performed on the blend films. The diffraction spectra of both P3HT and P3HT:PCBM blends are shown in Fig. 2.6. Three peaks are observed at $2\theta = 5.4^\circ$, 11° and 16° , corresponding to the (100), (200) and (300) reflections, respectively. The peak position, peak intensity and the full-width half-maximum (FWHM) of each peak are obtained with Gaussian fitting. The parameters acquired from the GIXRD data analysis are summarized in Table 2.1. The three peaks correlate with the degree of order along the *a*-axis (Fig. 2.4), which is along the direction of the interdigitating alkyl moieties. From Fig. 2.6(a), nanofiber P3HT (NF) can be qualitatively described as the most crystalline, due to its highest scattering intensity. The observed reflections indicate that the P3HT chains adopt an edge-on stacking orientation. Further analysis of the diffractogram data reveals that the crystallinity of the NF film, arbitrarily defined as the dot product of the peak intensity and FWHM, is 4.2 times higher than the as-cast NA P3HT film. On the other hand, thermal annealing (TA) only results in 1.9 times improvement in P3HT crystallinity. Although the mixing of P3HT with fullerene molecules generally reduces crystallinity, the degree of order in the blend system exhibits the same trend (Fig. 2.6(b)). The NF and TA blends are 3.5 and 1.6 times respectively more crystalline than the NA blend.

The interplanar distance *d*-spacing of the P3HT crystallites can be derived from the Bragg’s law²⁹

$$n\lambda = 2d \sin \theta \quad (2.4)$$

where $n = 1$ for the first-order (100) reflection, $\lambda = 0.154$ nm corresponding to Cu-K α radiation energy, and θ is the Bragg’s angle. For the neat P3HT films, the *d*-spacing increases with heat treatment (from 1.626 nm to 1.660 nm), suggesting that the thermal-activated diffusion induces molecular reorganization with increased distance between the neighboring alkyl

groups. Verploegen *et al.* attributed this change to the ordering of the alkyl groups during the cooling process.³⁰ By contrast, the $d_{(100)}$ -spacing decreases in the NF P3HT (1.617 nm). The reduced spacing correlates with the increase in the proximity between the P3HT molecules in the layers as they self-assemble in solution (refer to Fig. 2.4). The order-destructing nature of the incorporation of PCBM molecules into P3HT is expected to affect the $d_{(100)}$ -spacing, as the fullerene units can infiltrate in between the polymer chains. Nevertheless, as seen in Table 2.1, there is minimum change in the $d_{(100)}$ -spacing of the P3HT:PCBM blend and its trend is the same as that of the neat P3HT films.

Fig. 2.6 GIXRD patterns of: (a) P3HT films and (b) P3HT:PCBM blend films. Three types of P3HT used for the measurement: as-cast (NA), thermal-annealed (TA) and nanofiber (NF).

The crystallite size is the other parameter that can be calculated from the FWHM of the peaks in the diffractogram data. The relative FWHM are 0.76, 0.59 and 0.83 for the NA, TA and NF P3HT films, respectively. By using the following Scherrer equation³¹

$$D = \frac{K \lambda}{\beta \cos \theta} \quad (2.5)$$

where $K = 0.9$ and β corresponding to the FWHM of the peak (in radians), the crystallite size D are estimated to be 10.5, 13.4 and 9.6 nm for the NA, TA and NF P3HT, respectively. Thermal annealing increases the crystallite size due to the clustering of neighboring P3HT molecules. It is, however, unclear how the crystallite size can be correlated with the whisker-like P3HT nanofibers. The decrease in the crystallite size in NF P3HT could be due to averaging of the domain size with the small width/thickness (*ca.* 10 – 20 nm) of the fibers. The analysis of the FWHM of the blend systems gives crystallite sizes of 9.2, 12.5 and 9.5 nm for the NA, TA and NF blends, respectively. Other than the NF blend, both NA and TA blends exhibit decrease in crystallite size upon blending with PCBM. In summary, the GIXRD data show an

improvement in crystallinity in the NF system, which can lead to enhanced charge mobility, and thus, the performance of solar cell device.

Table 2.1 GIXRD parameters of P3HT films and P3HT:PCBM blend films.

Conditions	Peak Height	FWHM	Crystallinity	Crystallite size	$d_{(100)}$
	(count/s)	(°)	(a.u.)	(nm)	(nm)
P3HT (NA)	0.27	0.76	0.20	10.5	1.626
P3HT (TA)	0.63	0.59	0.37	13.4	1.660
P3HT-nf (NF)	1.02	0.83	0.84	9.6	1.617
P3HT:PCBM (NA)	0.12	0.86	0.10	9.2	1.634
P3HT:PCBM (TA)	0.25	0.64	0.16	12.5	1.657
P3HT-nf:PCBM (NF)	0.42	0.83	0.35	9.5	1.616

Mobility measurement Charge-carrier mobility can be defined by either lateral or vertical transport. The field-effect mobility, which is usually extracted from the saturation regime of the plot of the square root of drain current versus gate voltage of a transistor device,³² is one typical demonstration of the lateral geometry-based mobility. However, as the solar cell layers are stacked vertically, free charge-carriers are also transported in the direction perpendicular to the substrate. Space-charge-limited current (SCLC) method is a suitable approach to evaluate the charge-carrier mobility for P3HT:PCBM blend film.³³ Since both heat treatment and the application of pre-formed P3HT nanofibers have been demonstrated to improve P3HT crystallinity, it is of particular interest to correlate this observation with the change in the hole mobility. Hole-only devices with the following configuration: ITO/PEDOT:PSS/P3HT:PCBM/MoO₃/Al are used to extract the SCLC hole mobility. Molybdenum oxide (MoO₃), with its low LUMO (2.3 eV), is capable of blocking the electron transport to the top electrode (Al) since there is a substantial energy offset in the LUMO levels of MoO₃ and PCBM ($\Delta E_{\text{LUMO}} = 1.4$ eV). Besides, the oxide has similar HOMO level (5.3 eV) to the work function of PEDOT:PSS layer (5.2 eV). Therefore, the insertion of MoO₃ layer significantly enhances the hole-injection (or extraction) at the top electrode for P3HT:PCBM system.³⁴

Fig. 2.7 shows the double logarithmic plot of the current density-voltage (*J*-*V*) characteristics of the hole-only P3HT:PCBM devices measured in dark. The bias voltage has been corrected for the built-in potential ($V_{\text{bi}} = 0.1$ V),³³ which is determined from the work function difference between the two contacts. The SCLC charge-carrier mobility can be

measured by fitting the dark J - V plots (linear least-square fit) with the Mott-Gurney law³⁵

$$J = \frac{9}{8} \mu \epsilon \epsilon_0 \frac{V^2}{L^3} \quad (2.6)$$

where μ is the charge-carrier mobility, ϵ is the dielectric constant of the medium (*i.e.* typically 3.5 for organic materials), V is the applied bias voltage and L is the distance between the two electrodes (or the film thickness). By taking both the built-in voltage and the field-dependent Frenkel effect, Eq. 2.6 can be modified into³⁶

$$J = \frac{9}{8} \mu \epsilon \epsilon_0 \frac{(V - V_{bi})^2}{L^3} \theta_0 \exp \left(\frac{0.89}{kT} \sqrt{\frac{e^3 (V - V_{bi})}{\pi \epsilon \epsilon_0 L}} \right) \quad (2.7)$$

where θ_0 is the total charge ratio. Eq. 2.7 can in turn be simplified into the following equation

$$J = \frac{9}{8} \mu \epsilon \epsilon_0 \frac{(V - V_{bi})^2}{L^3} \exp \left(0.89 \gamma \sqrt{F} \right) \quad (2.8)$$

with γ as the field activation parameter and F is the electric field, which is defined as $F = (V - V_{bi})/L$. In the trap-free regime, the calculated SCLC hole mobilities are 1.53×10^{-5} , 3.00×10^{-4} and $5.50 \times 10^{-4} \text{ cm}^2/\text{Vs}$ for the NA, TA and NF P3HT:PCBM devices. The hole mobilities in both TA and NF blends are one-order magnitude higher than the one in NA blend. These values also correlate well with the trend in the blend crystallinity. As the degree of order in the blend increases, the hole transport becomes more efficient.

Fig. 2.7 Dark-current density – voltage (J_D - V) characteristics of hole-only P3HT:PCBM (10:8) devices.

Device performance Solar cell devices were fabricated and measured to confirm the effect of blend crystallinity. The device configuration: ITO/PEDOT:PSS/P3HT:PCBM(10:8)/Al is used for the power conversion efficiency (PCE) measurement. Fig. 2.8 shows the J - V

characteristics of the devices under AM 1.5G 100 mW/cm² (1 sun) illumination. The device merits are summarized in Table 2.2. The as-cast NA device gives J_{SC} of 4.56 mA/cm², V_{OC} of 0.7 V, FF of 0.33 and PCE of 1.08%. Both thermal annealing (TA) and application of P3HT nanofiber (NF) yield devices with higher J_{SC} and FF, although decrease in V_{OC} is observed. The increase in the photocurrent is related to the improvement in photon absorption and charge transport, which derives from the higher degree of crystallinity in the films. Similarly, as the charge transport within the bulk film becomes more efficient, the series resistance drops followed by an improvement in FF. The decrease in V_{OC} is another evidence of the change in the degree of order. As the π -conjugation length of P3HT increases, there is an upward shift in the highest occupied molecular orbital (HOMO) level. For organic solar cells, the photovoltage V_{OC} itself is largely dependent on the difference between the HOMO of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor. For PCBM as the acceptor, V_{OC} can be estimated from the following empirical relationship³⁷

$$V_{OC} = (1/e) (|HOMO_{donor}| - |LUMO_{acceptor}|) - 0.3 \text{ V} \quad (2.9)$$

Consequently, V_{OC} drop occurs as P3HT phase becomes more crystalline. The lower V_{OC} in the NF device also suggests more upward shift in the HOMO level, which correlates with its higher crystallinity.

Fig. 2.8 Current density – voltage (J - V) characteristics of P3HT:PCBM (10:8) devices under 1 sun (100 mW/cm²) illumination.

Despite the higher crystallinity in the NF blend, it is apparent from Table 2.2 that NF system is less superior to the TA blend in terms of device performance. With its superior absorption and charge transport properties, NF device is expected to yield higher J_{SC} , but NF

device has J_{sc} comparable to that of TA device (8.21 mA/cm^2 vs 8.57 mA/cm^2). The fill factor of NF device is also lower than that of TA device (by *ca.* 25%). Further analysis of the device series resistances (R_s), by calculating the slopes of the J - V curves at open-voltage condition ($V = V_{oc}$), reveals R_s of 49.5, 8.5 and $15.7 \text{ } \Omega \text{ cm}^2$ for the NA, TA and NF blends, respectively. The calculated resistance values do not relate well to the hole mobilities. Since series resistance is the accumulative manifestation of both bulk and contact resistances, the R_s data suggest that the worsening of the contact resistance in NF blend may have compromised the improvement in bulk resistance.

Table 2.2 Summary of photovoltaic device properties of P3HT:PCBM (10:8) devices.

Sample	PCE	J_{sc}	V_{oc}	FF	R_s
	%	(mA/cm^2)	(V)		($\Omega \text{ cm}^2$)
P3HT:PCBM (NA)	1.08	4.56	0.70	0.33	49.6
P3HT:PCBM (TA)	3.57	8.57	0.63	0.66	8.5
P3HT-nf:PCBM (NF)	2.40	8.21	0.58	0.50	15.7

The other possible source contributing to the photocurrent loss is the imbalance charge-carrier transport between holes and electrons.³⁸ As opposed to the thermal annealing, the pre-formed fiber approach only generates well-ordered donor polymer phase. On the other hand, heat treatment induces thermally activated molecular diffusion, which affects both donor and acceptor phases. In the thermal-annealed P3HT:PCBM blend, the acceptor phase can also crystallize and form percolation path, rendering a more efficient electron transport. It has been previously shown that the thermal annealing treatment can improve the SCLC electron mobility, although the extent of enhancement is dependent on the donor-acceptor ratio in the blend.³⁹ The balanced charge-carrier mobility ($\mu_h/\mu_e \approx 1$) reduces the likelihood of the build-up of space charges. In the NF device, μ_e could be significantly lower than μ_h , electrons may accumulate in the device, resulting in space-charge-limited photocurrent. Nevertheless, to get a more complete picture of the reasons behind the diminished photocurrent in the P3HT nanofiber device, the blends are to be subjected to further characterizations.

Dark current characteristics Fig. 2.9 shows the dark J - V characteristics of the same batch of devices used for PCE measurement. The curves can be further analyzed to obtain parameters, such as the reverse saturation current (J_0) and the diode ideality factor (n). The J - V

characteristics of a typical Shockley device can be described by the following relationship⁴⁰

$$J = \frac{1}{1 + \frac{R_s}{R_p}} \left[J_0 \left\{ \exp \left(\frac{V - J R_s A}{n k T / q} \right) - 1 \right\} + \frac{V}{R_p A} - J_{ph} \right] \quad (2.10)$$

Fig. 2.9 Dark current density-voltage (J_D -V) characteristics of P3HT:PCBM (10:8) devices. The solid lines in the inset are the exponential fits to the semilog J_D -V characteristics at the intermediate voltages.

where the R_s and R_p correspond to series and shunt resistance, respectively, q is the elementary charge (1.6×10^{-19} C), k is the Boltzmann constant, T is the temperature, A denotes the device area and J_{ph} corresponds to the photocurrent. In the dark ($J_{ph} = 0$) and by assuming close-to-ideal diode behavior (R_s is very small and R_p is very large), Eq. 2.10 can be simplified as

$$J = J_0 \left\{ \exp \left(\frac{qV}{nKT} \right) - 1 \right\} \quad (2.11)$$

Rearrangement of Eq. 2.11 thus yields

$$\ln(J + 1) = \ln J_0 + \frac{qV}{nKT} \quad (2.12)$$

which can be used for curve fitting of the dark J -V plots at the intermediate voltages in Fig. 2.9. The calculation reveals J_0 of 2.1×10^{-7} , 7.6×10^{-6} and 3.1×10^{-5} mA/cm² for NA, TA and NF P3HT:PCBM devices, respectively. The origin of J_0 has been proposed to result from a thermally activated electron excitation from HOMO level of the donor to the lowest energy charge-transfer (CT) state at the donor-acceptor heterojunctions.⁴¹ The higher J_0 for NF system can also be explained in terms of the higher upward-shift of the HOMO level, rendering a more efficient electron transfer to the CT state due to the reduction in the energy barrier. The reverse saturation current also correlates with V_{OC} , as seen from the following expression⁴¹

$$V_{OC} \approx n \frac{kT}{q} \ln \left(\frac{J_{SC}}{J_0} \right) \quad (2.13)$$

The J_0 is inversely proportional to the V_{OC} , *i.e.* device with higher reverse saturation current will have lower V_{OC} . There is an increasing trend in the J_0 for NA, TA and NF devices; this matches with the observed decreasing trend in the V_{OC} (*i.e.* 0.70, 0.63 and 0.58 V).

External quantum efficiency To probe the origin of the photocurrent loss, external quantum efficiency (EQE) measurement was conducted. Fig. 2.10(a) displays the EQE spectra of the P3HT:PCBM devices, while the normalized spectra are shown in Fig. 2.10(b). Maximum EQEs of 33%, 66% and 58% are obtained for the NA, TA and NF P3HT:PCBM devices, respectively. The normalized profiles (Fig. 2.10(b)) reflect the same pattern as the optical absorption data. The NF device appears to be most red-shifted and display the most pronounced shoulder at *ca.* 610 nm. By comparing the EQE ratio between the EQE at 610 nm, which corresponds to the vibronic absorption of P3HT, and EQE max (EQE_{610}/EQE_{max}), the values of 0.48, 0.68 and 0.85 are obtained for NA, TA and NF devices. The short-circuit current (J_{SC}) can also be estimated by integrating the EQE over the solar spectrum using the following relationship⁴²

$$J_{SC} = \frac{q}{A} \int EQE(\lambda) \Phi_{AM1.5}(\lambda) d\lambda \quad (2.14)$$

where A is the device area and $\Phi_{AM1.5}$ is the photon flux based on AM 1.5 solar spectrum. The calculated J_{SC} are comparable to the ones obtained from the PCE measurement: 4.2, 8.9 and 8.2 mA/cm² (< 8% difference). Apart from the red-shift in the EQE spectra, the NF device has almost identical feature to the TA device. The EQE decrease for the NF system could be resulting from any unoptimized mechanisms pertaining to the P3HT phase, since the lowering of the EQE signals is mainly in the range of 400 – 650 nm, *i.e.* the photoactive region of P3HT.

Fig. 2.10 (a) EQE spectra of P3HT:PCBM (10:8) devices and (b) the corresponding normalized spectra at EQE_{max} of each device.

Light intensity-dependent measurement To have an understanding on the fate of the photogenerated charge-carriers, the P3HT:PCBM devices were subjected to the light intensity dependence study. The double logarithmic plots of short-circuit current (J_{SC}) as a function of light intensity is shown in Fig. 2.11. Recombination parameters (α) can be extracted by fitting the plots with the power law⁴³

$$J_{SC} \approx P_{light}^{\alpha} \quad (2.15)$$

with P_{light} as the light intensity. Eq. 2.15 can be rewritten as

$$\log J_{SC} = \alpha \log P_{light} + K \quad (2.16)$$

Fig. 2.11 Double logarithmic plots of short-circuit current *vs* light intensity ($J_{SC} - P$) of P3HT:PCBM (10:8) devices. The slopes of the fits correspond to the recombination parameters (α).

The linear curve fitting of the double logarithmic plots gives the slopes (α) of 0.81, 0.99 and 0.95 for the NA, TA and NF devices, respectively. Recombination parameter close to unity ($\alpha = 1$) signifies a monomolecular-recombination-dominated charge-carrier loss, while $\alpha = 0.5$ indicates a bimolecular-recombination-dominated loss.⁴⁴ Under short-circuit condition, the amount of photogenerated charge-carriers extracted to the external electrodes are driven by the built-in electric field and affected by the lifetime and mobility of the charge-carriers. In the as-cast NA device ($\alpha = 0.81$), the blend morphology is unoptimized with inefficient charge transport. This increases the likelihood for both holes and electrons in the donor and acceptor respectively to annihilate each other before they are extracted to the external electrodes. The crystallinity increase in TA and NF devices both yield α close to 1. This indicates that the improved charge mobility results in reduction of bimolecular recombination. In other words,

the major source of photocurrent loss in these systems is the recombination of the coulombically interacting geminate electron-hole pairs. The NF device has a smaller recombination parameter ($\alpha = 0.95$) as compared to the TA device ($\alpha = 0.99$), indicating a minor contribution of bimolecular recombination. In the nanofiber P3HT:PCBM blend, a small portion of the charges generated recombine before they reach the external electrodes. The proposed explanation can be proven from the ultrafast spectroscopy measurement, as presented in a later discussion (section 2.3.3).

Photoluminescence spectroscopy Photoluminescence (PL) measurement also provides another insight into the mechanism affecting the photocurrent loss in NF system. The various P3HT:PCBM (10:8 wt%) blend films are excited at 520 nm, which corresponds to the λ_{max} from the optical absorption, and the corresponding emission spectra are shown in Fig. 2.12, normalized to their respective absorption intensities at 520 nm. The inclusion of PCBM into the P3HT matrix, even at very low concentration (as low as 1 wt%), can quench the luminescence of P3HT.⁴⁵ Photoluminescence phenomenon involves a recombination process of the photoexcited excitons. The quenching of the PL indicates the suppression of the exciton recombination and the existence of alternative pathways for the excitons. By adding acceptor molecules into the donor material, the photogenerated excitons may dissociate into free charges. As a result, the amount of excitons available for recombination reduces and the quenching of the photoluminescence is observed. The efficiency of PL quenching is often correlated to the charge generation and is dependent on the distribution of the molecules. With an increase of the amount of donor-acceptor (D/A) interface, the excitons are more likely to dissociate into free charges; thus, more PL quenching is observed. In other words, the effectiveness of PL quenching depends on the morphology of the donor-acceptor blend.⁴⁶

As shown in Fig. 2.12, NF P3HT:PCBM exhibits the highest PL intensity (or the least quenching), followed by TA and NA blends. When compared to the as-cast NA blend, the thermally annealed TA blend shows an increase in PL by *ca.* 18%, while in the nanofiber NF blend the PL is even stronger (*ca.* 66% increase). Thermal annealing induces reorganization of the P3HT and PCBM molecules, resulting in phase separation and formation of crystallite regions with reduced D/A interface. The TA blend also demonstrates a more red-shifted PL characteristic than the NA system, which is an indication of the enhanced degree of order. The NF blend has the least efficient quenching, which can be correlated to the decrease in the number of free charges. This finding also suggests that with fibrillar morphology, there is less

D/A interface in the NF blend. In summary, the PL data imply that the photogeneration in the nanofiber blend could be less efficient than the thermal-annealed blend. To confirm this, an investigation of the blend morphology is carried out.

Fig. 2.12 Photoluminescence spectra of P3HT:PCBM (1:1) blends excited with 520 nm light source. The spectra are normalized with respect to their absorption at λ_{ex} .

Blend morphology Tapping mode atomic force microscopy (AFM) images ($1 \mu\text{m} \times 1 \mu\text{m}$) of the various blend films are shown in Fig. 2.13. From the phase image (Fig. 2.13(d)), the NA blend appears to be more homogeneously mixed than the other blend. Both the donor and acceptor phases appear indistinguishable from each other. As for the annealed P3HT:PCBM blend, larger phase separated domains can be observed (Fig. 2.13(e)). This observation agrees with the previous finding in the diffraction study, in which the average crystallite size is demonstrated to increase upon annealing treatment (Table 2.1). The nanofiber P3HT:PCBM blend (Fig. 2.13(f)) shows the fibrillar P3HT is preserved in the blend matrix. A few of the nanofibers appear overlapping with the others. The remaining P3HT and PCBM molecules are presumed to fill the space existing between the fibers, although they cannot be differentiated in the phase image. With nanofibrillar morphology the amount of the D/A interface in NF blend is less, due to the smaller surface area per unit volume (S/V) compared to the more-dispersed P3HT phase in the TA blend. The morphology data may support the observation of the previous PL quenching study (Fig. 2.12).

The height images (Fig. 2.13 (a–c)) are analyzed to yield the root-mean-square roughness (σ_{RMS}) of the blends. For $1 \mu\text{m} \times 1 \mu\text{m}$ scan size, the following σ_{RMS} values are obtained: 0.3, 0.8 and 1.8 nm for the NA, TA and NF P3HT:PCBM blends respectively. The

roughening of the blend surface upon thermal annealing has often been reported to manifest due to the enhanced polymer ordering in the blend. From σ_{RMS} calculation, the TA and NF blends are rougher by 2.6 and 6 times, respectively. The increase in the surface roughness may result in poorer contact between the blend layer (P3HT:PCBM) and the top electrode (Al). In the case of TA blend, the surface roughening may also be accompanied by the heat-induced formation of organometallic bonds.¹ Consequently, the overall contact resistance is improved. In comparison, the nanofiber blend is almost 3 times rougher than the thermally annealed blend. On top of this, NF system lacks of any post-fabrication heat treatment that leaves the contact resistance unrectified. The effect of the surface roughness correlates well with the higher series resistance (R_s) in the NF device, *i.e.* *ca.* 2 times higher than that in the TA device. The donor and acceptor phases in the blend film is difficult to resolve using either height or phase images. The conducting AFM results in the next section can help to resolve the phases better.

Fig. 2.13 Tapping mode height (top) and phase (bottom) AFM images of P3HT:PCBM (10:8): (a,d) as-cast (NA), (b,e) thermal-annealed (TA) and (c,f) nanofiber (NF) blends. The scan size is 1 μm $\times$ 1 μm .

Current mapping The spatial distribution of holes and electrons, corresponding respectively to the donor-rich and acceptor-rich regions, can be mapped using conducting atomic force microscopy (c-AFM) technique.⁴⁷⁻⁴⁹ It is therefore possible to distinguish the polymer region from the fullerene phase in typical organic solar cell blends, and hence

elucidate their nanoscale distribution. Fig. 2.14 demonstrates the current images of the various blend systems at 0 V bias (Fig. 2.14 (a–c)) and at -3 V substrate bias (Fig. 2.14 (d–f)). The sample configuration consists of ITO/PEDOT:PSS/P3HT:PCBM. The contact-mode imaging was done in dark. A gold-coated silicon nitride (Si_3N_4) tip was used for the measurement. The low force constant (0.06 N/m with resonant frequency of 10 kHz) renders the Si_3N_4 AFM probe suitable for soft-contact imaging.

Fig. 2.14 Contact mode dark current AFM images with 0 V substrate bias (top) and -3 V substrate bias (bottom) of P3HT:PCBM (10:8): (a,d) as-cast (NA), (b,e) thermal-annealed (TA) and (c,f) nanofiber (NF) blends. The right scale bars are the same for all images. The scan size is $4\ \mu\text{m} \times 4\ \mu\text{m}$.

When no voltage bias is applied to the substrate ($V = 0\ \text{V}$), all films appear featureless (Fig. 2.14(a-c)). All the three blends look similar to each other. Upon the application of a negative substrate bias (equivalent to a positive tip bias), the measured current should correspond to holes injected from the tip to the sample. In terms of the c-AFM images, the brighter areas correspond to the hole (donor)-rich regions, while the darker regions correspond to the electron (acceptor)-rich regions. This allows better visualization due to the enhancement in image contrast. As seen in Fig. 2.14(d), the substrate bias of -3 V is able to result in a distinction between the hole-rich and electron-rich regions in the NA blend. The contrast between the two regions in c-AFM image is related to the amount of local current generated. There is an increase in contrast from the as-cast NA to the nanofiber NF to the thermal-annealed TA blends. The average dark hole currents calculated from the brighter

regions of the images are 0.41, 3.59 and 0.81 pA for the NA, TA and NF blends, respectively; the corresponding average electron currents are -0.44, -3.10 and -0.80 pA. From these results, it could be inferred that in spite of the difference in the size of the hole-/electron-rich regions, the total amount of holes are counterbalanced by the amount of electrons. The data also indicate that with equal amount of donor and acceptor, there is no preferential distribution of either material in the blend. The lower local current indicates a poorer current injection into the surface of the NF blend as compared to the TA blend.

To summarize the discussions in this section, three P3HT:PCBM blends with distinct morphologies were analyzed and characterized. Both thermal-annealed (TA) and nanofiber (NF) blends are more crystalline than the as-cast (NA) blend. In fact, the NF blend has the highest crystallinity; thus, the strongest optical absorption and the highest SCLC hole mobility. Nevertheless, the TA device outperformed the NF device in terms of device PCE. As revealed by light-intensity dependent study, there is a small contribution of bimolecular recombination in photocurrent generation in NF device. Furthermore, its exciton dissociation (PL quenching) is also less efficient, and the contact resistance is higher due to its rougher surface (AFM). To understand how the morphology impacts the lifetime and the amount of excited species, “time-resolved” studies are presented in the following section. Through this discussion, we are able to gain a better understanding of how to improve NF devices.

2.3.3 Time-resolved spectroscopy of P3HT nanofiber blend

Time-resolved spectroscopy techniques are capable of providing molecular insights of the fundamental processes occurring in organic solar cells that cannot be captured by “steady-state” characterization methods.⁵⁰⁻⁵⁷ The understanding of such processes is essential to achieve high device PCE. The dynamics of the processes occurring in the organic solar cell devices, from the exciton generation until the charge formation and extraction, can be observed using such techniques. Thus this technique is useful in revealing the actual mechanism behind the photocurrent loss observed in the nanofiber device.

Femtosecond transient absorption spectroscopy The fs-TAS measurements of both the neat P3HT and the blend P3HT:PCBM films were carried out to gain an understanding of the exciton and charge dynamics in the ultrafast time regime with a time resolution between femtosecond and nanosecond (fs – ns). To simplify the discussions, there are only two types of P3HT compared in this study, *i.e.* the thermal-annealed (TA) and nanofiber (NF) systems. A

low pump laser fluence (*i.e.* integrated flux over time) of $10 \mu\text{J}/\text{cm}^2$ was used for the measurement. At high fluence, both excitons and charges are more likely to interact with each other since they are both generated within close temporal proximity.^{54,58} The interaction between those species may result in undesirable secondary-order effects, *e.g.* exciton–exciton annihilation or exciton–charge interactions. This fluence-dependent behavior has also been observed in different polymer blend systems at various wavelengths. Nevertheless, too low a fluence may also degrade the signal-to-noise ratio (SNR).

Fig. 2.15 Femtosecond transient absorption spectra of: (a) thermal-annealed (TA) and (b) nanofiber (NF) P3HT films. The films were excited at 500 nm, $10 \mu\text{J}/\text{cm}^2$.

Fig. 2.15 shows the femtosecond transient absorption spectra of the TA and NF P3HT films measured at different time delays (1 ps to 2 ns), while the corresponding decay dynamics are shown in Fig. 2.16. In general, both P3HT films exhibit similar characteristics, although the intensity of the induced transmissions ($\Delta T/T$) of the NF P3HT is slightly stronger than that of TA P3HT. Upon photoexcitation at 500 nm, the signals corresponding to the photobleaching (PB) of the ground-state absorption, *i.e.* the ground state bleaching (GSB), can be observed in the wavelength range of 500 – 620 nm. The three positive GSB signals at 520, 560 and 610 nm correspond to the absorption transitions, which are labeled as 0–2, 0–1 and 0–0 GSB, respectively. The features of these GSB signals are similar to the steady-state absorption of P3HT, and they demonstrate decaying behavior over time. Since the GSB reflects the presence of non-ground states, they are indicative of the presence of excitons and polarons. In the absence of acceptor molecules, polaron formation is not favorable. As such, the decay of GSB indicates the recombination of the singlet excitons. Besides the GSB, the transient spectra also exhibit negative $\Delta T/T$ signals at *ca.* 650 nm, which have been previously assigned to the photoinduced absorption (PIA).⁵⁴ The PIA feature is attributed to the population of

photogenerated charges. The last “fingerprint” of the transient absorption spectra of P3HT (wavelength region 520 – 760 nm) is the weak stimulated emission (SE) signal at 730 nm, which corresponds to P3HT photoluminescence.⁵⁴ The SE signal suggests the presence of singlet excitons, and its shape may be affected by the nearby PIA signal. However, the SE feature is not observed in the NF system (Fig. 2.15(b)), which could be due to the overlapping by the stronger PIA signal.

Fig. 2.16 Femtosecond transient absorption decays of thermal-annealed (TA) and nanofiber (NF) P3HT films corresponding to: (a) 0–0, (b) 0–1 and (c) 0–2 optical transitions.

At the early stages of the decay, the 0–0 vibronic transition at 610 nm appears the most pronounced among the three GSB peaks (Fig. 2.15). The 0–0 GSB peak correlates with P3HT crystallinity. Hence, by comparing the $\Delta T/T$ of the transient spectra of the P3HT films at 610 nm, it is possible to qualitatively infer the film crystallinity. In terms of the photobleaching (PB) dynamics, the NF P3HT exhibits stronger signals for both 0–0 and 0–1 transitions in the first 100 ps than the TA P3HT, as can be seen in Fig. 2.16(a) and (b), respectively. The increase in the signal strength could be due to the stronger absorption of the nanofiber system, which leads to an increase in the amount of photoexcited states. On the other hand, both TA and NF P3HT films show almost overlapping decay characteristics for the 0–2 transition (Fig. 2.16(c)), suggesting that the depopulation of the 0–2 states to the energetically lower states is similar in both films. Since the decay dynamics of the GSB do not show a full-recovery to the ground state, this suggests that a few of the P3HT molecules are still in the excited state up to 2 ns. Nevertheless, at this time delay the $\Delta T/T$ magnitudes of the TA and NF P3HT films are very similar, indicating comparable amount of excited states in both systems.

The same measurement technique is also extended for the P3HT:PCBM blend systems, *i.e.* the main subject of this thesis. The dispersion of acceptor (A) molecules in the donor (D) matrix gives rise to the formation of D/A heterojunctions. The electric field at the D/A interfaces induces exciton splitting leading to charge generation. Therefore, in a blend system

the decay of the photoexcited states is not only by means of exciton recombination, but also *via* exciton dissociation at the interface, followed by charge transport and recombination. Fig. 2.17 shows the transient absorption spectra of both TA and NF P3HT:PCBM blends and their GSB dynamics are presented in Fig. 2.18. At early delay times, both blends exhibit similar spectra, which are characterized by positive GSB below 630 nm and negative PIA extending to 760 nm. Unlike the neat TA P3HT film, no SE signal is observed in both blends. Both the PIA shape and the absence of SE are indicative of the presence of charges instead of excitons. The pronounced vibronic GSB features are still present in the TA and NF blends, similar to the neat P3HT films. This is consistent with the notion that both thermal annealing and application of pre-formed fiber recovers and maintains high degree of order in the blends. The photogenerated excited states (*i.e.* charges) can then delocalize in these crystalline domains.

Fig. 2.17 Femtosecond transient absorption spectra of: (a) thermal-annealed (TA) and (b) nanofiber (NF) P3HT:PCBM (10:8) blends. The blends were excited at 500 nm, $10 \mu\text{J}/\text{cm}^2$.

Fig. 2.17 shows a rapid initial decay within the first 100 ps in the transient absorption spectra of both TA and NF P3HT:PCBM blends, which could be attributed to the exciton-charge annihilation. Beyond the time delay of 100 ps, there is barely any change in both spectra. This implies that stages such as charge transfer and exciton recombination are completed over this time scale. In terms of the decay dynamics (Fig. 2.18), the NF blend still exhibits larger magnitude of $\Delta T/T$ as compared to the TA blend up to 2 ns, in particular for the 0-0 and 0-1 transitions. At time delay of 2 ns, the GSB signal in the NF blend is still stronger than TA blend, which indicates that there are more long-lived excited states in the NF blend than the TA blend. These states are believed to be the charges, after excluding the possible contribution of both singlet and triplet excitons. Singlet excitons tend to be short-lived, while the population of triplet excitons in regioregular P3HT is expected to be minimal.

To further investigate the fate of the charges in both TA and NF blends, nanosecond laser flash photolysis spectroscopy was performed.

Fig. 2.18 Femtosecond transient absorption decays of thermal-annealed (TA) and nanofiber (NF) P3HT:PCBM blends corresponding to: (a) 0–0, (b) 0–1 and (c) 0–2 optical transitions.

Nanosecond laser flash photolysis spectroscopy This technique is capable of revealing the kinetics and dynamics of transient species with a time resolution between nanosecond and microsecond (ns – μ s). Fig. 2.19 shows the decay dynamics of both TA and NF blends in the time scale of ns – μ s. Within this time scale, the dynamics of the charge recombination are investigated and correlated with the device performance. In agreement with the previous finding from the ultrafast spectroscopy measurement, the $\Delta T/T$ magnitude of the 0–0 and 0–1 transitions are larger in the NF blend than that of TA blend in the early ns time scale. Beyond hundreds of ns, a rapid decline in the GSB signal is observed in the NF blend. In the μ s regime, the magnitudes of the 0–0 and 0–1 GSB signals in the NF blend become comparable to those of the TA blend. A more prominent decay is observed for the 0–2 transition. The decay of the GSB signals could be resulting from an increase in the bimolecular recombination of the charges.^{51,59} Therefore, it can be concluded that the bimolecular recombination rate in the NF blend is higher as compared to the TA blend. This finding is also consistent with the previous data on the light-intensity dependent behavior in section 2.3.2.

Fig. 2.19 Nanosecond transient absorption decays of thermal-annealed (TA) and nanofiber (NF) P3HT:PCBM blends corresponding to: (a) 0–0, (b) 0–1 and (c) 0–2 optical transitions.

Photocurrent loss in nanofiber device Through time-resolved measurements, it can be seen that the nanofiber blend has the potential to yield more charges than the thermal-annealed blend. However, the PCE data (section 2.3.2) indicate that the device performance of NF system is inferior to that of the TA system. As revealed by the nanosecond time-resolved spectroscopy, the photocurrent generation in NF device is slightly dominated by bimolecular recombination. Although the charge transport along the nanofiber is efficient, it is hypothesized that the fibers may not form an entirely interconnected network, leaving a few “dead end” regions and resulting in the isolation of the fibers. In a solar cell device, charges are expected to transport in the direction perpendicular to the substrate, while nanofibers with high aspect ratio tend to lie parallel to the substrate. As such, there is a high likelihood that a few of the fibers are disconnected from the others. The holes generated in these fibers will recombine with the electrons before they get any chance to be transported to an electrode; hence, an increase in bimolecular recombination. It can be concluded from these studies that the lower performance in NF device is mainly due to morphological issue. This issue, however, can be resolved through proper control of the fiber growth. A “skillfully” self-assembled fibrillar network of polymer fibers may eventually become the panacea to achieve thermal-free highly efficient organic solar cell devices. The following sections (2.3.4 and 2.3.5) will demonstrate how the fiber morphology can be easily manipulated.

2.3.4 Effect of marginal solvent

The morphology of the fibers is dependent on the growth parameters, such as the choice of marginal solvent. To investigate the effect of marginal solvent on P3HT nanofiber formation, anisole and *p*-xylene were used to dissolve P3HT. For comparison, P3HT was also dissolved in good solvent chlorobenzene (CB), which was then processed similarly. P3HT was found to be less soluble in anisole. Therefore, the dissolution of P3HT in anisole at high temperatures required longer time in comparison to that in *p*-xylene due to the poorer solubility of P3HT in anisole. The color transition was observed earlier in anisole, roughly 2 h after the cooling started (*ca.* 60 °C). The difference in the rate of change in the color of the solution (*i.e.* the rate of transition from solvation-to-aggregation state) implies a more rapid self-assembly of P3HT in anisole than in *p*-xylene. Therefore, more P3HT nanofibers were expected to form in anisole, and this can be seen in the following absorption spectra, which will be discussed next.

Optical spectroscopy Fig. 2.20 shows the absorption spectra of P3HT in different solvents. The three curves are normalized at the isobestic point (475 nm), which generally indicates the transition from the weakly interacting P3HT chains to the ordered strongly interacting P3HT aggregates. P3HT in good solvent CB only shows a single absorption peak with λ_{max} at 454 nm, often assigned to the intrachain π - π^* transition.⁶⁰ P3HT in CB, as deduced from its absorption spectra, adopts more randomly twisted conformations that prevent further interchain interactions. When poorer solvent anisole or *p*-xylene is used, λ_{max} of P3HT is red-shifted following the appearance of two more vibronic or “shoulder” peaks at 550 and 610 nm. These additional peaks are attributed to the extension of conjugation length with an improved π - π stacking of the P3HT chains within the nanofibers.⁶¹ P3HT in anisole exhibits a more red-shifted λ_{max} at 495 nm and the two “shoulder” peaks show stronger absorption as compared to the similar solution prepared in *p*-xylene. This observation implies that the stronger solvophobic interaction between anisole and P3HT chains enhances the stacking between the chains resulting in an improved P3HT crystallinity. It should be noted that both solutions were left undisturbed for 12 h after the cooling process was completed.

Fig. 2.20 UV-Vis absorption spectra of P3HT in chlorobenzene and P3HT nanofiber suspensions in *p*-xylene and anisole. The nanofiber suspensions were left undisturbed for 12 h in dark after cooling process was completed. All curves were normalized at the isobestic point at 475 nm.

Morphology Fig. 2.21 shows the distinct features of P3HT nanofibers prepared in *p*-xylene and anisole, as characterized by using atomic force microscopy (AFM) operated in tapping mode. The anisole-based P3HT fibers (Fig. 2.21(a)) tend to be shorter (smaller than 3 μm), while the *p*-xylene-derived ones (Fig. 2.21(b)) can be longer than 10 μm . In the anisole

system, a few fibrillar aggregates can also be observed. Due the poorer solubility of P3HT in anisole, a more substantial nucleation could have taken place during the onset of fiber self-assembly. This, however, may have reduced the concentration of P3HT molecules, resulting in short fibers. As P3HT is less soluble in anisole, the nanofibers formed also disperse poorly resulting in aggregates of the fibers.

Fig. 2.21 Tapping mode height AFM images of P3HT nanofibers self-assembled in: (a) anisole and (b) *p*-xylene. The suspensions were aged for 24 h and were diluted by a factor of 10 before spincoating. The scan size is 10 μm $\times$ 10 μm .

On the other hand, the morphology of the P3HT nanofiber:PCBM blends are shown in Fig. 2.22. Fibrillar structures are visible in all images. The P3HT nanofibers in the anisole blend (Fig. 2.22(a)) appear to be denser as compared to those in *p*-xylene blend (Fig. 2.22(b)). The topographic AFM images also reveal that the anisole blend is much rougher with root-mean-square roughness (σ_{RMS}) of 12.3 nm, approximately 5 times higher than the *p*-xylene blend ($\sigma_{\text{RMS}} = 2.4$ nm). The rougher surface of P3HT-nanofiber:PCBM blend cast from anisole could be due to the presence of larger nanofiber aggregates in the blend.

Fig. 2.22 Tapping mode height AFM images of P3HT-nanofiber:PCBM (10:8) blends self-assembled in: (a) anisole and (b) *p*-xylene. The scan size is 10 μm $\times$ 10 μm .

Fig. 2.23 Current density-voltage (J - V) characteristics of P3HT-nanofiber:PCBM (10:8) devices processed from anisole and *p*-xylene under 1 sun (100 mW/cm^2) illumination. The as-cast DCB device is included as reference.

Device Characteristics Solar cell devices were fabricated from the blends of P3HT nanofiber with PCBM in the following configuration: ITO/PEDOT:PSS/P3HT-nanofiber:PCBM/Al. Fig. 2.23 illustrates the current density-voltage (J - V) characteristics of the nanofiber devices. It is shown that both nanofiber-based devices performed better than the as-cast non-fiber OPV with $\text{PCE} < 1\%$, emphasizing the role of the nanofiber in the enhancement of both the blend absorption and charge transport. The device photovoltaic parameters, which include short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF) and power conversion efficiency (PCE), are summarized in Table 2.3. Device based on *p*-xylene system resulted in a better PCE of 2% as compared to that of anisole system ($\text{PCE} = 1.5\%$). This could be because even though there is a higher degree of P3HT crystallinity in anisole system resulting in higher J_{sc} but its V_{oc} and FF are compromised. The increase in J_{sc} is due to the improved P3HT crystallinity resulting in the enhancement of photoabsorption and hole mobility.⁶² Nevertheless, the increased hole mobility in P3HT could result in an imbalance of the hole and electron charge transport leading to space-charge phenomenon with increased electrical resistance in the bulk; hence, reducing the FF.⁶² Therefore the ability to control the morphology is essential in getting the optimal performance from the OPV devices. As there are more fibers in anisole blend, the highest occupied molecular orbital (HOMO) level of P3HT is shifted closer to the lowest unoccupied molecular orbital (LUMO) level of PCBM, resulting in V_{oc} reduction.⁶³ This V_{oc} reduction can also be explained in correlation with the

decreased intermolecular charge transfer states energy (ECT), which has been demonstrated to decrease with a higher proportion of nanofiber in the blend.¹¹ In short, this section demonstrates that PCE depends strongly on the dimension and amount of P3HT fibers, which are direct consequences of the choice of marginal solvent used during P3HT self-assembly.

Table 2.3 Summary of photovoltaic device properties of P3HT-nanofiber:PCBM (10:8) devices cast from anisole and *p*-xylene.

Solvent	PCE	J_{sc}	V_{oc}	FF
	%	(mA/cm ²)	(V)	
anisole	1.45	7.13	0.50	0.41
<i>p</i> -xylene	2.03	6.48	0.61	0.51

2.3.5 Effect of good solvent in a mixed-solvent system

Despite the lower PCE, P3HT-anisole system remains an interesting system to investigate because the nanofiber formation is substantially less sensitive to the cooling rate. Hence, the nanofiber amount and morphology are expected to be more reproducible.¹⁸ Besides, the enhanced photoabsorption in the anisole system also implied that there is potentially more excitons generated and separation of these excitons may result in more charges harvested. As mentioned earlier, it is critical to obtain an optimum balance in the crystalline/amorphous P3HT in the blend to achieve high PCE. To do this, a small amount of good solvent for P3HT, CB, was added into the P3HT-anisole solution to manipulate the conformation adopted by P3HT in solution, which would in turn influence the P3HT intermolecular interaction. P3HT solutions in these mixed solvents were then subjected to heating-cooling process. P3HT molecules in CB have limited interchain interaction and therefore do not show any vibronic features upon the thermal treatment of the solution (Fig. 2.20). The CB addition into P3HT/anisole system was expected to disrupt nanofiber formation and result in more amorphous P3HT in the film. However, the UV-Vis absorption and GIXRD revealed results that are counter-intuitive and are further elaborated in the following discussions.

Optical spectroscopy and diffraction measurement Fig. 2.24(a) depicts the UV-Vis absorption spectra of the P3HT/anisole system with different amount of CB (%vol). The addition of CB results in an improvement of absorption, as indicated by both the more red-shifted absorption maximum (λ_{max}) and increased absorption (higher “shoulder” peaks). P3HT with 10% CB in anisole absorbs more strongly than the other two solutions, as observed from

the more intense brownish purple solution. Further CB addition to 20% neither shifts the $\lambda_{\max}$ nor increases the absorption intensity. Translating the absorption characteristics into degree of crystallinity, it is expected that 10% CB addition in P3HT/anisole system will lead to the highest crystallinity or more fiber formation. Increasing the amount of CB to 20% then reduces the crystallinity, although the amount of fibers is still expected to be more than the pristine (0% CB) solution.

Fig. 2.24 UV-Vis absorption spectra of: (a) P3HT in anisole with chlorobenzene (CB) addition and (b) P3HT-nanofiber:PCBM (10:8) blends cast from anisole with different amount of CB addition. The absorption profiles are normalized at PCBM peak at 330 nm.

These nanofibers were then blended with PCBM and then used in the fabrication of solar cell devices. Firstly, thin-film absorption and X-ray diffraction studies were carried out on the spin-coated blend to determine the degree of P3HT crystallinity. Figure 2.24(b) shows the absorption spectra of the P3HT:PCBM nanofiber blend film on quartz substrates. The profiles are normalized to PCBM absorption peak at 330 nm. The behavior of P3HT:PCBM blend film absorption is similar to P3HT nanofiber absorption in solution. This suggests that the degree of P3HT crystallinity is still well preserved in the blend film, even with PCBM incorporation. The blend film cast from anisole with 10% CB shows the strongest absorption with a more intense $\lambda_{\max}$ at 520 nm and two vibronic peaks at 550 and 610 nm. The addition of 20% CB generally still induces a stronger blend absorption than that without CB, but $\lambda_{\max}$ absorption is slightly reduced as compared to the blend with 10% CB. This trend in crystallinity is also qualitatively supported by the GIXRD spectra. Fig. 2.25 shows the GIXRD patterns of the P3HT-nanofiber:PCBM blends coated on Si/SiO₂ substrates. The crystallinity level, $d_{(100)}$ -spacing and the crystallite size of P3HT in the different blends are summarized in Table 2.4. These parameters were derived by fitting the diffraction peaks at $2\theta = 5.4^\circ$ using

Gaussian function. These peaks are often associated with the packing of P3HT chains in the direction of the interdigitating alkyl group. With CB addition, there is an increase in the relative diffraction intensity. The calculation of P3HT crystallinity further reveals an improvement by at least 2-fold. By employing the Debye-Scherrer's equation (Eq. 2.5), the mean P3HT crystallite size in the P3HT-nanofiber:PCBM blends was calculated from the FWHM of (100) reflection. The mean crystallite size increases by around 5% when CB was added to the P3HT/anisole solution. Therefore both absorption and diffraction studies have conclusively shown that addition of CB increases P3HT crystallinity in the PCBM blends.

Fig. 2.25 GIXRD patterns of P3HT-nanofiber:PCBM (10:8) blends cast from anisole, with and without chlorobenzene (CB) addition.

Table 2.4 GIXRD parameters of P3HT-nanofiber:PCBM (10:8) blends cast from different solvents.

Solvent/ Mixed Solvents	Peak Height	FWHM	Crystallinity	Crystallite size	$d_{(100)}$
	(count/s)	(°)	(a.u.)	(nm)	(nm)
anisole	0.097	0.837	0.081	9.5	1.640
anisole + 10% CB	0.235	0.782	0.184	10.2	1.638
anisole + 20% CB	0.229	0.799	0.183	10.0	1.651

Blend morphology The morphology of the blend films with PCBM has also been investigated using AFM as shown in Fig. 2.26. In all samples, fibrillar features could be observed throughout the surface of the blends. The phase images indicate that CB addition has indeed affected the amount of P3HT nanofibers. The nanofibers are more closely packed in the blend films with CB addition, particularly in the 10% CB system. P3HT:PCBM blend with 20% CB also reveals similar features, although the higher CB content may have slightly

reduced the nanofiber content as compared to the 10% CB system resulting in slightly larger smooth regions, presumably to be amorphous P3HT, present between the nanofibers. On the other hand, topography analysis of the images shows that addition of CB during the fiber growth results in a rougher blend ($\sigma_{\text{RMS}} = 18.0 - 26.4$ nm), approximately twice as high as the pristine anisole blend ($\sigma_{\text{RMS}} = 11.2$ nm). Rougher surface has often been correlated to the enhanced crystallinity, and particularly in this study, the rougher blend also shows the presence of more aggregated P3HT fibers. Qualitatively, the morphological studies of the blends show that the amount of P3HT nanofibers increased with CB addition, which leads to improved crystallinity, as evident in the previous absorption and diffraction studies.

Fig. 2.26 Tapping mode height (top) and phase (bottom) AFM images of P3HT-nanofiber:PCBM (10:8) blends cast from anisole with: (a,d) 0% CB, (b,e) 10% CB and (c,f) 20% CB. The scan size is $4\ \mu\text{m} \times 4\ \mu\text{m}$.

AFM studies were also conducted on diluted nanofiber systems to quantify their dimensions. The measurement was performed on single fiber that did not overlap with the other fibers. In the CB-added system, the height of the nanofibers was found out to be smaller. The measured average height of P3HT nanofibers are 15 ± 2 nm and 8 ± 2 nm for anisole-only and CB-added systems, respectively. The structure of the nanofibers has been proposed to consist of layers of extended polymer backbones stacking along the axis of the fibers and each layer is separated by alkyl side chains (Fig. 2.4).^{8,16} The height of the fibers can be correlated to vertical stacking of the extended polymer backbones along their alkyl side groups or, simply

put, it indicates the number of organized polymer layers perpendicular to the fiber axis. The GIXRD data in Table 2.4 shows that the interlayer spacing of P3HT nanofibers along the alkyl groups, $d_{(100)}$ -spacing was measured to be *ca.* 16 Å. Since the nanofiber height in pure anisole system is *ca.* 15 nm, it can be deduced that it consists of about 9 polymer layers. Table 2.4 also shows that the addition of CB at different concentrations results in different $d_{(100)}$ -spacing. Much thinner nanofibers (*ca.* 5 layers) are formed when CB is present throughout the self-assembly of P3HT chains. In short, this morphology study provides evidence that the vertical stacking of the P3HT backbone is limited upon the addition of good solvent CB to P3HT/anisole blend. The decrease in dimension and the increase in crystallinity suggest an increase in the amount of nanofibers in CB system that corresponds well with the AFM data. This variation in fiber dimensions in the presence of good solvent such as CB in this study is a strong indication of its role in modifying the extent of nucleation and growth process of the P3HT nanofibers and therefore opening up the possibility to modify the dimension and/or the quantity of the nanofibers formed. Together with the synchrotron studies presented next, this important observation will be used to explain the self-assembly mechanism of P3HT in mixed solvent system.

Fig. 2.27 (a) Current density-voltage (J-V) characteristics and (b) External quantum efficiency (EQE) spectra of P3HT-nanofiber:PCBM (10:8) devices cast from anisole, with and without CB addition.

Device performance Fig. 2.27(a) shows the device characteristics of the P3HT:PCBM blends processed with the mixed solvents. The summary of the device parameters is given in Table 2.5. The CB addition resulted in improved device performances as expected from the enhancement in P3HT crystallinity. The best device performance was achieved with 10% CB addition, in which $J_{SC} = 10.13 \text{ mA/cm}^2$, $V_{OC} = 0.53 \text{ V}$, $FF = 0.42$ and $PCE = 2.29\%$. The P3HT/anisole with 20% CB resulted in a slightly lower J_{SC} with similar V_{OC} and FF , an

indication of its lower crystallinity than 10% CB system. V_{oc} of the CB-added system increases slightly despite the increased crystallinity. This improvement in V_{oc} could be due to the fact that CB as a good solvent may induce a more favorable organization, and hence the morphology, of the PCBM in the blend. The EQE spectra of the blends are shown in Figure 2.27(b). The EQE trend fits well with the PCE behavior and the UV-Vis absorption characteristics. The addition of CB resulted in a higher photoresponse within the range of 350 – 650 nm. The highest EQE of 56% is obtained for 10% CB addition. The improvement in EQE should originate in the higher blend crystallinity in the mixed solvent systems.

Table 2.5 Summary of photovoltaic device properties of P3HT-nanofiber:PCBM (10:8) devices cast from different solvents.

Solvent/ Mixed Solvents	PCE	J_{sc}	V_{oc}	FF
	%	(mA/cm ²)	(V)	
anisole	1.45	7.13	0.50	0.41
anisole + 10% CB	2.29	10.13	0.53	0.42
anisole + 20% CB	2.13	9.51	0.52	0.43

Mechanism of nanofiber formation in mixed solvents The addition of CB generally increases the delay in any observable color transition; the higher CB content leads to a longer delay in the onset of color transition. The presence of CB molecules was initially suspected to affect the conformation of the chains, whereby a more extended or “open” chain may cause reduced aggregation of P3HT chains and therefore less nanofiber formation. However, from the previous results, it was observed that more nanofibers with reduced heights were formed suggesting that CB present in the system did not encourage further vertical stacking of P3HT chains. There are two possible mechanisms that might explain this phenomenon. The first possible mechanism assumes the amount of nucleation sites does not change with the addition of CB. P3HT chain stacks vertically until further stacking is offset by the shearing of P3HT chain to form new nuclei. The addition of CB assisted the dissolution of P3HT chain, facilitating the shearing the P3HT layers and resulting in new nuclei. The second possible mechanism assumes that CB induces the formation of more nuclei since extensive intermolecular interaction is discouraged with CB addition. As the solutions are cooled, solvophobic interaction induced by anisole overcomes the CB solvophilic interaction and fiber growth is enhanced.

Fig. 2.28 Kratky plots of P3HT nanofiber growth in different mixed solvent solution with temperature variation at: (a) 0% CB, (b) 10% CB and (c) 20% CB. Kratky plots of P3HT nanofiber growth solution with different amount of CB at specific temperatures: (d) 65°C, (e) 45°C, (f) 40°C and (g) 35°C.

To determine the actual mechanism of the growth of P3HT nanofiber, SAXS was performed using synchrotron source in order to collect real-time data during the cooling process. This technique can be used to provide structural information of macromolecular particle system with a broad range of sizes. The scattering of P3HT aggregates in solutions of different mixed solvents was obtained at different CB temperatures. The change in the scattering intensity can be further correlated with the change in polymer molecules during the self-assembly process. Using Guinier approximations, it is possible to derive the information on the effective size of the scattering particles based on the scattering data,⁶⁴ while Kratky analysis reveals the change in the folding nature of polymer chains during the aggregation.⁶⁵ Guinier approximations are used to study the structure of single particles, their spatial arrangement and orientation. By treating the polymer chains in solution as scattering single

particles, it is possible to identify how these chains distribute around the centre of gravity and their effective size. Table 2.6 shows the radii of gyration (R_g) of the polymer aggregates in the mixed solvents extracted from the linear region of the intensity plots $I(q)$ versus the square of the scattering vector q at low scattering angle based on the practical rule $qR_g < 1.3$ since the Guinier approximation⁶⁴

$$\ln I(q) = \ln(I_0) - \frac{q^2 R_g^2}{3} \quad (2.17)$$

is only valid at small q range for globular molecules.⁶² The radius of gyration, R_g , which approximates the effective size of the polymer chains, depends on the chain conformation. Large conformational change induced by the thermodynamic interactions between polymer chains and the solvent mixtures can alter the scattering behavior, and hence modify R_g . As shown in Table 2.6, at high temperature (75 °C) the polymer chains in different solvent mixtures have similar values of R_g of *ca.* 20 Å, indicating that all P3HT molecules are dissolved well in the solutions. In anisole-only system, R_g starts to increase when cooled to 45 °C, earlier than the systems with CB addition in which the R_g increase occurs at 35 °C. The final R_g is also found to be larger in the systems with CB addition indicating slightly P3HT chain expansion induced by the good solvent.

Table 2.6 Radii of gyration (R_g in Å) of P3HT aggregates in solvent mixtures at different temperatures as derived from Guinier analyses.

Solvent/ Mixed Solvents	Temperature (°C)					
	75	65	55	45	35	25
anisole	21.4	20.2	21.3	22.7	24	23.5
anisole + 10% CB	21.1	19.6	19.4	21.7	25.7	27.8
anisole + 20% CB	18.8	19.9	20.8	20.1	24.9	26.3

Fig. 2.28 shows the Kratky plots of P3HT in different mixed solvent at various temperatures. Kratky analysis emphasizes on the anisotropic nature of the particle system by considering their degree of freedom. Depending on the interaction strength between the polymer chains and their neighbors, the local polymer chains will have different degree of freedom to move around, which then affects their scattering characteristics. These Lorentz-correlated scattered intensity of $q^2 I(q)$ vs q gives good indication of the Gaussian nature of the polymer chains. The previous R_g evaluated from Guinier approximation is only sensitive to

the change in molecular volume. Therefore, complementary Kratky plots can be used to obtain information on the folding characteristics of P3HT chains. In general, the linear region in the plot indicates expanded polymer chains with higher degree of freedom, while the parabolic region indicates the folded chain region with less freedom. Figures 2.28(a-c) show the change in $q^2I(q)$ at low q values as the solutions were cooled from 75 °C to 25 °C. In all solvent mixtures, at high temperature (75 °C), $q^2I(q)$ vs q plots adopt linear shape, suggesting similar unfolded P3HT chains.⁶⁵ As the temperature is lowered, there is an increase in $q^2I(q)$ at lower q . This change can be correlated with the degree of folding of P3HT chains. Figures 2.27(d-g) show the evolution of Kratky plots at specific transition temperatures. Fig. 2.28(e) clearly shows that P3HT folding in anisole-only system starts earlier at 45 °C, while those with CB starts at 40 – 35 °C. This corresponds well with the R_g values obtained from the Guinier analysis, in which an increase in R_g is observed at 45 °C in anisole-only system and at 35 °C for CB-added mixed solvent system. From this observation, it is evident that the onset of nucleation is delayed in the presence of CB. At similar polymer concentration, this delay may increase the amount of P3HT nuclei and hence P3HT nanofibers in CB-added system. Finally, in-situ SAXS provides a good way to study the change in polymer chain conformation in different solvents. This can be correlated with the device performance and the degree of aggregation, which provides an insight of the physical change.

2.4 Conclusions

It has been demonstrated that the nanofiber blend is more superior in terms of the crystallinity and the optical absorption. With improved photon harvesting and charge transport, as measured from the SCLC measurement, nanofiber (NF) devices are expected to yield remarkable performance. Although the NF device is better than the as-cast blend, the thermal-annealed (TA) device still performs better than the NF device. Exciton quenching is not so efficient in the nanofiber system, and the contact resistance could be worse due to its rougher surface as revealed from the morphology study. The light-intensity dependent photocurrent measurement indicates that there is a small contribution of bimolecular recombination in the photocurrent generation in NF device. This finding has also been confirmed by the nanosecond laser flash spectroscopy. As the bimolecular recombination is mainly correlated to the morphology issues, it can be said that the nanofiber morphology can still be optimized. The ideal morphology consists of a fully interconnected fibrillar network, which ensures

minimum charge recombination and encourages efficient charge extraction to the external circuitries.

To have a control over the growth conditions of the fibers is one of the ways to achieve the ideal fiber morphology. In this chapter, it is shown that the fiber crystallinity and dimensions are dependent on the choice of marginal solvent. For example, anisole with a poorer solvent quality for P3HT at room temperature compared to *p*-xylene, can promote higher degree of nanofiber formation during the cooling process due to the stronger solvophobic interaction between P3HT chains and the solvent molecules. When these nanofibers are blended with PCBM to make photovoltaic devices, *p*-xylene system show higher performance with higher V_{oc} and FF, but with a lower J_{sc} . Furthermore, it is shown that P3HT nanofiber formation can be effectively driven and controlled in an unusual mixed-solvent environment whereby the majority is the poor solvent and the minority is the good solvent. Surprisingly by adding good solvent CB into poor solvent anisole, more nanofibers form as indicated by the enhanced absorption intensity and a more intense X-ray scattering. AFM characterization of the nanofibers shows that the height of nanofiber decreases by half due to the coexistence of CB in anisole. The SAXS analysis has also confirmed the delay in the onset of nucleation when CB addition leads to an enhanced P3HT nanofiber formation. OPV devices based on CB addition demonstrated higher PCE value due to improved crystallinity. In short, this investigation first shows that P3HT nanofiber with excellent morphology can be synthesized by using a large quantity of poor solvent and a small quantity of good solvent. It is proposed that the self-assembly of P3HT molecules into nanofibers is governed by the interaction between polymer and poor solvent which can be further manipulated by adding good solvent in order to achieve a more optimized morphology. This study provides a new insight into the self-assembly of polymer chains in a mixed-solvent system, paving the way to new approaches of controlled self-assembly of organic nanostructures, which includes self-assembly of small molecules, oligomers or other polymers in solution or on surfaces.

2.5 Experimental section

Materials Regioregular P3HT (regioregularity > 90%, $M_w = 48\,300$ g/mol) was purchased from Rieke Metals, Inc. and PCBM was purchased from Nano-C®. Solvents used include *p*-xylene (Fluka), anisole (Acros) and chlorobenzene (Aldrich). All chemicals were used as received.

Nanofiber solution preparation P3HT nanofiber solution was prepared by slow cooling of dissolved P3HT solution (7 mg/mL) in either *p*-xylene or anisole from 85 °C at the rate of 10 °C/h using refrigerated circulator (Julabo F25-EC). After being cooled to room temperature, the solution was then left undisturbed in dark for the next 12 h to ensure sufficient nanofiber formation before being mixed with PCBM. P3HT nanofiber suspensions in the mixtures of anisole and chlorobenzene were prepared the same way.

Device fabrication The P3HT:PCBM blend solution was prepared by blending the P3HT nanofiber solution with PCBM at 10:8 weight ratio and stirred for 1 h before spincoating. OPV devices were fabricated on indium-tin oxide (ITO) coated substrates (Kintec Company, 7 Ω /sq). The substrates were first successively cleaned with ultrasonication in deionized water, acetone and isopropanol for 15 min each. The substrates were then plasma cleaned for 2 min before being coated with 30 nm thick of PEDOT:PSS layer. Subsequently, the PEDOT:PSS coated substrates were baked at 140 °C for 10 min. The active blend solution was then spincoated onto the PEDOT:PSS layer to yield film with thickness of 110 ± 5 nm. Due to the difference in viscosity of the *p*-xylene and anisole blend solutions, the spincoating rate had to be adjusted to yield films with similar thickness. Finally a 100 nm thick of aluminum cathode was deposited through a shadow mask on the active layer in vacuum of 10^{-6} Torr. The active area for each device was 0.07 cm². No thermal annealing treatment was performed on the blends. Fabrication of the hole-only devices is essentially the same as the one described above. An extra layer of MoO₃ (10 nm) was evaporated (10^{-6} Torr) prior to Al deposition.

Device measurements and blend characterizations The current density-voltage (*J*-*V*) characteristics of the OPV devices were measured using a Keithley SMU 2400 under simulated AM 1.5G illumination. The light intensity was adjusted at 100 mW/cm². For power conversion efficiency (PCE) measurement, there was no spectral mismatch applied. External quantum efficiency (EQE) measurement was done using a Merlin radiometer (Newport) with a monochromator-calibrated wavelength control. A calibrated silicon photodiode was used as a reference device in counting incident photons. Film thickness was measured by Alpha-Step profilometer (KLA-Tencor). UV-Vis absorption spectra were recorded on a Shimadzu UV-2510PC spectrophotometer. The photoluminescence (PL) measurement was conducted using Perkin-Elmer LS 50B luminescence spectrometer. Grazing incident X-ray diffraction (GIXRD) patterns were collected using CuK α radiation in a ω -diffractometer (incident X-ray at 2.5°). Atomic force microscopy (AFM) images were obtained using Digital Instruments (Nanoscope IIIa) in tapping mode. Conductive atomic force measurement (c-AFM) was performed using Asylum system in contact-mode. The small angle X-ray scattering (SAXS) was performed at the SAXS/WAXS beamline in Australian Synchrotron. The SAXS samples were prepared by filling the P3HT solution into the quartz capillaries before being mounted onto a holder with temperature control capability. The solutions were heated to 80 °C and held

for about 5 mins. It was then cooled at 10 °C/h to room temperature. The scattering data was collected for 1 s at 4 mins intervals.

Transient absorption spectroscopy The measurements were performed using two different setups: (1) for the fs – ns temporal regimes (*i.e.* femtosecond transient absorption spectroscopy (fs-TAS)), and (2) for the ns – μ s temporal regimes (*i.e.* ns laser flash photolysis spectroscopy). For the former setup, excitation pulses were generated from an optical parametric amplifier (OPA) (Light Conversion TOPASTM) that was pumped by a 1 kHz regenerative amplifier (*i.e.* Coherent LegendTM with center wavelength of 800 nm; pulse width of 150 fs; power of 1 mJ/pulse), which in turn was seeded by an 80 MHz Coherent VitesseTM oscillator. Fs-TAS was performed in a non-degenerate pump-probe configuration where the pump pulses (500 nm) from the OPA were focused onto a 200 μ m² spot and overlapped with white-light continuum (*i.e.* 450 – 700 nm) probe pulses generated with a thin sapphire plate using 800 nm laser pulses. Pump-induced changes of transmission ($\Delta T/T$) of the probe beam were monitored using a monochromator/PMT configuration with lock-in detection. The pump beam was chopped at 83 Hz, which was used as the reference frequency for the lock-in amplifier. The pump fluence was kept to a minimal of 10 μ J/cm² per pulse. For the latter setup, the system used was the Applied Photophysics LKS.60 Nanosecond Laser Flash Photolysis Spectrometer which excitation pulses were from a Nd:YAG, Q-switched laser (532 nm, 7 ns pulse width) and the probe was a 150 nm Xe lamp aligned normal to the excitation source. Each time-resolved trace was acquired by averaging 100 laser shots at a repetition rate of 1 Hz. The sample was positioned 45° with respect to both the excitation source and probe light. The samples used for both measurements were prepared by spincoating P3HT or blend solutions on pre-cleaned quartz substrates.

2.6 References

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Effects of Solvent Additives on Blend Morphology and Device Performance of Organic Solar Cells

Summary. As seen in Chapter 2, the amount of interface between the donor and acceptor and the continuity of the phases are critical in achieving good photovoltaic device performance. Thus the key to achieve high power conversion efficiency in organic bulk heterojunction (BHJ) solar cells is the control of the blend morphology. One simple yet effective method is the “solvent additive” approach, which involves the addition of a small fraction of high boiling point solvent into the donor/acceptor dissolved in another host solvent. Even though this method has been successfully applied in a number of polymer/fullerene BHJ devices, the selection rule of the choice of additive and the host solvent has yet to be fully established. In this chapter, a systematic study of the effect of alkyl lengths of alkanedithiol additives on the nanoscale phase separation of P3HT:PCBM blend and consequently, the power conversion efficiency (PCE) of the devices, is presented. The extent of the additive-induced phase separation is related to the additive boiling point and the degree of interaction between the additive and the fullerene, as evident from grazing incidence X-ray diffractometry (GIXRD) and scanning transmission X-ray microscopy (STXM) data. It was found that both the boiling point and the degree of interaction are correlated and should be considered simultaneously in the selection of the appropriate solvent additives. The additive approach can also be applied for the nanofiber system, resulting in a more optimized morphology with improved device performance. As a result, both non-fiber and nanofiber devices can yield PCE in excess of 3% with additive treatment.

3.1 Background

As discussed in the previous chapter, the reason for the lower power conversion efficiency in nanofiber devices compared to the thermal-annealed counterpart is due to the lack of interconnectivity between the polymer nanofibers, which is limited by the morphology of the nanofiber blends. Although it is possible to manipulate the growth conditions to obtain desired morphology, this approach is challenging, as it requires an extensive amount of growth optimizations. The application of solvent additive approach is introduced as an alternative technique to overcome this limitation. In recent years, this approach has been used to assist the optimization of the blend morphology. In this chapter, the selection rules of the additive will be first refined based on the non-fiber P3HT:PCBM blend system. Following this, the effect of the additive molecules on the nanofiber blend system is presented.

3.2 Introduction

Organic solar cells based on polymer-fullerene bulk heterojunction (BHJ) have gained significant interest within scientific community in the past decade.¹⁻⁷ The optimization of nanomorphology of the BHJ blend is one of the important factors to be considered in order to achieve high power conversion efficiency (PCE) devices.⁸⁻¹¹ The optimum blend morphology should consist of a bicontinuous, interpenetrating, nanoscale network of both donor and acceptor materials giving rise to a large amount of donor/acceptor (D/A) interfaces. From the morphological studies of devices with high PCEs, it was found empirically that one of the important criteria for efficient devices is that the size of these nanodomains has to be smaller than 20 nm correlating with the exciton diffusion length.¹²

Annealing treatments, such as exposure of BHJ to elevated temperatures or control of the evaporation rate of the residual solvent in BHJ, are generally applied to enhance phase separation in polymer-fullerene blend films in an attempt to generate the ideal nanomorphology discussed above.^{4,7,13-15} Significant PCE improvement has been observed in the optimally annealed devices; nevertheless, precise control of the annealing conditions has to be imposed due to the sensitivity of device performance towards these treatments. In the pursuit of improving BHJ nanomorphology, a simpler alternative approach is through incorporation of a small amount of high boiling point (T_b) solvents into the D/A solution.^{6,16-24} Bazan *et al.* first reported a significant PCE improvement to higher than 5% for PC₇₁BM blends

of a low bandgap polymer (PCPDTBT) upon the addition of a few volume percent of either alkanedithiols or alkanedihalogens.^{6,17} Similar improvement has also been observed recently on the other new generation polymers whereby the morphologies cannot be optimized under conventional thermal annealing processes. The highest PCE reported to date was achieved from PTB7:PC₇₁BM with 1,8-diiodooctane giving a PCE in excess of 8%.^{25,26} Morphological studies and photophysical measurements performed on these systems have revealed that the improvement in the device PCE stems mainly from improved phase separation throughout the blend film giving rise to an enhancement in the photoconductivity of the free carriers.²⁷⁻³¹ Hoven *et al.* have also extended the range of solvent additives by including a solvent that could better dissolve the low bandgap polymer, *e.g.* 1-chloronaphthalene, leading to reduced phase separation between donor and acceptor and hence improved PCE.³²

The solvent additive approach has also been applied to optimize the morphology of P3HT:PCBM blends, following the success in the low bandgap polymers.^{19,20} In this case, P3HT organization is enhanced resulting in better phase separated blend films. Steady-state and transient photoconductivity measurements have also shown that carrier mobilities improved by an order of magnitude in the solvent treated blends as compared to those in the pristine blends, indicating the presence of interpenetrating network in the additive-processed BHJ.³³ One particular study by Yao *et al.* showed that the nanoscale phase separation in P3HT-PCBM BHJ can be induced by an additive that has a higher boiling point than the host-solvent and poor solubility of PCBM.¹⁹ However, to the best of our knowledge, the effect of boiling point and solubility parameters on the nanoscale phase separation have not been investigated systematically and compared concurrently.

In this chapter, the effect of the incorporation of alkanedithiols with varying alkyl lengths in P3HT:PCBM system is presented. These solvent additives possess similar chemical structures but different boiling points (T_b). The physical characteristics of the additives and the intermolecular interaction between the additive and the fullerene molecules could be correlated with the resulting morphology, and hence the device PCEs. It was found out that although all additives have T_b higher than that of host solvent and have similar chemical structures, the device PCE trend does not vary linearly with T_b . The correlation between the solubility parameters of the different molecules with the extent of intermolecular interactions will also be discussed.

Furthermore, the additive approach also opens up the possibility of optimizing blend morphology based on the system cast from non-chlorinated aromatic solvents. The high PCEs often observed for polymer solar cells are strongly affected by the processing solvents. Most of the highly performing solar cell materials are highly soluble in solvents such as chlorobenzene or dichlorobenzene. These solvents, however, impose high risk on the environment. For the case of P3HT, such solvents can be substituted with the non-chlorinated versions, such as toluene or xylene. Nevertheless, processing with these solvents cannot result in devices with favorable performance. To circumvent this issue, the polymer morphology can be first transformed into nanostructures with superior properties. The device performance of such nanostructured device can be further improved with additive treatment, through optimization of blend morphology. The additive improves the overall crystallinity of the blend, by inducing the crystallization of the amorphous phase bridging the nanostructures. The additive treatment alters the optical and electrical properties of the blends, which are in turn the manifestations of the change in the blend morphology.

3.3 Results and discussion

3.3.1 Additive selection rule

A few criteria have been empirically proposed to simplify the selection of the appropriate solvent additives.¹⁷ First, the solvent additive should have a higher boiling point than that of the host solvent as it allows the additive molecules to stay longer in the blend to interact with the active BHJ components upon the evaporation of the host solvent during spin-coating. Second, the additive should have a preferential solubility with either one of the D/A molecules.

A few mercaptan-based molecules were selected to systematically study the effect of varying alkyl chain length on the performance of the devices. The structures of the additives are shown in Fig. 3.1. The boiling points and vapor pressures of these molecules are listed in Table 3.1. The additives 1,5-pentanedithiol, 1,6-hexanedithiol, 1,8-octanedithiol and 1,9-nonanedithiol are termed as PDT, HDT, ODT and NDT, respectively. As shown in Table 3.1, the boiling point (T_b) of the molecule increases with the length of the alkyl group of the dithiol molecule due to the enhanced Van der Waals interactions. Because of their higher T_b , all the solvent additives evaporate more slowly than the host solvent, *o*-DCB ($T_b = 180\text{ }^{\circ}\text{C}$) allowing them to interact with the polymer and fullerene components after the evaporation of *o*-DCB

during the spin-coating process. The importance of the high boiling point of the solvent additive is emphasized by Yao *et al.* in their proposed post-host-solvent-removal mechanism whereby the poor interaction between additive molecules and the active material components resulted in enhanced phase separation and hence the formation of an interpenetrating network in the blend film.¹⁹

Fig. 3.1 Chemical structures of solvent additives used: (a) 1,5-pentanedithiol (PDT), (b) 1,6-hexanedithiol (HDT), (c) 1,8-octanedithiol (ODT) and (d) 1,9-nonanedithiol (NDT).

Table 3.1 Physical constants of the mercaptan-based solvent additives.

Solvent Additive		Boiling Point	Vapor Pressure
		(°C at 760 Torr)	(Pa at 25 °C)
1,5-pentanedithiol	PDT	216	14.27
1,6-hexanedithiol	HDT	242	6.85
1,8-octanedithiol	ODT	270	1.60
1,9-nonanedithiol	NDT	284	0.91

Device performance Fig. 3.2 shows the *J*-*V* characteristics of the additive-processed devices under AM 1.5G irradiation at 100 mW/cm² and the summary of the device performance is tabulated in Table 3.2. Both the pristine (NA) and thermally annealed (TA) devices are also included for comparison. The pristine device shows the lowest PCE (< 0.5%) due to its low short-circuit current (*J*_{sc}) and fill factor (FF). Heat treatment at elevated temperature (above the glass transition (*T*_g) of the active components) was reported to induce reorganization of both polymer and fullerene phases which leads to improved nanomorphology.¹⁴ Therefore, PCE increases by 7-fold to 3.5% in the thermal-annealed device which is a resultant of both increase in *J*_{sc} and FF. In general, the additive incorporation improves the device performance as compared to NA blend. However, these additive-processed devices exhibit huge variation in PCE ranging from 1 – 3% depending on the alkanedithiol chosen.

Fig. 3.2 Current density–voltage (*J*-*V*) characteristics of P3HT:PCBM (10:8) devices processed with different mercaptan-based additives. The measurement was done under 1 sun (100 mW/cm²) illumination. Both pristine (NA) and thermally annealed (TA) devices are included for comparison.

Table 3.2 Summary of photovoltaic device properties of P3HT:PCBM (10:8) devices processed with different solvent additives. NA refers pristine device and TA refers to thermally annealed device.

Conditions	PCE	J_{SC}	V_{OC}	FF	R_s	R_p
	%	(mA/cm ²)	(V)		(Ω cm ²)	(Ω cm ²)
NA	0.46	1.58	0.67	0.43	62.5	1127
TA	3.49	8.79	0.62	0.64	3.1	475
PDT	1.18	7.14	0.44	0.37	18	196
HDT	3.16	9.38	0.53	0.64	2.3	627
ODT	3.12	9.28	0.52	0.64	2.6	652
NDT	1.91	6.70	0.46	0.59	4.5	866

From Table 3.2, it can be observed that PCE increases as the alkyl chain length increases, with the exception of NDT device. This trend is expected because as the T_b of additive increases, it takes a longer time for them to evaporate and therefore allowing more time for phase separation. The best device is obtained from HDT with J_{SC} of 9.38 mA/cm², V_{OC} of 0.53 V, FF of 0.64 and PCE of 3.16%. The high PCE is comparable to that of annealed device. The significantly enhanced PCE stems from the improvement in J_{SC} . The relatively high FF of the devices also indicates a low internal resistance in the blend. The trend in J_{SC} and FF of the devices can be correlated with the series resistance (R_s) of the devices listed in Table 3.2. The low V_{OC} in additive-processed devices is attributed to the upward shift in HOMO level of P3HT as a result of its aggregation that has also been observed in both thermally and solvent annealed devices.^{4,7} On the contrary, when the higher boiling point additive NDT was added

into the blend, reductions of J_{sc} (by 30% as compared to HDT-added device), V_{oc} , FF and PCE were observed. The increase in R_s also suggests unoptimized blend morphology in NDT processed blend film. The V_{oc} reduction in NDT-added device might also be attributed to the less soluble fullerene derivatives with a tendency to aggregate in the blend, which would induce a lower V_{oc} in the organic solar cell devices.³⁴

Solubility of the components The different extent of PCBM aggregation can be correlated to the degree of intermolecular interactions between the additive molecules and the active materials, which are in turn dependent on the solubility parameter (δ) and the boiling point (T_b) of the solvents. Solubility parameter δ can be calculated from the following equation

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (3.1)$$

δ_d , δ_p and δ_h are the parameters corresponding to the contribution of dispersion forces, polar forces and hydrogen bonding, respectively. All parameters constitute the total cohesive energy. Based on approach developed by Hoftyzer and Van Krevelen³⁵, those parameters can be estimated based on group contributions using the following relationship

$$\delta_d = \frac{\sum F_{di}}{V} \quad (3.2)$$

$$\delta_p = \frac{\sqrt{\sum F_{pi}^2}}{V} \quad (3.3)$$

$$\delta_h = \frac{\sqrt{\sum E_{hi}}}{V} \quad (3.4)$$

where F_d , F_p , E_h and V are the dispersion force, polar force, hydrogen bonding energy and molar volume, respectively.

Solubility parameter, often used to estimate the miscibility between organic solvents, is applied to estimate the interaction strength, while the duration of the molecular interaction is directly related to the boiling point of the additive. In this discussion, we determine the interaction parameters between the alkanedithiol and fullerene molecules. The interactions between the additive molecules and the host solvent are not considered based on the assumption that the host solvent molecules have evaporated during the initial stage of spin-coating. By using the group theory based on Van Krevelen's approach, the solubility parameters were calculated for PDT, HDT, ODT and NDT giving values of 19.7, 19.2, 18.6 and 18.36 J^{1/2}/cm^{3/2} respectively. The δ for PCBM using the same approach yields a value of 7.8

$\text{J}^{1/2}/\text{cm}^{3/2}$. Two molecules are considered to have good interactions if the solubility parameter difference $\Delta\delta$ between the two molecules is as small as possible.

Fig. 3.3 Correlation between boiling point (T_b), variation in solubility parameter ($\Delta\delta$) and device PCE of the different additive systems.

Fig. 3.3 shows the correlation between the PCE of the devices with different additives, the variation in the solubility parameter and the boiling point of the additives. It can be observed that the optimum PCE is achieved at an optimal combination of both T_b and solubility parameter. Solvent additives with longer alkyl group and higher T_b favor the interaction with PCBM molecules, as suggested from the smaller $\Delta\delta$. Although the difference in solubility parameter between NDT and PCBM is the smallest ($\Delta\delta_{\text{NDT-PCBM}} = 10.56$), its high T_b induces NDT to stay longer in the blend film during spin-coating. This provides sufficient time for NDT to interact with PCBM and resulting in aggregation of the fullerene molecules. Conversely, PDT with the lowest T_b gives the largest difference in solubility parameter with PCBM ($\Delta\delta_{\text{PDT-PCBM}} = 11.9$) suggesting that the poor interaction between the two molecules may enhance the aggregation of PCBM. The PDT device performance (Table 3.2) is indeed lower than both HDT and ODT devices. The above observations imply that the extent of interaction between the additive and fullerenes depends on the strength and the duration of the interaction. The enhanced interaction can be obtained by choosing a solvent additive with as large $\Delta\delta$ as possible and by selecting additive with high T_b . By modulating the choice of both δ and T_b of the additive, it is possible to adjust the extent of phase separation when the additive molecules are incorporated into the blend. This investigation reveals that the optimized blend

morphology is obtained when either HDT or ODT is used which provides moderate degree of interaction with the fullerene molecules.

Absorption spectroscopy and grazing incidence X-ray diffraction Both UV-Vis absorption and X-ray diffraction measurements can give insight to the aggregation and degree of order of the polymer chains. Fig. 3.4 depicts the UV-Vis absorption spectra of the blend films with the different additives. It can be seen that both the absorption profiles of TA and PDT blends have higher intensity and are more red-shifted than the NA blend. PDT blend even possesses higher absorption intensity than that of TA blend, although the positions of the main absorption peak at *ca.* 520 nm, which corresponds to π - π^* transition, and the two vibronic “shoulders” at *ca.* 550 nm and *ca.* 620 nm, which indicate the interchain interaction are very similar. The redshift in absorption and the more prominent “shoulder” peaks are often correlated to a more extensive P3HT crystallinity in the blend. This indicates PDT addition to the blend indeed has increased the amount of ordered regions in the blend. On the other hand, there is no significant variation observed from the absorption profiles of the different alkanedithiol blends in the main figure. Nevertheless, comparison across the different additive-added blends shows that PDT has slightly stronger absorption characteristics. The fact that the film containing PDT has the most intense absorption is a direct indication that PDT induces P3HT interchain organization most strongly. The other supporting evidence of this enhanced crystallinity will be provided in the subsequent discussion on XRD.

Fig. 3.4 UV-Vis absorption spectra of P3HT:PCBM (10:8) blends processed with different solvent additives. The profiles are normalized at PCBM peak at 330 nm. The spectra of the pristine (NA) and thermally annealed (TA) blends are shown as reference.

To further quantify the extent of the P3HT crystallization in the different blends, grazing incidence X-ray diffraction study was carried out on the different films. Fig. 3.5 shows the X-ray diffractograms of the different P3HT:PCBM blends. All blend films have similar thicknesses. The relative degree of P3HT crystallinity and the domain sizes of the different blend films are obtained by fitting the diffraction patterns of the (100) peaks at $2\theta = 5.2^\circ$ followed by the extraction of the diffraction intensity and the full-width half-maximum (FWHM) respectively. The (100) reflection corresponds to the spacing between P3HT lamellae.³⁶ Fig. 3.5 shows that all the additive-processed blends possess higher degree of crystallinity than the ones without additive. Comparison of the area under the curve of the (100) peaks reveals that P3HT phase in PDT blend is the most crystalline, at least 25% more than the other blends. The relative FWHM as calculated from the peaks are 0.77, 0.88, 0.90 and 0.91 for PDT, HDT, ODT and NDT blends respectively. By using Debye-Scherrer relationship (Eq. 2.5), it can be estimated that the domain size of P3HT in PDT processed blend is the largest. The higher degree of crystallinity and the increased domain size of P3HT in PDT blend are not attributed to T_b variation since the low T_b of PDT implies less opportunity for PDT to interact with P3HT after the host solvent evaporation. Instead, the increase in domain size should be attributed to the stronger interaction between PDT and P3HT molecules. In addition, the large P3HT domain size also implies that severe P3HT and PCBM segregation are present in PDT blend. Finally, the GIXRD data indicate that the increase in both P3HT and PCBM phase segregation, which implies a reduction in the donor-acceptor interfacial area, causes a decrease in the exciton dissociation efficiency and hence lowers the device PCE.

Fig. 3.5 GIXRD patterns focusing on the (100) peaks of P3HT phase in the P3HT:PCBM (10:8) blends processed with different solvent additives.

External quantum efficiency measurement and light intensity-dependent studies

The EQE, or IPCE, measurements were performed and the spectra for all the devices are shown in Fig. 3.6. The EQE results are consistent with the optical absorption of the different P3HT:PCBM blend films. The spectra of both annealed (TA) and additive-processed blends are more red-shifted than the pristine blend (NA) with the maximum EQE around 55 – 65% in the wavelength range of 500 – 550 nm. Even though EQE has often been correlated with the trend in J_{sc} and hence PCE,^{21,23} the J_{sc} of the additive-processed devices could not be correlated with their EQEs. Fig. 3.2(b) shows that the J_{sc} of NDT is lower than HDT and ODT, while PDT results in the lowest J_{sc} . In Fig. 3.6, NDT device has comparable spectra to those of HDT and ODT, while PDT addition results in the highest EQE spectra in spite of its lowest J_{sc} . The variation from the two measurements could be due to the difference in light intensity used for illumination. Low-intensity monochromatic light illumination, significantly lower than the standard 1 sun PCE measurement, was used for EQE measurement without any background white light bias. Photovoltaic behaviors of solar cell devices may vary under different light intensities due to the change in recombination losses, charge-density dependent mobilities and space-charge effect.³⁷⁻⁴⁰ With respect to the quantum efficiency (QE) characteristics, Szymtowski has theoretically derived a set of relationships which show QE decreases as light intensity increases and bimolecular recombination increases with increased light intensity.⁴⁰ Consequently, the deviation in the PCE-EQE relationships for PDT and NDT devices could be attributed to the reduced bimolecular recombination at low light intensity.

Fig. 3.6 EQE spectra of the P3HT:PCBM (10:8) devices processed with different solvent additives.

To investigate the loss of photocurrent in the alkanedithiol-added PV devices, the light intensity-dependent study was performed. Fig. 3.7 shows a double logarithmic diagram of the intensity dependence of J_{SC} of the devices, as well as the recombination parameters α derived from the power law (Eq. 2.15).⁴¹ The α values can be correlated to the trend in PCE and this shows that the device performance is influenced by recombination process, whether it is geminate ($\alpha = 1$) or bimolecular recombination ($\alpha = 0.5$). The current densities of both HDT and ODT devices possess a close-to-linear dependence on the light intensity, implying the free charges are limited by geminate recombination. Both NDT and PDT devices have lower α indicating an increased contribution of bimolecular recombination. This loss may be correlated with the change in blend morphology where more severe phase separation will induce an increase in bimolecular recombination.³⁹ So far, the deviation between the EQE and PCE behaviors is explained in terms of the contribution of the bimolecular recombination. In the following sections, the effect of the different additives on morphology is presented.

Fig. 3.7 Double logarithmic plots of short-circuit current *vs* light intensity ($J_{SC} - P$) of P3HT:PCBM (10:8) devices processed with different solvent additives. The slopes corresponding to the recombination parameters (α) are also shown.

Blend morphology From previous discussions, we suggested that the low device performance was caused by the unoptimized blend morphology with aggregation of P3HT and/or PCBM molecules into domains with non-ideal size for exciton dissociation and transport. To show conclusively that unoptimized morphology is the reason for the variation in the device behaviors, both AFM and STXM techniques were used to investigate the samples. AFM operated in tapping mode was used to verify the extent of phase separation in the

blends. Fig. 3.8 shows the $4\ \mu\text{m} \times 4\ \mu\text{m}$ topographical and phase images of the different P3HT:PCBM blends. Pristine (NA) blend appears to be smooth and featureless with root-mean-square roughness (σ_{RMS}) of 0.9 nm. Thermal treatment of the same blend resulted in slight increase in the surface roughness ($\sigma_{\text{RMS}} = 1.4\ \text{nm}$) and interconnected fibrillar features are also observed in this blend. The addition of high boiling point solvents such as alkanedithiols tends to enhance the aggregation of the polymer blends resulting in rougher surfaces.^{19,20} From the AFM study, it is difficult to resolve any significant difference among the additive-added blend films although their features are distinctly different from the non-additive counterparts. Regardless of the additive molecules used, these blends feature irregular domains ranging from $0.1 - 1\ \mu\text{m}$ in size and the surface roughness of the blend films is found to vary from 10 – 14 nm. In short, although AFM has often been used to resolve the difference between pristine and additive-treated samples, it may not be the most effective method to distinguish the nanomorphology and the phase segregation of the blend films treated with alkanedithiols. On top of this, it was reported that P3HT-rich phase tended to segregate vertically on top of PCBM-rich phase in additive-treated blends.¹⁹ Hence AFM, which is a surface technique, does not have the capability to provide sufficient information about the phase segregation in the blend films with additives.

Fig. 3.8 Tapping mode height AFM images of P3HT:PCBM (10:8) blends with different treatments: (a) NA, (b) TA, (c) PDT, (d) HDT, (e) ODT and (f) NDT. The scan size is $4\ \mu\text{m} \times 4\ \mu\text{m}$.

Scanning transmission X-ray microscopy (STXM), a powerful synchrotron-based technique capable of resolving morphology and blend composition with nanoscale resolution, has been recently applied to investigate the effect of nanomorphology on photovoltaic device characteristics.⁴²⁻⁴⁶ STXM can provide information on the bulk morphology and is therefore a good complementary technique to AFM in investigating the phase separation in polymer-fullerene blend. In this section it will be shown that the decrease in device performance may be related to the increased PCBM phase aggregation in the blend film upon NDT addition. The increase in the degree of phase separation of fullerene component is believed to be unfavorable for a balanced hole-electron transport that results in the low FF in NDT system. In short, the choice of additive will affect the device performance, which can be correlated with the change in blend morphology.

Fig. 3.9 Scanning transmission X-ray microscopy (STXM) images for P3HT:PCBM blends processed with: (a) HDT and (b) NDT. The left images are taken at 200 eV and the right images are taken at 285 eV, corresponding to the sulfur-rich and carbon-rich regions, respectively. The scan size is 15 μm x 15 μm .

Fig. 3.9 shows the 15 μm x 15 μm STXM images of HDT and NDT blends obtained at both photon energy (E) of *ca.* 200 eV and *ca.* 285 eV, which are sensitive to sulfur and carbon X-ray absorption edges, respectively. The choice of the beam energies for STXM measurement is based on the near-edge X-ray absorption fine structure (NEXAFS) spectra of P3HT and PCBM demonstrated by Watts *et al.*⁴⁶ For the image taken at E *ca.* 200 eV, the darker region corresponds to the sulfur-rich region; while for the image taken at E *ca.* 285 eV, the darker region corresponds to a carbon-rich region. Due to the varying contrast, the P3HT (sulfur-rich) and PCBM (carbon-rich) regions in the sample could be differentiated. It is clear that the

contrast difference between the domains/matrix areas of the images taken at E *ca.* 285 eV is more obvious than the contrast difference of those taken at E *ca.* 200 eV. This implies that the phase segregation of PCBM is more distinct and the domains are PCBM-rich. On the other hand, the P3HT distribution in the domains and matrix regions are more uniform as can be seen from the low contrast difference of these two regions. It should also be noted that no further thickness and chemical mappings were done for this study. As revealed from the STXM measurement, P3HT:PCBM blend processed with NDT has larger “PCBM-rich” domains (around 2 – 3 μm) distributed throughout the bulk whereas the corresponding domains are smaller (around 0.5 – 1 μm in diameter) in the HDT-processed blend. The size difference of these micro-domains plays an important role in the device performance of the blend. Blend with HDT has smaller “PCBM-rich” domains and does not suffer any loss in photocurrent suggesting exciton dissociation and charge transport are equally optimized. This observation agrees with previous studies in that the smaller domains reduce the recombination probability and favor efficient exciton dissociation.^{47,48} In NDT-processed blend, the larger PCBM phase separation would promote an efficient electron transport but compromises the amount of free charges generated due to the smaller D/A interfacial area. The lower PCE with low J_{sc} in NDT system suggests that exciton dissociation as the limiting factor rather than charge transport. The poorer performance in PDT system may be contributed by similar factor, *i.e.* significantly aggregated PCBM phase in addition to the more severe P3HT aggregation as revealed from the GIXRD study.

The selection of the solvent additive is an important factor to obtain the ideal nanomorphology in a thermal-free organic solar cell device. By choosing additive with proper solubility parameter and boiling point, it may be more feasible to generate optimal phase separation, crucial in improving device performance. The application of solvent additives can also be extended for nanofiber blend system, which is presented in the following discussions.

3.3.2 Additive approach to optimize nanofiber blend

An alkylhalide compound, 1,6-dibromohexane (DBH), was used as the additive for the blends of P3HT nanofiber and PCBM. The halide has higher boiling point ($T_b = 243\text{ }^\circ\text{C}$) and therefore has the potential to induce molecular interactions with the active components in the semi-dry nanofiber blend cast from *p*-xylene ($T_b = 138\text{ }^\circ\text{C}$). The incorporation of a small amount of DBH

(2%V/V) into the non-fiber blends resulted in device improvement comparable to those of the alkanedithiols.

Absorption spectroscopy and X-ray diffraction Fig. 3.10(a) depicts the normalized UV-Vis absorption characteristics of the nanofiber blend films with and without additive processing. In Fig. 3.10(b), the additive-processed blend appears to be darker than the as-cast fiber blend. Both vibronic “shoulders” (Fig. 3.10(a)) at *ca.* 550 nm and *ca.* 600 nm can be clearly seen in the nanofiber blend. As discussed earlier in Chapter 2, these are the distinctive characteristics of well-organized P3HT. The additive-processed nanofiber blend film also demonstrates the two “shoulder” peaks without any significant red-shift. In addition, the blend possesses higher normalized intensity as compared to as-cast nanofiber blend. Assuming the same thickness for the two blends, the integration of the absorption spectra reveals that the nanofiber blend with additive processing has absorption enhancement of *ca.* 15% as compared to the one without. The increase in absorption intensity indicates there are more photons making transitions between the ground and the excited states. This could in turn be due to an increase in π - π interactions in the additive-treated blend. In short, addition of the additive molecules during the processing of the nanofiber blend resulted in an increase in blend crystallinity.

Fig. 3.10 (a) UV-Vis absorption spectra of the nanofiber P3HT:PCBM (10:6) blends with and without additive processing. (b) As-cast nanofiber blends: the left image is without additive and the right image is with additive. Blends were prepared on quartz substrates.

Fig. 3.11 shows the X-ray diffractograms of the nanofiber blends and their analyses are presented in Table 3.3. The scattering peaks at $2\theta = 5.6^\circ$ are related to P3HT (100) reflections. The peak integration of the (100) reflections reveals an improvement of *ca.* 69% in P3HT crystallinity for the additive-treated nanofiber blend as compared to the as-cast blend. The increase in the crystallinity agrees with the optical absorption results. The narrowing of the (100) peak is also observed upon additive treatment, resulting in *ca.* 17% decrease in the FWHM, which is translated into *ca.* 22% increase in the crystallite size. The processing with solvent additive also results in decrease in the $d_{(100)}$ -spacing. This means that the P3HT molecules are closer to each other in the additive-treated blend, which may facilitate charge transport. Considering the fact that P3HT nanofibers are crystalline in nature, the additive molecules should have affected the amorphous non-fiber P3HT in the blend. In the previous chapter, it has been pointed out that self-assembly of P3HT in solution does not yield a complete conversion to nanofiber. This well-dissolved P3HT, which remains in the suspension after the growth, further crystallizes with the help of solvent additive during the spin-coating process. The crystallization of the initially amorphous P3HT phase may also be contributing to the increment of the average size of the ordered crystallites. These crystallized non-fiber P3HT regions, which fill the space between the nanofibers, are expected to enhance the fiber-to-fiber charge transport. In short, the processing with high T_b solvent additive resulted in improvement in the crystallinity of nanofiber blend.

Fig. 3.11 GIXRD patterns of the nanofiber P3HT:PCBM (10:6) blends with and without additive processing.

Table 3.3 GIXRD parameters of the nanofiber P3HT:PCBM (10:6) blends with and without additive processing.

Sample	Peak Height	FWHM	Crystallinity	Crystallite size	$d_{(100)}$
	(count/s)	(°)	(a.u.)	(nm)	(nm)
NF + 0% additive	330.4	0.88	290.8	9.0	1.590
NF + 2% additive	672.4	0.73	490.9	11.0	1.574

Fig. 3.12 (a) Photoluminescence spectra of nanofiber P3HT:PCBM (10:6) blends with and without additive processing, excited with 520 nm light source. (b) Corresponding PL spectra normalized at their respective λ_{max} .

Photoluminescence spectroscopy The steady-state PL spectra of the nanofiber blend in Fig. 3.12 exhibit intense peaks at $\lambda_{\text{max}} = ca.$ 625 nm and “shoulder” at 680 nm, *i.e.* typical characteristics of P3HT. As seen in Fig. 3.12(a) the PL of the nanofiber blend exhibits an even stronger quenching with additive processing. This finding suggests that the additive-

processed blend may have induced a more homogeneously mixed P3HT and PCBM phases. The normalization of the PL spectra of both nanofiber blends at their respective $\lambda_{\max}$, as shown in Fig. 3.12(b), also provides another evidence for the increase in the degree of order in the additive-processed blend. Firstly, there is a slight red-shift in the $\lambda_{\max}$ of *ca.* 5 nm as well as the regions at the vicinity of the “shoulder”. Secondly, the “shoulder” also appears to be more prominent in the blend processed with solvent additive. This “shoulder” observed in the PL spectra derives from the aggregated emissions, resulting from the increase in the planarity of the polymer backbones with improved π - π interactions.⁴⁹ The intensity ratio between the $\lambda_{\max}$ (*ca.* 625nm) and the “shoulder” (*ca.* 680 nm) is also higher for the additive-processed blend (0.82 *vs* 0.72). The PL results are also qualitatively consistent with the change observed in the optical absorption features, in which the vibronic “shoulders” appear to be more pronounced with additive treatment. The existence of the better-intermixed blend along with the improved crystallinity may lead to increase in device performance. The former helps to promote a more efficient charge transfer between the donor and acceptor phases, while the latter assists in a better post-separation charge transport. Miller *et al.* also discovered that the solvent-vapor annealing treatment on P3HT:PCBM led to a distinct improvement in the ordering of P3HT, followed by further quenching in the PL intensity.¹⁵ Both factors were then attributed to the overall improvement in the device performance.

Fig. 3.13 Tapping mode height AFM images of nanofiber P3HT:PCBM (10:6) blends: (a) without and (b) with additive processing. The scan size is 4 μm x 4 μm .

Blend morphology Fig 3.13 shows the 4 μm x 4 μm topographical images of the nanofiber blends. The change due to the additive treatment can be easily noted from the roughening of the blend surface. The incorporation of DBH molecules preserves the fibrillar features. The nanofibers in the additive-processed blend also appear to be more

distinguishable. The surface roughness analysis reveals $\sigma_{\text{RMS}} = 2.6$ nm when there is no additive and $\sigma_{\text{RMS}} = 9.4$ nm when there is DBH addition for $4 \mu\text{m} \times 4 \mu\text{m}$ scan images. It is noted that the root-mean-square values calculated for the nanofiber blend ($\sigma_{\text{RMS}} < 10$ nm) are generally lower than those of the non-fiber blend ($\sigma_{\text{RMS}} > 10$ nm) presented in the previous discussion. The roughening of the blend also suggests the presence of the more organized P3HT moieties.¹⁹ This results, again, correlates well with the previous optical spectroscopy measurements. The difference in the blend morphologies with additive treatment also implies that the additive molecules may have affected the molecular distribution of donors and acceptors, favoring a more intimate contact between both phases.

Fig. 3.14 Current density – voltage (*J*-*V*) characteristics of nanofiber P3HT:PCBM (10:6) blends with and without additive processing. The measurement was done under 1 sun ($100 \text{ mW}/\text{cm}^2$) illumination.

Device performance The solar cell device structure consists of ITO/PEDOT:PSS/P3HT:PCBM(10:6)/TiO_x/Al. The buffer layer titanium suboxide (TiO_x) is applied to enhance hole blocking at the cathode. The current density-voltage (*J*-*V*) characteristics of the nanofiber-based devices are shown in Fig. 3.14. Table 3.4 summarizes the device parameters extracted from the *J*-*V* characteristics. The as-cast fiber device yields J_{sc} of $6.0 \text{ mA}/\text{cm}^2$, V_{oc} of 0.68 V , FF of 0.60 and PCE of 2.45% . As compared to the nanofiber device characteristics in section 2.3.2 (Table 2.2), the J_{sc} here is lower due to thinner film used (*ca.* 70 nm *vs ca.* 90 nm). The reasonably high V_{oc} could be attributed by the presence of the blocking layer TiO_x.²⁴ The high J_{sc} and FF are also the traits of nanofiber devices, which stems from the high degree of crystallinity even when no post-fabrication treatment is applied. The processing with alkylbromide additive significantly improves the short-circuit current by 37% ,

yielding J_{sc} of 8.2 mA/cm². The improvement in J_{sc} is expected as the blend film has stronger absorption (better photon harvesting) as well as higher crystallinity (better charge transport). Similar to what observed in the non-fiber system, the high T_b additive also induced a higher FF. This confirms with the drop in the internal series resistance (R_s) of *ca.* 35%. Another similar feature common to the additive-treated P3HT:PCBM devices is the decrease in the photovoltage. Comparison across the additive-treated devices reveals a higher V_{oc} in the nanofiber system (0.61 V) than those of the non-fiber one (0.53 V), owing to the TiO_x layer. Overall, the increase in both J_{sc} and FF with slight compromise in the V_{oc} yields a PCE of 3.12%, improvement of *ca.* 27%. The PCE obtained for the nanofiber devices (with TiO_x) becomes comparable to the non-fiber ones with additive treatment. As comparison, the pre-deposition annealed non-fiber P3HT:PCBM device yields PCE of 3.46%, J_{sc} of 8.42 mA/cm², V_{oc} of 0.63 V and FF of 0.65 with TiO_x insertion.

Table 3.4 Summary of photovoltaic device properties of nanofiber P3HT:PCBM (10:6) devices with and without additive processing.

Sample	PCE	J_{sc}	V_{oc}	FF	R_s
	%	(mA/cm ²)	(V)		(Ω cm ²)
NF + 0% additive	2.45	6.0	0.68	0.60	19.5
NF + 2% additive	3.12	8.2	0.61	0.62	12.6

Fig. 3.15 EQE spectra of nanofiber P3HT:PCBM (10:6) devices with and without additive processing.

The external quantum efficiency (EQE) spectra of the devices are presented in Fig. 3.15. The maximum EQE increases from 43% to 56% following the treatment of the nanofiber devices. The trend observed for the EQE spectra can be correlated with that of the J_{sc} . The integration of the spectra over the solar spectrum yields J_{sc} of 5.8 mA/cm² and 7.8 mA/cm²

for the as-cast and additive-treated nanofiber devices, respectively. These values are not more than 5% different when compared to those obtained from the PCE measurement. The EQE spectra also correlate well with the optical absorption results. The red-shift characteristic, which indicates the presence of well-ordered structures, is also present in the EQE spectra of the additive-treated device.

The additive-induced “reorganization” of the non-fiber P3HT phase during the fast-drying process to generate more ordered structures should be facilitated by phase separation of PCBM molecules from the well-mixed amorphous portion of the blend. This results in an increase in the blend crystallinity, evidenced from the XRD, absorption and photoluminescence measurements. Based on the earlier study on the non-fiber system, it was discovered that the acceptor molecules could also aggregate when treated with solvent additive. Nevertheless, in the nanofiber system, there is no excessive aggregation of PCBM phase. The higher degree of PL quenching in the additive-treated blend suggests that even with crystallization of both P3HT and PCBM, the molecules can reorganize themselves in such a way that a balanced amount of D/A interfaces can be obtained. As a result, both exciton dissociation and charge transport can be optimized, leading to devices with higher PCEs.

3.4 Conclusions

In this chapter, the systematic study of the effect of alkanedithiols with varying alkyl length on the photovoltaic behavior of the P3HT:PCBM BHJ has been presented. It was found that both boiling point (T_b) and solubility parameter (δ) of the additives should be considered simultaneously. Solvent additives with different T_b and δ can be used to modify the degree of intermolecular interaction in order to achieve phase segregation with the ideal domain size for optimal exciton dissociation and minimal bimolecular recombination. More PCBM aggregation was observed either when PDT was used, due to the poor intermolecular interaction (*i.e.* high $\Delta\delta$), or when NDT was used, because of its sufficiently long interaction duration with the active materials due to its high T_b . The blend morphologies with extensive phase separation such as in the PDT and NDT-added blends are unfavorable for exciton dissociation and charge transport. Nonetheless, optimization of blend morphology as in the HDT and ODT systems can lead to the improvement of device PCE to 3.1%.

The same technique has also been applied for the nanofiber system. In the previous chapter, it has been pointed out from the transient absorption measurement that some of the charges generated recombine before being extracted to the external electrodes. Although the transport along the fiber is efficient, there could be a lack in the fiber-to-fiber connectivity in the nanofiber system. Furthermore, the as-cast nanofiber device also lacks in the percolation path for the acceptor phase. The processing of the nanofiber blend with solvent additive results in an increase in polymer crystallinity. The additive molecules also facilitate the crystallization of fullerene phase. However, as has been shown in this chapter, the molecular reorganization of both the donor and acceptor does not compromise the amount of D/A interfaces. As a result, improvement in device efficiency to 3.1% can be obtained for the additive-treated nanofiber devices.

3.5 Experimental section

Materials The active BHJ materials, regioregular P3HT ($M_w = 50\,000$ g/mol, head-to-tail regioregularity > 90%) and PCBM (99.5% purity) were obtained from Rieke Metals, Inc. and Nano-C[®] respectively. The host solvents, 1,2-dichlorobenzene (*o*-DCB) and 1,4-dimethylbenzene (*p*-xylene), as well as the solvent additives were all purchased from Sigma-Aldrich. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (CLEVIOST[™] P VP Al 4083, HC Starck) was used as hole transport layer. All chemicals were used as received without any further purification.

Device fabrication P3HT (10 mg/mL) was mixed with PCBM in *o*-DCB with weight ratio of 10:8. The blend solution was stirred overnight at 50 °C in N₂ glovebox. P3HT (7 mg/mL) fiber suspension was prepared in *p*-xylene, as earlier described in Chapter 2, and was added with PCBM to yield a weight ratio of 10:6. 10 μ L of the solvent additive was added into 500 μ L of the P3HT:PCBM blend solution, which was then stirred for another hour before spin-coating. The additives chosen for this study have higher T_b than that of *o*-DCB ($T_b = 180$ °C) and are therefore potentially effective in affecting the organization of the active materials upon evaporation of the host solvent during the fast-drying process. The organic photovoltaics were fabricated on indium-tin oxide (ITO) coated glass substrates (7 Ω /sq, Kintec Company). The substrates were cleaned sequentially by using deionized water, acetone and isopropyl alcohol in ultrasonic bath. A thin layer of PEDOT:PSS was spin-coated onto the plasma-treated substrates at 3000 rpm for 60 s to give a thickness of 30 nm. The substrates were then transferred into a N₂ glove box and were baked on a hotplate at 140 °C for 10 min. Subsequently, the P3HT:PCBM blend solutions were filtered through 0.45 μ m PTFE syringe filter and spin-coated at 700 rpm for 2 min resulting in BHJ film thickness of 100 ± 5 nm as measured using a profilometer (KLA-Tencor Alpha Step

500). The prolonged period of spin-coating was to ensure that there is sufficient time for most of *o*-DCB to evaporate leaving the higher T_b additive to interact with the polymer and fullerene phases. Blend films with additives underwent significant color change within 30 ± 2 s of spin-coating process. For nanofiber blends, TiO_x solution (in ethanol)⁵⁰ was spin-coated to generate additional buffer layer, followed by hydrolysis in the ambient for 1 h. Eventually, the photovoltaic devices were loaded into a thermal evaporator and were left overnight (> 6 h) in vacuum ($< 10^{-6}$ Torr) before Al cathode (100 nm) with an active area of 0.1 cm^2 was deposited. No thermal treatment was done for the additive-processed blends. For comparison, one set of the additive-free device was also subjected to post-evaporation thermal annealing at 150°C for 20 min.

Device measurement The current density-voltage (*J*-*V*) characteristics of the organic solar cell devices were measured in ambient under AM 1.5G illumination ($100 \text{ mW}/\text{cm}^2$) using a Keithley SMU 2400 sourcemeter. The light intensity was calibrated by using an NREL-calibrated silicon photodiode. No spectral mismatch correction was applied to the calculation of power conversion efficiency (PCE). Filters were used for light intensity-dependence study. External quantum efficiency (EQE) measurement was performed in N_2 glove box with Merlin radiometer (Newport) and the wavelength adjustment was done using monochromator (Oriel Cornerstone 130 1/8 m). The light from the xenon lamp, after being chopped at 60 Hz and wavelength adjusted, was passed into the glove box using an optical fiber (Ocean Optics). A calibrated silicon photodiode (Hamamatsu) was used as reference to count the signal generated by the solar cell devices.

Blend characterization The UV-Visible absorption spectra were characterized using Shimadzu UV-2510PC spectrometer on BHJ-coated quartz substrates. The photoluminescence (PL) measurement was conducted using Perkin-Elmer LS 50B luminescence spectrometer. The λ_{ex} used was 520 nm corresponding to the absorption maxima (λ_{max}) of the blend. The diffraction patterns of BHJ film on Si/ SiO_2 substrates were collected using grazing incidence X-ray diffraction (GIXRD) with CuK_α radiation of a ω -diffractometer (incident X-ray angle is 2.5°). Atomic force microscopy (AFM) imaging was done on the films of actual photovoltaic devices in tapping mode by using Digital Instruments (Nanoscope IIIa). The chemical composition distribution of the BHJ was confirmed using scanning transmission X-ray microscopy (STXM). For the STXM study, the blend solution was spin-coated onto silicon nitride membranes and the samples were air-dried before analysis. STXM measurements were performed at the elliptical polarizing undulator (EPU) beamline 11.0.2 at the Advanced Light Source in Berkeley, California (USA). Photon energy of 200 eV and 285 eV was used for the investigations. STXM images were taken at normal incidence with a lateral resolution of approximately 35 nm. All measurements were performed at room temperature in He atmosphere.

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The Role of Poly(3-hexylthiophene) Nanofibers in an All-Polymer Blend with Polyfluorene Copolymer for Solar Cell Applications

Summary. Unoptimized morphology in an all-polymer solar cell is often caused by the strong interaction between polymeric chains. Due to this interaction, the organization of the first component in the blend may be disrupted by the other, eventually leading to poor solar cell device performance. For the first time, the use of highly crystalline poly(3-hexylthiophene) (P3HT) nanofibers as a way to control the morphology in an all-polymer blend was demonstrated. An improvement in the short-circuit current (J_{sc}) by a factor of 10 was observed when P3HT nanofibers were incorporated into the blends with polyfluorene copolymers as compared to the as-cast blends. These nanofiber blends outperformed the devices subjected to thermal annealing. This enhanced current density in nanofiber system comes from better optical absorption and improved charge transport; both improvement being the manifestation of high degree of crystallinity as evident from grazing incidence X-ray diffraction (GIXRD) measurement. In brief, this chapter demonstrates the potential of using polymer nanofibers to improve the efficiency of all-polymer solar cell devices.

4.1 Background

The preceding chapters exhibit the potential of nanofiber as a thermal-free approach to obtain efficient organic solar cell devices based on the polymer-small molecule system. The blend morphology can be further optimized with the assistance of morphology modifying agent, such as high boiling point solvent additive. Nevertheless, the nanofiber-based devices are still unable to perform better than the devices that undergo the conventional thermal annealing. The value of nanofiber-based devices can be seen in systems in which thermal annealing is not able to optimally improve the phase separation and the ordering of the film to sufficient extent after deposition. In this chapter, the application of polymer nanofiber in an all-polymer solar cell is presented. Unlike polymer-small molecule system, all-polymer blend may suffer a more serious morphological issue, either extreme phase separation or excessive intermixing. As such, the inclusion of pre-formed polymer fibers becomes a better alternative to control the blend morphology.

4.1 Introduction

Polymer solar cells have emerged as an increasingly attractive class of photovoltaic technology in recent years. The current state-of-the-art architectures are based the bulk heterojunctions (BHJ) made up of donor (D) and acceptor (A) blends.¹ The current power conversion efficiency (PCE) records for polymer-small molecule and polymer-polymer BHJ are 8.4% and 1.8% respectively.^{2,3}

Despite the lower PCE, all-polymer solar cells could potentially surpass the performance of polymer-small molecule due to the versatility of chemical synthesis which facilitates the precise control over optical and electrical characteristics of novel conductive polymers.⁴ Absorption properties of the blend can be carefully tailored by having donor and acceptor polymers with complementary absorption profiles. The absorption profiles of these polymers can be tuned through bandgap engineering to maximize photon capture throughout the solar spectrum. The adjustment of highest-occupied molecular orbital (HOMO) and lowest-unoccupied molecular orbital (LUMO) of the polymers, both essential for bandgap alteration, also provides a straightforward approach in maximizing device photovoltage. Furthermore, all-polymer blends offer superior flexibility in controlling solution viscosity, an important factor to consider in large scale solution processing such as printing.⁵ However, the

performance of all-polymer solar cells is often restricted by low fill factor (FF), which can hardly go beyond 40%. This low FF is the result of poor charge transport in the bulk and inefficient extraction of free charges to the electrodes in all-polymer solar cells.^{6,7}

Due to the similarity in the chemical structures between the components of an all-polymer solar cell, generally the organization of one or both polymers is disrupted when the polymers are blended together. As discussed in the earlier chapters, one method to achieve optimized morphology without subjecting blend films to any annealing treatment is to integrate pre-assembled one-dimensional (1-D) polymeric nanostructures into the blend.⁸⁻¹¹ The main advantage of these 1-D nanostructures is the enhanced charge mobility induced by the strong π - π interaction resulting in efficient charge transport. Among the reported conjugated polymers, the poly(3-alkylthiophene) (P3AT) series has been extensively investigated due to their ability to self-assemble into well-ordered structures such as lamellae or whiskers.¹²⁻¹⁴ Poly(3-hexylthiophene) (P3HT), for example, can form whisker-like structures in marginal solvents such as *p*-xylene and anisole.^{8,15,16} In these poor solvents, self-assembly of P3HT occurs readily in solution as the saturated solution undergoes supercooling with decreasing temperature. Blends of these P3HT nanofibers with PCBM small molecules resulted in devices with comparable PCE to those subjected to annealing treatments.^{8,11} To optimize device performance, it is of paramount importance to fine-tune the ratio between amorphous P3HT and crystalline P3HT nanofibers. The presence of amorphous P3HT regions in the BHJ is believed to promote the interconnectivity between the nanofibers, much likened to the role of adhesive, thus increasing charge pathways between the nanofibers. This results in enhanced charge mobility and reduction in charge recombination.

In this chapter, the first application of the pre-assembled P3HT nanofibers with poly(9,9-dioctylfluorene-co-benzothiadiazole) (F8BT) in an all-polymer solar cell is discussed. This atypical system is chosen to investigate the role of polymeric nanofibers in morphological control of the blends. The earlier reports on as-cast P3HT:F8BT BHJ showed inferior device PCE due poor charge transport, which is attributed to poor morphology.^{17,18} To enhance phase segregation and reorganization of P3HT, thermal annealing has been the only adopted technique thus far.^{18,19} The best PCE obtained for annealed P3HT:F8BT is 0.13% with insertion of LiF layer.¹⁸ The first demonstration that morphological control of all-polymer blend can be achieved without annealing by pre-assembly of P3HT nanofibers is presented in this chapter. The unoptimized nanofiber-based devices show better PCE than those of thermally annealed

ones, because of the enhanced absorption and charge transport originating from the high crystallinity of these nanofibers.

4.3 Results and discussion

Absorption spectra and photoluminescence Fig. 4.1 shows the chemical structures, energy levels (HOMO-LUMO) and optical absorption along with photoluminescence (PL) spectra of both regioregular P3HT and F8BT in thin films. P3HT with smaller bandgap ($E_g = 2$ eV) has a broader absorption feature in comparison to F8BT ($E_g = 2.4$ eV). In addition to the absorption peaks at *ca.* 510 nm and *ca.* 560 nm, P3HT exhibits distinct vibronic features at higher wavelengths, *i.e.* “shoulder” at *ca.* 610 nm. These features, which are originally absent in the absorption profiles of P3HT in solution, indicate the presence of strong interchain π - π interactions because of the high degree of crystallinity in the blend.²⁰ Morphologically, these ordered structures can manifest themselves as lamellar structures when P3HT is cast from solution. Being a polyfluorene copolymer, two absorption peaks of F8BT film at lower and higher wavelengths can be observed and they emanate from the BT units and π -conjugation of F8BT main chain, respectively.²¹ In terms of photoluminescence characteristics, F8BT is found to be much more luminescent, with PL intensity around 20-fold more than that of P3HT. The strong interchain coupling in P3HT films is also apparent from observation of the much red-shifted PL spectra and vibronic features at *ca.* 700 nm. From the observed optical characteristics of the two components, it is evident that the emission of F8BT in the 500 – 700 nm range falls within the absorption of P3HT. This perfect emission-absorption overlap has high likelihood of inducing resonance energy transfer from F8BT to P3HT.²²

Fig. 4.1 (a) Chemical structures and energy level diagrams of P3HT and F8BT and (b) Normalized optical absorption (solid line) and photoluminescence spectra (dashed line) of P3HT (purple) and F8BT (orange) films ($\lambda_{\text{ex P3HT}} = 520$ nm and $\lambda_{\text{ex F8BT}} = 460$ nm).

Fig. 4.2(a) and (b) show the absorption and photoluminescence spectra of P3HT:F8BT blend films – as-cast, thermally annealed, and pre-assembled P3HT nanofiber:F8BT blend. The film thickness of these blends was carefully controlled at 90 ± 5 nm for comparative study. The absorption profiles of the blends in Fig. 4.2(a) are normalized with respect to F8BT peak at lower wavelength, *i.e.* 330 nm. The bulky dioctyl groups in the polyfluorene units (F8) prevent F8BT backbones from packing closely.²³ Therefore, the variation in processing conditions should not alter F8BT absorption profile. The absorption spectra of the blend films shown in Fig. 4.2(a) consists of the superposition of individual P3HT and F8BT absorption characteristics with relatively equal contribution, with peak at *ca.* 480 nm. Absorption shoulders of P3HT at 560 and 610 nm in the blend is more blue-shifted as compared to pristine P3HT, overlapping with the second peak of F8BT at higher wavelength. Although this blue-shift phenomenon has been observed in the well studied P3HT:PCBM system, the degree of shift in P3HT:F8BT is more extensive. For the same weight ratio, blue-shift of P3HT absorption peak in P3HT:PCBM is *ca.* 10 nm, *i.e.* 3 times lower as compared to our observation in P3HT:F8BT system.²⁴ This indicates a more disrupted P3HT organization when F8BT is introduced into the blend. This higher degree of disruption can be attributed to the relatively strong interaction between the two polymers, thus phase separation of the components becomes unfavorable.

Thermal annealing is employed to trigger reorganization of P3HT in the blend to a more crystalline nanostructure. The annealing condition, *i.e.* 150 °C for 20 min, is chosen because this temperature is above the glass transition temperature of both polymers (T_g of P3HT *ca.* 12 – 110 °C depending on M_w of the polymer and material purity; and T_g of F8BT *ca.* 140 °C). This heat treatment facilitates the reorganization of the polymers to a more thermodynamically stable state. The absorption profile of the heat-treated blend exhibits a distinct “shoulder” peak at *ca.* 560 nm, while a slight increase in intensity is observed at the 480 nm peak. Since F8BT has no significant absorption above 550 nm, this “shoulder” is attributed to reorganization of P3HT chains into crystallites. Thermal annealing facilitates the diffusion of polymers and their phase separation, enhancing the interchain π - π interaction of P3HT chains, and eventually improving the absorption of the blend around 480-630 nm.²⁵

Similar improvement in absorption is also observed when pre-assembled P3HT nanofibers are integrated into the blend, even when no post-fabrication annealing is carried out. A stronger absorption is observed at 480 nm, while vibronic features at *ca.* 560 nm and *ca.*

610 nm become more prominent as shown in Fig. 4.2(a). These “shoulders” are the fingerprints of crystalline P3HT, indicating the presence of significantly undisrupted well-ordered P3HT regions in the blend. The inset in Fig. 4.2(a) shows the normalized absorption profiles of the blends, clearly showing the superior absorption intensity of P3HT nanofiber blend. In organic solar cells, the improved absorption efficiency is often associated with the improved photon harvesting which in turn increases the probability of charge generation and as a result, a higher photocurrent density.²⁶

Fig. 4.2 (a) UV-Vis absorption spectra of P3HT:F8BT (1:1) blends normalized at 330-nm peak. (Inset shows same spectra normalized at 460 nm absorption peak) (b) Normalized PL spectra of P3HT:F8BT (1:1) blends excited with 460 nm light source together with PL of pure P3HT and F8BT.

Steady-state photoluminescence (PL) study is carried out to investigate the efficiency of exciton dissociation after they are generated through photoabsorption. Fig. 4.2(b) shows the photoluminescence behavior of the blends and their parent materials upon excitation with 480

nm light source. The PL profiles are normalized with respect to the maximum absorption of the thin films to eliminate any variation induced by difference in photon absorption. The blends exhibit efficient PL quenching of F8BT. This is expected from the observation of the good overlap between F8BT emission and P3HT absorption which has been shown earlier in Fig. 4.1(b). This type of Förster energy transfer is not beneficial for solar cell application due to the lack of free charge generation although the excitons could be harvested over large distances.²⁷ The spectra of the blends show the remnant from P3HT emission in the red region as well as a new emission peak at *ca.* 620 nm. The vibronic features, *i.e.* “shoulders” at *ca.* 660 nm, are observed in the profiles. These new peaks suggest the presence of charge transfer (CT) states, formed due to interfacial electronic interaction between the donor and acceptor materials.^{28,29} The CT state density correlates strongly with the donor/acceptor (D/A) interfacial areas and they have been reported to influence charge separation.³⁰ The emission of CT states is likely to originate from geminate recombination, which depends on the polymer intrachain conformation and blend morphology.

The PL intensity quenching of these CT states is proposed to be the result of the following processes that prevent charge recombination at D/A interface: (1) efficient dissociation of polarons with different polarities at the interface, (2) efficient charge transfer away from the interface and (3) reduction of donor-acceptor interfacial area. In both thermally annealed and nanofiber blend systems, PL intensity is quenched more as compared to the as-cast blend, with a more significant quenching observed in nanofiber system. This indicates a decrease in geminate recombination through these states or increase in charge generation when blend is either annealed or in the presence of nanofibers. The decrease in PL intensity could also be a result of phase segregation induced by both treatments, which in turn reduces the D/A interfacial area. In addition, this phase segregation creates interconnected pathways that facilitate a more efficient charge transport which contribute to the reduced recombination at the interface. It should also be noted that the reduction of D/A interfacial area may induce the reduction of CT density, therefore contributing to the PL intensity quenching. From the PL analysis above, we can conclude that P3HT nanofiber blend system with the highest degree of PL quenching is likely to generate the largest short-circuit current due to better charge transport and reduced recombination.

Grazing incidence X-ray diffraction Previously, optical absorption spectra of the blends indicate that “aggregated” or phase-separated regions exist in thermally annealed and

nanofiber blends. Grazing incidence X-ray diffraction (GIXRD) measurements are performed to investigate the degree of P3HT organization in P3HT:F8BT blends and to examine the changes in P3HT lattice parameters after blending with F8BT. Fig. 4.3 shows the diffraction patterns of the blends spincoated on Si substrates and their crystallinity data, as extracted from the diffraction patterns, are shown in Table 4.1.

Fig. 4.3 (a) GIXRD patterns of P3HT:F8BT (1:1) blend films. (b) X-ray profiles of P3HT:F8BT (1:1) blends extracted from (a). (Inset shows the reflections of P3HT in comparison to P3HT:F8BT blends).

The GIXRD results in Table 4.1 qualitatively describes P3HT crystallinity in the different P3HT:F8BT blends. The degree of crystallinity in P3HT can be derived from the product of peak height and width, which are obtained by fitting the peak at 2θ ca. 5.4° with Gaussian function. From the inset in Fig. 4.3(b), we could observe that blending of P3HT with F8BT without any treatment results in a profile with significantly reduced peak intensity. The presence of F8BT in the blend greatly disrupts the formation of P3HT crystallites. Annealing of this blend is shown to restore the P3HT crystallinity as reflected in the distinct diffraction peak at 5.4° . Thermal treatment provides the energy required for the diffusion of both types of polymer chains, resulting in a more phase-segregated D/A distribution leading to the formation of P3HT crystallites. Comparable degree of order is also observed when P3HT

nanofiber is blended with F8BT without any thermal annealing, as shown from the relatively high yet broader peak at 5.4° . Comparing the degree of crystallinity between the annealed and nanofiber blends, we notice that pre-assembled P3HT nanofibers can indeed maintain high crystallinity of around 25% more than that of the thermally annealed blend. Although heat treatment can induce crystallization of P3HT, it appears that comparable, if not better, degree of crystallinity is obtained in the pre-assembled P3HT nanofiber blend. In addition, the higher order (200) reflection at 10.8° is observed in the annealed blend. This implies that the degree of crystallinity in the nanofiber blend is more localized than that in the annealed blend.

Table 4.1 GIXRD parameters of P3HT nanofiber and P3HT:F8BT (1:1) blends.

Conditions	Peak Height	Peak Width	Crystallinity	$d_{(100)}$
	(count/s)	($^\circ$)	(a.u.)	(nm)
P3HT-nanofiber	1.02	0.83	0.84	1.617
Pristine P3HT:F8BT	0.04	1.28	0.06	1.645
Annealed P3HT:F8BT	0.28	0.73	0.20	1.663
P3HT-nanofiber:F8BT	0.19	1.28	0.25	1.640

The interplanar distance of the crystallites, *i.e.* d -spacing, is derived using Bragg's law (Eq. 2.4) and serves as a good indication of the extent of F8BT interference to the structural order of P3HT. The peak at 2θ *ca.* 5.4° is generally assigned to (100) reflection, which indicates the degree of order along the a -axis (Chapter 2), in the direction of interdigitating alkyl groups. This d -spacing corresponds to the distance between the neighbouring P3HT chains which are kept apart by their alkyl groups. The presence of F8BT increases the $d_{(100)}$ of P3HT from 1.617 nm to 1.645 nm. Since P3HT and F8BT interact strongly, good intercalation of F8BT chains into the P3HT units may be the origin of expansion of $d_{(100)}$. The "swelling" of $d_{(100)}$ is slightly reduced in the nanofiber blend compared to pristine blend where P3HT regions are highly disorganized.

The final aspect in the discussion of GIXRD is the broadening of the (100) peak for the nanofiber P3HT:F8BT blend, which implies the presence of crystallite defects.³¹ The defects can be caused by the strong interaction between F8BT units with P3HT nanofibers upon blending. This is similar to the "scission" of the crystallite regions in nanofibers as they prefer to interact with F8BT rather than to maintain the coherency within the P3HT nanofibers. More crystal defects could be present in P3HT nanofiber blend, while thermal annealing induces

more defect-free crystallite regions. This broadening is slightly asymmetric as there is also contribution for the shift in the d -spacing. Nevertheless, solar cells devices based on both approaches are expected to show comparable charge transport characteristics as both have high P3HT crystallinity.

Morphology study Atomic force microscopy (AFM) operated in tapping mode is used to investigate the blend surface morphology, and transmission electron microscopy (TEM) is used to reveal the film bulk morphology. As seen in the previous X-ray diffraction discussion, there is a strong interaction between P3HT and F8BT, which could lead to unfavorable morphology. The interaction between P3HT and F8BT is stronger than the interaction between similar P3HT molecules and similar F8BT molecules ($E_{AB} < E_{AA}$ or E_{BB} , where A refers to P3HT, B refers to F8BT and E refers to the interaction energy). We observed this strong interaction when F8BT aided the dissolution of P3HT in *p*-xylene and it was not possible to grow P3HT nanofiber in the presence of F8BT. Simulated morphology based on the relative strength of different interaction energies predicted morphology with larger interfacial area of the interacting P3HT–F8BT chains, leading to higher probability of charge dissociation but fewer aggregated domains.³² With this type of morphology, although the charge generation is improved, the recombination also becomes more pronounced due to large interfacial areas because of the reduction in domain size.

Fig. 4.4 shows the AFM morphologies of the different P3HT:F8BT blends. The AFM phase image of the as-cast P3HT:F8BT blend film shows a smooth, featureless surface as shown in Fig. 4.4(d). This type morphology with abundant nanoscale D/A interfacial areas, lacks of phase separation, which conforms to the reported simulation results as well as our PL study.³² Thermal annealing induces organization of P3HT and the phase image in Fig. 4.4(e) shows a very faint presence of phase segregation. In Fig. 4.4(f), obvious fibrillar morphology can be observed in the nanofiber blend with a more interconnected network of the fibers. As compared to fiber-only morphology, this blend shows a more compact film with spaces in between the fibers occupied by both amorphous P3HT and F8BT molecules. On the contrary, Kim et al. demonstrated a featureless morphology for P3HT:F8BT cast from *p*-xylene, which was also the host solvent used for the nanofiber self-assembly.¹⁸ The lack of surface features indicates a vertical phase separated of P3HT to the bottom of the blend, leaving F8BT phase on the top. Average surface roughness (σ_{RMS}) is obtained by analyzing height images of the blends, giving 0.8, 1.0 and 1.9 nm for pristine, thermally annealed, and nanofiber blends,

respectively. The surface roughness is often correlated to the degree of order of P3HT in the bulk.³³ Post-fabrication treatment such as thermal annealing improves packing of P3HT chains, while pre-assembled P3HT nanofibers inherently possess better crystallinity. Both phase and height analysis provide concurring conclusion for P3HT nanofiber role, *i.e.* better chain order and interconnectedness between the nanofibers, offering possible charge transport enhancement which could lead to an improved short-circuit current.

Fig. 4.4 Tapping mode height (top) and phase (bottom) AFM images of P3HT:F8BT (1:1): (a,d) pristine blend, (b,e) annealed blend and (c,f) blend with nanofibers. The scan size is 4 μm $\times$ 4 μm .

Transmission electron microscopy is used as a complementary technique to study the bulk morphology. Fig. 4.5 shows the bright field TEM images of the blend films prepared by drop-casting the solution on carbon-coated copper grids. Similar to the surface morphology of the films, pristine blend film does not show any specific features. Annealing at temperature above T_g of both polymers encourages polymer chain ordering resulting in phase segregation in the blend where domains with different contrast appear on the TEM image. P3HT, which can self-assemble to form ordered structures after annealing, has higher electron density and diffracts more and hence appears darker under bright field TEM. On top of this, blend of nanofibers shows distinct presence of fibers with an interconnected network of P3HT nanofibers. These fibers have width of *ca.* 20 nm, which is in good agreement with value determined from AFM. The less diffracting amorphous P3HT and F8BT components should fill the space between these nanofibers. Comparing the size of crystalline regions in both thermally annealed and nanofiber blends, it appears that thermal annealing results in homogeneous distribution of the dark and bright regions, implying a more homogeneous

distribution between donor and acceptor. Nevertheless, the interconnected network in nanofiber blend, which can enhance hole transport, still gives an advantage over annealed blend.

Fig. 4.5 TEM images of P3HT:F8BT (1:1) blends: (a) pristine blend, (b) annealed blend and (c) blend with nanofibers. The scale bar is 50 nm.

Device characterization The optical, structural and morphological studies have indicated that P3HT nanofiber approach as a promising annealing-free technique for morphology optimization. Fig. 4.6 shows the current density–voltage (J - V) characteristics of the devices based on the different P3HT:F8BT blends under AM 1.5G 1 sun illumination. The statistical distribution of the device parameters is shown in Fig. 4.7, calculated from 30 devices prepared from 3 different batches of devices for each sample. Summary of the device parameters is given in Table 4.2. Two common traits for all the BHJ devices are the low fill factor (FF), not exceeding 30%, and the high open circuit voltage (V_{OC}) close to 1 V. The different treatments were found to affect the short-circuit current (J_{SC}) significantly which depends strongly on various factors, such as: (1) amount of photons absorbed, (2) efficiency of exciton dissociation and (3) effectiveness of free charge transport.

Fig. 4.6 Current density-voltage (J - V) characteristics of devices made from P3HT:F8BT (1:1) blends under AM1.5G illumination at 100 mW/cm².

Table 4.2 Summary of photovoltaic device properties of P3HT:F8BT (1:1) devices.

Sample	PCE	J_{sc}	V_{oc}	FF
	%	(mA/cm ²)	(V)	
Pristine P3HT:F8BT	0.008	0.029	0.98	0.29
Annealed P3HT:F8BT	0.045	0.223	0.99	0.20
P3HT-nanofiber:F8BT	0.055	0.291	0.93	0.20

Fig. 4.7 Statistical distribution of device parameters of P3HT:F8BT (1:1) blends.

Low FF in this study may indicate imbalance between positive and negative charge (hole and electron) transport ($\mu_{h\nu}$ P3HT of *ca.* 10^{-4} cm²/Vs and μ_{ev} F8BT of *ca.* 10^{-5} cm²/Vs) and poor morphology.^{7,18,34} The one order of magnitude difference in charge mobility can induce build-up of space-charge region which can further impede charge extraction, increasing internal resistance in the blend.³⁵ Improvement in hole mobility induced by both annealing and nanofiber approaches may intensify the charge transport imbalance, leading to their even lower FF. Similar to the blends of poly(dialkoxy-*p*-phenylene vinylene)⁷, the strong interaction between P3HT and F8BT will give rise to molecular scale intermixing resulting in strongly bound electron-hole with small separation distance and hence the dissociation efficiency is reduced. V_{oc} is often correlated with the energy difference between HOMO of the donor and LUMO of the acceptor.³⁶ The high V_{oc} in this system is agreeable with the lower LUMO level of F8BT, *i.e.* 3.5 eV, in comparison to the generally used fullerene-based acceptor PCBM with LUMO level of 3.7 eV, which generally yields V_{oc} of *ca.* 0.6 – 0.7 V in P3HT blends. While both as-cast and annealed blends possess similar V_{oc} , P3HT nanofiber shows a 5% reduction in V_{oc} , which can be explained from the decrease in HOMO of P3HT due to the high crystallinity of P3HT nanofibers.³⁷

In terms of J_{SC} , thermal annealing and application of nanofiber leads to a 7-fold and 10-fold improvement, respectively. This increase in J_{SC} can be derived from the improved degree of crystallinity, which results in enhanced absorption and charge transport. Comparing these two treatments, nanofiber approach appears to have more potential to improve the PCE of an all-polymer solar cell due to its better optical absorption characteristics at the higher wavelength and more crystallites with good interpenetrating network that are beneficial for efficient charge transport. As shown in the PL study above, the improved charge transport is one of the contributing factors to the PL quenching in P3HT-nanofiber:F8BT blend.

Finally, primarily due to its high J_{SC} , nanofiber blend device results in the best PCE in this study. These preliminary device results can be further optimized to yield more efficient solar cells by various methods, such as varying D/A ratio or inserting a hole blocking layer. Nevertheless, in this study we have shown the great potential of nanofiber as the ideal morphology in an all-polymer solar cell which performance depends strongly on an optimized morphology.

4.4 Conclusions

In this chapter, we have introduced the first application of polymeric nanofibers in an all-polymer solar cell to control the blend morphology. In all-polymer blends, both conjugated polymers may have strong interactions that could lead to unoptimized morphology. To induce phase segregation in the blends, thermal annealing serves as the only approach to modify the morphology thus far. We showed that the pre-assembled P3HT nanofibers, when blended with a polyfluorene copolymer, F8BT, resulted in a superior device performance compared to the annealed blend. GIXRD, AFM and TEM observations show that the nanofiber approach is beneficial in an all-polymer system because it preserves high crystallinity and minimizes the interaction between P3HT and F8BT chains, leading to a more optimized morphology for charge transport. The superior device performance is also attributed to the more efficient photon absorption and charge dissociation as shown by UV-Vis absorption and PL spectra, respectively. In short, we believe this thermal-free approach is a promising one in optimizing device performance for all-polymer blends, including blend of P3HT with poly((9,9-dioctylfluorene)-2,7-diyl-alt-[4,7-bis(3-hexylthienyl-5-yl)-2,1,3-benzothiadiazole]-2'-2''-diyl) (F8TBT), which is the current-state-of-the-art for all-polymer solar cells with PCE close to 2%.³

4.5 Experimental Section

Materials Regioregular P3HT ($M_w = 48.3$ kg/mol, regioregularity >90%) was purchased from Rieke Metals, Inc. F8BT ($M_w = 22$ kg/mol) was obtained from American Dye Source, Inc. The solvents *p*-xylene and 1,2-dichlorobenzene (*o*-DCB) (Chromasolv® HPLC grade, 99%) were purchased from Fluka and Aldrich respectively. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (CLEVIOS™ P VP Al 4083, HC Starck) was used to enhance hole transport. All materials were used as received without any further purification.

Preparation of P3HT nanofibers and P3HT:F8BT blend solutions P3HT nanofiber was prepared by gradual cooling of P3HT solution (7 mg/ml) in a marginal solvent *p*-xylene from 85 °C to room temperature at the rate of 10 °C/h using refrigerated circulator (Julabo F25-EC). P3HT solutions were prepared in N₂ glovebox and were protected from light and ambient atmosphere exposure throughout the cooling process to avoid P3HT photooxidation. P3HT organization into nanofibers was indicated by the color change from bright orange to dark purple. To ensure completion of the self-assembly process of P3HT molecules, the solution was left undisturbed in the dark for 48 h. Subsequently, P3HT-nanofiber suspension was mixed with F8BT at 1:1 weight ratio and stirred for 2 h at room temperature before spincoating. Non-fiber solution was prepared by blending the as-received P3HT and F8BT in a good solvent, *i.e.* *o*-DCB.

Device fabrication Polymer solar cells were fabricated with the following structure: ITO/PEDOT:PSS/P3HT:F8BT/Al. Patterned indium tin oxide (ITO)-coated glass substrates (Kintec Company, 7 Ω/sq) were successively cleaned by ultrasonication in deionized water, followed by acetone and finally in isopropanol for 15 min each. They were subsequently plasma cleaned for 2 min. A 30 nm thick PEDOT:PSS layer was spincoated onto the ITO-coated glass substrates, followed by baking at 140°C for 10 min. Spincoating of the active layer was done in N₂ glovebox. No filtration was done for nanofiber solutions while the non-fiber solutions were filtered using 0.45 μm PTFE filter. The P3HT:F8BT composite films thickness was adjusted to around 90 nm by controlling the spincoating rate. Eventually, the coated substrates were transferred to thermal evaporator and pumped down to < 10⁻⁶ Torr before depositing a layer of 80 nm thick aluminum (Al) cathodes. Thermal annealing of non-fiber P3HT:F8BT blend film was performed on a hotplate inside the glovebox at 150°C for 20 min. No hole blocking layer was deposited before Al cathode.

Device measurement and blend characterization The *J*-*V* characteristics for all devices were measured under AM 1.5G illumination from a calibrated solar simulator with irradiation intensity of 100 mW/cm² using Keithley SMU 2400 sourcemeter. No spectral mismatch correction was applied for power conversion efficiency (PCE) measurement. A calibrated Si-photodiode (Hamamatsu) was used as a

reference device in counting the incident photons. The optical absorption spectra were taken using Shimadzu UV-2510PC spectrometer on quartz substrates. The photoluminescence (PL) measurement was conducted using Perkin-Elmer LS 50B luminescence spectrometer. Grazing incident X-ray diffraction (GIXRD) patterns were collected using CuK_α radiation of a ω -diffractometer (incident X-ray angle at 2.5°). Film thickness was measured using Alpha-Step profilometer (KLA-Tencor). Atomic force microscopy (AFM) images were obtained using Digital Instruments (Nanoscope IIIa) in tapping mode while transmission electron microscopy (TEM) of the blend film was performed on JEOL 2010 TEM fitted with a LaB_6 filament and operated at an acceleration voltage of 200 kV.

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Triplet-Sensitized Organic Solar Cells: Importance of Blend Morphology and Role of Polymer Nanofibers

Summary. The effect of the incorporation of iridium(III)-based metal complex as triplet exciton sensitizer on the bulk heterojunction (BHJ) organic photovoltaics (OPV) based on P3HT and PCBM is discussed in this chapter. The extensive crystallization of regioregular (rr-) P3HT promotes molecular aggregation of the dopant molecules, while the amorphous regiorandom (ra-) P3HT forms a more homogeneously mixed blend. As a result, the triplet-doped ternary devices based on ra-P3HT experienced significant improvement ($> 60\%$) in the short-circuit current (J_{sc}). By contrast, triplet sensitized ternary devices of rr-P3HT experienced a significant degradation in performance, which was further aggravated upon thermal treatment. As described later in this chapter, in order for triplet sensitizer to improve the device performance, the active donor polymer has to be amorphous. However, the effect of sensitization could also be observed in the semicrystalline polymer that has undergone morphological transformation into nanofiber such as the P3HT nanofiber system that is discussed in this thesis. Due to their excellent optoelectronic properties, the post-fabrication annealing, which turns out to be detrimental for the ternary blends of such polymers, can be avoided. Thus it is important when working with ternary systems, to consider the effect of polymer configuration on the blend morphology and by using the concept of nanofiber, it is possible to circumvent this issue.

5.1 Background

In Chapter 4, the polymer nanofibers are demonstrated as a potent alternative to other conventional treatment techniques to optimize the blend morphology for improving device efficiencies. It becomes clear that another advantage of the nanofibers is that the fibrillar features, along with their excellent optoelectronic properties, are retained even when they are blended with other components. This is extremely important in ternary systems where even more components are involved. In recent years, there has been a significant development in the use of a third component in the conventional donor-acceptor binary blend system to improve the performance of the device. Unlike the solvent additive molecule in Chapter 3, which eventually vaporizes and leaves, the dopants stay in the samples. The morphology of the blend may be affected by the presence of the dopant. This chapter first explores the effect of the third component on the blend morphology in a triplet-doped ternary system. Subsequently, the discussion will be extended to the application of polymer nanofibers as the way to maintain good morphology in the triplet system.

5.2 Introduction

The field of organic solar cells has become progressively more attractive in the recent decade and has been regarded as one of the most promising emerging technologies for renewable energy industry. Significant improvement in power conversion efficiencies (PCE) of bulk heterojunction (BHJ)-based organic solar cell devices in excess of 8% and 4% has been demonstrated for the binary blends of fullerene derivatives with thieno[3,4-*b*]thiophene–benzodithiophene-based polymers and diketopyrrolopyrrole-based small molecule, respectively.^{1,2} Various attempts such as thermal annealing,^{3,4} solvent annealing,^{5,6} solvent additive,⁷⁻⁹ and application of pre-formed polymer nanostructures¹⁰⁻¹² have been applied to BHJ blends to induce a more thermodynamically stable and optimally phase-separated blend morphology.

A simple yet effective method to improve device performance is to generate ternary blends through the incorporation of dopant materials with superior optical and electrical properties into the original mixtures. For instance, the optical absorption range of the binary blends can be extended to longer wavelength through the addition of low band-gap materials (including conjugated polymers and oligomers)¹³⁻¹⁶ or dyes¹⁷⁻²⁰. Besides complementary

absorption characteristics, the electronic levels of the dopants should also be considered in the design of a ternary system. The position of these levels should promote energetically favorable photo-induced charge transfer between the dopant and active materials, as well as hole/electron transport to the respective donor/acceptor materials. In general, the photosensitization effect can be achieved when the highest-occupied molecular orbital (HOMO) level of the dopant lies between those of the donor and acceptor; likewise for the lowest-unoccupied molecular orbital (LUMO) level. The morphology of the active layer can also be altered upon blending the dopants into the active materials.²¹⁻²³ Kim *et al.* pointed out that the surface chemistry of the dopant molecules could affect the thermodynamics of donor-acceptor phase separation in the blend.²¹ On the other hand, Campoy-Quiles *et al.* showed that a higher degree of crystallinity with reduced crystallite size was obtained when an amorphous polymer was added into a binary blend.²² Similar improvements in crystallinity resulting in enhanced charge transport were also observed by Shin *et al.* through incorporation of *p*-type small molecules.²⁴ Carbon-based derivatives, such as carbon nanotubes (CNT) and graphene, form another class of additive materials for OPV.²⁵⁻²⁷ Both materials possess remarkable electronic properties and their incorporation into BHJ improves the charge percolation in the ternary composite, as shown by the increased photocurrents. However, proper dispersion of these materials in organic solvents has been demonstrated to be critical since aggregation of the material may severely affect the device properties. The other type of additive used in ternary systems is triplet material, which is the primary discussion in this chapter.²⁸⁻³⁰

The concept of triplet exciton was first introduced as a prospective panacea for the issue of short exciton diffusion length (L_D) universal in OPV field.³¹ Due to the low degree of order in OPV materials, L_D is typically in the order of 5 – 20 nm for singlet exciton.³² To allow efficient dissociation of these excitons, the thickness of the active layer has to be within L_D . Unfortunately a thickness (d) of ≥ 100 nm is required to ensure maximum absorption of the incident photons. Increasing the lifetime of excitons, which can in turn increase L_D , increases the probability of exciton-to-carrier conversion before they decay. Since radiative decay of triplet excitons is dipole-forbidden, their lifetime is typically longer (μ s to ms) as compared to that of singlet excitons (ns) rendering them attractive as a potential solution to the L_D vs d dilemma. This issue can also be overcome by using the bulk heterojunction concept, which requires the domain size be smaller than twice the diffusion length; with the presence of more triplet excitons, the tolerable domain size becomes greater. Organic materials have weak spin-

orbital coupling, and therefore are mostly populated by singlet excitons upon photoexcitation. The triplet exciton population in OPV can be increased through intersystem crossing (ISC) from singlet states by incorporating phosphorescent sensitizers as shown by photo-induced absorption measurements.³³ Despite the longer lifetimes of triplet excitons, which diffuse via short-range Dexter energy transfer, have lower mobility as compared to the singlet counterparts which can diffuse via longer-range Förster energy transfer.³⁴ Moreover, due to their different binding strengths, triplet excitons undergo different pathways to produce photocurrent in OPV depending on the strength of donor-acceptor interactions.³⁵

Although the efficacy of triplet exciton-enhanced photovoltaics remains controversial, research in the field has shown a few encouraging results leading to an increasing number of publications in recent years. Strengthening the spin-orbital coupling of organic systems can be done through introduction of transition metals into OPV systems (*e.g.* Ir, Pt, or Pd complexes) which act as platforms for singlet states to intersystem cross to form triplet states.³⁶ These metal complexes can be either chemically tethered to the backbones of conjugated polymers³⁷⁻⁴¹ or physically dispersed in the donor-acceptor BHJ.²⁸⁻³⁰ Direct chemical attachment of the metal complex units requires delicate organometallic synthetic procedures, while physical dispersion of these complexes is limited by the materials solubility, which may also affect the blend morphology. Triplet OPV has also been successfully applied in planar double heterojunction configuration, in which the complexes are only mixed with either one of the active materials, usually the donors.⁴²⁻⁴⁵

The effect of P3HT regioregularities and morphologies on the device performance of ternary blends doped with triplet sensitizer, namely iridium tris(2-phenylpyridine) (Ir(ppy)₃) (Fig. 5.1) was examined. Regioregular (rr-) P3HT with regioregularity (RR) of 90 – 94% and regiorandom (ra-) P3HT with RR of 50% are used as the prototypes for semicrystalline and amorphous polymeric systems, respectively. The two types of P3HT are different in terms of the position of the alkyl side groups in the polymer backbone. It was found out that the distribution of the transition metal complex in the blend depended on the regioregularity, and hence the morphology, of the polymers. Small molecules, such as fullerene and metal complex, tend to disperse more homogeneously in the matrix of ra-P3HT. The high molecular miscibility of fullerene in amorphous systems has been earlier demonstrated by Collins *et al.* as evident from the compositional mapping results.⁴⁶ On the other hand, it was also demonstrated that fullerene molecules could be effectively dispersed in the disordered regions

of rr-P3HT although the miscibility limit was only as high as 20 %vol.^{47,48} Therefore, a more pronounced ISC effect was observed in the better-mixed ra-P3HT blend, resulting in J_{SC} and PCE being increased by more than 60%. This improvement, however, was not observed for rr-P3HT blend; instead, degradation in device performance was observed.

Fig. 5.1 Chemical structure of the triplet sensitizer Ir(ppy)₃.

The polymer nanostructure approach also widens the possibility for ternary blend systems in particular when the conventional post-fabrication treatment fails to improve the device performance. In the following discussions, the virtues of P3HT nanofibers for triplet sensitization will be presented and emphasized. In a broader context, the findings presented in this chapter emphasize the importance of polymer morphologies in small molecule-doped ternary composites and their implications on the device characteristics.

5.3 Results and discussion

5.3.1 Triplet sensitization in P3HT:PCBM

Fig. 5.2 shows the electronic energy diagram of the components in the ternary blend devices. The solid lines represent the molecular orbital energy levels (HOMOs and LUMOs) while the dotted ones represent the estimated triplet energy levels. The molecular orbital energy level values shown were extracted from established literatures, with justified approximation.⁴⁹⁻⁵¹ The triplet levels for both P3HTs were estimated based on the exchange energy between the lowest singlet state and the triplet state (ΔE_{ST}), which was found to hold a value of *ca.* 0.7 eV for various amorphous π -conjugated polymers⁵² and *ca.* 0.45 eV for ordered poly(3-alkylthiophene).⁵³ The triplet energy level for Ir(ppy)₃ was derived from its phosphorescence peak.⁵¹ The LUMO level, or lowest excited singlet state (S_1), of both rr-P3HT and ra-P3HT is similar to that of the Ir(ppy)₃ (*ca.* 3 eV) suggesting that upon excitation singlet excitons in the donor P3HT may readily delocalize between the two materials, followed by rapid intersystem

crossing (ISC) to the triplet state (T_1) in the triplet dopant. Furthermore, the triplet excitons in Ir(ppy)_3 may either back-transfer and populate T_1 of P3HT or get quenched via electron transfer to S_1 of PCBM. Due to the rapid (in picoseconds range) photoelectron transfer to PCBM, the latter is the kinetically more preferred process.³⁷ Following the charge transfer, intersystem crossing from S_1 to T_1 states in PCBM is also possible depending on the energy of the charge-separated state.⁵⁴ The HOMO level of Ir(ppy)_3 , which is between those of P3HT and PCBM, not only prevents hole trapping in the dopant material, but also allows hole transfer between the donor and acceptor. To sum up, the introduction of iridium-based dopant does not pose any energetic barrier to the photoinduced charge generation. Nevertheless, the physical distance between the triplet and the donor molecules has to be kept minimal to ensure efficient triplet sensitization. As will be shown later, this limitation is closely related to the issue of the optimal blend morphologies.

Fig. 5.2 Energy level diagram of the materials used for the solar cell devices. The dotted lines represent the triplet energy levels (with respect to the HOMO levels).

5.3.2 Importance of blend morphology

To explore the effect of Ir(ppy)_3 incorporation in the blends, optical, electrical and morphological characterizations were performed on both polymer systems.

Absorption spectroscopy Fig. 5.3(a) shows the solid state UV-Vis absorption spectra of both rr-P3HT:PCBM and ra-P3HT:PCBM nanocomposites (before and after addition of the triplet dopant). The profiles are normalized at PCBM peaks at $\lambda_{\text{max}} = 330$ nm. The absorption spectra from 400 to 650 nm, which corresponds mostly to that of P3HT, show noticeable

difference between rr-P3HT ($\lambda_{\text{max}} = 520 \text{ nm}$) and ra-P3HT ($\lambda_{\text{max}} = 460 \text{ nm}$) blends. The blue-shifted spectra of ra-P3HT:PCBM together with the absence of well-resolved vibronic shoulders at higher wavelengths (560 and 620 nm) indicate a more inferior degree of order in the blends with reduced conjugation length, which is the result of increased steric repulsions of the alkyl side groups due to their random positioning in ra-P3HT. On top of this difference in regioregularity, ra-P3HT in this study has a higher molecular weight (M_w), which further restricts its ability to organize. The lack of the π - π interchain interaction in solid-state ra-P3HT results in optical transition at lower wavelength with a broader optical gap ($E_g = 2.3 \text{ eV}$), *i.e.* an offset of 0.3 eV compared to rr-P3HT ($E_g = 2.0 \text{ eV}$). Furthermore, the blends of ra-P3HT have slightly lower optical density (OD) than rr-P3HT. Transferring the optical characteristics into the device properties, it is expected that ra-P3HT:PCBM will perform worse than rr-P3HT:PCBM due to the unoptimized photon harvesting and poor charge transport resulting from the combination of the blue-shifted weak blend absorption along with the low degree of structural order. The triplet sensitizer Ir(ppy)₃ absorbs throughout the visible spectrum extending to the UV region with absorption band at 390 nm (Fig. 5.3(b)). The absorption of the polymer blends was enhanced by 1 – 3% with the addition of 5 wt% of iridium complexes, primarily in the 340 – 450 nm region, corresponding to the contribution of the sensitizer absorption.

Fig. 5.3 UV-vis absorption spectra of: (a) binary and ternary blends of ra-P3HT and rr-P3HT with PCBM (1:1), and (b) Ir(ppy)₃.

Device performance Fig. 5.4 displays the current density-voltage (J - V) characteristics of the devices under AM1.5G 1 sun (100 mW/cm^2) standard illumination. The device performance data is provided in Table 5.1. The non-annealed (NA) binary device of rr-P3HT:PCBM exhibits a low PCE of 0.88% with short-circuit current (J_{sc}) of 3.86 mA/cm^2 ,

open-circuit voltage (V_{OC}) of 0.68 V and fill factor (FF) of 0.34. The low J_{SC} and FF are associated with the unoptimized blend morphology with low polymer crystallinity. The incorporation of $Ir(ppy)_3$ molecules into rr-P3HT:PCBM blend further degrades device PCE to 0.44% (*ca.* 50% reduction). This suggests the presence of the triplet molecules may result in less efficient charge generation and charge transport in the rr-P3HT ternary blend.

Fig. 5.4 Current density–voltage (J - V) characteristics of: (a) rr-P3HT:PCBM and rr-P3HT:PCBM:Ir(ppy)₃, and (b) ra-P3HT:PCBM and ra-P3HT:PCBM:Ir(ppy)₃ devices. The types of devices were also subjected to thermal annealing at 150 °C for 20 min. The measurement was performed under 1 sun (100 mW/cm^2) illumination.

Post-deposition heat treatment at 150 °C for 20 min was performed to restore the crystallinity of rr-P3HT. The thermally annealed (TA) rr-P3HT:PCBM device shows a three-fold PCE improvement to 2.98%, with J_{SC} , V_{OC} and FF of 9.02 mA/cm², 0.57 V and 0.58, respectively. As discussed earlier in Chapter 2, the thermally activated diffusion of both rr-

P3HT and PCBM molecules results in enhanced molecular reorganization with increased degree of crystallinity for both materials.⁵⁵ On the other hand, annealing of the ternary rr-P3HT:PCBM:Ir(ppy)₃ device only resulted in a slight increase in PCE from 0.44% to 0.81%, with moderately improved J_{sc} and FF. Comparing both annealed devices, it is evident that the blending of Ir(ppy)₃ into rr-P3HT:PCBM device has significantly reduced device performance as seen by the PCE reduction of *ca.* 70%, due to decrease in J_{sc} , FF and even V_{oc} . The considerably reduced V_{oc} from 0.58 to 0.43 V in the TA rr-P3HT:PCBM:Ir(ppy)₃ might be attributable to substantial PCBM aggregation.⁹ The decrease in FF also indicates the impediment of charge transport with increased series resistance (bulk and contact resistances). In short, for rr-P3HT:PCBM systems, the inclusion of Ir(ppy)₃ resulted in decreased device performance, which was further worsened by thermal annealing.

Table 5.1 Summary of photovoltaic device properties of binary and ternary P3HT devices. The thermal annealing was done at 150 °C for 20 min.

Sample	PCE	J_{sc}	V_{oc}	FF
	%	(mA/cm ²)	(V)	
rr-P3HT:PCBM (as-cast)	0.88	3.86	0.68	0.34
rr-P3HT:PCBM (annealed)	2.98	9.02	0.57	0.58
rr-P3HT:PCBM:Ir(ppy) ₃ (as-cast)	0.44	2.53	0.67	0.26
rr-P3HT:PCBM:Ir(ppy) ₃ (annealed)	0.81	4.06	0.42	0.47
ra-P3HT:PCBM (as-cast)	0.33	1.29	0.88	0.29
ra-P3HT:PCBM (annealed)	0.16	0.98	0.58	0.29
ra-P3HT:PCBM:Ir(ppy) ₃ (as-cast)	0.54	1.96	0.90	0.29
ra-P3HT:PCBM:Ir(ppy) ₃ (annealed)	0.14	0.90	0.54	0.29

In comparison, PCE enhancement is observed in the triplet-doped ra-P3HT:PCBM devices, as shown in Fig. 5.4(b). The reference binary device gives PCE of 0.33%, with J_{sc} of 1.29 mA/cm², V_{oc} of 0.88 V and FF of 0.29, while the ternary device shows improved PCE of 0.54%, with J_{sc} , V_{oc} and FF of 1.96 mA/cm², 0.90 V and 0.29, respectively. The V_{oc} for ra-P3HT devices is higher due to its deeper HOMO level than that of rr-P3HT. The low PCE for the binary ra-P3HT:PCBM devices derives from the poor absorption properties and poor charge transport, *i.e.* hole mobility of an order of magnitude smaller than that of rr-P3HT.^{56,57} The PCE improvement exceeding 60% in the triplet devices correlates well with the increase in J_{sc} while the other device parameters remain unchanged. Thermal annealing of both binary and ternary

devices based on ra-P3HT blends resulted in decreased device PCE. Comparison between the thermal-annealed binary and ternary devices reveal that inclusion of Ir(ppy)₃ in ra-P3HT blend only resulted in *ca.* 10% degradation in performance. This is remarkably lower than that observed for the rr-P3HT system.

External quantum efficiency (EQE) measurement also shows that the incorporation of triplet sensitizer significantly enhances the photoresponse of ra-P3HT:PCBM, as shown in Fig. 5.5. Along with the photocurrent improvement, the appreciable EQE signal enhancement (EQE_{max} increases from 8% to 12%) suggests that the presence of Ir(ppy)₃ molecules may have enhanced spin-orbital coupling resulting in enhanced triplet state population in P3HT donor *via* intersystem crossing. The longer-lived triplet excitons with longer diffusion lengths have a higher probability of diffusing to the D/A interfaces and dissociating, thus aiding to the more-readily dissociated singlet excitons in generating charges. These triplet excitons can also produce free charges via exciton-charge reactions, *i.e.* upon encountering other free charges.^{28,35} In addition, recombination of the dissociated charges can also be suppressed if they possess different spins.

Fig. 5.5 EQE spectra of ra-P3HT:PCBM (1:1), before and after incorporation of Ir(ppy)₃ molecules.

To probe the effect of polymer regioregularities and morphologies on the device performance, a few transient absorption measurements of both the pristine polymer films and their binary blends have been reported.⁵⁸⁻⁶² Guo *et al.* argued that in the more intimately mixed amorphous ra-P3HT and PCBM, charge generation is more efficient due to the abundance of D/A interfaces and hence, less need for extended exciton migration.⁵⁸ Following this process, however, efficiency is lowered by major geminate recombination of dissociated charges as

well as the poor charge collection at the electrodes. On the other hand, the semicrystalline rr-P3HT possesses an inherent tendency to phase separate, thereby reducing the efficiency of exciton collection to the interfaces in the blend with PCBM. However, in such blends with sufficient percolation network, charge dissociation and transport are more efficient, which further improve upon thermal annealing. It was also reported that the formation dynamics of the quasiparticles is different for P3HT films with different regioregularities.⁵⁹⁻⁶² Triplet excitons are generated in ra-P3HT films via singlet exciton-exciton annihilation and intersystem crossing from singlet excitons, while in rr-P3HT triplet formation is not observed due to the more competitive formation of polarons.

Triplet exciton enhancement in a BHJ can only be realized if the transition metal complexes are in close proximity to the active materials. In the amorphous ra-P3HT system, the presence of molecular disorder hinders the phase separation, which leads to a more homogeneously dispersed blend with increased donor/dopant and acceptor/dopant interfaces. By contrast, the semicrystalline rr-P3HT has a strong tendency to crystallize and phase separate in the blends, increasing the possibility for molecular aggregation for both acceptor PCBM and dopant Ir(ppy)₃. The molecular miscibility of PCBM and Ir(ppy)₃ in the rr-P3HT matrix is limited by the amount of disordered phase present.^{47,48} It is therefore of the utmost importance to investigate the morphologies of the ternary blends.

Fig. 5.6 Tapping mode height AFM images of Ir(ppy)₃ in rr-P3HT matrix. The scan size is: (a) 50 μm x 50 μm, and (b) 10 μm x 10 μm.

Blend morphology Fig. 5.6 shows the morphology of rr-P3HT film doped with Ir(ppy)₃ (5 wt%). It is obvious that needle-like features with lengths ranging from 1 – 5 μm and an aspect ratio of *ca.* 8 are present throughout the film surface. These structures are assigned as nanorods of Ir(ppy)₃. Wang *et al.* also reported formation of similar structures by a gradual solvent evaporation technique.⁶³ As discussed here, Ir(ppy)₃ can also self-assemble to form the

nanostructures even in a rapid solvent evaporation condition during spin-coating from polymer blend solution. Further blending with PCBM preserves these structures, as seen in Fig. 5.7(b) and 5.7(e), while the binary blends of polymers and fullerene exhibit featureless surfaces (Fig. 5.7(a) and 5.7(d)). The presence of PCBM in the ternary blends, which is ten times higher in concentration than the triplet dopant, may have interfered in the self-assembly of the triplet molecules. This could have affected the dimensions of needles, *i.e.* shorter length ($<1 - 3 \mu\text{m}$) yet with significantly increased aspect ratio (*ca.* 10 – 40). Both regioregular and regiorandom P3HT blends exhibit similarly distribution of the needle-like structures on the surface.

Fig. 5.7 Tapping mode height AFM images of (a) rr-P3HT:PCBM (b) rr-P3HT:PCBM:Ir(ppy)₃, (c) annealed rr-P3HT:PCBM:Ir(ppy)₃, (d) ra-P3HT:PCBM (e) ra-P3HT:PCBM:Ir(ppy)₃, (f) annealed ra-P3HT:PCBM:Ir(ppy)₃. Thermal annealing was performed at 150 °C for 20 min. The scale bar indicates length of 5 μm .

To further elucidate the molecular distribution of the polymer, fullerene and dopant molecules in both polymer systems, the ternary blends were subjected to heat treatment at 150 °C. As shown in Fig. 5.7(c), large cube-like particles with diameter *ca.* 1 – 3 μm and height of greater than 1 μm emerged in the thermally annealed ternary blend of rr-P3HT:PCBM:Ir(ppy)₃. These features are also visible from scanning electron microscope (Fig. 5.8) and they demonstrate a time-dependent growth behavior. Fig. 5.9 shows an increase in the density of the particles over annealing time. On the contrary, such massive particles are absent in the thermally annealed ra-P3HT:PCBM:Ir(ppy)₃ blend (Fig. 5.7(f)), although the

surface becomes rougher as compared to the non-annealed blend (Fig. 5.7(e)). Thermally annealed blend of rr-P3HT is generally rough ($\sigma_{\text{RMS}} > 110$ nm) for the regions with the particles, but is smoother in the particle-free regions ($\sigma_{\text{RMS}} = \text{ca. } 10 - 20$ nm). On the other hand, thermal annealing coarsens the ra-P3HT blend surface uniformly ($\sigma_{\text{RMS}} = 17$ nm), although the root-mean-square surface roughness only increase slightly compared to its non-annealed blend ($\sigma_{\text{RMS}} = 11$ nm).

Fig. 5.8 SEM image of the annealed rr-P3HT:PCBM:Ir(ppy)₃ measured at 15kV. The scale bar indicates length of 20 μm .

Fig. 5.9 Visible light optical microscope images of rr-P3HT:PCBM:Ir(ppy)₃ ternary blend films prepared on glass substrates and annealed at 150 °C for: (a) 0 min, (b) 10 min, (c) 20 min and (d) 30 min. Ir(ppy)₃ concentration in the blends is 5 wt%. The micron-sized structures (>100 nm) correspond to PCBM needles. The scale bar indicates length of 100 μm .

Thermal annealing drives phase segregation of the blend materials. Depending on the nature of polymer morphology as well as the preferential distribution of the small molecules in the polymer matrix, this phase segregation can be modulated. Regiorandom P3HT, which is inherently amorphous, lacks the ability to pack to generate P3HT-rich regions even under elevated temperature conditions. On the contrary, regioregular P3HT readily undergoes local molecular packing, which becomes more pronounced upon thermal treatment. Thermal annealing beyond glass transition temperatures (T_g) of the materials magnifies the extent of molecular phase segregation in rr-P3HT blends, since the strong crystallization of the polymer phase will in turn provide a large free volume for the small molecules to interact with and thus coalesce into larger aggregates. It is proposed that the observed particles in the ternary blend of rr-P3HT in Fig. 5.7(c) are hybrid structures of both the triplet dopants and the fullerene molecules. PCBM molecules tend to form needle-like crystals with lengths of *ca.* 100 μm (observed in Fig. 5.9). When the binary blend of rr-P3HT:PCBM is annealed, there is an enhancement in the formation of PCBM crystals due to its increased tendency to phase segregate.⁶⁴ Moreover, a separate annealing treatment of rr-P3HT:Ir(ppy)₃ did not induce any significant change in the smaller micron-sized needle-like features. Nevertheless, in the doped blends, thermal annealing resulted in formation of the large cube-like particles, suggesting the presence of the triplet dopants triggered the emergence of these particles. Therefore, it is suggested that PCBM molecules may have diffused and nucleated on the surfaces of Ir(ppy)₃ crystals. This type of heterogeneous nucleation and growth resulted in Ir(ppy)₃/PCBM core/shell hybrid nanostructures. The ternary blend based on amorphous ra-P3HT, however, should suffer a lesser extent of phase separation because small molecules are somewhat retained in the immobile polymer matrix. The roughening of the blend surface (Fig. 5.7(e)) upon thermal annealing suggests that local aggregation of the small molecules occurred homogeneously in the blend.

Scanning transmission X-ray microscopy (STXM) was performed to further investigate the components of the different nanostructures observed in the ternary blends, *i.e.* the needle-like and cube-like particles. This powerful synchrotron-based microscopy technique is capable of spatially resolving the chemical difference in the samples through the variation in their photon energies. The contrast in STXM images derives from the differences in X-ray absorption spectra at the carbon K-edge of the constituting components, which in turn stem from the differences in their anti-bonding electronic structures.⁶⁵ STXM has been

applied as a characterization tool to investigate the morphologies of various organic systems.^{9,46,66-68} The selection of the photon energies for STXM measurement depends on the near edge X-ray absorption fine structure (NEXAFS) spectra. The NEXAFS spectra of the ternary blend components are shown in Fig. 5.10, in which each component has its own spectroscopic fingerprints. A set of calibrated C1s NEXAFS spectra of some commonly encountered organic electronic materials have been reported by Watts *et al.*⁶⁹ Both NEXAFS and STXM measurements were performed on the samples prepared on Si₃N₄ membranes. For STXM imaging, photon energies of 280 eV, 284.8 eV and 286.2 eV were used, corresponding to the background absorption, absorption peaks of Ir(ppy)₃ and PCBM, respectively. The difference in the X-ray absorption intensity between Ir(ppy)₃ and PCBM at 284.8 eV is marginal, while the absorption intensity of PCBM is much higher for 286.2 eV.

Fig. 5.10 NEXAFS spectra of P3HT, PCBM and Ir(ppy)₃. The vertical lines indicate the photon energies used for STXM imaging (*i.e.* 284.8 eV and 286.2 eV, corresponding to Ir(ppy)₃ and PCBM absorption peaks, respectively).

Fig. 5.11 shows the X-ray microscopy images of both non-annealed (Fig. 5.11(a-c)) and thermally annealed (Fig. 5.11(d-f)) ternary blends of the rr-P3HT:PCBM:Ir(ppy)₃ taken at various photon energies. As seen in Fig. 5.11(a), at 280 eV which corresponds to the pre-edge absorption of carbon, the equally low x-ray absorption intensity of PCBM and Ir(ppy)₃ lead to almost featureless blend images. A weak X-ray absorption at this wavelength results mostly from the x-ray absorption of sulfur in P3HT. A few needle-like structures can be observed on the blend at both 284.8 eV and 286.2 eV, agreeable to the previous AFM result (Fig. 5.7(b)). These features appear to be slightly darker at 284.8 eV, suggesting that they are made up of

Ir(ppy)₃-rich phase. However, the fact that the features also absorb at 286.2 eV suggests that PCBM may also be present. Upon thermal treatment, the STXM images reveal the disappearance of the needle-like structures, followed by the emergence of large particles. This observation is also in good accordance with the surface information observed under AFM (Fig. 5.7(c)). It is to be noted that the STXM images have not been calibrated with respect to the blend thickness. As such, taller features may have more pronounced absorption. These particles absorb strongly at 284.8 eV and 286.2 eV, which indicates the possibility of formation of Ir(ppy)₃/PCBM hybrid structures. At 286.2 eV (PCBM absorption), these micron-sized particles appear to be darker suggesting that they are rich in PCBM (Fig. 5.11(f)). As discussed before, thermal treatment may induce diffusion and aggregation of PCBM molecules. In addition, there are also many nano-sized particles surrounding the larger ones which appear darker at 284.8 eV (Ir(ppy)₃ absorption). Since these features were not observed under AFM, it is possible that Ir(ppy)₃ may have undergone some morphological deformation in the bulk film.

Fig. 5.11 STXM images of P3HT:PCBM:Ir(ppy)₃ ternary blends: (a-c) unannealed and (d-f) annealed. Left images are taken at 280 eV, middle images are taken at 284.8 eV and right images are taken at 286.2 eV. Thermal annealing was done at 150 °C for 20 min. The scan size is 15 μm x 15 μm.

Proposed mechanism The schematic of a plausible mechanism of how materials are distributed in the ternary blends based on rr-/ra-P3HT:PCBM:Ir(ppy)₃, as well as how they are redistributed is shown in Fig. 5.12. From our observations, the ternary blend of amorphous

polymer (ra-P3HT) tends to have a more homogeneous material distribution as opposed to that of crystalline polymer (rr-P3HT). The high regioregularity of rr-P3HT promotes material packing and phase separation, and therefore, also encourages the organization of the PCBM and Ir(ppy)₃ molecules. In addition, high miscibility of fullerene and iridium molecules in rr-P3HT is limited to its more disordered regions. Therefore, in such blends the small molecules are more likely to form clusters among themselves. Further thermal annealing treatment increases the organization of rr-P3HT, resulting in enhanced phase separation of both the polymers (forming crystalline lamellae) and the small molecules. As seen before, there is a possibility that both small molecules may interact to form larger aggregates. On the other hand, the lack of polymer ordering in ra-P3HT blends hinders polymer phase separation, which also retards the aggregation of both PCBM and Ir(ppy)₃. The use of amorphous polymer helps to enhance the thermal stability of the blend morphologies. The concept of introduction of certain amount of disorder through reduction in material regioregularity has been shown as one of the approaches to promote a more thermally stable morphology for binary blends by suppressing the excessive destructive phase separation.^{64,70-72}

Fig. 5.12 Proposed mechanism of the effect of thermal annealing performed on ternary blends of P3HT:PCBM:Ir(ppy)₃ with different morphologies. rr-P3HT represents the semicrystalline polymer, while ra-P3HT represent the amorphous polymer.

The morphological change upon thermal treatment provides some hints to the material distribution of the non-annealed material ternary blends. In the ra-P3HT:PCBM:Ir(ppy)₃ blend, all components are closely mixed resulting in increased polymer/dopant and fullerene/dopant interfaces, along with the polymer/fullerene

interfaces. The triplet excitons from Ir(ppy)₃ can be transferred more effectively to the triplet states of donor ra-P3HT due to the small spatial gap between dopant and active materials, resulting in improved triplet sensitization. Besides, the more homogeneously distributed dopants should have minimal adverse effect on the charge transport. On the other hand, the lack of the active material/dopant interface in the semicrystalline polymer system (rr-P3HT) reduces the efficiency of the triplet exciton sensitization. Moreover, the formation of the aggregates in the blend upon thermal annealing may negatively affect the charge transport in the otherwise efficient device. To sum up, the poorer device performance in the annealed ternary devices based on rr-P3HT could be due to the impediment of the charge transport both in the bulk film and at the contact with the top electrode. The effective PCBM concentration in the polymer matrix could have reduced due to the formation of the micron-sized cubic-like structures. This could in turn decrease the total possible amount of donor-acceptor interface, eventually leading to decline in charge generation.

5.3.3 Role of Polymer Nanofibers

As discussed earlier, the semicrystalline polymers, *e.g.* regioregular poly(3-alkylthiophene)s, tend to be more superior in terms of their electronic properties as compared to their amorphous analog. However, their molecular miscibility with small molecules, either acceptors or dopants, may become an issue due to their propensity to interact among themselves and self-organize. The phase separation is aggravated when thermal treatment is required, which unfortunately is the case in order to achieve excellent electronic properties. Furthermore, the presence of a third component in the system to a large extent may also affect the blend morphology. The blends of non-fiber rr-P3HT, PCBM and Ir(ppy)₃, for instance, upon thermal annealing generate microstructures believed to induce negative influence on the device performance. However, with polymer nanofiber approach, it is possible to obtain highly efficient solar cell devices without undergoing any post-fabrication annealing treatment. Therefore, by eliminating the detrimental annealing step, ternary blend consisting of nanofiber of regioregular P3HT (P3HT-nf) system may show triplet sensitization effect and hence improvement in device performance.

Absorption spectroscopy Fig. 5.13(a) depicts the normalized steady-state UV-Vis absorption spectra of the binary (P3HT-nf:PCBM) and ternary (P3HT-nf:PCBM:Ir(ppy)₃) blends. The absorption features are generally similar to the ones in Fig. 5.3(a), except that

nanofiber blends exhibit more pronounced vibronic “shoulders” at *ca.* 560 nm and *ca.* 620 nm, which have been discussed in the previous chapters. The incorporation of the Ir(ppy)₃ molecules do not affect the absorption characteristics of P3HT, as seen from the nearly overlapping of the profiles. The triplet dopant (5 wt%) has also increased the blend absorption around 340 – 450 nm by *ca.* 2%, similar to the previous observation on rr-P3HT:PCBM blends.

Fig. 5.13 (a) UV-Vis absorption and (b) PL spectra of nanofiber P3HT:PCBM (10:6) blends, before and after Ir(ppy)₃ incorporation. The Ir(ppy)₃ concentration is 5 wt%. The excitation wavelength used for PL measurement is 520 nm.

Photoluminescence spectroscopy The role of the heavy metal complexes is to strengthen the spin-orbital coupling, thereby increasing the chance for ISC to occur. Consequently singlet excitons from the active materials can be converted to triplet excitons. Due to their long lifetime, triplet excitons have higher chance of reaching the D/A interfaces and thereafter, dissociated into free charges. Fig. 5.13(b) shows the normalized thin-film PL

spectra of the nanofiber blends. The typical PL characteristics of P3HT-nf:PCBM with an excitonic peak at *ca.* 620 nm and vibronic “shoulder” *ca.* 680 nm can be observed; discussions of which are presented in the earlier chapters. The doping of 5 wt% of Ir(ppy)₃ considerably alters the PL features of the blend. In general, there is a reduction in the PL intensity throughout the range of interest, *i.e.* 600 – 750 nm corresponding to the luminescence range for P3HT. However, the energy used to excite the P3HT molecules may have also affected the phosphorescent triplet molecules present in the blend. Ir(ppy)₃ absorbs throughout the visible window (Fig. 5.3(b)), and its emission covers the range from 500 – 700 nm, peaking at 520 nm. Therefore, it is suspected that the extra PL intensity around 660 nm is attributed partly to Ir(ppy)₃ luminescence. Such metal complexes tend to have high quantum yield (*i.e.* highly luminescent) and may interfere with the interpretation of the result.⁵¹ Considering the contribution of the complexes, the ternary blend was expected to have even higher PL intensity. Nevertheless, the observation of PL quenching around P3HT excitonic peak (620 nm) suggests that the heavy metal complexes may have induced an efficient singlet-to-triplet exciton conversion in P3HT. The decrease in radiative recombination implies better efficient charge generation, and thus better device performance.

Device performance The *J*-*V* characteristics of the P3HT-nf:PCBM and P3HT-nf:PCBM:Ir(ppy)₃ devices under 1 sun illumination are shown in Fig. 5.14. The device parameters are summarized in Table 5.2. The control binary device shows *J*_{SC} of 6.3 mA/cm², *V*_{OC} of 0.684 V, FF of 0.55 and PCE of 2.37%. On the other hand, the triplet-doped device has *J*_{SC} of 6.75 mA/cm², *V*_{OC} of 0.673 V, FF of 0.55 and PCE of 2.49%. There is a slight improvement in the photocurrent by *ca.* 6% while the FF remains the same. These results show a noticeable difference from the previous data of the non-fiber rr-P3HT (both as-cast and thermally annealed). The non-fiber blends experience *ca.* 50% and *ca.* 70% drop in PCE (or *ca.* 30% and *ca.* 50% drop in *J*_{SC}) after the incorporation of Ir(ppy)₃ molecules for both the as-cast and annealed devices, respectively. In contrast, the nanofiber device not only does not deteriorate in performance, but there also is a slight increase in PCE of *ca.* 5%. The increase in the PCE is solely due to the improvement in the *J*_{SC}, implying the possibility of the enhancement in the triplet excitons as induced by the intersystem crossing (ISC) process. It is also noteworthy to point out that the incorporation of triplet molecules into the non-fiber rr-P3HT devices has substantially reduced the FF by *ca.* 20%. As FF correlates more with the device resistance, this suggests triplet molecules in the non-fiber system may have impeded the charge transport.

This, however, is not observed in the nanofiber system since the FF remains unchanged. The pre-formed fibrillar structures in the nanofiber system are not affected by the presence of Ir(ppy)₃ molecules.

Fig. 5.14 Current density-voltage (*J*-*V*) characteristics of nanofiber P3HT:PCBM (10:6) devices, before and after Ir(ppy)₃ incorporation. The measurement was done at 1 sun (100 mW/cm²) illumination.

Table 5.2 Summary of photovoltaic device properties of nanofiber P3HT:PCBM (10:6) devices, before and after Ir(ppy)₃ incorporation.

Sample	PCE	<i>J</i> _{sc}	<i>V</i> _{oc}	FF
	%	(mA/cm ²)	(V)	
P3HT-nf:PCBM	2.37	6.30	0.684	0.55
P3HT-nf:PCBM:Ir(ppy) ₃	2.49	6.75	0.673	0.55

External quantum efficiency To understand the origin of the photocurrent (*J*_{sc}) enhancement observed in the nanofiber system, external quantum efficiency (EQE) measurement was performed. Fig. 5.15 shows the EQE spectra of the nanofiber devices. There is an apparent increase in the maximum EQE from 45% to 48% after the incorporation of the iridium complexes. Unlike the triplet-sensitized ra-P3HT:PCBM system, in which the increase in the EQE signal can be observed throughout the photoactive region (Fig. 5.5), the EQE enhancement in P3HT-nf:PCBM is observe to come from two main regions, *i.e.* around 420 nm and 500 – 620 nm.

Rand *et al.* proposed multiple roles a triplet dopant may assume in the photocurrent generation in an OPV: (1) increasing triplet population in the donor material *via* sensitized phosphorescence, (2) directly absorbing photons followed by charge transfer to the nearby

acceptor molecules, and (3) acting as auxiliary donor sites to help exciton dissociation from the acceptor molecules.²⁹ The increase in the EQE signal in Fig. 5.15 suggests that the Ir(ppy)₃ molecules fulfill the first two roles. The region around 420 nm corresponds to the absorption maximum of the complex, and Fig. 5.13(a) also shows the contribution of iridium complex absorption. This suggests that iridium complexes have assisted the current generation through direct photoabsorption. Furthermore, the signal enhancement at 500 – 620 nm implies a selective triplet sensitization of the P3HT nanofiber. This also agrees with the PL measurement that shows the quenching of P3HT luminescence upon blending with Ir(ppy)₃. The triplet-induced fullerene sensitization is not observed in this system. The data indicate that the triplet complexes must have distributed at the proximity of the polymer nanofibers.

Fig. 5.15 EQE spectra of nanofiber P3HT:PCBM (10:6) devices, before and after Ir(ppy)₃ incorporation.

Fig. 5.16 4 μm x 4 μm tapping mode AFM images of: (a) P3HT-nf:PCBM and (b) P3HT-nf:PCBM:Ir(ppy)₃. 10 μm x 10 μm AFM images of P3HT:PCBM:Ir(ppy)₃: (c) height and (d) phase images.

Blend morphology Fig. 5.16 shows the AFM images of both the binary and ternary blends. The fibrillar features can be observed throughout the blend surface coexisting with amorphous-like regions (Fig. 5.16(a)). On the other hand, the triplet-doped blend film reveals a similar morphology with embedment of micron-sized needle-like structures (bright features in Fig. 5.16(b)). These Ir(ppy)₃ needles are <100 nm in height, overlaid by the P3HT fibers. From the 10 μm $\times$ 10 μm AFM images, it is noticeable that the density of the needles is smaller than those observed in both rr-P3HT and ra-P3HT blends, although the needles are similar in dimension (*ca.* 1 – 3 μm in length). This suggests that Ir(ppy)₃ molecules are more well-spread in the bulk of the blend, and are thus more likely to sensitize the active materials. From this observation, it also becomes apparent that formation of the Ir(ppy)₃ needles is independent of the choice of the processing solvent.

The triplet concept can also be extended for various low bandgap polymer systems, which are predominantly amorphous in nature. Advanced organometallic synthetic approaches also enable fine-tuning of the dopant energy levels to match those of the polymers. Besides, the versatility of the synthesis techniques also enables the incorporation of a range of functional groups to the metal complexes, which can then be used to moderate molecular aggregation via steric control and T_g adjustment. When the use of semicrystalline polymer is inevitable, there is an option to transform the polymers into nanostructures. Although the triplet sensitization of the nanofiber device presented in this chapter is yet to be fully optimized, it is obvious that the approach is promising; particularly when severe morphological issue occurs upon dopant incorporation.

5.4 Conclusions

In summary, it has been shown that the morphology and regioregularity of donor polymers plays significant role on the device performance of a ternary system. In the blend consisting of amorphous polymer such as regiorandom (ra-) P3HT, both fullerene acceptor and dopant molecules are distributed homogeneously, which results in a more preferable interaction between the active materials and the dopants. Semicrystalline regioregular (rr-) P3HT tends to crystallize and phase separate, promoting a more substantial aggregation of the small molecules in the ternary blend as compared to ra-P3HT. The small amount of active material/dopant interface also reduces the interaction among the blend components. Iridium

metal complex was added to improve the singlet-to-triplet exciton conversion. As expected, device performance enhancement was only observed in the amorphous ternary blend while the semicrystalline polymer blend experienced degradation in the device efficiency. The improvement in the device short-circuit current (J_{sc}) agrees well with previous reports on the other triplet-doped amorphous polymer systems, such as MEH-PPV:PCBM and MDMO-PPV:PCBM. Although there is no direct evidence that the triplet excitons are harvested, it can be inferred from the device data that triplet sensitization may have taken place.

The concept of ternary blends opens up the possibility of simple bulk heterojunction (BHJ) device enhancement through incorporation of an optoelectronically compatible material. As shown here, in order to obtain this enhancement, the issues of chemical nature and morphology of the polymers need to be carefully addressed as part of the optimization of blend morphology. The approach can be extended to other types of donor systems, in particular the low bandgap polymers, which are often reported to be amorphous in nature. The properties of dopant material have to match those of the active materials and if necessary, the dopant properties can be fine-tuned through various organic synthetic approaches. Furthermore, it is also possible to alter the organization properties of semicrystalline polymer by introducing some more bulky groups, which may interrupt the packing and hence prevents the aggregation of the dopant materials. This may give good performance if the charge transport characteristics of the original polymer are not compromised due to changes in the organization behavior of the polymers. If the morphology of the conventional semicrystalline polymer blend is severely affected by the dopant molecules, polymer nanostructures can be used instead. By using the new materials for the ternary devices, we hope more morphologically stable and efficient OPV devices can be realized through sensitization.

5.5 Experimental section

Materials Regioregular poly(3-hexylthiophene-2,5-diyl) rr-P3HT ($M_w = 50$ kDa, regioregularity > 90%) and regiorandom poly(3-hexylthiophene-2,5-diyl) ra-P3HT ($M_w = 95.8$ kDa) were purchased from Rieke Metals, Inc., while [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) (99.5% purity) was obtained from Nano-C®. The triplet metal complex, fac-tris(2-phenyl-pyridinato-C²,N)iridium(III) (Ir(ppy)₃) (99% purity), solvent 1,2-dichlorobenzene (*o*-DCB) (Chromasolv® HPLC grade, 99%) and *p*-xylene were purchased from Sigma Aldrich. Poly(3,4-ethylenedioxy-thiophene):poly(styrenesulfonate) (PEDOT:PSS)

(P VP Al 4083) was purchased from CLEVIOS™. All chemicals were used as received without further purification.

Device Fabrication The blend solutions were prepared by mixing rr-/ra-P3HT (10 mg/mL) with PCBM in *o*-DCB with weight ratio of 10:10. P3HT fiber suspension was prepared from slow cooling of P3HT solution in *p*-xylene (7 mg/mL), followed by 48h ageing. To prepare the ternary blend solutions, 5 wt% of Ir(ppy)₃ was added into the previously prepared binary blends of rr-/ra-P3HT:PCBM (P3HT:PCBM:Ir(ppy)₃ = 10:10:1). The D:A ratio for the nanofiber blend was 10:6, and the Ir(ppy)₃ amount was adjusted accordingly. The mixtures were stirred overnight at 50 °C in N₂ atmosphere, while the nanofiber blend was stirred at room temperature. The devices were prepared on indium-tin oxide (ITO) coated glass substrates (7 Ω/sq, Kintec Company). The substrates were consecutively ultrasonicated in cleaning concentrate (Hellmanex®), deionized water, acetone and isopropanol. After the substrates were dried under a stream of N₂, they were plasma cleaned for 2 min (Harrick PDC-32G plasma cleaner). Subsequently, PEDOT:PSS solution was filtered through 0.45 μm PVDF syringe filter and spin-coated onto the ITO-coated glass substrates at 3000 rpm for 60 s to give films of *ca.* 30 nm thickness. The PEDOT:PSS coated substrates were transferred into a N₂ glovebox and were baked on a hotplate at 140 °C for 10 min. The active layers were then deposited by spin-coating the blend solutions without any filtration at 700 rpm for 60 s, resulting in thicknesses of 90 ± 10 nm. TiO_x solution (in ethanol) was spin-coated at 1000 rpm followed by hydrolysis in the ambient for 1 h, to generate an additional buffer layer only for the nanofiber blend. To complete the device fabrication, *ca.* 100 nm of Al was deposited onto the samples in vacuum (< 10⁻⁶ Torr) resulting in devices with an active area of 0.1 cm². The rr-P3HT based binary and ternary devices were subjected to further post-deposition thermal annealing under N₂ at 150 °C for 20 min. No annealing was performed for the fiber-based devices.

Device measurement and blend characterization The electrical properties of the OPVs were characterized by measuring their current density-voltage (*J*-*V*) characteristics in ambient under AM 1.5G illumination with a sourcemeter (Keithley 2400). The light intensity was adjusted to 1 sun (100 mW/cm²) with an NREL-calibrated silicon photodiode. The obtained *J*-*V* characteristics were not corrected with mismatch factor. The UV-Visible absorption spectra of the blend films prepared on quartz substrates were characterized using Shimadzu UV-2510PC spectrometer. The film thickness was measured with a surface profilometer (Alpha Step 200, KLA-Tencor™). Atomic force microscopy (AFM) was done in tapping mode on the active layers of the devices with a surface probe microscope (Digital Instruments, Nanoscope IIIa). Near edge X-ray absorption fine structure (NEXAFS) spectroscopy and scanning transmission X-ray microscopy (STXM) were performed at the elliptical polarizing undulator (EPU) beamline 11.0.2 at the Advanced Light Source in Berkeley, California (USA). Photon energies of 280 eV, 284.8 eV and 286.2 eV were used for the STXM imaging. For both NEXAFS and STXM studies, the

samples were prepared by spin-coating the active material/ blend solutions on silicon nitride membranes. All measurements were done at room temperature in He atmosphere. Each image was taken within 5 – 8 min, which means that one molecule is exposed to X-rays for less than 10 ms. The radiation damage is negligibly low and does not influence the experimental results.

5.6 References

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CHAPTER
SIX

Summary and Outlook

6.1 Summary

Ever since the pioneering work done by Tang at Kodak in 1980s, the field of organic solar cells has grown extensively in less than three decades. The research in the field is also getting more competitive, as scientists and industry players are contending to improve not only the device efficiency, but also the lifetime and, ultimately, the cost of the solar cells. The milestone efficiency of organic solar cells is close to 10%, almost reaching a stage where commercialization might be viable. The efficiency breakthroughs are often supported by the use of new and better materials. Although the inherent advantage of organic solar cells is its low-cost solution processibility, the final module pricing should also include the cost of raw materials, which is often the bottleneck due to the low-yield, laboratory-scale synthesis. Furthermore, additional processing steps are generally required to enhance device performance. The application of organic nanostructures, which is the main subject of this thesis, provides an alternate approach by which the extra steps can be forsaken. The thesis focuses on the electrical and optical characterizations of the self-assembled P3HT nanostructures and their applications for organic solar cells.

The P3HT nanofibers demonstrate strong π - π interactions between the polymer molecules, affecting the optical and charge transport properties. The optical absorption is stronger and more red-shifted than non-fiber system, while the high degree of order along the nanofiber results in high charge mobility. In addition, the width of the nanofiber is within the range for exciton diffusion. Due to these features, nanofiber ought to be the ideal donor material for organic solar cells. Nevertheless, when used in the blend with PCBM acceptor, the nanofiber device performs below expectation. In terms of the device efficiency, nanofiber device demonstrates PCE of 2.4%, while the control device treated with conventional heat treatment reaches 3.6%. Further investigations reveal that nanofiber system may have suffered from loss in exciton quenching, greater charge recombination and poor charge extraction. By using time-resolved spectroscopy techniques, the root-cause of the poor device performance was found to be charge recombination. The problem is strongly related to the blend morphology, and this suggests that the morphology of most nanofiber systems is still suboptimal. Some P3HT fibers could be isolated from the others, and charges generated recombine before they could be extracted. Improving the interconnectivity among the nanofibers may circumvent the issue.

To verify the proposition on the fiber connectivity, the effect of mixed solvents on P3HT nanofibers was investigated. The self-assembly of polymer nanostructures, including both nucleation and growth steps, is largely dependent on the solvent environment. The second half of the discussion in Chapter 2 focused on the effect of the mixed solvent on the nanofibers and thus the device performance. To modify the growth conditions, a second solvent, chlorobenzene, is added into P3HT solution in anisole. Consequently, an improvement in the crystallinity, *i.e.*, more fibers, was observed. In the in-situ study using synchrotron SAXS, it was found that the onset of P3HT nucleation in the mixed solvent system occurs at lower temperature, producing an effect similar to supersaturation, and hence the system ends up with more nuclei. By having more nanofibers, the interconnectivity should also improve. The mixed-solvent system exhibits an improved efficiency by more than 50%, with PCE of 2.3% (In the single-solvent anisole system, the nanofiber device performance is 1.45%).

The mixed-solvent approach has huge potential in modifying the nanofiber device performance. However in order to establish the optimal nanofiber growth conditions, parameters such as solvent, concentration and temperature have to be varied and studied. A simpler approach is by adding high boiling point molecules, also known as “solvent additive”, into the blends, as described in Chapter 3. During the spin-coating process, the host solvent will be first removed, leaving the additive molecules to interact with the blend active components. To date, there are only two empirical rules to select the appropriate additive from the extensive libraries of molecules: (1) boiling point has to be higher than the host solvent and (2) additive needs to have selective miscibility with the active components. In this thesis work, a systematic study was performed based on dithiol molecules as additives for P3HT:PCBM, and it was found that the device performance does not have a direct correlation with both criteria. It was hypothesized that the phase separation of the active components that determines the morphology of the blend is highly dependent on both the strength of the intermolecular interactions and the duration of these interactions between the additive molecules and active components. With this in mind, the selection of the suitable additive for any blend system can be made, as long as the molecular interactions can be parameterized. For the non-fiber P3HT:PCBM blend, we obtain PCE of 3.1% with additive processing. When extended to the fiber system, the additive induces a more crystalline nanofiber blend, which suggests the crystallization of the non-fiber. The blend absorption was also found to improve

upon additive incorporation. A PCE of 3.1% was obtained for the nanofiber blend, which is comparable to the non-fiber counterpart. Therefore, this showed that additive processing could help to improve the blend morphologies and to reduce the device dependence on the processing solvents. Non-fiber P3HT is often prepared in halogenated solvents, in which the P3HT is highly soluble. With the solvent additives, it is now possible to obtain highly efficient P3HT nanofiber device prepared cast from different solvents. Since halogenated solvents are harmful towards the environment, the combination of nanostructuring and application of solvent additive can serve as a more environmentally friendly and thermal-free processing approach.

In Chapter 4, the application of pre-assembled P3HT nanofibers for polymer-polymer blends is discussed. Unlike polymer-small molecule system, such as P3HT:PCBM discussed in the previous chapters, polymer-polymer blends have often been reported to suffer from severe morphological issues, either extensive phase separation or intermixing. The extreme of either case is unfavorable for organic solar cell device, as it limits either the charge generation or the charge transport. P3HT:F8BT system is one such system which suffers from the latter situation, which is evident from the blue-shifted P3HT absorption in the blend and a much reduced blend crystallinity. With the use of P3HT nanofibers, the extent of the intermixing could be reduced. Consequently, both absorption and crystallinity are improved. In terms of device performance, the nanofiber P3HT:F8BT blend showed increase in both the photocurrent and PCE by 1.2 times as compared to the conventionally annealed blend. This result emphasizes the importance of the nanofiber to control the blend morphology.

If the absorption has to be enhanced in the infrared region since a huge fraction of the sunlight falls in the infrared range, theoretically an IR absorber can be added as the third component in the blend. This is the core concept of a ternary blend whereby a new component with complementary optoelectronic properties is added into a binary blend to improve the overall blend properties. The main limitation of this approach is the detrimental alteration of blend morphology when the third component is added. In Chapter 5, the effect of triplet sensitizer in the blends of P3HT and PCBM was presented. The sensitizer assists the conversion of singlet excitons to triplet excitons. The latter tend to have longer lifetime and can thus be converted into charges more efficiently. To probe the change in morphology, the sensitizers are added into the blends containing PCBM and P3HT of different regioregularities: highly regioregular (rr-) and regiorandom (ra-) P3HT; the former one is

semicrystalline in nature, while the latter one is amorphous. The sensitizer molecules aggregate more easily in the blend of rr-P3HT upon annealing, while they are more homogeneously distributed in the ra-P3HT blend. Thermal annealing is a prerequisite to improve the device performance of rr-P3HT:PCBM blend. On the other hand, one criterion for sensitization is that the sensitizer molecules have to stay close enough to the to-be-sensitized components, *i.e.* the P3HT molecules. Furthermore, the molecular aggregation may impede the charge transport. Consequently, favorable effect of triplet sensitization can only be observed in the amorphous regiorandom P3HT. In terms of the device performance, upon addition of the triplet sensitizer, PCE improves from 0.33% to 0.54% for ra-P3HT device, but it degrades from 2.98% to 0.81% for rr-P3HT. The approach can be extended for other polymer systems, most of which are amorphous and, therefore, may exhibit distinct effect of triplet sensitization.

It would be possible to also observe triplet sensitization in regioregular systems that have the propensity to aggregate. To do this, the process of thermal annealing to improve device performance has to be avoided. In order to avoid thermal annealing and yet have good device performance, P3HT nanofiber can be used for the ternary blends instead. The nanofibers are self-assembled from rr-P3HT, and are therefore good candidates to study the effect of morphology while keeping the same active components. Expectedly, the P3HT nanofiber system, which is able to retain the superior properties of enhancement in absorption and charge transport, demonstrates a slight improvement in PCE upon addition of triplet sensitizers. Again, this emphasizes the role of organic nanostructures to maintain the morphological stability of the blends.

6.2 Outlook

In this thesis, the potential of organic nanostructures for solar cell applications, as well as possible approaches to overcome their limitations has been shown. Although the research shown in this thesis is only based on poly(3-hexylthiophene) (P3HT), it is expected that similar properties can also be observed from the nanostructures self-assembled from other conjugated polymers and small molecules. Likewise, the concepts established, including solvent additive incorporation, all-polymer blends and ternary systems, can essentially be extended to other nanostructure systems. The formation of 1-D nanostructures is not only limited to polythiophene and its derivatives. There are accounts on other conjugated polymers that also

unveil the nanofibrillar morphology, such as PCDTBT with PCE exceeding 6% or diketopyrrolopyrrole polymer with PCE of 5.5%. The effects of molecular weight (M_w), polydispersity index (PDI) as well as end groups of conjugated polymers on the formation of organic nanostructures also need to be further explored to anticipate the batch-to-batch variation of the materials synthesized.

The other novel application of the organic nanostructures is by decorating them with other moieties with complementary properties. Conceptually, this is similar to the conventional ternary blend; however, it gives the freedom to manipulate the positioning of the dopants. For instance, dye molecules with absorption characteristics in the infrared region can be hybridized onto P3HT nanofibers. These hybrid nanostructures are expected to exhibit superior absorption properties. Furthermore, the morphology issue is unlikely to occur as the dye molecules only sit on the P3HT fibers. By selecting dyes with appropriate energy levels, the dye molecules may also assist the charge transfer between the P3HT donor and neighboring acceptor molecules. Definitely, the choice of the decorating units is not limited to dye molecules – semiconducting nanoparticles can improve absorption or metallic nanoparticles can induce plasmonic effect. By using these hybrid nanostructures, it is possible to achieve enhancement in optoelectronic properties, without having to deal with any morphological issues.

LIST OF PUBLICATIONS

1. *Influence of an iridium(III)-based sensitizer on nanoscale morphology and device performance of P3HT:PCBM solar cells*
Teddy Salim, Jun Yan Lek, Björn Bräuer, Denis Fichou and Yeng Ming Lam, *submitted to ChemSusChem*.
2. *Carrier dynamics in polymer-nanofiber:fullerene solar cells*
Michael Kurniawan, Teddy Salim, Kong Fai Tai, Shuangyong Sun, Edbert Jarvis Sie, Xiangyang Wu, Edwin Kok Lee Yeow, Cheng Hon Alfred Huan, Yeng Ming Lam and Tze Chien Sum, *submitted to Journal of Physical Chemistry C*.
3. *The role of poly(3-hexylthiophene) nanofibers in an all-polymer blend with a polyfluorene copolymer for solar cell applications*
Teddy Salim, Shuangyong Sun, Lydia Helena Wong, Lifei Xi, Yong Lim Foo and Yeng Ming Lam, *Journal of Physical Chemistry C*, 2010, **114**, 9459.
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Hairong Li, Shuangyong Sun, Teddy Salim, Swarnalatha Bomma, Andrew C. Grimsdale and Yeng Ming Lam, *Journal of Polymer Science Part A: Polymer Chemistry*, 2012, **50**, 250.