Morphology dependent photophysics in bulk heterojunction organic solar cells

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**MORPHOLOGY DEPENDENT PHOTOPHYSICS IN BULK
HETEROJUNCTION ORGANIC SOLAR CELLS**

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2017

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HETEROJUNCTION ORGANIC SOLAR CELLS**

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List of Abbreviations

AFM	Atomic Force Microscope
AM 1.5 G	Air Mass 1.5 global
B3LYP	Becke-Lee-Yang-Parr hybrid exchange co-relation three parameter function
BHJ	Bulk Heterojunction
BTU	British thermal unit
CT	Charge Transfer
CTS	Charge Transfer States
D	Donor
D/A	Donor/Acceptor
DFT	Density Functional Theory
EFT	Electric field Treated
ETL	Electron transport layer
EQE	External quantum efficiency
FF	Fill Factor
FWHM	Full Width Half Maxima
GIXRD	Grazing Incidence X-ray Diffraction
HOMO	Highest Occupied Molecular Orbital
IPCE	Incident photon to current efficiency
LUMO	Lowest Unoccupied Molecular Orbital
MESP	Molecular Electrostatic Potential Surface
nm	Nanometer
OLED	Organic Light Emitting Diode

OPV	Organic Photovoltaics
OSC	Organic Solar Cells
PCE	Power Conversion Efficiency
PL	Photoluminescence
PV	Photovoltaics
RMS	Root Mean Square
SCLC	Space Charge Limited Current
TFLC	Trap Filling Limited Current
TA	Transient Absorption
TAS	Transient Absorption Spectroscopy
UOS	Ultrafast Optical Spectroscopy
UV	Ultraviolet
UV-vis	Ultraviolet-visible
XRD	X-ray Diffraction
μm	micrometer

Materials

Al	Aluminum
ITO	Indium Tin Oxide
P3HT	Poly-(3-hexylthiophene)
P3BT	Poly-(3-butylthiophene)
PTB7	Poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]]
PCPDTBT	Poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)]

DRCN5T	(2,2'-((5Z,5'Z)-5,5'-((3,3'',3''',4'-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-ethyl-4-oxothiazolidine-5,2-diylidene))dimalononitrile
PCBM	[6,6]-thienyl C 61 Butyric acid Methyl ester
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene):Poly-(styrene sulfonate)
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
Si	Silicon
SiO ₂	Silicon dioxide

LIST OF SYMBOLS

d	Thickness of a Film
J	Current Density
J_D	Diode Current Density
J_L	Light Current Density
J_{ph}	Photocurrent Density
J_{sc}	Short-Circuit Current Density
J_{sat}	Saturation Current Density
k_B	Boltzmann Constant
n_e	Number of collected electrons
q	Charge of an Electron
R_s	Series Resistance
R_{sh}	Shunt Resistance

S	Number of photons available at a particular wavelength in AM 1.4G solar spectra
T	Temperature
V	Voltage
V_{bi}	Built-In Voltage
V_o	Compensation Voltage
V_{oc}	Open Circuit Voltage

Greek Symbols

β	FWHM of the Gaussian fit at the peak
ϵ_0	Free space permittivity
ϵ_r	Relative permittivity
η_A	Absorption Efficiency
η_{CC}	Charge Collection Efficiency
η_{CT}	Charge transfer efficiency
η_{ED}	Exciton diffusion efficiency
η_{EQE}	External quantum efficiency
μ	Charge carrier mobility
λ	Wavelength
θ	Angle

Abstract

The morphology of organic active layer plays a crucial role in the performance of organic solar cell devices. Understanding of charge carrier mechanism governed by the distinct morphologies of the active blend systems is required to enhance the power conversion efficiencies in solar cells. In this work, we have investigated the ultrafast photophysics in a wide range of active blend systems and correlated with their nano-morphology and optoelectronic properties in solar cell devices. External electric field treatment, inclusion of the solvent additive and solvent vapour annealing of the active layer were adopted as three different processing methods to modify the morphology of the active blend system in bulk heterojunction solar cells. External electric field treatment on the active layers based on semicrystalline donor polymers (*i.e.* P3HT and P3BT) promotes self-organization in the system and enhances the exciton/polaron generation, which results in improved device efficiency. On the other hand, inability of self-organization, complex molecular structure and larger molecular size of the amorphous donor polymers (*i.e.* PTB7 and PCPDTBT) make this approach unsuitable, resulting in invariant optoelectronic performance. Addition of a small fraction of poor solvent in P3HT:PCBM blend system is a room temperature processing approach to improve the device efficiency, which is suitable for roll-to-roll applications. The performance enhancement by solvent additive is comparable to the thermally annealed devices, however certain additives cause strong phase separation of the donor and acceptor, which result in higher charge carrier recombination. Similar to conjugated polymer systems, the suppression of charge carrier losses is also important in solution processed small molecule blend system. Solvent vapour annealing of DRCN5T:PCBM active blend layer helps to reduce the predominant monomolecular recombination in the finely mixed system. Hence, this improved the performance from 3.3 % to 10%. This work provides new in-depth understanding on the morphology dependent charge carrier dynamics, which will lead to further improvements in organic solar cell devices.

Publication List

- Ankur Solanki, Bo Wu, Yeng Ming Lam and Tze Chien Sum, “Correlation between blend morphology and recombination dynamics in additives-added P3HT:PCBM solar cells”, *Phys. Chem. Chem. Phys.*, **17**, 26111-26120 2015- **doi:10.1039/C5CP03762J**.
- Ankur Solanki, Bo Wu, Yeng Ming Lam and Tze Chien Sum, “Charge dynamics in alkanedithiols-additives in P3HT:PCBM bulk heterojunction solar cells”, *Proc. of SPIE* Vol. 9184, San Diego 2014 - **doi:10.1117/12.2061434**.
- Ankur Solanki, Bo Wu, Teddy Salim, Edwin Kok Lee Yeow, Yeng Ming Lam, and Tze Chien Sum, “Performance Improvements in Polymer Nanofiber/Fullerene Solar Cells with External Electric Field Treatment”, *J. Phys. Chem. C*, **118**, 11285 – 11291, 2014 - **doi:10.1021/jp5040097**.
- Ankur Solanki, Anirban Bagui, Guankui Long, Bo Wu, Teddy Salim, Yongsheng Chen, Yeng Ming Lam and Tze Chien Sum, “Effectiveness of the external electric field treatment on conjugated polymers in bulk-heterojunction organic solar cells”. *ACS Appl. Mater. Interfaces*, **8**(47), 32282–32291, 2016- **doi:10.1021/acsami.6b08012**.
- Guankui Long, Bo Wu, Ankur Solanki, Xuan Yang, Bin Kan, Xinfeng Liu, Miaomiao Li, Xiangjian Wan, Tze Chien Sum and Yongsheng Chen, “New Insights into the Correlation between Morphology, Excited State Dynamics and Device Performance of Small Molecule Organic Solar Cells”. *Adv. Energy Mater.* **6**, 1600961, **2016**. **doi:10.1002/aenm.201600961**.

Chapter 1

Introduction

1.1 Background

Issues of General Interest: Renewable Energy and Photovoltaics

Modern civilization is highly dependent on energy. Our daily activities from small scale applications such as home appliances to large scale industries are all driven by energy. The energy demand in the modern world is increasing every year as it can be seen from the plot of annual world energy consumption as shown in **Fig 1.1**.¹ World's primary energy consumption has increased ~86% in last three decades and will continue to rise rapidly with the establishment of new metropolitan cities and large scale industries around the world. To accomplish these requirements, our dependency on fossil fuels like coal, petroleum, oil, and natural gas to meet its energy requirements has also increased. Some of the techniques employed to harvest the energy from these resources has been recognized as causing heavy environmental pollutants. Since all these energy sources are non-renewable, we are concerned about their complete depletion in near future.

Figure 1.1: World's total primary energy consumption by year in quadrillion BTU. (1 British thermal unit = 1055 Joule). Source:, U.S. Energy Information Administration.¹

In view of the increasing energy demand, renewable sources are alternatives which also have advantages of being perpetual and environment friendly. These are widely available and well suited for applications in off-grid remote locations. In addition, photovoltaic technology has other advantages such as being noiseless, can be aesthetically pleasing when incorporated into building designs and allow for small-scale plant deployment in unused areas compared to other renewable sources. The potential for the different renewable energy sources is listed in Table 1.1. It clearly shows that solar energy (photovoltaics) has the maximum potential to meet the increasing energy demands.^{2,3} According to the world energy scenario report from the energy revolution series for the year 2010 prepared by the Greenpeace International and the European Renewable Energy Council, the cost of PV energy is expected to reduce drastically over the next few decades as the installed capacity increases.⁴

*Table 1.1 The renewable energy potential³

Energy Source	Generation potential (billion kW-h)
Photovoltaics	283,664
Wind	49,760
Biomass	488
Hydro	536
Solar Concentrators	116,146
Geothermal	31653

*Source: "U.S. Renewable Energy Technical Potentials: A GIS-Based Analysis", National Renewable Energy Laboratory, July 2012.

There is potentially an inexhaustible supply of energy resources to sustain the worldwide demand, ranging from photovoltaic, wind, biomass, hydroelectric and geothermal, (Table 1.1). To illustrate this abundance, the approximate annual solar radiation received on the earth after reflection by the upper atmosphere is 283,664 billion kW-h. It shows that by simply harnessing the solar energy efficiently for a day, it is more than sufficient to sustain global energy consumption for whole of the next decade. This bright outlook on solar energy provides a huge motivation for moving towards PV as the major source for energy production to improve the existing PV systems and enable them to take lead over other sources.

Since the discovery of photovoltaic effect by Becquerel in the early 19th century, silicon solar cell has progressed tremendously in terms of performance with the best-reported PCE of 26% based on monocrystalline silicon.⁵ However, to achieve the higher performance of the solar cells, it is possible to use the multi-junction technologies, which allows the capture of a wider spectrum of sunlight. To date, the best certified efficiency reported for multi-junction solar cell is 46%.⁶ The data collected from national renewable energy laboratory for some of the best efficiencies of different kinds of solar cells are listed in Table 1.2.

Table 1.2 certified highest efficiencies of various types of solar cells measured under standard solar spectrum.⁶

Type of Solar cell	Highest Efficiency Reported (%)
Multi-junction	46.0
Si(Single Crystal)	26.0
GaAs (Thin Film Crystal)	28.8
CIGS (Thin Film)	22.6
CdTe (Thin Film)	22.1
Dye-Sensitized (Thin Film)	11.9
Amorphous Si (Thin Film)	13.6
Perovskite	22.1
Organic (Thin Film)	11.5

*Data is presented till December 2016.

Although multi-junction solar cells demonstrate higher efficiency, they have comparatively higher cost of production relative to their thin film counterparts using materials like amorphous Si, Copper Indium Gallium Selenide (CIGS), CdTe, GaAs, etc. Also, the processing of both single crystal and multi-junction crystalline solar cells is highly energy-intensive.⁷ The substrate preparation and thin film deposition covers the major part of the production cost in thin film solar cells technology. In this aspect, organic solar cells are an attractive alternative. These solar cells have the potential to be manufactured using low-cost, flexible and low-temperature processing methods. In addition, organic photovoltaic materials are bio-degradable^{8,9} which can solve the problem of disposing the solar cells after their lifetime. Thus, these solar cells can become environmentally friendly. All these aspects provide great motivation to develop organic photovoltaic (OPV) systems.

1.2 Organic Solar Cells

Generally, organic solar cells (OSCs) are widely categorized into two types based on the kind of photoactive materials used as (a) Conjugated polymer based OSCs and (b) Small molecule based OSCs. The former OSCs are fabricated by solution processing techniques while the latter are

fabricated using thermal evaporation (some small molecules are also developed which are solution processed). In both kinds of OSCs, the required amount of energy to fabricate cells is considerably lower than inorganic cells using conventional methods. In addition, lightweight, mechanical flexibility as well as having the capability of tuning the optoelectronic properties during the synthesis and processing are the other advantages. Organic light emitting diodes (OLEDs) are the best example of this technology which contains all the mentioned features and available commercially.

In the PV market, polymer solar cell technology has also taken the lead in solution processing and large scale industrial manufacturing of solar panels has also began recently.^{10 11,12} A flexible and light weight manufactured panel is shown in **Fig. 1.2**. Some building-integrated photovoltaic modules are also being developed which contain transparent and flexible solar cells.¹³ In terms of life time and efficiency, these solar cell modules are still under performing compared to those of inorganic solar cells. The highest certified efficiency of an organic sub module is presently at 5.5%, reported by Imec and Solvay.¹⁴ Hence, this field needs to be pursued further in order to reach the ultimate goal of developing of cheaper, more efficient, and easily accessible PV technology.

Figure 1.2 Flexible organic solar cells (Photograph source: www.pinterest.com).

1.2.1 Advantages of Organic materials: Besides the nature of the flexibility, low-temperature processing and cost effectiveness, the pursuit of OSC has other important unique benefits from the basic device operation point of view.¹⁵ These include:

1. Tuning of the molecular properties: Organic materials possess the versatility for their molecular properties to be tailored for various applications. Tuning of the bandgap, molecular weight, conjugation length and functional group is possible through molecular engineering. Moreover, new compounds can also be developed with the incorporation of the inorganic part and explored for flexible applications.

2. High absorption coefficient: These photoactive materials have higher absorption coefficients values in the range 10^5 cm^{-1} .¹⁵ Such intrinsic property of the material enables to make thinner devices, typically up to only a few hundred nm¹⁶ and reduce the material usage.

3. Efficient ultrafast charge generation mechanism between donor and acceptor materials: The electron donation from donors to acceptors has been shown to be very efficient and to take place in the time scales of sub-pico seconds.¹⁷

Poly-(3-hexylthiophene) (P3HT) as the donor and [6,6]-thienyl C₆₁ butyric acid methyl ester (PCBM) as the acceptor are the organic materials mainly used in this work. **Fig 1.3** shows the chemical structures P3HT and PCBM.¹⁶

Figure 1.3 Chemical structures of the organic materials used in this work. (a) poly-(3-hexylthiophene) (P3HT) which is a conjugated polymer. (b) [6,6]-thienyl C₆₁ butyric acid methyl ester (PCBM) which is a functionalised C₆₀ fullerene. P3HT and PCBM are donor (electrical conduction is dominated by holes) and acceptor (electrical conduction is dominated by electrons) materials respectively.

1.2.2 Disadvantages of Conjugated Polymers: Apart from the above mentioned advantages, achieving highly efficient device remains a highly challenging task because there are certain drawbacks with these organic materials. The most important of them are as follows:

1. Limited absorption range: Though the capability of the absorption tunability of organic photoactive materials in entire solar spectrum, most commonly used materials like polythiophene and other recently developed small molecules absorb a narrow part of the entire solar spectrum (visible). **Fig 1.4** displays comparison of the absorption spectra of some of the commonly used organic semiconductors to the solar spectrum.¹⁵ The lack of crystalline structure of these kind of materials is the main cause of this which results in low bandgap of the π and π^* bands. Thus, to harvest the complete solar spectrum in a solar cell device, a multi-layers structure has to be used possibly in a tandem solar cell structure.

Figure 1.4 Comparison of absorption coefficients of commonly used organic semiconductors with photon flux of standard AM 1.5G solar spectrum.¹⁵ It can be clearly seen that the absorption band of any of these materials does not cover the entire range of the solar spectrum.

2. Low charge carrier mobility: Organic semiconductors are heavily disordered materials by nature where intrinsic hopping is the basic charge carrier transport mechanism. The hopping of the charges in these materials is thermally activated and affected by both positional and disorders energetic and hence the mobility.¹⁸ Consequently, the organic materials show the mobility much lower than that of their inorganic counterparts. Typical reported bulk mobility values are of the order of 10^{-7} to $10^{-2} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ for organic solar cells.

3. High exciton binding energy: In organic materials, photo-absorption always produces localized bound excitons having large binding energies due to their low dielectric constants (typically in the range of 2 to 4). In some cases, the binding energy can be more than 1 eV.¹⁹ Hence, room temperature thermal energy of 0.026 eV is insufficient to dissociate the excitons, unlike in inorganic semiconductors. The presence of asymmetric junctions is required to dissociate these excitons. However, low exciton diffusion lengths (typically in the range of 5 to

20 nm)²⁰, causes a larger population of excitons to recombine before reaching a junction. The bulk heterojunction (BHJ) structure is thus developed to overcome this problem. The details of BHJ device structure are discussed in the next section.

1.2.3 Mechanism of Organic Bulk Heterojunction Solar Cells

In BHJ structure, numerous combinations of polymers as donor and fullerenes as acceptors have been used to attain high efficiency solar cell devices. Here the donor represents the electron donating material and acceptor represents the electron accepting material. In these materials, polarons are the fundamental charge carriers. Therefore, the transport mechanism should include charge movement along with the local distortion of the molecule. For the conventional p-n junction, donor conducts the holes, hence it can be considered as p-type material; while the acceptor conducts the electrons, therefore it can be considered as n-type material. Moreover, due to the higher defect density as compared to traditional inorganic semiconductors (*i.e.* Si, Ge etc.), these materials are relatively lower conducting materials.

The fundamental operating principle of BHJ solar cells can be divided into four basic steps and will be explained with the help of the following cross-section schematic (**Fig. 1.5**), energy level diagrams (**Fig. 1.6**), and device schematic (**Fig. 1.7a**).²¹⁻²³ In the first step of the operation, absorption of the incident light takes place by the both materials (donor and acceptor) in their respective wavelength ranges and results in the excitons generation in them. P3HT and PC60BM are widely used donor and acceptor respectively and also used as photoactive materials in this research work. Since the exciton generation yield is higher in the donor than those generated in the acceptor, the exciton generation is mainly considered to be in the donor for the following discussion. However, some other acceptors which absorb photons in blue and green wavelength region have also emerged recently. PC70BM is one of the best example based on

fullerene acceptors. Since exciton entity is electrically neutral hence we can assume that these remain unaffected by an electric field. These excitons are also known to be Frenkel-type due to their higher binding energy (order of $\sim 1\text{eV}$).

Figure 1.5 Cross-sectional schematic of the active layer of a polymer-fullerene solar cell showing the various steps of photo-carrier generation. Each of the steps with regards to photon absorption, exciton formation, polaron generation, and charge transport are explained in the text.

In the second step of BHJ operation, excitons in the donor material diffuse from a high to low concentration region (**Fig 1.5**). During diffusion towards the nearest D/A interfaces, the probability of annihilation rises with the increase of distance. Generation of excitons in the donor near the interface (within 10-20 nm as exciton diffusion length) is important to overcome the annihilation process. However, the good intermixing of donor and acceptor in photo-active layer of bulk-heterojunction solar cell structure easily provides D/A interface for the exciton dissociation

Dissociation of the excitons at the D/A interfaces is the third step of BHJ operation. At the D/A interface, excitons dissociate into positive and negative polarons (i.e. generate a polaron pair which is energetically favourable). The positive polaron remains in donor while the negative polaron is transferred to the acceptor. These polaron pairs are called charge transfer (CT) states,

which are not completely spatially separated from each other and may still recombine. Such recombination process is known as geminate or monomolecular recombination. Several models have been proposed to explain the role of CT states in OSCs operation. According to the Onsager-Braun model, the relaxation of the hot CT states (generated from the exciton quenching) to the lowest CT state is very fast (~ 100 fs scale).^{24,25,26} Theoretically, these CT states are long lived (~ 10 μ s,²⁷) but these are found to be very short lived ($\sim$ ns)²⁸ in experiments. Recently it was found that the hot CT states in certain D/A systems are highly delocalized and easily dissociate into free charges but also behave conversely in some other systems (poly[(9,9-dioctylfluorene)-2,7-diyl-alt-(4,7-bis(3-hexylthien-5-yl)-2,1,3-benzothiadiazole)-2',2''-diyl] - F8TBT).²⁹ Moreover, direct generation of polarons are also seen in single-junction regioregular P3HT film, with generation efficiency $\sim 30\%$.³⁰

After separation, free positive and negative polarons migrate through the donor and acceptor phases towards the anode and cathode, respectively and subsequently get collected at the respective electrodes (fourth step of the process). However, free polarons also encounter their oppositely charged counterparts during the transport and recombine. This loss channel is termed as non-geminate or bimolecular recombination which is always dependent on the polaron density. The remaining charges that did not undergo recombination can also be trapped during transport and may not be collected at the respective electrodes. As a result, charge collection efficiency at electrodes is always lower than charge generation efficiency. In addition, lower charge carrier mobilities in organic semiconductors also generate space charges, which in turn limit the overall photocurrent density J_{ph} generated from the device. Therefore, charge carrier mobilities are also very crucial characteristics of these materials, which is highly dependent on the degree of the ordering of the donor and acceptor phases. Typically, organic semiconductors

have very low charge carrier mobilities, ranging from 10^{-6} to $10^{-3} \text{ cm}^2\text{-V}^{-1}\text{s}^{-1}$, while highly crystalline inorganic semiconductors exhibit higher mobility ($\sim 10^2 \text{ cm}^2\text{-V}^{-1}\text{s}^{-1}$).³¹⁻³³ In BHJ solar cells, donor and acceptor phases are randomly intermixed with each other. For efficient BHJ, the selection of the photo-active materials (i.e. donor and acceptor) and their distribution (i.e. blend morphology) are two key criteria. The maximum amount D/A interfaces are required for efficient exciton generation in this configuration. They must be balanced with sufficient continuous percolation pathways which are important for uninterrupted charge transport. The optimization of the exciton dissociation and transport by controlling the blend morphology is an alternative for higher photocurrent generation. Certain properties of organic materials such as molecular weight, regioregularity, molecular design, side groups etc. are morphology determining factors in the blend system.³⁴ Moreover, the selection of the host solvent, blend composition and processing conditions are other external factors which strongly influence the blend organization.^{32,35-37} Therefore, to make efficient BHJ solar cell devices it becomes vital to engineer the percolation pathways for both charge carriers to ensure minimum losses and efficient charge transport to the respective electrodes.

Figure 1.6 Simplified energy level diagrams of polymer-fullerene bulk heterojunction solar cell under short circuit condition. These energy levels represent the HOMO and LUMO levels of polymer and fullerene. These correspond to π and π^* bands respectively. The thick dark lines represent the two electrodes. Four steps (photon absorption, polaron generation, charge transport and charge collection) in the process of photogeneration are explained in the text with the help of these figures. (Courtesy: Arun Tej, Indian Institute of Technology Kanpur)

1.2.4 Device architecture

Bulk-heterojunction is the commonly used device architecture as shown in **Fig 1.7**. This architecture consists of a transparent electrode ITO (Indium-tin-oxide) as anode and aluminum as cathode. Poly(3,4-ethylenedioxythiophene):Poly-(styrene sulfonate) (PEDOT:PSS), nickel oxide (NiO_x), tungsten trioxide (WO_3) etc. are the hole transport layers (HTL) which are inserted between anode and active layer. Lithium fluoride (LiF), calcium (Ca), titanium oxide (TiO_x) etc. are the optional electron transport layers (ETL) between cathode and active layer. These layers facilitate easier charge transport to their respective electrodes by suppressing the interface barrier. A blend of the donor and acceptor materials which is the main photoactive layer to

absorb the photon and generate free charge carriers is sandwiched between PEDOT:PSS (HTL) and ETL (or cathode).

Figure 1.7 Device architecture of BHJ solar cell device.

1.2.5 Organic solar cell device Physics and analysis

The simplest organic semiconductor device is the metal-insulator-metal diode with asymmetric work function metal electrodes as shown in **Fig 1.8(a)**, with the assumption that the non-illuminated polymer has a negligible amount of intrinsic charge carriers and can therefore be regarded as an insulator. Due to the asymmetry of the work function of the two electrodes the forward bias current for a single charge carrier material is orders of magnitude larger than reverse bias current at low voltage.

Short circuit current: **Fig 1.8(b)** shows the energy level diagram of BHJ in short circuit condition under illumination. In short circuit condition the Fermi Level of the two electrodes aligns together and therefore zero potential exists across the device. When light is incident on the device, the excitons and subsequently charge carriers are generated. Generally, the work function of the anode is considerably higher as compared to the cathode. This leads to the origin of electric fields inside the device and generate a drift current which is termed as short circuit

current (J_{SC}). In bulk heterojunction system, J_{SC} depends on several parameters including absorption spectrum, absorption coefficient, hole and electron mobilities, charge carrier lifetime, film morphology and the incident light intensity.^{38,39} The charge carrier mobilities and their lifetime are real material parameters and therefore determined by the nano-morphology of the active layer. J_{SC} also depends on proper organic/electrode interface because poor contact may lead to high resistance region, which causes a drop in most of the in-built field.⁴⁰

Figure 1.8: Energy level diagram for (a) Metal-organic semiconductor-metal (E_g is the band gap of semiconductor) (b) short circuit condition (c) flat band or open circuit condition (d) at forward bias voltage.

Open circuit condition (V_{OC}): Under the open circuit condition, as depicted in **Fig 1.8(c)**, the photo generated current is zero across the device. Under this condition, the diffusion current originated from the charge diffusion is balanced by the equal and opposite drift current which is due to the finite field across the device. This field leads to the potential difference across the electrodes and hence the open circuit voltage in device. V_{OC} is limited by several factors including interfacial energy levels, shunt losses, interfacial dipoles and morphology of the active film. For bulk heterojunction organic solar cells with Ohmic contacts, V_{OC} is mainly determined

by the difference between the HOMO of the donor polymer and the LUMO of the acceptor polymer.⁴¹

Fill Factor (FF): The fill factor (*FF*) is defined as the fraction of the photogenerated charge carriers that are collected at the electrodes, which is in fact a competition between charge carrier recombination and transport.⁴¹ The *FF* of a device is defined as:

$$FF = \frac{J_{mpp} \times V_{mpp}}{J_{sc} \times V_{sc}} \quad (1.2)$$

The maximum power point (*MPP*) represents a point along the *J-V* curve with the highest power product per area (i.e. $J_{MPP} \times V_{MPP}$) as shown in **Fig 1.9(a)**. High *FF* values are expected for diode with a strict selection principle for the separation of positive and negative carriers. There are two main loss mechanisms that suppress the *FF*; (i) high series resistance (R_s), which flattens the *J-V* characteristics and thereby reduce J_{sc} , and (ii) low shunt resistance (R_{sh}), which reduces the open circuit voltage by leakage currents. For high fill factor, R_{sh} should be high to reduce leakage current and R_s should be low to increase the collected current.^{42,43}

Fig. 1.9(a) shows the typical current density-voltage (*J-V*) characteristics of a solar cell device. At certain illumination intensity (P_{in}), the power conversion efficiency (PCE) of a device can be calculated using the relationship:

$$PCE = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}} \quad (1.3)$$

Figure 1.9: (a) Current density-voltage (J - V) characteristics plot and (b) equivalent circuit model for solar cell

Fig 1.8(b) shows the equivalent circuit diagram used for organic solar cells. The current source (I_L) in this model depicts the current generated from the illuminated device, shunt resistance (R_{sh}) represents the losses due to recombination of charge carriers and series resistance (R_s) represents the conducting resistance of the device. R_{sh} is the inverse of the slope of I - V characteristics around 0 V.

$$R_{sh} = \left[\frac{dI}{dV} \right]_{V=0}^{-1} \quad (1.4)$$

R_{sh} gives the potential leakage current through the device. R_{sh} should be maximum to achieve high efficiency cells. Generally, R_{sh} is inversely proportional to the thickness and light intensities^{44, 45}. Series resistance R_s of device is dependent on various parameters like the charge mobility, thickness, trap density and electrode contact resistance. R_s can be estimated from the inverse slope of I - V characteristics at a positive voltage around V_{oc} .

$$R_s = \left[\frac{dI}{dV} \right]_{I=0}^{-1} \quad (1.5)$$

Moreover, the ohmic contributions of the electrode and the contact between the organic semiconductor and the metal also contribute to R_S . Besides, R_S reflects the capability of the organic bulk to transport charge carriers. R_S has to be lowered to ensure a maximum efficiency.

1.2.6 Efficiency limiting factors

Under illumination, current flows in opposite direction of the injection current. The electric current corresponds to the number of incident photons and therefore the created charges. The fraction of photons to create charge carriers can be described by equation (1.6). It depends on the fraction of absorbed photons η_{Abs} , the fraction of dissociated excitons η_{diss} , and the fraction of separated charges η_{out} that reach the electrodes.⁴⁶

$$\eta_{PCE} = \eta_{abs} * \eta_{diss} * \eta_{out} \quad (1.6)$$

The fraction of absorbed photons η_{Abs} can be tuned by the absorption spectrum of the materials, its absorption coefficient, its thickness and the number of internal reflections. The fraction of dissociated excitons η_{diss} is determined by the fraction of the diffused excitons at the dissociation site (polymer-electrode or polymer-fullerene interface) and the fraction of dissociated excitons at these interfaces before decaying. The fraction of separated charges that reach the electrodes η_{out} is controlled by the morphology of the active layer as well as the electrodes work-function.⁴⁷ Thus, the efficiency of organic solar cell mostly depends on the selection of the absorber (for the efficient photon absorption and charge generation), combination of D/A (for higher V_{OC}), active layer morphology (for efficient charge transport) and selection of electrodes (for the efficient charge collection).

1.3 Organic nanostructured solar cells and ultrafast dynamics

In addition to the BHJ, one dimensional (1-D) nanostructures have also emerged in the last few years showing great potential and also garnering significant attention in the community.⁴⁸⁻⁵⁰ This group of structures is able to provide the anisotropic excitonic confinement along their long axis and improved fluorescence may also be acquired due to the extension of the exciton diffusion length in the structure. Moreover, there are certain advantages of using the nanostructures in OPV. These are: (1) easier to control the blend morphology, (2) dimensions of the nanostructures are comparable to the exciton diffusion length, (3) better exciton diffusion within the same crystalline region (4) interpenetrating network for uninterrupted charge carrier transport, (5) thermal free approach well-suited for the flexible technology and (6) improved stability.⁵¹

Different 1-D nanostructures such as nanotubes, nanofibres, nanoribbons etc., can be produced using the appropriate tactics like molecular self-assembly, nanolithography template-assisted synthesis, electrospinning, layer-by-layer (LBL) deposition, etc.^{49,50,52} Two different types of approaches have been introduced to grow the nanostructures: (a) hard template and (b) soft template approach.⁵¹ The hard template approach is generally used to fabricate hard 1-D nano-structures such as nanorods, nanowires and nanotubes. Some other nanomaterials such as polyaniline (PANI) and polypyrrole (PPy) have also synthesized using this approach. In the soft approach, surfactants, liquid crystals, block copolymers etc. are employed to develop the nanostructures. Supramolecular self-assembly of π -conjugated polymers has developed as one of the best approach of produce the nanostructure. This approach is mainly subjected to the intermolecular interactions among the molecules or between the molecules and substrates and can be employed both in bulk solution and at the interfaces or surfaces. Nevertheless, Kim et al.⁵¹ also pointed out the simplicity, large-scale synthesis, fine tuning of the dimensions, high

reproducibility and possible hybridized nanostructures, as the advantages. The self-assembly of P3HT has also been successfully demonstrated several nanostructures such as nanofibers,⁵³ nanowires,⁵⁴ nanosheets,⁵⁵ and 2-D nanoribbons⁵⁶. In this thesis, we will focus on the solution-phase self-assembly of the organic nanostructures because of its adaptability in generating reproducible structures. Both nanofibers and nano-domains are generated in P3HT (Poly(3-hexylthiophene)) and DRCNT ((2,2'-((5Z,5'Z)-5,5'-((3,3'',3''',4'-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-ethyl-4-oxothiazolidine-5,2-diylidene))dimalononitrile) as the donor materials for solar cell applications. To further organizing the distribution of the orderderd/disordered structures of in different D/A, an external electric field treatment was used as an alternative approach.

The discovery of the ultrafast mechanism in BHJ solar cells has opened a new field for optimization of the morphology by creating the bicontinuous inter- penetrating network with optimal domain size.^{57,58} For the highly efficient BHJ structure, an interpenetrating morphology along with large amount of D/A interfacial area is the most common believed objective of the research. In this structure, excitons are believed to diffuse to the interface where dissociation is energetically possible.⁵⁹ However, in over-phase-separated nanostructure (>20 nm in size), diffusion of the excitons over such distance within its life span appears to be impossible where it requires hundreds of picoseconds.⁶⁰ In addition to this, ultrafast charge carrier formation (~100 fs) has also been observed in some BHJ system which accounts for the yield of the free charges responsible for the device performance comparable to one Sun illumination. A block diagram, drawn in **Fig. 1.10** provides a complete picture of the time scale range of all mechanisms from photo-absorption to the charge extraction in BHJ solar cell devices. It should be noted here that the given time value is an approximate range reported by several research groups mainly for the

most common P3HT:PCBM BHJ. Two life times from exciton to polaron generation assigned to two different mechanisms. The prompt charge generation (~ 1 ps) occurs usually in finely mixed phase of acceptor and donor phase while delayed generation (~ 300 ps) occurs due to the migration of excitons to the interface in the larger and well separated polymer domains. These polaron pairs are also called geminate pairs, charge transfer states, loosely bound exciton or bound radicals. The dissociation of polaron pair to free polaron occurs very fast, on the scale of 100 fs. Comparatively, process of the charge transport and collection at the electrodes takes a longer time. Within 10 μ s most of the charges are collected at their respective electrodes under short circuit condition. A schematic depicting the photo-physical mechanism at the D/A interface is also shown in **Fig 1.11**. Hence to achieve the best nanomorphology of the BHJ, new molecules are being designed with optimum optoelectronic properties such as bandgap, energy levels and absorption wavelength range to enhance of the power conversion efficiency.^{61,62} The importance of nano-morphology for efficient solar cells was also confirmed by structural characterization techniques such as scanning probe microscopies, X-ray scattering and numerous type of electron microscopies.³⁹

Figure 1.10 Block diagram of typical photo-physical mechanism displaying their approximate time scale.

Figure 1.11 Schematic diagram depicting the typical photo-physical process and their approximate time scale at polymer:fullerene interface in BHJ solar cell.

1.4 Scope and objectives

Study of the different approaches used for various D/A systems in OPVs applications and investigation of their fundamental photophysics are the main objectives of this work. P3HT, as one of the widely used conjugated polymer in organic devices is used as the focus to study

different nanostructures. DRCN5T ((2,2'-((5Z,5'Z)-5,5'-((3,3'',3''',4'-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-ethyl-4-oxothiazolidine-5,2-diylidene))dimalononitrile), a recently developed highly efficient (~10%) small molecule is also included as the different category of the organic material for OPV to broaden the scope of the study. The objectives of this thesis are to: (a) develop different approaches to improve the performance of the various nanostructured BHJ solar cell devices, (b) investigate the structural and electrical properties of different blend films and to correlate them with solar cells performance, (c) gain a clear understanding of the effects of developed approaches (electric field/ additives/solvent annealing) on the carrier dynamics in organic PV materials (d) correlate the carrier dynamics from ultrafast optical spectroscopy (UOS) with electrical probes, and (e) to gain a clear understanding of the origin/mechanisms of the device enhancement following electric field treatment/adding of additives and solvent annealing.

In-depth study of such BHJ structures is necessary to gain a better understating of the limiting factors of OSC device performance. On the basis of the optical and time resolved characterization, either geminate or non-geminate recombination mechanism was found to be the major limiting factor depending on the morphology of the D/A systems. The external electric field treatment of the P3HT nanofiber-based devices helped to improve the device performance but the non-geminate recombination of the charge carriers remains the main loss channel. Therefore, (i) blend morphology of the blend systems and (ii) charge carrier extraction pathways, strongly determine the recombination dynamics of the system and device performance thereof. However, this method is not applicable for all organic materials used for OPVs. Thermal annealing of the active blend layer in the presence of external electric field promotes self-organization in semi-crystalline conjugated polymers and improves device performance. The

inability of self-organization of polymer chains in intrinsically amorphous blend systems causes ineffective electric field and molecular dipole interaction and hence the invariant device performance. On the other hand, inclusion of "solvent additive" to optimize morphology by crystallization of the disordered phase in P3HT is another thermal-free approach to enhance the overall device performance. Certain thiol-based additives definitely promote the crystallization in P3HT system and reduce the charge recombination but over-crystallization invites the dominance of trap-assisted geminate recombination with lower average charge carrier lifetime as compared to the optimum morphology. Charge carrier dynamics are directly correlated to the blend morphology induced by the different solvent-additives and solar cell device performances. In the series of the development of new organic materials, DRCN5T (which is a small molecule) is also developed as donor material for solution processed high efficiency photovoltaic devices. Solvent thermal annealing of the blend active layer based on this small molecule improves the devices efficiency by changing the finely mixed grain system to the well phase separated fibrillar crystalline structure. Fine intermixing of the D/A causes the formation of the strongly bound charge transfer states which do not contribute to the free charges and recombine to the ground state. However, solvent thermal annealing of this system causes the conversion of most of these states into free charges which are easily collected at their respective electrodes, resulting in improved device performance.

1.5 Thesis outline

The organization of work of this thesis is divided into six chapters including the present chapter. This chapter is the introduction of the thesis which provides the background information of the solar cell, including basic operational mechanism and recent developments of the organic

nanostructures for the solar cell applications. It also includes the motivation behind the research. The second chapter explains the methodology used for the optical and electrical characterization of films and solar cell devices respectively. In the third chapter, the effect of the external electric field treatment during the drying of P3HT-nanofibers based blend film is presented. By analyzing the current – voltage characteristics of electric field treated and control device, the charge transport properties and solar cell device performance is determined. Further, the performance of these devices is correlated with the charge carrier dynamics. In the fourth chapter, the relation between morphology and external electric field treatment is investigated using different conjugated polymers with different intrinsic morphologies. In addition to the ability of self-organization, the monomer structure of organic molecules is also found to be the limiting factor for constructive performance of devices although these conjugated polymers have higher electric dipole moment. In the fifth chapter, it is demonstrated that certain thiol-based solvent additive can further improve the morphology of the P3HT:PCBM blends and can enhance the device efficiency of approximately three times of the pristine device. These results are validated using time-resolved measurements and the recombination mechanisms are investigated. In chapter six, a systematic investigation of the origin of the enhanced device performance in small molecule based devices by solvent thermal annealing have been carried out, and the relationship between charge generation dynamics and device performance is established. Large amount of strongly bounded CTSs were formed in the pristine BHJ blend due to the well-miscible morphology without expediting the charge transport channel. The enhanced device performance by solvent annealing of DRCN5T is mainly ascribed to the increased effective photon absorption in the active layer and reduced geminate/non-geminate recombination owing to improved charge transport channels in the crystallized fibril

morphology. The last chapter provides a summary of the conclusions from the thesis along with the suggestions for further improvements in organic solar cell devices based on different D/A combination.

Chapter 2

Experimental Techniques

2.1 Introduction

In this chapter, details of the experimental techniques used in this thesis which include the material and experimental setups are presented. It will start with the working principles and setups descriptions of optical characterization techniques as different spectroscopies including steady-state UV-Vis and ultrafast spectroscopy and photoluminescence. Atomic force and X-ray diffraction microscopy will be other structural characterization techniques used for the morphological study. Finally, the electrical characterization techniques to perform the current-voltage and incident-photon-to-current efficiency measurements for the solar cell device characterization will be presented.

2.2 Optical Spectroscopies

2.2.1 Steady State Absorption Spectroscopy

Steady-state absorption is the basic technique to measure the linear absorption of the different molecules and it guides us for the appropriate selection of pump excitation wavelength in both photoluminescence and transient absorption spectroscopy measurements. When a molecule absorbs the incident light, the excess energy promotes the electrons from ground state to any other optically coupled higher excited state. The selection of the excited states to occur this transition depends on the oscillatory strength, parity and conservation of angular momentum in the absorption process. Other factors such as incident radiation flux, sample thickness and the

optical cross section of the system are a few factors that influence the absorption. The ‘strength’ of this transition is generally determined by the wave function overlap of the upper and lower energy states; known as the Frank Condon principle. The absorption of various polymers films in the visible range is measured using the Shimadzu UV-3600 UV-Vis-NIR spectrophotometer. It consists of three detectors: a PMT detector (photomultiplier tube) for the ultraviolet and visible regions, with additional InGaAs and PbS detectors for near infrared region. To eliminate the substrate effects the absorption spectrum of the blank substrate was subtracted during the measurements. Apart from this, scattering and reflection from the sample are assumed to be negligible and no other process taken place.

2.2.2 Transient Absorption Spectroscopy

Transient absorption spectroscopy (TAS) is a fundamental and versatile technique to probe and characterize the excitation dynamics in many photo-sensitive chemical, physical and biological systems. In this technique, two ultra-short pulses are required (See **Figure 2.1**), namely pump and probe pulses. Pump beam is used to promote a fraction of molecules to excited states. Meanwhile, probe beam that passes through the sample with a delay of Δt with respect to the pump is used to probe the perturbation effect by the pump beam in the sample. The probe beam should be much weaker than the pump beam so as to avoid significant secondary perturbation to the system by the probe. By means of measuring the difference with and without pumping of the probe in either transmission (ΔT) or reflection (ΔR) geometry, one can determine the difference in light absorption (ΔA) between the excited sample and that in equilibrium. Through varying the delay time Δt and recording the ΔT or ΔR at each delay time, the temporal profile of the dynamics can be obtained. By choosing different wavelengths λ , the spectral profile of the

dynamics can also be acquired. In general, there are several sources that contribute to the transient absorption signals.

Figure 2.1 Schematic of the pump-probe operation.

Ground State Bleaching (GSB). When the system is excited with a high fluence pump pulse, fraction of molecules (0.1% to 10%) are promoted from the ground state to excited states. As a result, fewer molecules are left in the ground state compared to that of equilibrium condition. The excited molecules gradually decay to the ground state and the system tries to relax back to the thermally equilibrium distribution. (**Fig 2.2 Process 1**). After excitation and before the full relaxation of the system, at delay time Δt , the probe beam passes through the sample and will be partly absorbed. For the probe beam at certain energy, it will be less absorbed due to the fact that less molecules reside in the ground state. Hence, the probe transmission (T) will increase ($\Delta A < 0$, $\Delta T > 0$).

Photo-induced Absorption (PIA): After the pump excitation, in certain wavelength region the optical transition to higher excited states from the lower excited states might also occur. In this wavelength region, the probe beam is absorbed by these lower excited state, which results in weaker transmission of the system ($\Delta A > 0$, $\Delta T < 0$) (**Fig 2.2 Process 2**).

Stimulated Emission (SE): The stimulated emission from the populated excited states to the ground states occurs when the probe beam goes through the excited system. This emission is occur only optically allowed transition and can be observed in fluorescence spectrum range of the excited system. Typically, this region is Stokes shifted (red shifted) with respect to the

ground state bleaching region. During the mechanism of stimulated emission, photons from the probe beam induce the emission of the other photons from the excited states of the system to come back to the ground states. The stimulated emission and probing photon are unidirectional and hence both can be detected. Note that probe beam is assumed to be much weaker than the excited-state population hence it is expected not to appreciably deplete the excited state population. The existence of the stimulated emission enhances the light collection on the detector which results in a stronger transmission ($\Delta T > 0$, $\Delta A < 0$) (**Fig 2.2 Process 3**). For some systems, the Stokes shift is very small and stimulated emission band overlaps with ground state bleach region.

Figure 2.2 (a) Schematic processes of transient absorption spectrum signal contribution, (b) Schematic for transient absorption spectrum indication ground state bleaching (GSB, process 1), photoinduced absorption signals (PIA process 2) and stimulated emission (SE, process 3).

Absorption by New Species: This process is contributed by the product absorption. In photobiological or photochemical systems, certain reactions may take place after photoexcitation. As a result of these reactions some new species such as isomerized states, charge-separated states, and triplet states are formed. These product also have its new absorption which yields a $\Delta A > 0$ and $\Delta T < 0$ at corresponding wavelength. For example, in organic solar cell,

the photoexcitation will yield charge (polaron) states after exciton undergoes charge transfer. Charges will have their corresponding absorption which does not happen at equilibrium condition. (**Fig 2.2 Process 4**)

Transient absorption measurements were performed using a commercially available HELIOS and EOS setups (Ultrafast Systems LLC) as shown in **Fig. 2.3**. HELIOS and EOS were used to measure transient absorption dynamics in the fs-ns and ns- μ s time regimes, respectively. The pump pulse (500 nm) was generated from an optical parametric amplifier (OPerA Solo) that was pumped by a 1-kHz regenerative amplifier (Coherent Libra). The beam from the regenerative amplifier has a centre wavelength at 800 nm, a pulse width of around 50 fs and a power of 4 mJ per pulse and was seeded by a mode-lock Ti-sapphire oscillator (Coherent Vitesse, 80MHz). OPA can produce a tunable pumping wavelength range from 230-3100nm. The probe beam for Helios was a white light continuum generated from either a 2 mm sapphire plate for visible part (400 nm-800 nm) or 1 cm sapphire plate for NIR part (800 nm-1600 nm) using 800 nm fs pulse from the regenerative amplifier above. The probe beam for EOS was a white continuum generated from a photonic fiber using a Nd:YAG laser (center wavelength: 1064 nm). The probe beam was collected using a dual detector for UV-Vis (CMOS sensor) and NIR (InGaAs diode array sensor). Here, we have delayed the probe beam instead of the pump beam. In our transient absorption measurements, a portion of the fundamental 800 nm is split off from the amplifier output to the OPA. This small amount of the 800 nm is delayed via a delay line and then focused into a sapphire crystal to generate the white light continuum probe beam. Due care was taken to ensure that we have good alignment of the beam within the 2 ns window to ensure a stable white light continuum.

Figure 2.3 Schematic of the Helios pump-probe setup in our lab.

2.2.3 Photoluminescence

Photoluminescence (abbreviated as PL) is a subsequent emission of photons following photoexcitation process. Quantum mechanically, an excitation to the higher energy states occur as a result of the absorption and then relaxed to the ground state (or lower energy state) with a simultaneous emission of the photon. On the basis of the nature of the excited state, PL is categorized as fluorescence and phosphorescence. According to the Jablonski diagram as seen in **Fig 2.4**, the photon absorption of the molecule populates singlet excited states (S_1 or S_2) which relax to the lower vibrational energy level of S_1 . Following photoexcitation, optically allowed transition (photon emission) in the order of ps to μ s may occur from S_1 to the ground state (S_0). This relatively fast radiative mechanism is called fluorescence. The other interesting processes also occur when the photoexcited electrons undergoes internal energy transitions (intersystem crossing) to a triplet state (T_1) where direct optical transition to the ground state is forbidden.

Emission from triplet state might still occur, but with a much lower probability, *i.e.* comparatively much slower process, in order of ms to s. Such effect is known as phosphorescence. The generated photon in this case is said to be red shifted, referring to the loss of energy as Jablonski diagram shows.

Figure 2.4 Jablonski diagram of the physic process of photoluminescence.⁶³

2.3 Structural Characterizations

2.3.1 Atomic force microscopy

Atomic Force Microscopy (AFM) is a surface characterization technique to measure morphology of polymer-fullerene solar cells. AFM works in two different modes: tapping mode and contact mode. AFM is operated in tapping mode to obtain the height, amplitude and phase images of the film surface which provide the information about the crystallinity, surface roughness, and qualitative nature of phase separation. 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. A gold-coated silicon nitride (Si_3Ni_4) tip was used for the measurement. The low force constant (0.06 N/m with resonant frequency of 10 kHz) renders the Si_3Ni_4 AFM probe suitable for soft-contact imaging.

2.3.2 Grazing incidence X-ray diffraction crystallography

The X-ray diffraction is one of the non-destructive analytical methods to extract the information about the crystallographic structure in different form of the materials. This technique is based on the intensity of the collected beam of the diffracted X-rays after hitting the material as a function of the incident angle or energy. Conventional $\theta/2\theta$ scanning method is not applicable for the thin films (1-1000nm) and very low crystalline or amorphous materials like polymers because intensity of the diffracted signal from material is much weaker diffracted from the substrate. A modified method is used for this kind of materials where incident x-ray beam is fixed at grazing angle to avoid the intense signal from the substrate and detector detect the diffracted beam from the sample. This technique is known as Grazing incidence X-ray diffraction (GIXRD). As the beam of the X-rays strike at the sample during the experiment, it is diffracted in all direction. A movable detector scans vertically and detects the signal diffracted as shown in **Fig. 2.5**. Most of the conjugated polymers are amorphous in nature while some of them are semi-crystalline. P3HT, mostly used in this thesis is semi-crystalline and have out of plane orientation of backbone and hence this is the right approach to obtain the information about the structural arrangement of the polymer. In this work, the X-ray Diffraction (XRD) Bruker D8 Advance is used to do the structural characterization of different polymer films coated on glass substrates. The XRD patterns in the 2θ range of (2° - 50°) were recorded using Cu $K\alpha$ radiation ($\lambda = 15.418$ nm) at room temperature.

Figure 2.5 Schematic of GIXRD setup for out-of-plane measurements with scan of 2θ . The incident X-rays are at small angle ω to the plane of the sample surface.

The thickness of the nanostructured films were measured by a surface profiler (Alpha step IQ) using a step height analysis. The scanning details are as follows: scan length 2000 μm , scan speed 100 $\mu\text{m/s}$, sampling rate 50Hz and sensor range 550 μm -33 pm. The stylus force was manually adjusted to 5-6 mg for scanning of the materials.

2.4 Electrical Characterizations

2.4.1 Current-Voltage measurements

A Keithley 4200 Semiconductor Characterization System (K4200 SCS) was used for the current density-voltage (J-V) measurements in Energy Research Institute at Nanyang Technological University (ERI@N). The system was auto-calibrated frequently and tested with standard devices before connecting our solar cells. The voltage step size in mV was varied according the device characterization requirements. The K4200 SCS was used along with the solar simulator for light characteristics.

2.4.2 Solar Simulator

Radiation from the Sun interacts with Earth's atmosphere before reaching its surface. Thus, at

any place, along with its dependence on time and Earth-Sun distance, solar radiation significantly varies with location, cloud cover, aerosol content, and ozone layer conditions. Near the surface of the Earth, the reflection from surroundings like trees and buildings also changes the available intensity at any location. Hence, standard spectra have been developed to provide a basis for any theoretical and laboratory experimental investigations. Solar simulator provides these spectra with collimated beams of different areas and intensities. These standard spectra are given in terms of Air Mass (AM) and angle between Sun and Earth for direct and reflection conditions. Air Mass is defined as the ratio of the slant optical thickness, to the vertical optical thickness of the standard atmosphere. In other words, it is the secant of the angle between sun at its zenith and at any slant angle as shown in the **Fig. 2.6**. For example, AM 2.0 indicates that the sun is at an angle of 60.1° from zenith since $\sec(60.1^\circ) = 2.0$. AM 0 is the direct sun light above the Earth's atmosphere. Standard optical filters for simulating AM 0, 1, 1.5, and 2.0 are usually available. Of these, AM 1.5 G is the most commonly used standard for comparison of solar cell efficiencies world over. Here G indicates 'global' which means that the spectrum includes the direct sun light as well the scattered and reflective components of the radiation. The total intensity of AM 1.5 G equals 100 mW cm^{-2} for the standard of CEI/IEC 904-3 (Commission Electrotechnique Internationale/International Electrotechnical Commission) and 963.8 mW cm^{-2} for the standard of ASTM E 892 (American Society for Testing and Materials).

Figure 2.6 Illustration of the concept of Air Mass and the standard angles associated with it. (Picture source: www.newport.com).

In this work, we have used Air Mass 1.5 Global (AM 1.5 G) solar simulator (Sanei XES-300, AAA rating) with an irradiation intensity of 100 mW-cm^{-2} coupled with exposure control equipment to illuminate the solar cells to measure the I - V characteristics. The light intensity of the solar simulator was calibrated using a solarimeter.

2.4.3 IPCE measurement

Internal photon to current efficiency (IPCE) of solar cells represents the photocurrent at each wavelength of incident light and calculated by:

$$\text{IPCE} = \frac{J_{sc}}{G \times \lambda} \times \frac{hc}{e} \quad (2.1)$$

where J_{sc} represents the short circuit current density at wavelength λ , G is the illumination power, h is plank constant, c and e is light speed and elementary charge, respectively. IPCE can be used to understand the origin of photocurrent in the cell which will, eventually, help in understanding the device physics. The external quantum efficiency (EQE) of the solar cell is determined as:

$$EQE = \frac{P_{\max}}{G \times S} \quad (2.2)$$

where $P_{\max}$ represents the maximum extracted electric power, G represents the incident illumination while S is the illuminated surface area. To record the IPCE spectra, a Merlin radiometry system is used including 150 W Newport-Oriel Xenon lamp as the light source. Spectra is resolved using a Cornerstone 260 ¼ m monochromator and chopped at 60 Hz by an optical chopper. The light power-density was calibrated with a Hamamatsu silicon photodiode. All the device measurements were performed in nitrogen filled glove box.

2.5 Device Layout

The design of the solar cell devices on ITO coated glass substrate is shown in **Fig. 2.7**. 1”x1” glass substrates in size with ITO at the center as shown in **Fig. 2.7** were used as the substrates to fabricate the ten cells on common anode contact. The cells were designed circular with an area of 0.07 cm² to minimize the leakage current from the periphery.

Figure 2.7 Layout of ten devices on the substrate. The white color dumbbells represent Al cathodes; the blue color represents ITO anodes while pink color represents the glass substrate. The solar cells are located at the intersection of the Al and ITO. The configurations use common PEDOT:PSS and active layer at the anode interface.

2.6 Conclusions

In this chapter we gave a brief introduction of the experimental techniques and instruments used in the thesis. The main experimental techniques used to investigate different organic photovoltaic systems were discussed, which includes steady-state and transient absorption spectroscopies, AFM, XRD and, *I-V* and IPCE measurements.

Chapter 3

Influence of external electric field treatment on poly(3-hexylthiophene) nanofibers based organic solar cell devices

Summary

For the higher efficiency organic solar cells, self-assembled organic nanostructure is an interesting alternative. However, the performance reported by different research groups using the polymer nano-structure (i.e. nanofiber) is comparable but incapable of crossing the limit set by the most promising method – annealing. In this chapter, we propose the electric field treatment as a processing method to improve the photovoltaic device performance of nanofibre:fullerene system and establish its correlation with the charge dynamics. Since the performance of the devices is directly correlated to the system morphology, the organization polymers are also discussed. The steady state and transient techniques are employed here in order to get insight on possible photophysics on the effect of external electric field and hence other possible ways for further development.

3.1 Introduction

In the past few years, regioregular poly(3-hexylthiophene) (P3HT) is the most widely focused donor material among all poly(3-alkylthiophene)s (P3ATs) group due to its encouraging properties such as easy processibility and self-assembling potential. The bulk heterojunctions (BHJ) organic solar cell based on P3HT as electron donor and methano-fullerene derivatives ([6,6]-phenyl-C61-butyric acid methyl ester (PCBM)) as electron acceptors is the most promising system with efficiencies^{64,65} approaching 5%. To achieve such outstanding performance, the devices entail some additional processing such as solvent annealing⁶⁶⁻⁶⁸, ordered organization of blend⁵⁴, self-assembly with marginal solvents,⁶⁹ etc. Without such treatments, the low degree of crystallinity of P3HT during P3HT:PCBM blend film formation results in poor charge carrier mobility which limits the device performance.³⁹ Although all these techniques are capable of improving the solar cells performance but all such post processing methods are not compatible for large scale roll-to-roll applications⁷⁰. Therefore, for the high volume, cost effective production, it is essential to develop a low-temperature solution-processable technique which is compatible with mechanically flexible substrates^{37,71-}

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So far, numerous annealing free techniques such as poor solvent-induced aggregation⁷⁴, use of crystallizable solvent⁷⁵, marginal solvent method⁷⁶ etc. have been developed to promote the one-dimensional nanostructures in P3HT. In 1993, Ihn et al. first reported the nanostructured behaviour of P3HT dissolving in cyclohexanone and n-decane, as poor solvents.⁷⁶ Later, Yang et al. also reported the existence of the fibrillar network of P3HT and demonstrated the relation between morphology and solar cells performance.⁷⁷ The crystalline P3HT nanofibers blended with PCBM as an acceptor in organic solar cell devices have achieved around ~3.4% efficiency.⁷⁸⁻⁸¹ This improved performance of P3HT nanofibers devices as compared to the annealing free conventional P3HT solar cell devices attribute to

the improved charge carrier mobility. In nanofibers based system, comparable dimensions of the nanofibers to exciton diffusion length (10-20 nm) results in better charge separation and subsequently improved charge transport in these devices. However, further improvement in PCE without thermal annealing can also be achieved by optimizing the acceptor content, nanofiber-amorphous polymer ratio, selecting stronger acceptor (such as PC71BM) or by organization of the blend morphology.

According the previous reports, the fibrillar network of P3HT is interconnected and oriented parallel to the surface of electrode with improved properties such as absorbance and crystallinity to perform light connecting antennas in OSCs.^{53,82} However the performance of the P3HT-NF:PCBM blend devices are found to be lower than the conventional nanoscale phase separated structure.⁶⁹ Kurniawan, M. et al. reported the loss of charge carriers by higher bimolecular recombination resulted from the poor interfibrillar charge transport between the NFs as the main cause of underperformance.⁸³ Nevertheless, the compatibility of P3HT-NF system for low temperature processing flexible substrates for roll-to-roll application proves it relevant. Therefore, to realize the full potential of the fibrillar network it becomes important to reduce the charge carrier losses and therefore develop a technique to overcome the poor interfibrillar charge transport.

P3HT is a molecule polar in nature with a dipole moment of $\sim 1.0\text{--}1.6\text{ D}^{84}$ (arising from the negative charge distribution around sulfur atom in the heterocyclic ring that is more than that for hydrogen, carbon and nitrogen as shown in **Fig 3.1**) and P3HT-NF system comprises of both fibrillar and amorphous phases (randomly distributed polymer chains).^{53,85,86} Therefore perpendicular alignment of the randomly distributed NFs to the electrodes would be the approach to avail the higher intra-fibrillar charge carrier mobility and hence reduce the bimolecular recombination. In addition, the alignment of the P3HT

molecules in amorphous phase as a result of dipole polarization may also improve the interfibrillar charge transport. At the present, the role of the existing random phase on the device behaviour and its interactions with acceptor are vague; nevertheless, this phase can be imagine as analogous to the “glue” between the P3HT NFs.

Figure 3.1 The molecular electrostatic potential map (in a.u.) of P3HT monomer based on DFT method. Blue and red regions represent positive and negative potentials, respectively. Arrow illustrates the direction of the dipole moment in a monomer.

We speculate that P3HT chains act as “connections” between P3HT nanofibers (NFs) and can be organized by applying the external electric field (E-field) during the solvent-drying stage of the processing and hence improving the device performance of P3HT-NF:PCBM OSCs. Investigating the electrical properties and photovoltaic performance of functional devices and correlating them with the charge carrier dynamics of E-field-treated P3HT-NF:PCBM thin films are the main objectives of this work. In this chapter the capability of external E-field treatment of P3HT-NF to improve the performance of P3HT-NF:PCBM OSCs is presented.

3.2 Experimental Procedure

3.2.1 Growth of P3HT nanofibers: To grow the nanofibers, regioregular P3HT (rr > 90%) and p-xylene as a solvent were purchased from Rieke Metals Inc. and Fluka respectively. The processing method to grow the P3HT nanofiber in p-xylene was as follows: P3HT was first dissolved in p-xylene (8 mg/mL) and heated to 80 °C to confirm complete dissolution of the

polymer before being gradually cooled down to room temperature at a rate of $-10\text{ }^{\circ}\text{C/h}$ (Julabo F25-EC). To encourage self-assembly of the P3HT NFs, the suspension was left uninterrupted in the dark for 20 h. Two different physical changes, color from bright orange to dark brownish and increase in solution viscosity can be observed as P3HT undergoes the transition. This physical behaviour of the solution can also be directly correlated to the change in optical absorption and presence of non-dissolved nanofiber respectively. The presence of nanofibers prepared by this procedure is also previously reported by Teddy Salim *et.al.*⁸⁷ To observe the existence of nanofibers, P3HT NFs suspension was diluted in p-xylene solution and spin-coated on glass substrate. The AFM scan of this film verified the presence of P3HT-NFs and the dimension these nanofibers were measured to be around 2 - 5 μm in length and 20 - 40 nm in width as shown in **Fig 3.2 (a)**.

3.2.2 Film preparation for optical characterizations: To prepare the NF blend solution P3HT-NF suspension was mixed with PCBM (purchased from Nano-C) with a weight ratio of 10:8 and was stirred thoroughly at room temperature for 2 h before spin-coating as active layer. For all optical measurements, P3HT-NF:PCBM thin films were prepared on indium-tin oxide (ITO) coated glass substrates. The substrates were first thoroughly cleaned by detergent solution followed by ultrasonication in deionized water, acetone and isopropanol for 15 min each and kept in oven at $90\text{ }^{\circ}\text{C}$ for overnight to remove the moisture. Later these substrates were transferred to the N_2 filled glove box for processing. P3HT-NF:PCBM blend solution was then spin-coated on top of ITO at 700 rpm for 120 second to yield films thicknesses of $100 \pm 5\text{ nm}$. Solvent drying of these substrates were performed in two different sets. For one group of devices, an electric field was applied across the blend film as they were drying at room temperature for 30 min, i.e., the “electric-field dried” (E-field treated) devices. On the basis of preceding reports, a static electric field of 1.4 kV/cm was applied using a metallic plate (aluminum) separated by a spacer above the active layer while ITO was used as the

counter electrode.^{88,89} A static field was achieved by applying a constant DC 600 V between the metallic plate and ITO at a fixed distance of 4.3 mm. The improvement in E-field treatment was validated by fabricating 50 cells of each set in different batches. The schematic of the arrangement used for E-field treatment is shown in **Fig. 3.2 (b)**.

Figure 3.2 (a) AFM scan of the P3HT-nanofibers⁸⁷ and (b) schematic of the electric field treatment of P3HT-NF:PCBM blend films.

3.2.3 Device fabrication: To fabricate the organic solar cell (OSC) devices the cleaned substrates were further treated with plasma for 5 min to make the ITO surface hydrophilic and to increase the work function. A thin film of Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (CLEVIOSTM P VP Al 4083, HC Starck) layer of ~30 nm was deposited by spin-coating on the substrates (at 3000 rpm for 60 s), followed by annealing at 100 °C for 15 min in a N₂-filled glove box. PEDOT:PSS smoothens the ITO surface and also works as the hole transport layer for charge extraction from the active layer. The P3HT-NF:PCBM active blend solution was then spin-coated and dried with and without electric field as mentioned above. Finally, a cathode contact of 100

nm thick aluminium layer was deposited on the active layer was through a shadow mask (with active area of 0.07 cm^2) in a vacuum of 10^{-6} Torr.

3.3 Results and interpretations

3.3.1 Linear Absorption: The measured linear absorption spectra of both P3HT-NF:PCBM blend films (with and without E-field treatment) of similar thicknesses coated on ITO deposited glass substrate are shown in **Fig. 3.2**. The maximum absorption peak (λ_{max}) is observed at 510 nm and the other two vibronic “shoulders” are found to be at 550 and 605 nm. These profiles and position of the absorption peaks typical resembles of P3HT. The peak at the lower wavelength ($\lambda = 510\text{nm}$) represents the π - π^* intrachain transition, while the vibronic features at longer wavelengths are correlated to the π - π^* stacking strength. The vibronic features at 605, 555, and 510 nm resembles to the 0–0, 0–1, and 0–2 transitions of P3HT, respectively. The degree of the order of P3HT in blend film is directly proportional to the absorption intensity of the vibronic shoulder at 605 nm.^{90,91} A slight stronger absorbance is observed in E-field dried film, as shown in **Fig. 3.3 (a)**. The presence of the structured peaks is attributed to the increased ordering and crystallinity of the system irrespective of E-field treatment. To exclude the role of active layer thickness, the linear absorption spectra was normalized at 340 nm (where the absorption is dominated by PCBM instead of P3HT) and is presented in **Fig. 3.3 (b)**. The stronger 0-0 peak intensity in E-field treated film confirms the stronger interchain interaction in the E-field treated P3HT-NF:PCBM samples. These improved characteristics attribute to better molecular organization in the external E-field treated blend film. Hence, enhanced exciton generation is expected in E-field treated P3HT-NF:PCBM system.

Figure 3.3 (a) Linear absorption spectrum of P3HT-NF:PCBM film without and with E-field treatment (at $1.4 \text{ kV}\cdot\text{cm}^{-1}$). The absorption below 400 nm is due to the presence of PCBM in the blend, (b) the absorption spectra normalized at 340nm.

3.3.2 Absorption Efficiency Calculation: The absorption coefficients (α) for the films were calculated using the Beer-Lambert's law ($A = A_0 e^{-\alpha x}$, where x is the film thickness). The relation used to estimate the absorption efficiency of these blend films is⁹²

$$\eta_A = \frac{\int (1 - 10^{-\alpha d}) S(\lambda) d\lambda}{\int S(\lambda) d\lambda} \quad (3.1)$$

where d is the blend film thickness and $S(\lambda)$ represents the number of available photons at a particular wavelength λ in AM1.5G solar spectra. As a result of the integration between the wavelengths from 300 nm to 800 nm, the absorption efficiency η_A is found to be 38.5%, and 40.8% for the films without and with E-field treatment respectively. Therefore, the active layer treatment by the external E-field during the solvent-drying process improves the photon absorption in the active layer slightly.

3.3.3 Nanofiber morphology: The film morphology of the P3HT-NF:PCBM layers has been visualized using AFM in tapping mode directly on the active layers prepared for solar cell devices. **Fig. 3.4** shows the $5 \times 5 \mu\text{m}^2$ topographical and phase images of both kinds of active layers. It should be noted that P3HT-NF:PCBM blend films also consists of some fraction of

P3HT molecules (which are not formed into nanofibers) and PCBM phases. The presence of higher fraction of these two phases covers P3HT nanofibers from surroundings which block the direct AFM scanning of P3HT nanofibers and therefore the topography of the blend film appears as shown in **Fig 3.4**. The surface topography of the active layer dried in E-field is found to be smoother than that of without treatment film. The root mean square (RMS) surface roughness is found to be 2.6 ± 0.1 nm and 2.1 ± 0.1 nm for without and with E-field dried film respectively. In addition, the peak height for these films is measured to be 9.3 ± 0.2 nm and 8.4 ± 0.2 nm respectively. The lower roughness and peak height in E-field dried active layer attributes to the improved crystallinity and better ordering in the film. On the comparison of phase images, E-field treatment was not observed to induce any phase separation.

Figure 3.4 AFM scan image of the surface topography and phase **a, b)** without and **c, d)** with E-field dried P3HT-NF:PCBM blend films respectively. The scan area is $5 \times 5 \mu\text{m}^2$ for all images.

3.3.4 Grazing-incidence X-ray diffraction: **Fig. 3.5** shows the XRD pattern of P3HT-NF:PCBM blend films coated on ITO/glass substrates. The pattern of both samples show a clear single peak at $2\theta \sim 5.48^\circ$ (100).⁹³ This diffraction peak in P3HT is often associated with

interdigitation of the alkyl chains. John D. Roehling *et. al.* also measured the XRD pattern of the P3HT-only nanofiber system prepared using different solvents.⁹⁴ The position of (100) diffraction peak of P3HT- nanofiber system was the same as that for crystalline P3HT at $2\theta \sim 5.4^\circ$. Therefore, diffraction peak of P3HT-NF:PCBM system reveals the information collectively about nanofibres and P3HT. Lattice spacing in the system was calculated using Bragg's diffraction law ($2d \sin \theta = n\lambda$, where θ = Bragg angle, $n = 1$ for the first-order (100) reflection, $\lambda = 0.154$ nm corresponding to Cu-K α radiation energy) and found to be 1.65 nm and 1.58 nm for without and with E-field treated films respectively. This decrement in d spacing suggests the electric field induced molecular reorganization with increase in proximity between P3HT molecules. The intensity of 100 diffraction peak is found to be higher for the E-field treated P3HT-NF:PCBM film. The closer proximity of P3HT molecules and higher diffraction intensity of 100 peak in E-field dried film suggests higher crystallinity as compared to non-treated film.

Figure 3.5 GIXRD patterns of P3HT-NF:PCBM blend films. The samples were prepared on Si/SiO₂ substrates.

3.3.5 Photoluminescence: A steady-state photoluminescence (PL) study was performed to investigate the exciton dissociation efficiency after generation through photo absorption. **Fig.**

3.6 shows the photoluminescence behaviour of the film dried without and with E-field upon excitation with a 530 nm light source. The film dried in E-field exhibit better PL quenching which has been earlier expected. The lower intensity of PL in E-field treated film indicates more excitons dissociates into free charge carriers before they relax back to the ground state or recombine. The PL emission is likely to originate from monomolecular recombination of CT states, which depends on the nanofibers conformation and blend film morphology. The quenching of these charge transfer states can be proposed to be the consequences of the following processes which prevent charge recombination at the D/A interface: (a) efficient dissociation of excitons at the interface, (b) efficient charge transfer away from the interface through the organized structure, and (c) reduction of D/A interfacial area due to enhanced crystallinity. PL quenching in presence of the electric field as shown in **Fig. 3.6** indicates a drop in recombination through CT states or an increase in charge extraction.

Figure 3.6 PL Intensity of P3HT-NF:PCBM thin film dried without and with electric field treatment.

Photovoltaic Performance

3.3.6 Dark Characteristics: Two different set of BHJ devices (ITO/PEDOT:PSS/P3HT-NF:PCBM/Al) with and without E-Field treatment of ten devices of each set were prepared and their current density–voltage (J – V) characteristics were measured in dark. The devices

fabricated with E-field dried active layer exhibits higher forward current density relative to the control device (**Fig. 3.7a**). Here, we would like to highlight the different components of blend system (*i.e.* P3HT-nanofibers, amorphous P3HT and PCBM) causing the flow of current in device. Since the dimensions of the P3HT nanofibers are around 2 - 5 μm in length and 20 - 40 nm in width⁸⁷, the reorganization of nanofibers are therefore impossible under the influence of the external E-field treatment. The lack of strong polarizability of the PCBM molecules also makes the fullerene inappropriate for such treatments. Thus, the remaining amorphous P3HT phase in the blend system is the only component which is reorganized by the field, resulting in dark current improvements.

Figure 3.7 (a) Linear and (b) log-log scale plot of dark current density–voltage characteristics of P3HT-NF:PCBM devices without and with E-field treatment.

Since the fraction of amorphous P3HT is small in P3HT-NF:PCBM blend system, this give rise to a smaller re-organization and hence only a slight improvement in the dark current. This improvement in the dark current is attributed to better charge transport in E-field dried devices even though the built in potentials are found to be similar (*i.e.*, $\sim 0.7\text{V}$) for both devices. Better charge transport can further suppress charge carrier recombination in the E-field dried devices, which can further generate more charge carriers and thus photo-current.

Fig. 3.7 (b) shows the double logarithmic plot of the current density-voltage (J - V) characteristics of the P3HT-NF:PCBM devices measured in dark. The dark J - V characteristics as shown in **Fig 3.7 (b)** consist of three distinct regions. In the first region at low voltage range (0-0.3 V), the relationship between current density and voltage follows Ohm's law ($J \propto V$). In this region, the quantity of the injected charge carriers is not strong and current is dominated linearly by thermally generated free charge carriers in BHJ devices. In the middle voltage range (0.3 - 1 V), current is rapidly rising as a result of filling of the trap states with applied voltage ($J \propto V^m$ where $m > 2$) and termed as trap filling region.^{95,96} **Fig 3.7 (b)** display that both types of devices show an Ohmic region below 0.3 V and then switch to trap-filling region (0.3 – 1 V). Since traps are main cause for the underperformance of nanofiber based devices as observed by M. Kurniawan *et. al.*⁸³, it is useful to analyse the trap-filling region to investigate the influence of E-field treatment. In this region, contribution from injected carriers to dark current is proportional to the applied voltage and swift rise of current in this region indicates the accumulation of the injected charges in bulk. This phenomenon is generally observed similar to the power law which indicates that traps are exponentially filled in the bulk system. Thus, the slope of current rise in this region can be used for the relative comparison of trap filling mechanism in these devices. Therefore, a faster rise in current of the trap filling region (**Fig 3.7 (b)**) indicates faster trap filling process or relatively less amount of charge carrier trapping sites which are easily filled in E-field dried devices as compared to the control device. Finally, in the third region ($V > 1$ V), all the traps in the bulk system are filled by the injected carriers and resist further injection and therefore collection rate at the electrode is dropped as compared to trap-filling region. As a result, the accumulation of charges create a space charge region near the electrode, and hence field dependent injection where trap free space charge limited current (SCLC) flows through the device which obeys $J \propto V^2$ law.⁹⁷

3.3.7 IPCE Measurements: The measured incident-photon-to-collected-electron efficiency (IPCE) of these devices is plotted in **Fig. 3.8**. IPCE of both types of devices fabricated on active layer with two different treatments is derived from their spectral response of devices. The following relation has been used to calculate the IPCE for a given wavelength:

$$\text{IPCE}(\lambda)[\%] = 1240(J_{sc}/I_p) \quad (3.2)$$

where I_p ($\text{W}\cdot\text{m}^{-2}$) stands for the incident light intensity and J_{sc} ($\text{mA}\cdot\text{cm}^{-2}$) is the short-circuit current density measured at corresponding wavelength λ (nm). For the devices fabricated on E-field dried active layer shows significant improvement in IPCE from wavelength range 370-650 nm (**Fig. 3.8**). The maximum of ~55% IPCE at a wavelength of 470 nm is observed in the device with active layer dried without electric field while maximum IPCE reaches to ~57% for solar cell devices made with E-field dried active layer.

Figure 3.8 IPCE plots for of the devices fabricated on active layer (P3HT-NF:PCBM) dried film without and with E-field.

Improvement of IPCE at 610 nm is more pronounced than at 560 nm in E-field-treated P3HT-NF:PCBM devices which resembles the absorption spectra as shown in **Fig. 3.3**. Integrated J_{sc} is also calculated for these devices using the measured IPCE spectra. Devices fabricated with E-field dried active layer generates higher current density ($\sim 7.6 \text{ mA}\cdot\text{cm}^{-2}$) than the device fabricated without E-field treated active layer as $\sim 7.1 \text{ mA}\cdot\text{cm}^{-2}$. The

improvement in IPCE and integrated current density indicates better charge collection at the electrodes in E-field treated devices. The external quantum efficiency (η_{EQE}) is also calculated to get a quantitative idea of the electric field effect on device efficiency of P3HT-NF:PCBM solar cell and compared with the control sample. The external quantum efficiency η_{EQE} is defined as the ratio of total number of charge carriers collected at the electrodes to the number of photons of a given energy incident on the solar cell, i.e.

$$\eta_{EQE} = \frac{\int \frac{n_e(\lambda)}{n_p(\lambda)} S(\lambda) d\lambda}{\int S(\lambda) d\lambda} \quad (3.3)$$

where n_e/n_p represents the ratio of the number of collected electrons to the number of photons at a particular wavelength, $S(\lambda)$ refers to the number of available photons at that corresponding wavelength of the AM1.5G solar spectrum. The η_{EQE} for device fabricated with E-field and naturally dried active layer is calculated to be 37.6 % and 34.7 % respectively. To perform this calculation, integration is carried out over the IPCE spectrum from 300 to 700 nm. Generally, the external quantum efficiency of OSC depends on photo-absorption of active layer to excitons generate (η_A), diffusion of excitons to form the charge transfer states or dissociation to free charge carriers (η_{ED}), transport of the charges towards the respective electrodes (η_{CT}) and charge collection at the electrodes (η_{CC}). Hence, the total external quantum efficiency is OSC is represented by:

$$\eta_{EQE} = \eta_A \times \eta_{ED} \times \eta_{CT} \times \eta_{CC} \quad (3.4)$$

In bulk heterojunction solar cells structure, polymer grains sizes are found to be the order of the exciton diffusion length. This means that the exciton reaches the donor–acceptor interface before its annihilation, thus η_{ED} can be assumed to be one. The collection efficiencies η_C (η_{CT}

$\times \eta_{CC}$) for both devices are estimated using the values of η_A determined from equation 3.1. The estimated values of the different efficiencies for both solar cell devices are tabulated in **Table 3.1**. These values indicates that electric field treatment on P3HT-NF:PCBM blend film also improves charge carrier transport and collection over non-treated device.

Table 3.1: Summary of calculated efficiencies for standard and E-field dried devices

Devices	η_{EQE} (%)	η_A (%)	η_C (%)
Standard	34.7	38.5	89.9
Electric Field Dried	37.6	40.8	92.1

The calculated external quantum efficiency (η_{EQE}) and absorption efficiency (η_A) for AM 1.5G spectrum.

3.3.8 Illumination Characteristics: J – V characteristics of the solar cell devices fabricated with and without E-field dried active layer, measured under $100 \text{ mW}\cdot\text{cm}^{-2}$ standard illumination of AM 1.5G spectrum are shown in **Fig. 3.9**.

Figure 3.9 Current density–voltage (J – V) plots for the P3HT-NF:PCBM devices without and with electric field treatment measured at an intensity of $100 \text{ mW}\cdot\text{cm}^{-2}$ at AM1.5 Sun.

Table 3.2 summarises the relevant parameters e.g., short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF) and power conversion efficiency (PCE) determined from J – V characteristics as shown in **Fig. 3.9**. These results are validated by testing 50 devices of each set fabricated in different batches. Both solar cell devices display comparable values of

V_{oc} and FF . Devices fabricated on E-field dried active layer exhibits an improvement of $\sim 0.3\%$ in PCE and $\sim 1.0 \text{ mA}\cdot\text{cm}^{-2}$ in J_{sc} as compared to the control devices. The improved current density in E-field dried solar cells is consistent with the higher integrated current density as estimated from the measured IPCE (**Fig 3.8**). Therefore, higher PCE of E-field dried solar cell devices is attributed to high photon absorption and better ordering in the P3HT-NF:PCBM active layer, which indicates efficient charge generation and better transport to the electrodes.

Table 3.2: Summary of the performance of devices under illumination.

Devices	PCE (%)	$J_{sc} (\text{mA}\cdot\text{cm}^{-2})$	$V_{oc} (\text{V})$	FF
Standard	1.7 ± 0.1	7.2 ± 0.4	0.54 ± 0.01	0.45 ± 0.02
Electric Field dried (4.0 kV·cm⁻¹)	2.0 ± 0.1	8.0 ± 0.3	0.56 ± 0.02	0.46 ± 0.01

3.3.9 Charge Generation: We have also analyzed the photocurrent as a complementary approach in order to clarify whether ordering in P3HT-NF system due to the E- field treatment could resulted in any excess carrier generation. As **Fig. 3.10** shows, the photocurrent for both devices at 1 sun intensity is almost saturated around $V = 1.0 \text{ V}$, which indicates that nearly all photogenerated carriers are extracted from the devices. In order to determine the saturated photocurrent J_{sat} at large enough reverse bias we have used a model developed for insulators by A.M. Goodman and A. Rose⁹⁸. According this model:

$$J_{sat} = qGd \quad (3.5)$$

where G is generation rate, d is device film thickness and q stands for the electronic charge. This model can also be applied to organic BHJ solar cells as well.^{99 100} Comparing J_{sat} values for both kinds of devices, we can investigate if more photo-generation takes place as result of improved ordering. **Fig. 3.10** shows a log-log plot of photocurrent against $(V_o - V)$, where V_o refers to compensation voltage. At this particular voltage, dark current (J_D) equals light

current (J_L), in other words, where the photocurrent in device is zero¹⁰¹. Thus, $(V_o - V)$ represents the effective voltage available for generation of photocurrent. V_o values for without and with electric field dried P3HT-NF:PCBM devices were measured to be 0.67 V and 0.72 V respectively. The lower value of dark current and photocurrent in non-treated devices are responsible for lower value of V_o as compared to E-field dried devices.

Figure 3.10 Log scale photocurrent- voltage plot measured at 1 sun intensity for P3HT-NF:PCBM devices, dried with and without E-field. The symbols are: d = Film thickness; V_o = Compensation voltage; G = Carrier generation rate; J_D = Dark current density, J_{sat} = Maximum photocurrent generated at saturation.

From **Fig. 3.10**, it can be observed that at low effective voltages, i.e., around V_{oc} where available drift field is small, E-field dried devices show higher photocurrent. As the voltage is increased, i.e., large reverse bias, photocurrents for both devices saturate at different values: $J_{ph} = 8.7 \text{ mA·cm}^{-2}$ for E-field dried devices and $J_{ph} = 7.5 \text{ mA·cm}^{-2}$ for non-treated devices. This means that the total photo-generated carrier density is higher in devices having electric field dried active layer. Hence, the possibility of excess charge generation by efficient exciton dissociation is consistent reasons for J_{sc} improvement.¹⁰² To validate these results, we also measured charge generation and recombination dynamics in these blend films using transient absorption spectroscopy.

Femtosecond Transient Absorption

3.3.10 Charge carrier dynamics in fs-ns temporal regime: For further understanding of generation and recombination mechanism of photoexcited species, transient absorption measurements were performed on P3HT-NF:PCBM active layer (100 ± 5 nm thick) dried without and with E-field. The representative differential transmission (DT) spectra measured from 520 nm to 750 nm at varying delay times following photoexcitation by 500 nm pump wavelength for both kinds of film are shown in **Fig. 3.11**.

Figure 3.11 Femtosecond transient absorption spectra of P3HT-NF:PCBM film treated (a) with E-field and (b) without E-field.

The vibronic peaks corresponding to 0-0 (at 610 nm), 0-1 (at 560 nm) absorption transitions apparent as ground state bleaching (GSB) peaks.⁹² The positive photobleaching (PB) signal (*i.e.*, $\Delta T/T > 0$ or relative DT > 0) is related to the population of the photoexcited species *i.e.* excitons and polarons in the blend films,¹⁰³ and this signal is directly correlated to the population of filled excitonic and polaronic states. The negative $\Delta T/T$ signal appears around 700 nm refers to photo-induced absorption (PIA) which arises from the presence of photogenerated species (polarons, excitons, or charge transfer excitons) in blend film. The evolution and relative magnitude of DT signal obtained from photoexcited blend film

provides information related to the population of residual excited species and their average life time after photoexcitation.

The GSB spectral profiles of both P3HT-NF:PCBM films, E-field treated and untreated control are largely similar (**Fig. 3.11**). However, the E-field dried film shows more pronounced DT signal at 0-0 and 0-1 GSB band compared to the film without E-field treatment at early times. The PB signal for the 0-0 transition is 20% larger at 1 ps onset and continue up to 1.5ns (**Fig. 3.12(a)**). This increased PB signal arises from higher photo-absorption and hence larger yield of photogenerated excitons and polarons in E-field dried P3HT-NF:PCBM film. This behaviour of higher magnitude of PB signal is invariant in the entire GSB region of the films. This is consistent with the enhanced ordering of polymer chains in P3HT.^{88,104}

Figure 3.12 The dynamics of (a) 0-0 GSB, (b) 0-1 GSB peak of the E-field dried P3HT-NF:PCBM film.

Moreover, the incorporation of electric field on P3HT-NF:PCBM does not affect the GSB decay profile within the first 500 ps and exhibits a similar decay profile as the one without field (**Fig. 3.12**). Both peaks (0-1 and 0-0 GSB) in films dried without and with electric field decay swiftly in first 100 ps and relax in long-lived species with a life time beyond the time window of our TAS setup. There are two possibilities of this rapid GSB decays within first 100 ps: (1) annihilation of charges with excitons or (2) variation in

bleaching cross sections of the P3HT exciton and polaron.⁹² However, the E-field dried P3HT-NF:PCBM blend film shows 44% and 50% larger DT signal of 0-0 and 0-1 GSB peaks respectively than the untreated film from over 1 ps to 0.5 ns time scale, which implies larger population of photogenerated excitons and long-lived polarons.^{105,106} In addition, the slight increment of 0-0 GSB signal at longer time scale (i.e. > 500 ps) is also observed in non-treated film (Fig 3.11a). This rise of GSB signal indicates the accumulation of long lived or trapped excitons and polarons in disordered P3HT phase. On the other hand, EF-treatment of P3HT-NF:PCBM film improves ordering of system and reduces trapping sites by creating efficient transport channels, thus preventing the accumulation of these photospecies.

Generally, in solar cell devices, the monomolecular and bimolecular recombinations are two loss mechanisms. The former mechanism occurs by the annihilation (dominate in picoseconds to few nanosecond time windows) of positive and negative charges near the D/A interface which originate from the same exciton. This is often reported as Shockley-Read-Hall trap-assisted recombination process.^{107,108} However in bimolecular recombination process, two spatially-separated charges away from the polymer interfaces recombines and generally this process dominates the recombination dynamics over ns- μ s time scale. This is also known as Langevin recombination.¹⁰⁹ To probe the dynamics of these long-lived charges at even longer time scales in both types of blend films, nanosecond laser flash photolysis spectroscopy was performed.

Fig. 3.13 shows the normalized decay profile of 0-0 and 0-1 GSB peak of E-field treated and non-treated blend films measured by the ns-transient absorption spectroscopy at $\sim 60 \mu\text{J}\cdot\text{cm}^{-2}$ pump fluence excitation. Both GSB peaks of E-field dried P3HT-NF:PCBM film decays faster in first sub-microsecond compared to the control film which then followed by long lived tail. This faster decay of GSB signal can be attributed to the dominance of bimolecular recombination in E-field treated film than without any E-field treatment. Here

are two possible causes for the presence of higher bimolecular recombination in E-field dried blend film: (a) the higher population of photogenerated carries arises from the improved photo-absorption which leads to higher recombination in lacking of sweep-out voltage which extract them before recombination, and (b) the presence of considerable increased charge trapping sites which causes higher charge concentrations.¹¹⁰

3.3.11 Modelling the Charge Carrier Recombination Dynamics: For further understanding of the dynamics occurring in these blend films at longer time scales, an analytical model developed by our group was modified and employed to analyze the branching ratios of monomolecular versus bimolecular recombination in these films. In previous model, these two processes are assumed to occur independently.¹¹¹ The expressions describing the charge dynamics are derived as follows

$$\frac{dN_{mon}}{dt} = -\gamma_1 N_{mon}^\alpha N_{mon}^1 \quad (3.6)$$

$$\frac{dN_{bim}}{dt} = -\gamma_2 N_{bim}^\alpha N_{bim}^2 \quad (3.7)$$

$$\frac{N}{N_0} = ((1-f)^{-\alpha} + \alpha\gamma_1 N_0^\alpha t)^{-\frac{1}{\alpha}} + (f^{-(\alpha+1)} + (\alpha+1)\gamma_2 N_0^{(\alpha+1)} t)^{-1/(\alpha+1)} \quad (3.8)$$

$$= ((1-f)^{-\alpha} + k_1 t)^{-\frac{1}{\alpha}} + (f^{-(\alpha+1)} + k_2 t)^{-1/(\alpha+1)} \quad (3.9)$$

where N_{mon} and N_{bim} represents the population of charges undergoing monomolecular and bimolecular recombination. The fraction (f) refers to initially generated charges which annihilate by bimolecular recombination while rest ($1 - f$) undergo monomolecular recombination.^{110,112} α is the concentration dependent exponent while γ_1 and γ_2 are the recombination prefactors. The third expression represents the sum of both recombination mechanism and corresponds to the transient absorption signal of GSB.

In this model, GSB decay occurs via two channels: monomolecular (or Shockley-Read-Hall trap-assisted recombination) and bimolecular (or Langevin type) recombination. This model yields a good fit at higher pump fluence where long lived species dominates in GSB. Bimodal polaron recombination was previously reported and the long life species ($>10 \mu\text{s}$) was ascribed to polarons that are deeply trapped and undergo trap-limited recombination in P3HT:PCBM system.¹⁰⁹ Meanwhile, the recombination in sub microsecond time scale is from polarons in mobile states and/or from shallow traps.¹¹³ The increase of contribution from long-lived species may also originate from a large number of deep traps or from some irreversible change created by the high intensity laser pulses. As the long-lived species have a much longer lifetime than the time region we measured, we can simply put it as a constant. The equations of this modified model are:

$$\frac{N}{N_0} = ((1-f)^{-\alpha} + kt)^{-1/\alpha} + f \quad (3.10)$$

where k is the average recombination rate and $(\alpha+1)$ is the average recombination order related to the type of recombination and concentration dependence of carrier mobilities. The recombination rate k may come from Langevin process and/or trap-assisted recombination.

Table 3.2: Fitting parameters for the ns-TAS data.

Device	$k \text{ (ns}^{-1}\text{)}$	$\alpha + 1$	f	$*R^2$
0-1 GSB w/o EF	$(2.5 \pm 0.2) \times 10^{-3}$	1.1 ± 0.1	0.45 ± 0.01	0.992
0-1 GSB w EF	$(4.4 \pm 0.3) \times 10^{-3}$	1.4 ± 0.1	0.26 ± 0.01	0.993
0-0 GSB w/o EF	$(0.7 \pm 0.1) \times 10^{-3}$	1.3 ± 0.02	0.41 ± 0.01	0.992
0-0 GSB w EF	$(1.1 \pm 0.1) \times 10^{-3}$	1.5 ± 0.03	0.32 ± 0.01	0.993

$*R^2$ Represents the degree of the fitting.

A representative plot of fits for the decay of 0-0 and 0-1 GSB peak for film treated with E-field and standard is shown in **Fig. 3.13**. The fitting parameters from this model are listed

in Table 3.2. For 0-1 GSB peak, the recombination order enhances from 1.1 to 1.4 (1.3 to 1.5 for 0-0 GSB peak) on E-field treatment which represents higher contribution of Langevin process to the recombination. Moreover, the fraction of long lived species *i.e.* f for 0-1 GSB is also dropped from 0.45 to 0.26 for E-field treatment which attribute to decrease in deeper trap states. The similar trend is also observed from 0-1 GSB decay dynamics.

Figure 3.13 Nanosecond transient absorption decay dynamics of film dried without and with electric field at ns– μ s time scale (circle and square) for (a) GSB 0–0 and (b) GSB 0-1 peaks. The analytical model fits to the decay dynamics is represented by the solid lines.

Apparently, the E-field dried film exhibits higher bimolecular recombination which is inconsistent with improved performance of E-field dried devices. However, one has to note that the dynamics were measured at open circuit voltage condition where sweep-out voltage is completely absent. Therefore, higher mobility of the charge carriers following E-field treatment promoted more opportunities for free charges to encounter one another and undergo recombination, or be trapped in the lack of any external voltage which helps in extraction of charges from the film before recombination occur. Hence, in consistent with our previous findings of enhanced performance and improved charge carrier mobility measured in E-field-dried devices along with higher bimolecular recombination in E-field dried film as observed

here, we proclaim that E-field treatment promoted the P3HT molecules organization in amorphous phase and hence improved the inter fibrillar charge transport.

3.4 Conclusions

In conclusion, we find that E-field treatment is an alternative approach to improve the device performance of P3HT-NF:PCBM OSCs which is feasible for low temperature processing. Based on findings from electrical and optical characterizations, the performance improvement in E-field dried devices can be attributed to: (a) higher photoabsorption which resulted in higher population of exciton formation; (b) efficient charge transport resulting from better oriented polymer chains at the polymer nanofibers interfaces; and (c) facilitate efficient inter-fibrillar charge transport and extraction due to the oriented polymer chains. All these findings are found to consistent with the speculation of bridging the P3HT chains between nanofibers to improve charge transport by orientation management of these chains using the external electric field treatment; thereby improving the performance of P3HT-NF:PCBM OSC devices.

Chapter 4

Investigation of the relationship between external electric field treatment and blend morphology in bulk heterojunction solar cell

Summary

As seen in chapter 3, the external electric field treatment of active layer blend system is an effective technique to enhance the organic solar cell performance. However, the effectiveness of electric field (E-field) interaction in a wide family of conjugated polymers is severely lacking. In this chapter, we investigate the effects of external electric field treatment on different polymer/fullerene blend films based on different intrinsic morphologies to establish a morphology-function-charge dynamics relationship to the photovoltaic performance. The study reveals the importance of electric dipole moment, intrinsic molecular structure and self-organization ability of conjugated polymers for the effective e-field and polymer interaction. The external E-field treatment promote self-organization of thiophene-based semicrystalline conjugated polymers i.e. P3HT and P3BT and hence improve the crystallinity, absorption and hence PCE of OSC devices. On the other hand, the lack of lamellar packing and longer molecular length of amorphous polymers (such as PTB7 and PCPDTBT) causes ineffective dipole and E-field interaction despite their higher dipole moment. In addition, the ultrafast dynamics also reveal the importance of blend morphology to control loss mechanism in E-field treated blend system.

4.1 Introduction

As seen from the previous chapter, the molecular organization of polymer is very essential for the efficient charge transport as well as better crystallinity and hence better performing BHJ devices. Tuning the blend morphology to obtain desired nanoscale structure has been proven to be an effective method to optimize solar cell efficiency. Thermal annealing⁶⁶⁻⁶⁸, ordered organization of blend⁵⁴, self-assembly with marginal solvents,^{69,114} etc are some of the best examples of morphology tuning methods to improve solar cell device performance. Processing of active layer in the presence of external electric has also emerged as an attractive approach to control the nanomorphology of active layer to improve photo-absorption and charge carrier mobility.¹¹⁵ Researchers have also successfully used this approach for organizing the photoresists and carbon nanorods.¹¹⁶⁻¹¹⁸ H. L. Cheng *et. al.*¹¹⁹ and A. M. Hiszpanski *et. al.*¹²⁰, reported an improvement of in-plane charge carrier mobility by tuning the structural organization of organic semiconductor in organic thin film transistor. Feasibility of this approach at different stage of device processing as used by various research groups prove the importance of the external electric field treatment to improve PCE of solar cells .

In this work we have investigated the relationship between the optoelectronic properties, nanomorphology, molecular orientation and charge dynamics influenced by external electric field treatment in polymer based organic solar cells. This study would provide better insights into the effects of external electric field on organic solar cells fabricated with different D/A systems. To accomplish this work, two different groups of polymers are chosen which have different nanomorphologies in active blend films. The first polymer group, P3HT and P3BT are semi-crystalline in nature and show inherent self-organization and crystallization capabilities in active blend films.^{121,122} While the other group, PTB7 (Poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-

[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl])) and PCPDTBT (Poly[2,6-(4,4-bis-(2-ethylhexyl)-4*H*-cyclopenta [2,1-*b*;3,4-*b'*] dithiophene)-*alt*-4,7(2,1,3-benzothiadiazole)]) were chosen because they are amorphous polymers which are inherently unable to self-organize in long-range order but show finely intermixing with acceptor in active blend.^{123,124} These polymers are intrinsically polar in nature ($\mu_{\text{P3HT}} = 1.0 - 1.6\text{D}^{88}$, $\mu_{\text{P3BT}} = 1.0 - 1.5\text{D}$, $\mu_{\text{PTB7}} = 3.76\text{ D}^{125}$) and can interact with an external field by dipole polarization. The solar cell devices based on first group of semicrystalline polymer (*i.e.*, P3HT:PC60BM and P3BT:PC60BM) shows improved power conversion efficiency when an optimal external electric field (E-field) of $4.0\text{ kV}\cdot\text{cm}^{-1}$ was applied during thermal annealing of active layer before cathode deposition. On the other hand, the performance of latter group of polymer based devices (*i.e.*, PTB7:PC70BM and PCPDTBT:PC60BM) remained almost unchanged in the range of $2.0\text{--}8.0\text{ kV}\cdot\text{cm}^{-1}$ electric fields even though a more effective dipole interaction could have been conjectured on account of their higher ground states dipole moments. The reasons for the anomalous behaviour of polymers to electric field interaction were further investigated by optical characterizations and nanoscale analysis of active blends and DFT simulation of their monomers. The semicrystalline group of polymers shows better photo-absorption and improved crystallinity ($\sim 16\%$ in P3HT:PC60BM and $\sim 35\%$ in P3BT:PC60BM) to the devices subjected to E-field treatment compared to those without E-field treatment. Transient absorption spectroscopy measurements also revealed higher generation of the excitons and polarons and significant reduction of losses through monomolecular recombination of charge transfer states in E-field treated devices. However, amorphous polymers did not show any significant optical/structural changes between EFT and control samples.

4.2 Experimental Procedures

Film preparation for optical characterizations: The blend solutions of different combinations of D/A were prepared in 1,2-dichlorobenzene (DCB) and stirred overnight. The concentrations of different blend solutions and stirring temperatures were as follows: P3HT:PC60BM (1:0.8, 18 mg/ml, 50 °C), P3BT:PC60BM (1:0.8, 18 mg/ml, 50 °C), PTB7:PC70BM (1:1.5, 25 mg/ml, 22 °C), and PCPDTBT:PC60BM (1:3, 28 mg/ml, 22 °C). To fabricate organic solar cell (OSC) devices, ITO coated glass substrates were first thoroughly cleaned by detergent solution followed by ultrasonication in deionized water, acetone and isopropanol for 15 min each and kept in oven at 90 °C for overnight to remove moisture. These cleaned substrates were further treated with plasma for 5 min to make the ITO surface hydrophilic and to increase work function. A thin film of Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (CLEVIOSTM P VP Al 4083, HC Starck) PEDOT:PSS layer of ~30 nm was deposited by spin-coating on these substrates (at 3000 rpm for 60 s), followed by annealing at 100 °C for 15 min. Later these substrates were transferred to the N₂ filled glove box for further processing. Different blend solutions were then spin-coated on top of PEDOT:PSS. Based on previous reports, solvent drying of these active layers were performed in two different sets for 30 min each to maintain similar processing conditions.⁸⁹ On the first set of films, an external electric field was applied across the active layers by means of ITO and aluminium plate as counter electrode i.e., the “electric field treated” film (EFT) as shown in **Fig. 4.1**. Constant electric fields (2, 4, and 8 kV-cm⁻¹) were applied at 140 °C and at room temperature for 30 min during the active layer drying of semicrystalline and amorphous blend systems respectively. Finally cathode contact as a 100 nm thick aluminium layer was deposited on the active layer through a shadow mask (with active area of 0.07 cm²) in a vacuum of 10⁻⁶ mbar. For all optical measurements, different blend films were directly prepared on cleaned indium-tin oxide (ITO) coated glass substrates.

Figure 4.1: Schematic of the electric field treatment of active blend films.

4.3 Results and Discussions

4.3.1 Photovoltaic Characteristics: J - V characteristics of P3HT:PC60BM, P3BT:PC60BM PTB7:PC70BM and PCPDTBT:PC60BM solar cell devices fabricated with and without electric field treated active layer, measured under $100\text{-mW}\cdot\text{cm}^{-2}$ standard illumination of the AM1.5G spectrum are shown in **Fig. 4.2**. A blend of PTB7 with PC70BM was chosen instead of PC60BM because the former is considered to be one of the most efficient BHJ OSCs.¹²⁶ The behaviour of PCPDTBT:PC60BM is very similar to that of PTB7:PC70BM; hence discussion of amorphous polymers will be represented by the latter blend system. **Table 4.1, 2, 3 and 4** summarize the relevant parameters e.g., short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factors (FF) and power conversion efficiency (PCE) determined from J - V characteristics of semicrystalline and amorphous group of polymers based devices treated with external electric fields as shown in **Fig. 4.2**. For the convenience, devices fabricated with external electric field treatment are termed as "EFT" devices while those prepared without any E-field treatment are termed as "standard" device. It should also be noted here

that discussion on the EFT semicrystalline devices are only based on those prepared under 4.0 kV-cm^{-1} (an optimum field) E-field treatment as “EFT” devices throughout this chapter.

Figure 4.2: *J-V* Characteristics of (a) P3HT:PC60BM, P3BT:PC60BM (b) PTB7:PC70BM and (c) PCPDTBT:PC60BM devices fabricated under different electric field and measured under 100 mW-cm^{-2} illumination of AM1.5 Sun.

Table 4.1: Summary of the P3HT:PC60BM solar cell devices under illumination

EF/Parameters	PCE (%)	J_{sc} (mA-cm^{-2})	V_{oc} (V)	FF
0.0 kV-cm^{-1}	3.0 ± 0.2	8.8 ± 1.2	0.57 ± 0.01	0.61 ± 0.02
2.0 kV-cm^{-1}	3.3 ± 0.1	9.6 ± 1.0	0.58 ± 0.01	0.61 ± 0.01
4.0 kV-cm^{-1}	3.5 ± 0.1	9.5 ± 0.8	0.58 ± 0.01	0.63 ± 0.02
6.0 kV-cm^{-1}	2.7 ± 0.1	8.4 ± 0.6	0.56 ± 0.02	0.58 ± 0.01

Table 4.2: Summary of the P3BT:PC60BM solar cell devices under illumination

EF/Parameters	PCE (%)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF
0.0 kV-cm ⁻¹	1.4 ± 0.1	4.0 ± 0.6	0.58 ± 0.01	0.61 ± 0.02
2.0 kV-cm ⁻¹	1.5 ± 0.2	4.0 ± 0.8	0.65 ± 0.02	0.58 ± 0.02
4.0 kV-cm ⁻¹	1.8 ± 0.1	4.9 ± 0.9	0.64 ± 0.02	0.58 ± 0.01
6.0 kV-cm ⁻¹	1.6 ± 0.2	4.7 ± 0.5	0.62 ± 0.01	0.55 ± 0.01

Table 4.3: Summary of the PTB7:PC70BM solar cell devices under illumination

EF/Parameters	PCE (%)	J_{sc} (mA-cm ⁻²)	V_{oc} (V)	FF
0 kV-cm ⁻¹	5.36± 0.3	13.8± 1.3	0.72 ± 0.02	0.54 ± 0.03
2 kV-cm ⁻¹	5.54± 0.2	13.5± 1.7	0.72 ± 0.02	0.57 ± 0.03
4 kV-cm ⁻¹	5.34± 0.2	14.0± 1.2	0.72 ± 0.01	0.53 ± 0.01
8 kV-cm ⁻¹	5.44± 0.3	13.7± 2.1	0.71 ± 0.02	0.56 ± 0.02

Table 4.4: Summary of the PCPDTBT:PC60BM solar cell devices under illumination

EF/Parameters	PCE (%)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF
0 kV-cm ⁻¹	2.2 ± 0.2	11.6 ±0.4	0.58±0.01	0.34±0.03
2 kV-cm ⁻¹	2.2 ± 0.2	9.2 ± 0.8	0.61±0.01	0.39±0.01
4 kV-cm ⁻¹	2.3 ± 0.2	10.0 ± 0.3	0.57±0.02	0.40±0.02
8 kV-cm ⁻¹	2.3 ± 0.2	10.8 ± 0.5	0.56±0.01	0.39±0.01

EFT solar cell devices based on semicrystalline polymers (i.e., P3HT:PC60BM and P3BT:PC60BM) exhibit higher PCE as compared to standard devices as shown in **Table 4.1** and **4.2**. In P3HT:PC60BM devices, PCE improvement occurred mainly by enhancement of J_{sc} while it was cumulative improvement of all parameters in P3BT:PC60BM solar cell devices. J - V characteristics of these devices were also measured in the dark to explore the effect E-field treatment on charge transport properties as shown in **Fig 4.3**. Dark current in P3HT:PC60BM device is observed to be one order of magnitude higher than P3BT:PC60BM devices. It indicates that P3BT:PC60BM system has relatively poor morphology (or fine intermixing of P3BT and PC60BM) which causes inefficient charge transport. Ming He *et. al.* also found this to be the same reason which causes higher charge carrier recombination and lower charge carrier mobility in P3BT blend system and thus lower device performance as

compared to P3HT based devices.¹²⁷ However, the higher dark current in both P3HT:PC60BM and P3BT:PC60BM EFT devices indicate efficient charge transport with respect to their standard samples. This could result from an improved organization of the polymers by dipole-E-field interaction, which leads to better connectivity inside the blend system.^{128,129} A significant V_{oc} improvement of 0.06 V V_{oc} in EFT P3BT solar cell devices is also attributed to the reduced recombination sites in EFT system.⁴¹ In contrast to this group of polymers, PTB7:PC70BM (**Fig. 4.2b**) and PCPDTBT:PC60BM (**Fig. 4.2c**) based solar cells were found to be unresponsive to the applied external electric field treatment from 2 kV-cm⁻¹ to 8 kV-cm⁻¹ during active layer drying process at room temperature. PTB7:PC70BM solar cell devices displayed 5.6 ± 0.4 % PCE ($J_{sc} = 14.9 \pm 1.5$, $V_{oc} = 0.72 \pm 0.01$, $FF = 0.52 \pm 0.02$) while PCPDTBT:PC60BM displayed 2.2 ± 0.2 % PCE ($J_{sc} = 11.6 \pm 0.4$, $V_{oc} = 0.58 \pm 0.01$, $FF = 0.34 \pm 0.02$) irrespective of applied electric field (see **table 4.3, 4.4**). These results are contradicting the hypothesis of better ordering of polymers by dipole polarization under the influence of external electric field due to higher dipole moment. To investigate the reason for anomalous behaviour of different polymers to the external electric field treatment, optical and structural characterizations were performed on these blend films.

Figure 4.3: Linear J - V characteristics in the dark for the standard and E-field (4.0 kV-cm⁻¹) treated (a) P3HT:PC60BM and (b) P3BT:PC60BM.

4.3.2 Linear Absorption: The linear absorption spectra of standard and EFT for P3HT:PC60BM and P3BT:PC60BM blend films coated on ITO/glass substrates are shown in **Fig 4.4**. In semi-crystalline group of polymers, absorption enhances in EFT films as compared to the standard. In P3HT:PC60BM, the maximum absorption peak (λ_{max}) is observed at 513 nm and other two vibronic “shoulders” are found to be at 550 and 600 nm in both films. The peak at the lower wavelength ($\lambda = 513$ nm) represents the π - π^* intrachain transition, while the vibronic features at longer wavelengths are correlated to the π - π^* stacking strength. P3BT:PC60BM blend films also exhibits similar spectral profile but “vibronic shoulders” are more prominent in P3HT:PC60BM blend films. In addition, the absorption also maximize at 488 nm which is blue shifted relative to P3HT:PC60BM ($\lambda_{\text{max}} = 500$ nm) which indicates poor crystallinity of P3BT:P60CBM blend relative to P3HT:PC60BM. Thus, in the standard devices, more organized P3HT molecules in blend films results in higher absorption and improved charge transport that would eventually account for better performance of P3HT:PC60BM devices over P3BT:PC60BM devices. The EFT on polymer blends improves photoabsorption compared to their respective standard blend films (**Fig. 4.4a**). Cheng Lin *et. al.* also observed significant improvements for P3HT:PCBM absorption in the 300-650 nm wavelength range when the active layer was dried under external electric field.⁸⁹ A stronger absorption in EFT blend films indicates further improvement to the molecular organization which enhances exciton and polaron generation. This is also consistent with improved short-circuit current density in the EFT devices (**Fig. 4.2a**). Thus, a combination of increased absorption and better charge transport (as the result of improved molecular organization) accounts for performance improvement in these EFT devices. On the contrary, EFT blend films of PTB7:PC70BM and PCPDTBT:PC60BM display similar absorption spectra and device performances compared with that of their standard blend films (**Fig. 4.2b** and **4.2c**).

Figure 4.4: Absorbance in standard and electric field treated (a) P3HT:PC60BM, P3BT:PC60BM and (b) PTB7:PC70BM and (c) PCPDTBT:PC60BM blend films. EFT blend film of P3HT:PC60BM and P3BT:PC60BM was treated at 4.0 kV/cm⁻¹.

4.3.3 Photoluminescence: A steady-state photoluminescence (PL) study was performed to investigate the exciton dissociation efficiency after they are generated through photo absorption. Photoluminescence phenomenon involves a recombination process of photoexcited excitons and monomolecular recombination of CT states. The quenching of PL indicates the suppression of this recombination and the existence of alternative pathways for excitons and charge carriers. The efficiency of PL quenching is often correlated to charge generation and is dependent on the distribution of molecules. With an increase of D/A interfaces, 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 D/A blend. **Fig. 4.5 (a)** and **4.5 (b)** shows the photoluminescence spectra of

standard and EFT active layers of P3HT:PC60BM and P3BT:PC60BM upon excitation with a 530 nm light source. The EFT samples exhibit stronger PL intensity which indicates more radiative recombination of excitons compared to standard films. This could be due to the effects of EF-induced higher photo-absorption and reorganization of D/A molecules, which promotes more phase separation and formation of more extended ordered regions with reduced number of D/A interfaces. Excitons that are generated in the extended regions beyond the exciton diffusion length recombine radiatively before approaching D/A interface and this results in higher PL intensity. The PL spectra of standard and EFT films of PTB7 and PCPDTBT upon excitation with a 630 nm light source are also shown in **Fig 4.5 (c)** and **4.5 (d)**. Due to strong quenching of PL in the presence of relatively higher fraction of fullerene (PTB7:PC70BM – 1:1.5 and PCPDTBT:PC60BM – 1:3) in these blend films, these spectra were measured on PTB7 and PCPDTBT films. As a result of EFT on these films, slight quenching of PL intensities is observed, but it is not as significant as observed in P3HT and P3BT based systems (**Fig 4.5 (a)** and **4.5 (b)**). Such small variations in PL intensities indicate that the recombination mechanism is not influenced significantly in blend systems and thus the photovoltaic performance is not affected. Next, we discuss about the effects of electric field treatment on the organization and nanomorphology of blend films as characterized by X-ray diffraction and atomic force microscopy.

Figure 4.5: PL Intensity of (a) P3HT:PC60BM and (b) P3BT:PC60BM, (c) PTB7 and (d) standard and electric field treated films.

4.3.4 Nano-morphology: The surface morphology of P3HT:PCBM and P3BT:PCBM (standard, EFT) blend films have been visualized using AFM in contact mode. **Fig. 4.6** shows $5 \times 5 \mu\text{m}^2$ topographical AFM images and corresponding histogram of all different films. The surface topology of EFT was found rougher than standard active layers in both polymer blends. The root mean square (RMS) surface roughness of P3HT:PCBM active layer is $0.87 \pm 0.02 \text{ nm}$ ($0.42 \pm 0.03 \text{ nm}$ for P3BT:PCBM) for “standard” film, and $1.08 \pm 0.04 \text{ nm}$ ($0.52 \pm 0.04 \text{ nm}$ for P3BT:PCBM) for “EFT” film. The rougher surface is most likely a signature of self-organization of polymer molecules which in turn enhances the formation of ordered structures in blend film.⁷⁰ The electric-field treatments might also have changed the vertical composition of active layer and leads to the variations of distribution between P3HT and

PCBM which caused higher surface roughness which is also shown by S. Y. *et.al.*¹³⁰ A rough surface at the metal electrode could enhance internal light scattering and hence improve light absorption. At the same time, roughness could also increase the metal–semiconductor interface area, decrease the contact resistance and enhance the charge collection at the electrodes.⁸⁸ All these effects as a consequence of external EF help in increasing J_{sc} in solar cells fabricated with these films.

Figure 4.6: Topography AFM scan of (a) P3BT:PC60BM standard, (c) P3BT:PC60BM EFT, (e) P3HT:PC60BM standard and (g) P3HT:PC60BM EFT. Their corresponding three dimensional holograms are shown in (b), (d), (f) and (h) respectively.

4.3.5 Grazing-incidence X-ray diffraction: Fig. 4.7 shows the XRD pattern of all these blend films of polythiophenes coated on ITO/glass substrates. The pattern of both samples show a clear single peak at $2\theta \sim 5.48$ (100) for P3HT:PC60BM and at $2\theta \sim 6.78$ in P3BT:PC60BM. The diffraction patterns in P3HT and P3BT derive from the lamellar structure of these polymers which corresponds to a parallel edge-on π - π stacking among the thiophene chains with respect to substrate. The (100) peak intensity in EFT films is stronger as compared to that of corresponding standard films, suggesting that the crystallinity of both active layers is enhanced under the influence of E-field treatment. The relative degree of crystallinity and crystal sizes of different blend films are obtained by fitting the diffraction

patterns of (100) peaks and summarized in **table 4.5**. The crystallinity of blends is calculated by the dot product of diffraction peak intensity and full-width half-maximum (FWHM). Thus the crystallinity is improved by ~ 15.8% in P3HT:PC60BM and 35% in P3BT:PC60BM blend film as a result of EFT. By employing Debye-Scherrer's equation ($D = k\lambda/\beta\cos\theta$), where $k = 0.9$ and β corresponds to FWHM of peak (in radians), crystallite size (D) the mean polymer crystallite size in blends was calculated as shown in **table 4.5**. The increase in crystallite size in EFT blend films (from 7.2 nm to 7.8 nm in P3HT:PC60BM and 6.1 to 7.2 in P3BT:PC60BM) confirms the enhanced ordering of blend films. The (100) reflection corresponds to the spacing between P3HT lamellae. The processing of blend films with EF also results in an increase in the d (100)-spacing from 1.63 to 1.78 nm in EFT P3HT:PC60BM blend. This increased lamellar spacing inside polymer crystallite is believed to be result of higher ordering. Therefore, the polymer chains are better organized and result in more ordered structures with simultaneous external EFT during thermal annealing of systems. XRD measurements were also performed on standard and EFT ($4.0 \text{ kV}\cdot\text{cm}^{-1}$) PTB7 and PCPDTBT films as shown in **Fig. 4.7c** and **4.7d**. It is important to note that fullerene is used in much higher amounts compared to the donor polymer to fabricate the devices (*i.e.*, PTB7:PC70BM – 1:1.5 and PCPDTBT:PC60BM – 1:3). This is in contrast to the blend D:A ratio of 1:0.8 for both P3HT:PC60BM and P3BT:PC60BM. To disregard the effect of fullerene organization (due to the higher PCBM loading in the former films), which could mask the effect of EFT on the orientation of amorphous polymers, we measured XRD of only donor polymers. No clear diffraction peaks corresponding to any crystallographic plane were observed from either of amorphous polymer films. The invariance in the XRD profiles of untreated and E-field treated films shows that E-field interaction with polymer dipoles is ineffective in promoting any structural reorientation in these polymers.

Figure 4.7: GIXRD patterns of standard and EFT (a) P3HT:PC60BM and (b) P3BT:PC60BM, (c) PTB7 and (d) PCPDTBT films. The samples were prepared on ITO coated glass substrates.

Table 4.5. Summary of the XRD parameters of different P3HT:PC60BM and P3BT:PC60BM blend films.

Blend film/Parameters	FWHM ($^{\circ}$)	Crystallinity (a.u.)	Crystallite size (nm)	d (100) (nm)
P3HT:PC60BM Standard	1.13	1203	7.2	1.63
P3HT:PC60BM EFT	1.05	1393	7.8	1.78
P3BT:PC60BM Standard	1.35	448	6.1	1.29
P3BT:PC60BM EFT	1.14	605	7.2	1.31

Thus we conclude that polymer chains of semicrystalline donors (P3HT and P3BT) are predominantly self-organized with lamellar stacking perpendicular to the substrate. As the E-field is applied concurrently during thermal annealing, the lamellar stacking of donor polymer is promoted in field direction with elongated lamellar spacing. We attribute this to

the interaction of the electric dipole moment of thiophene ring with external E-field which enhances vertical ordering of donor molecule in the direction of applied field.⁸⁸ However, E-field interaction with molecular dipole moments was ineffective in amorphous polymers blend systems due to the constraint imposed by the inability of polymer molecules to form ordered phase. Hence, the respective electric-field treated blends did not undergo any noticeable change in nanomorphology, leading to indistinguishable optical and electrical properties, and expectedly similar solar cell device performance.

4.3.6 Analysis of molecular electrostatic potential, dipole moment and molecular

orientations: To find the main cause for different interaction behaviour of these polymers to the external electric field, the electrostatic charge distribution and orientation of electric dipole is visualized in both groups of polymers. To simulate charge distribution and to compare the ground state dipole moments of these polymers, theoretical calculations were performed on monomer of these donor polymers. The geometries of monomers were obtained using B3LYP model with 6-311G** basis set^{131,132} and frequency analysis was followed to assure stability of the optimized structures. The molecular electrostatic potential (ESP) surface is then calculated based on optimized geometry of these monomers. Gaussian 09 was used as a tool to perform all these calculations.¹³³

Fig. 4.8 represents the electrostatic potential (ESP) distribution in monomer of these conjugated polymers. Red and blue regions in the ESP diagram of these monomers represent negative and positive potentials, respectively. The negative charge mainly exists on sulphur atom in the heterocycle of P3HT, P3BT and PTB7, while it is localized on the nitrogen atom (with lone pairs) in PCPDTBT. The electrons tend to be distributed around the sulphur atom more than hydrogen, carbon and nitrogen atoms causing sulphur to be negatively charged. This imbalance of the electronic charge distribution gives a polarity to polymers. The black

arrows in **Fig. 4.8** represent the direction of ground state dipole moments in each monomer, which are calculated to be 0.99 D, 0.97 D, 4.02 D and 1.53 D for P3HT, P3BT, PTB7 and PCPDTBT, respectively. The monomer lengths were also examined using this model and found to be $L_{\text{P3HT}} = 0.99$ nm, $L_{\text{P3BT}} = 0.76$ nm, $L_{\text{PTB7}} = 2.19$ nm and $L_{\text{PCPDTBT}} = 1.41$ nm. **Fig. 4.8a** and **4.8b** show that the direction of the intrinsic dipole moment in P3HT and P3BT is along the polymer chain and these monomers are also smaller in size than other polymers. When an external E-field is applied during thermal annealing of the films, thiophene molecules get polarised and molecular dipoles in amorphous region align themselves with E-field. In organic solar cell device structure under illumination, charge carriers transport occur out-of-plane towards their respective electrodes. Therefore, increase in the vertical ordering of the system is also important for efficient charge transport in these devices. The advantage of polymer alignment was also observed by Paul Meredith *et. al.* where one order higher hole mobility was observed from vertically aligned DPP–DTT based system.^{134 135} On the other hand, our results suggest that the orientation and packing of larger and more branched PTB7 and PCPDTBT monomers under EFT (at the largest applied E-field of $8 \text{ kV}\cdot\text{cm}^{-1}$) is still inhibited despite their higher dipole moment than semicrystalline conjugated polymers. Therefore, the organization within blends of amorphous polymers remains unaffected due to steric constraints imposed by the inability of polar molecules to orientate.

Figure 4.8: Electrostatic charge distribution and dipole direction (by black arrow) in the monomer of (a) P3HT, (b) P3BT, (c) PTB7 and (d) PCPDTBT.

On the basis of above discussion, thermally annealed semicrystalline blend systems, P3HT and P3BT are organized with lamellar stacking perpendicular to substrate accompanied by surrounding amorphous phase.¹³⁶ When an external E-field is applied during thermal annealing of these blend films, the lamellar stacking of polymers is further promoted in field direction. The growth of lamellar stacking in P3HT and P3BT blend systems is confirmed by an increase of the (100) peak intensity in the GIRXD measurements. This results in polarization of polar polymer molecules in system due to dipole-E-field interaction, which enhances ordering of blend in E-field direction. Higher crystallinity improves photo-absorption and ordering of originally amorphous polymer phase also provides more efficient charge transport, thus improving PCE. On the other hand, PTB7 and PCPDBT exhibit neither improvement in solar cell performance nor change in structural properties. Although PTB7 and PCPDBT monomers have higher dipole moments than their P3HT and P3BT

counterparts, the ineffectiveness of EFT in former is likely due to their larger and more complex monomers rendering them less easy for reorientation and packing/stacking under external E-field for lamellar formation. Thus, the intrinsic dipole moment of a molecule is not the sole criteria to assess its suitability for EFT, but the intrinsic lamellar structure and molecular organization are also, and perhaps even more, essential. Hence, we infer that the EFT of active layer in OSCs to improve the performance is best used only for molecules that have: (i) electric dipole moment, (ii) intrinsic lamellar packing and (iii) smaller linear monomer units.

Lastly, the effects of external electric field on exciton/polaron formation and recombination mechanisms in P3HT:PC60BM and P3BT:PC60BM blend films are further investigated by time-resolved spectroscopy and correlated with their solar cell device performances.

Ultrafast Spectroscopy Measurements

4.3.8 Charge carrier dynamics in fs-ns temporal regime: For further understanding of generation and recombination mechanism of photoexcited species, transient absorption measurements were performed using ultrafast spectroscopy on EFT and standard active layers of P3HT:PC60BM and P3BT:PC60BM. The representative differential transmission (DT) spectra measured spanning from 520 nm to 1500 nm at varying delay times following photoexcitation at 500 nm for all these active layers are shown in **Fig. 4.9**. Both P3HT:PC60BM and P3BT:PC60BM shows similar TAS profile. Because they have a similar absorption profile and molecular structure (P3BT has only shorter side chain by two methyl group), TAS profile was also found to be similar. The vibronic peaks corresponding to absorption transitions at 605 nm and 555 nm apparent as ground state bleaching (GSB) peaks⁹² in both active layers. P3HT:PC60BM blend film shows strong and sharper GSB

peaks as compared to P3BT:PC60BM films. This arises due to the dominant crystallinity of P3HT in active layer as compared to P3BT which is consistent with XRD analysis and topographical AFM scans. Relatively higher magnitude of GSB signal in both types of EFT blend films indicates higher population of excitons and polarons as compared to standard blend films which is also consistent with enhanced photo-absorption in EFT blend films.¹⁰³ The transient signal around 700 nm in P3HT:PC60BM active layers are due to stimulated emission of the probe pulse. Short lived SE signal in EFT P3HT:PC60BM blend film as compared to standard blend films indicates faster charge transfer to PC60BM. On the other side, the absence of SE signals in P3BT:PC60BM blend is consistent with finely mixed morphology where charge transfer is completed before 1ps.

Figure 4.9: Transient absorption spectrum of (a) P3HT:PC60BM standard, (b) P3HT:PC60BM EFT, (c) P3BT:PC60BM standard, and (d) P3BT:PC60BM EFT blend films at $35 \mu\text{J}\cdot\text{cm}^{-2}$ pump fluence.

The broad negative $\Delta T/T$ signal between 850 – 1500 nm in near-infrared region represents the photo induced absorption in polymer of blend films. The most prominent peak at the initial time is ascribed to excitons population while a wide band between 850 nm to 1000 nm is correlated to the population of polymer polarons and charge transfer states in these blend films. On comparing the peak position of excitons in these active layers, excitons in P3BT are generated at lower wavelength range (1100 - 1200 nm) relative to P3HT (1250 -1300 nm). Generally, such red-shift in the transient absorption spectra occurs due to increased contribution of absorption in the region of polymers with stronger intermolecular ordering.^{110,137} Higher GSB signal in **Fig. 4.4 (a)** also validates better photoabsorption in P3HT:PC60BM blend system as compared to P3BT:PC60BM. Since P3HT and P3BT both are semicrystalline polymers with the resemblance of steady state absorption (**Fig 4.4 (a)**) and also originated from same thiophene family, the appearance of exciton peak at longer wavelength range in P3HT indicates stronger intermolecular ordering and relatively higher crystallinity as compared to P3BT. It confirms that these excitons in P3HT are generated in larger size (or highly ordered) polymer domains while excitons in P3BT are generated relatively smaller size (or less ordered) polymer domains.

The excitons in P3HT:PC60BM blend system is approximately 10 times longer-lived compared to P3BT:PC60BM blend system (**Fig. 4.9a** and **4.9c**). This is attributed to the donor and acceptor in the latter to be more finely mixed and that the abundant excitons encountered nearby dissociation sites after generation. This quick decay of exciton signal in P3BT:PC60BM signal also confirmed their origin from the relatively low crystalline polymer which is consistent with the XRD and AFM scans. Exciton peaks are found to be red shifted ($\Delta\lambda_{\text{P3HT}} = 22 \text{ nm}$, $\Delta\lambda_{\text{P3BT}} = 90 \text{ nm}$) in EFT films as compared to standard films in both D/A systems, which suggests that singlet excitons in these EFT blend systems are not localized on single chains but delocalized over the crystalline phase.¹³⁷ Such delocalization of excitons

also confirms better ordering and enhanced crystallinity in E-field treated systems. The stronger peak shift of P3BT as compared to P3HT ($\Delta\lambda_{\text{P3HT}} = 22 \text{ nm}$, $\Delta\lambda_{\text{P3BT}} = 90 \text{ nm}$) system indicates that excitons are more delocalized in former EFT blend system. Thus, EFT is enhancing the contributions from weakly interacting H-aggregates and also enhancing the intermolecular ordering to form J-aggregate-like excitons in P3HT.^{92,110}

Fig. 4.10 shows the normalized decay dynamics of 0-0 GSB peak and exciton peak in standard and EFT blend films. Slower decay of GSB signal in EFT P3BT:PC60BM blend film (**Fig 4.10 (b)**) confirms increased crystallinity of system where photoexcited species has longer lifetime ($> 2 \text{ ns}$) as compared to standard film ($\sim 50 \text{ ps}$). Exciton signal in EFT films also decay at a slower rate as compared to standard P3HT:PC60BM and P3BT:PC60BM films as shown in **Fig 4.10 (c)** and **4.10 (d)**. It also suggests that, excitons in EFT blend films are generated in larger or more ordered P3HT/P3BT domains and annihilation rate of these excitons by recombination is slower. On the other hand, GSB decay dynamics in P3HT:PC60BM (**Fig 4.10(a)**) is different where GSB signal in standard film rises at longer time scale. We attribute this rise of signal to the accumulation of photo-excited species in disordered P3HT:PC60BM system while enhanced self-assembly of EFT system provides easier pathways for charge-transfer and hence suppresses accumulation.

Figure 4.10: Normalized decay dynamics of (a) P3HT:PC60BM GSB peak at 610 nm, (b) P3BT:PC60BM GSB peak at 605 nm (c) P3HT:PC60BM peak at 1332 nm, and (d) P3BT:PC60BM peak at 1220 nm.

To address the mechanism of the formation of excitons and polarons in different blend films, a singular value decomposition (SVD) and global fitting analysis for the transient absorption spectra was performed. The global analysis separates the spectral features that have different time evolutions in these blend films. **Fig. 4.11** shows the separation of the different features in all different blend films over the time range from 100 fs to 5 ns in NIR spectral range where dynamics evolution determine the different species. In P3HT:PC60BM, first two most prominent decay time constants are mainly due to singlet excitons (dominant around 1300 nm); the first time constant is due to excitons present in amorphous or intermixed phase of P3HT:PC60BM while second is assigned to delayed exciton dissociation due to the migration in larger P3HT domains. The prompt charge generation (< 2 ps) indicates that no exciton diffusion is needed to reach PC60BM molecules to dissociate into free carriers. This is probably because PC60BM molecules are likely to be dispersed

homogeneously in amorphous region. The similar values of decay time constant in different P3HT:PC60BM blend films indicate that the external electric field treatment does not make any significant difference to excitons evolution mechanism. On the other hand, standard P3BT:PC60BM blend film shows four different decay channels as compared to three decay channels in EFT blend film (**Fig. 4.11c** and **4.11d**). The first two decay constants in this system can also be assigned to the excitons dissociation. The lengthening of first two decay processes in EFT P3BT:PC60BM (from 0.33 ps to 0.75 ps and 11.0 ps to 19.4 ps) corresponds to the transformation of intermixed phase of D/A to crystalline phase and expansion of polymer crystallites (**Fig. 4.11**). The addition decay channel ($1.0 \text{ ns} \pm 0.1$) in standard blend film can be correlated to strongly bound short lived CT states. These CT states are long lived (i.e. beyond 5 ns) in P3HT:PCBM blend films and EFT P3BT:PCBM blend as well. The last (longest) decay constant in all four blend films are ascribed to polarons and long lived CT states which decays beyond our measurement time window. In addition, the loss decay channel by CTS P3BT blend system is diminished by faster charge transfer between P3BT and PC60BM with vertically organized morphology in EFT samples. On comparing the decay dynamics in fs-ns time scale of all four blend films, the external electric field does not influence decay dynamics significantly in P3HT:PC60BM while excitons and CT states are found to be long lived in P3BT:PC60BM which contribute to higher photocurrent. This occurs due to improved crystallinity of blend and self-organized P3BT lamellae in EFT blend system which assists a faster charge transfer and charge transport to the electrodes in device.

Figure 4.11: Pre-exponential coefficient spectrum obtained by SVD and global fitting analysis of (a) P3HT:PC60BM standard, (b) P3HT:PC60BM EFT, (c) P3BT:PC60BM standard, (d) P3BT:PC60BM EFT blend films at $35 \mu\text{J}\cdot\text{cm}^{-2}$ pump fluence.

4.3.9 Modelling the Charge Carrier Recombination Dynamics: In order to further understand the slow transient signal of remaining polarons band (at around 1000 nm) beyond 1 ns (**Fig 4.9**), we measured the decay dynamics in nano-second to micro-second (ns- μ s) timescale when polaron and CTS population decay due to the recombination processes. The decay dynamics of these photoexcited species in standard and EFT blend films were investigated in region between 950 nm to 1050 nm as a function of excitation pump fluence (from 35 - $140 \mu\text{J}\cdot\text{cm}^{-2}$). P3HT and P3BT are from the same thiophene family and show a resemblance of steady state and transient absorption spectra. Since excitons are dissociated within the first nanosecond, measured dynamics in this time window represents bound charge transfer (CT) states and free (delocalized or spatially separated) polaron.¹¹⁰ The linear

relationship between the rise of DT signals and absorbed photon density in these blend films shows that CT states and free polarons have similar cross sections in this wavelength range (**Fig. 4.12**). Generally, CT states which are not converted to free carriers and decay by monomolecular (geminate) recombination while other free polaron population decay by bimolecular recombination.

Figure 4.12: Linear fitting of the DT signal vs no of absorbed photon for standard and EFT blend films of (a) P3HT:PC60BM and (b) P3BT:PC60BM.

Fig. 13a and **13b** shows that these decay dynamics are pump fluence dependent in P3HT:PC60BM blend films from first nanosecond onwards while **Fig. 13c** displays fluence independent dynamics within first 8 ns in standard P3BT:PC60BM blend film. Here we assume that these dynamics in P3BT also arises from the same photoexcited species as in P3HT. Thus, the dynamics measured between 950-1050 nm wavelength owing to the presence of CT states and localized polarons, as seen by Laquai et. al. in P3HT:PC60BM blend system.¹¹⁰ The fluence dependent dynamics in P3HT:PC60BM shows that these dynamics are dominated by free charge carriers, occurred from ultrafast dissociation of bound charges. On the other hand, the fluence independent decay in standard P3BT:PC60BM shows dominance of photoexcited species by strongly bound charges which persists for approximately 8 ns before dissociating or recombining to the ground state. This indicates that

these bound charges act as interfacial traps for charge carrier recombination. Such recombination is Shockley-Read-Hall (SRH) type trap-assisted recombination is usually a monomolecular process. On the other hand, the dynamics in EFT P3BT:PC60BM blend film exhibits shorter fluence independent dynamics (< 2 ns), indicating that these CT states dissociate earlier (within 2 ns). This suggests that Coulombic binding force within bound charges is weakened which enable them to dissociate easily (**Fig 11d**). The change in Coulombic binding energy is subjected to improved crystallinity and organization of blend components in the system.¹³⁷ Deibel *et.al.* has also observed the fall in Coulombic attraction and increases of dissociation efficiency in P3HT after the increase of crystallization in P3HT. At longer timescales, losses of free charges carriers in polaron band of both systems are strongly intensity dependent and recombine via Langevin type trap-free bimolecular (non-geminate) recombination.

For quantitatively understanding of dynamical processes in these blend films, an analytical model developed by our group was employed to analyze the branching ratios of monomolecular versus bimolecular recombination in these films. The expressions describing the charge dynamics are derived as follows:

$$\frac{dN_{mon}}{dt} = -\gamma_1 N_{mon}^\alpha N_{mon}^1 \quad (4.1)$$

$$\frac{dN_{bim}}{dt} = -\gamma_1 N_{bim}^\alpha N_{bim}^2 \quad (4.2)$$

$$\frac{N}{N_0} = ((1-f)^{-\alpha} + \alpha\gamma_1 N_0^\alpha t)^{-1/\alpha} + ((1-f)^{-(\alpha+1)} + (\alpha+1)\gamma_2 N_0^{(\alpha+1)} t)^{-1/(\alpha+1)} \quad (4.3)$$

where fraction (f) represents the initially generated charges undergo bimolecular or nongeminate recombination while rest ($1 - f$) undergo monomolecular or nongeminate recombination.^{110,112} Also N_{mon} and N_{bim} refer to charges undergoing monomolecular and

bimolecular recombination, respectively. N_0 is the total charge carrier density; α represents the concentration dependent exponent while γ_1 and γ_2 are the recombination prefactors.

Fig. 4.13 shows the global fitting of this model to the normalized decay dynamics of different blend films as a function of pump fluence. The obtained values from fitting of the model are inferred in **Table 4.6**. In thermally annealed P3HT:PC60BM blend film, only 83.96 % (f) of the CTSs are converted into free polarons while rest of CTSs are tightly bound and decay at the rate of $\gamma_1 = 1.1 \pm 0.1 \times 10^6 \text{ ns}^{-1}$. While in EFT P3HT:PC60BM blend film, more photoexcited species ($89.07 \pm 1.0 \%$) are converting into free polarons though these species decay at similar rates. It shows that improvement of PCE in EFT P3HT:PC60BM devices are mainly resulted from higher photoabsorption in the system while recombination mechanism is not significantly affected by improved ordering. On the other side, standard P3BT:PC60BM blend film shows only $63.81 \pm 0.95 \%$ available excitons to convert into free charges as compared to $76.55 \pm 0.18\%$ in EFT blend. In addition, the decay rate of these strongly bound states is also reduced drastically (from $\gamma_1 = 1.8 \pm 1.2 \times 10^8 \text{ s}^{-1}$ to $\gamma_1 = 4.0 \pm 2.7 \times 10^6 \text{ s}^{-1}$) in EFT blend films. The bimolecular recombination losses have also been reduced one order in magnitude (from $\gamma_2 = 8.2 \pm 2.3 \times 10^{-11}$ to $2.3 \pm 1.1 \times 10^{-12}$) which is agree with efficient charge transport. The lower value of γ_1 in EFT samples indicates the delocalization of bound charge carriers and suppression of first order interfacial trap assisted recombination (monomolecular). As we observed, the strong delocalization of excitons in EFT P3BT:PC60BM blend film, more delocalized polarons are likely to form and hence more efficiently dissociated into free carriers than in standard P3BT:PC60BM.²⁴ The simulation of hopping transport mechanism of bound charges performed by Deibel revealed that delocalization of hole polarons along the polymer chains reduces Columbic attraction and enhances separation efficiency.¹³⁸ The effective charge separation in CT state would be increased by such charge delocalization in more crystalline phases. Thereby we propose that

longer effective charge separation distance due to hole delocalization in crystalline phases in EFT P3HT:PC60BM would promote dissociation into free charge carriers while ordered amorphous phases (donor or intermixed) would promote efficient interconnecting pathways.

Figure 4.13: Global fitting of pump fluence dependent DT signal between 950-1000 nm in (a) P3HT:PC60BM standard, (b) P3HT:PC60BM EFT, (c) P3BT:PC60BM standard, and (d) P3BT:PC60BM EFT blend films.

Table 4.6: Summary of the fitting parameters for the ns-TAS data.

Blend films/ Parameters	f (%)	$\alpha+1$	γ_1 $(\times 10^{-3} \text{ ns}^{-1})$	γ_2 (s^{-1})
P3HT:PC60BM Standard	83.89 ± 0.92	1.47 ± 0.02	9.5 ± 2.5	$1.6 \pm 1.4 \text{ E-18}$
P3HT:PC60BM EFT	89.07 ± 1.68	1.52 ± 0.02	2.4 ± 1.8	$0.2 \pm 0.1 \text{ E-18}$
P3BT:PC60BM Standard	63.81 ± 0.95	1.01 ± 0.02	$1.8 \pm 1.2 \text{ E8}$	$8.2 \pm 2.3 \text{ E-11}$
P3BT:PC60BM EFT	76.55 ± 0.18	1.09 ± 0.01	$4.0 \pm 2.7 \text{ E6}$	$2.3 \pm 1.1 \text{ E-12}$

4.4 Conclusions

In conclusion, the performance of solar cell devices based on semicrystalline conjugated polymers *i.e.* P3HT:PC60BM and P3BT:PC60BM is improved while thermal annealing and external E-field treatment of active blend are performed concurrently. The structural measurements and analysis confirms the improved crystallinity and larger crystallite size in E-field treated blend films which results in higher photo-absorption and more efficient charge transport. On the contrary, the performance of solar cell devices based on amorphous conjugated polymers, *i.e.*, PTB7:PC70BM and PCPDTBT:PC60BM, was found to be almost unchanged irrespective of different magnitude of E-field treatment. The DFT calculations of monomers indicate higher dipole moment and large complex structure of PTB7 and PCPDTBT as compared to semicrystalline polymers. Therefore, electric dipole moment, intrinsic lamellar packing and smaller linear monomer units are three essential requirements in conjugated polymers for effective E-field induced ordering. Transient absorption spectroscopy reveals the higher photo-generation in both P3HT:PC60BM and P3BT:PC60BM EFT blend films with faster charge transfer mechanism as confirmed by SVD analysis. The reduced interfacial trap-assisted monomolecular recombination in EFT P3HT:PC60BM along with reduced trap-free bimolecular recombination in EFT P3BT:PC60BM blend is also an additional source for higher short circuit density in these

solar cell devices. Hence, our finding reveals the role of the electrostatic charge distribution in polymer molecule for effective E-field interaction to enhance the ordering of system which resulted in reduced recombination losses and thus improved photovoltaic performance.

Chapter 5

Influence of alkanedithiols as additives on morphology and ultrafast charge dynamics in P3HT:PCBM solar cell devices

Summary

As discussed in chapter 3 and 4, the organization of the D/A is a predominant factor to obtain the optimal performance of the organic solar cell devices. Therefore, control of the blend morphology remains the biggest challenge to achieve the high PCE in organic bulk heterojunction (BHJ) solar cells for low temperature applications. “Solvent additive” is another simple and effective approach in the direction of the developing high performance solar cell devices for flexible application. In this method, a small fraction of the high boiling point solvent is added to the host solvent in organic blend system to control the morphology organization. This approach has been widely used to improve the performance of BHJ devices using different D/A systems. However, systematic study of the photophysical processes governing charge dynamics using different solvent additive from the same family are still lacking. In this chapter, we present detailed study of the optoelectronic properties, morphology and charge carrier dynamics using ultrafast spectroscopy in pristine, thermally annealed and different thiol-based additive-added P3HT:PCBM blend devices. The degree of the interaction between additive and P3HT as apparent from XRD, AFM and charge carrier recombination dynamics are found correlated. A poor interaction between additive and P3HT is also possible which results in over-phase-separation to promote the trap assisted recombination and hence inferior solar cell device performance. Therefore, choice of balanced additive:polymer interaction is highly desirable for optimal blend morphology and higher performing additive-added solar cell devices.

5.1 Introduction

The conjugated polymers are widely used for the application of bulk heterojunctions (BHJs) OSCs because of the ease in fabrication, higher light absorption coefficient and compatibility with flexible substrates.^{15,16} Among the numerous combinations, blends of regioregular-P3HT as a donor and PCBM as a acceptor are one of the most commonly studied polymers in recent years.¹³⁹ To obtain the high performance BHJ devices, optimal blend morphology is always required for maximum photo-absorption, efficient free charge generation, transport and collection at the electrodes. In this regard, several methods such as, solvent annealing⁶⁶, ordered templates¹⁴⁰, self-assembly with marginal solvents⁶⁹, drying in the presence of electric field¹¹⁵ etc. have been used to optimize the nanomorphology of P3HT:PCBM as active blend. Although, all these approaches improve the solar cells device performance but such post processing methods are not compatible for large scale roll-to-roll applications.⁷⁰ In some cases, these techniques are found to be not applicable to some D/A systems (e.g., PTB7, PCPDTBT etc.) as presented in chapter 4.¹⁴¹ Therefore, for high volume production, it is essential to develop a technique that is compatible with mechanically flexible substrates.^{37,71-73}

In the last few years, two different methods have been developed to fabricate the thermal-free BHJ organic solar cell devices. In the first approach, Zhang *et. al.* reported a solvent mixing method where two solvents of different boiling points were added to the APFO-3:PCBM system.¹⁴² The aggregation of the polymers indeed occurred in active blend but the devices still yielded low PCE. On the other hand, significant improvements in PCE were reported with the other method employing PCDTBT and PTB7-based organic solar cell devices following the addition of a small volume fraction of alkanedithiols.¹⁴³⁻¹⁴⁵ Bazan *et. al.* used a similar method with P3HT:PCBM system where toluene was used as the host solvent.¹⁴⁶ Salim et al. further investigated deeper into the effects of this solvent additives on

the solubility and boiling point of the additives and the phase separation of P3HT:PCBM blend system.¹⁴⁷ They found that PCE improvement was dependent on the miscibility of these additives and the acceptor molecules but it had nonlinear relationship with the boiling point of solvent additive. The in-depth morphology study revealed that the improved phase separation of donor and acceptor in the blend film causes the photoconductivity improvement of charge carriers and hence the improved PCE.¹⁴⁸⁻¹⁵⁰

Despite the potential of the higher PCE of P3HT:PCBM OSCs by appropriate selection of the additive than those without, the organized studies on the charge carrier dynamics in these systems are still lacking. For further optimization of materials properties and morphology of additives-added P3HT:PCBM blend to achieve higher PCE of solar cells, it is essential to understand fundamental photo-physics with charge carrier dynamics and correlate them with the performance of solar cell. In this chapter, we present a comprehensive investigation of the carrier dynamics in the blend films that have undergone different treatments (i.e. non-annealed (NA), thermally annealed (TA) and thiol based additives added P3HT:PCBM blends) using transient absorption spectroscopy. Our findings reveal that the addition of 1,6-hexanedithiol (HDT) or 1,8-octanedithiol (ODT) yielded a Langevin-type free charge carrier bimolecular recombination as compared to a trap-assisted recombination in additive-free non-annealed (NA) P3HT:PCBM blend. This is attributed to the formation of optimum-size crystalline domains and effective percolation of the donor acceptor phases. However, any further enlargement of the polymer domains disrupts the percolation pathways, as in the case of 1,5-pentanedithiol (PDT) blend films. This is detrimental to the solar cell device performance where trap-assisted recombination prevails. We infer that a careful balance of the crystalline order, intermixed phases (*i.e.*, comprising of disordered/ordered P3HT and PCBM) and percolation pathways is essential for the optimal performance of additive-added devices.

5.2 Experimental Methods

For OSC device fabrication and film preparation for optical characterizations, a blend solution of P3HT and PCBM (18 mg mL^{-1} in 1,2-dichlorobenzene (o-DCB)) was prepared in 1:0.8 weight ratio. (P3HT, PCBM and o-DCB were purchased from Rieke Metals, Inc., Nano-C and Sigma Aldrich respectively). For complete mixing of the polymers blend the solution was stirred overnight at 50°C in a N_2 glovebox. Based on previous reports, the optimum amount alkanedithiols (2% by volume) was added into this solution which was then stirred for further two hours before spin-coating.^{147,151} The alkanedithiols chosen for photo-physics study were 1,5-pentanedithiol (PDT, $T_b = 216^\circ\text{C}$), 1,6-hexanedithiol (HDT, $T_b = 214^\circ\text{C}$) and 1,8-octanedithiol (ODT, $T_b = 272^\circ\text{C}$) which were also bought from Sigma Aldrich. The chemical structures of these thiols are shown in **Fig 5.1**. All these additives have boiling points (T_b) higher than that of o-DCB ($T_b = 180^\circ\text{C}$) and therefore potentially would be affecting the organization of the polymers upon evaporation of the host solvent (i.e. o-DCB) during the spin coating.

The indium-tin oxide (ITO) deposited glass substrates were cleaned and a thin hole transporting layer (HTL) of PEDOT:PSS was spin coated on ITO as mentioned in previous chapters. The different active blend solutions were then spin coated on top of the HTL layer in N_2 filled glove box at 700 rpm for 2 minutes to yield a uniform film with thickness of $100 \pm 5 \text{ nm}$. Unlike the widely used spin time, the longer duration of the spin coating was required in our case to ensure the complete evaporation of o-DCB leaving behind the alkanedithiols to interact with the polymer and fullerene phases. Cathode contact of 100 nm thick aluminium was thermally evaporated through the shadow mask (with 0.07 cm^2 device area) in a vacuum of 10^{-7} Torr. No thermal treatment was performed on the additive added blends and non-additive added set of devices. For comparison, another set of the additive free

device was subjected to post-evaporation thermal annealing at 140 °C for 20 min. Different active blend layers were directly prepared on glass substrates for optical and other thin film characterizations.

Figure 5.1: Chemical structure of (a) 1,5-pentanedithiol (PDT) (b) 1,6-hexanedithiol (HDT) and (c) 1,8-octanedithiol.

5.3 Results and Discussions

5.3.1 Linear Absorption Measurements: Fig. 5.2 exhibits the UV-Visible absorption spectra of different P3HT:PCBM blend films of equal thickness prepared on glass substrates without any additive and thermal annealing (NA), only thermally annealed (TA) and those treated with 2% of PDT, HDT and ODT as processing additive. The linear absorption profiles in Fig 5.2 (a) show TA and additives added blend films have higher absorption intensity as compared to the NA blend film for the entire visible spectrum range. Among the all additives added blends, PDT added film possesses the highest absorption intensity. Although the position of vibronic peak at ~510 nm (related to π - π^* transition) and other peaks at ~555 nm and ~610 nm (represents the interchain interactions) are found to be very similar. The prominence of these peaks in the normalized absorption spectra are often attributed to the highly ordered P3HT chains in the P3HT:PCBM blends (Fig. 5.2 (b)).¹⁵² This indicates that the addition of PDT in the blend resulted in the highest improvement of crystallinity in the film. While it can indeed be surmised that the π - π^* transition (510 nm) in the TA film gives the highest peak absorption, the additive-added blend films are more organized as a result of the stronger interchain interactions. The total amount of absorbed photons is further calculated by integrating the absorption spectrum of these blend films by overlapping the

solar spectrum and it is found that more photons are absorbed in the additive-added blend compared to the non-additive added films ($\eta_{A-NA} = 1.58 \times 10^{22}$, $\eta_{A-TA} = 2.06 \times 10^{24}$, $\eta_{A-HDT} = 2.18 \times 10^{24}$, $\eta_{A-ODT} = 2.24 \times 10^{24}$, $\eta_{A-PDT} = 1.73 \times 10^{25}$). This clearly shows that the addition of the additives improves the organization of P3HT, thereby enhancing the photo absorption (highest in PDT-added film) as compared to the NA and conventional TA blend film.

Figure 5.2: (a) Linear, (b) normalized absorption spectra of NA, TA and additive-added P3HT:PCBM blend films.

For the further estimation on the presence of the ordered region from absorption ratio between the crystalline and amorphous regions in different blend film, the degree of crystallinity, χ_C , is evaluated using the following relation:¹⁵³

$$\chi_C = (\epsilon_{460} / \epsilon_{600}) A_{600} / \{(\epsilon_{460} / \epsilon_{600}) A_{600} + A_{460}\} \quad (5.1)$$

where A_{460} and A_{600} represents the amount of absorption at 460 nm (amorphous) and 600 nm (crystalline) respectively while $\epsilon_{460} / \epsilon_{600}$ refers to ratio of the extinction coefficient between the amorphous and crystalline P3HT. The ratio of the extinction coefficients for each blend film were calculated by assuming negligible absorption by PCBM at these wavelengths.¹⁵⁴

The degree of P3HT crystallinity is calculated to be minimum 31% in NA blend and to be the

highest 50% PDT added blend film. Generally, in the presence of the high boiling point solvent (additive), the polymer chains start aggregating to minimize the interactions between the polymer and the poor solvent. Though the alkyl groups might have good interaction with polymer, the interaction between -SH end group in thiol and thiophene along polymer backbone cannot be omitted. The presence of the -SH end group might interfere the interaction between the alkyl groups. The two molecules (additive vs polymer) could also have different polarities that will affect their interactions. Yang Yang *et. al.*¹⁵¹, T. P. Russell *et.al.*¹⁵⁵, D. M. DeLongchamp *et. al.*¹⁵⁶, *etc.* also observed the poor solubility of different polymers in thiol additives. Based on our own experience, under the naked eye, P3HT is indeed barely soluble in 1,8-octanedithiol (ODT), which should also applicable for the other additives that we used. Moreover, the aggregation of the polymer also depends on the interaction time (i.e., evaporation time which is in turn dependent on the boiling point of the additive). The improved crystallization of P3HT and ordering with these additives can be explained as follows: during the spin-coating of the blend, the lower boiling point of the host solvent (o-DCB) evaporates faster than the additives and leaves behind decreased volume ratio of o-DCB to poor soluble additives. As a consequence, P3HT molecules start agglomerating to minimize the internal energy of the system and promote grain formation. To verify the existence of the larger grains, photoluminescence, X-ray crystallography and topography phase scans of these blend films were performed and discussed in subsequent section.

5.3.2 Photoluminescence Measurements: Photoluminescence (PL) phenomenon involves a recombination of the photoexcited excitons in the lack of required exciton separation energy or the existence of discontinuous pathways. Thereby, the quenching of the PL indicates the suppression of the exciton recombination and the existence of alternative pathways for the

excitons. By tuning the organization of the donor/acceptor, the fraction of excitons dissociation into free charges can be improved. Thus efficiency of PL quenching is correlated to the charge generation and is dependent on the distribution of the blend components. With an increase in the amount of donor-acceptor (D/A) interface, the excitons are more likely to dissociate into free charges carriers and higher PL quenching is observed. In other words, the effectiveness of PL quenching depends on the morphology of the donor-acceptor blend. To measure the PL intensity from different P3HT:PCBM blend films, an incident light of 520 nm corresponding to the λ_{max} from the optical absorption was used to excite the P3HT molecules and the corresponding emission spectrums are shown in **Fig. 5.3**. The steady-state PL spectra of NA, TA and additives-added blends in Fig. 4.3 exhibit intense peaks at $\lambda_{\text{max}} = 720$ nm and shoulder at 660 nm. From **Fig. 5.3**, the PL of the NA blend exhibits strongest quenching which attributes to the homogeneously mixing of P3HT and PCBM phases where excitons find myriad of donor/acceptor interfaces to dissociate. On the other hand, PDT-added P3HT:PCBM exhibits the highest PL intensity (or the least quenching), followed by HDT, ODT-added and TA. Higher PL intensity in additives-modified film suggest that phase separation and crystallite formation are stronger in these blends as compared to NA film which causes higher exciton recombination and hence higher PL intensity.^{157 158}

Figure 5.3: Photoluminescence of NA, TA and different additive-added P3HT:PCBM blend films.

5.3.3 X-ray Diffraction: Grazing incidence X-ray diffraction measurements were performed to further quantify the degree of organization in different blend films. The X-ray diffractograms of the all P3HT:PCBM blend films are shown in **Fig. 5.4**. The peak observed at $2\theta = 5.4^\circ$ corresponds to the reflection from (100) plane of P3HT. This peak comes from the lamellar structure of these polymers which is corresponding to thiophene chains with alkyl stacking normal to the substrate and $\pi - \pi^*$ stacking between thiophene chains parallel to the substrate. The higher intensity at (100) peak in additive-added blend films describes the improved crystallinity of these blend as compared the controlled NA and TA blend films. The relative full width half maxima (FWHM) from the peaks for NA and TA blend films are calculated to be 0.44 and 0.65 respectively. The incorporation of the additive increase the FWHM to 0.75, 0.73 and 0.77 in HDT, ODT and PDT-added P3HT:PCBM blend films respectively. The crystallinity of these blend films can be arbitrary obtained from the product of the maximum peak intensity and FWHM. Thus, the arbitrary crystallinity calculated for these blend films are 135, 426, 889, 990 and 1159 for NA, TA and HDT, ODT, PDT-added blend films respectively. The highest degree of crystallinity and highest FWHM of P3HT in PDT-added blend film can be attributed to stronger interaction between P3HT and PDT and

thus also indicate the stern phase separation between P3HT and PCBM. The highest crystallinity in PDT-added blend will indeed improve the photoabsorption but reduce D/A interfaces and may cause the inferior exciton dissociation efficiency.

Figure 5.4: X-ray diffraction patterns of different P3HT:PCBM blend films.

5.3.4 Atomic Force Microscopy (AFM): On the basis of XRD measurements, PDT-added P3HT:PCBM blend system indeed shows the highest crystallinity among non-additive and additive-added system. We have further investigated the distribution of the D/A by the topographic scan of all these blend films using AFM which influences the exciton and polaron pair dissociation. **Fig. 5.5** displays the phase images of $20 \times 20 \mu\text{m}^2$ scan area of the different P3HT:PCBM blend films scanned in tapping mode. The morphology of the additive-added P3HT:PCBM blend films is significantly different from the control sample and shows a phase separation with improved crystallinity. The control sample shows a finely mixed blend with poor phase separation (having the smallest phase difference $\Delta\Phi = 4.91^\circ$), while the presence of the additives promotes phase separation with $\Delta\Phi = 66.83^\circ$ (HDT), 67.42° (ODT) and 88.43° (PDT). This segregation increases the P3HT aggregate size which agrees with the XRD results. As discussed earlier, polymer aggregation commences at an early stage of film formation where longer time is required to evaporate the higher boiling

point additive (ODT) as compared to the lower boiling point additive (PDT). In the case of PDT-added blend film, another factor that promotes P3HT polymer aggregation is its poorer interaction with P3HT as compared to HDT and ODT. Consequently, larger sized P3HT polymer aggregates with extreme phase separation which is formed through the stronger P3HT–PDT interaction. This is further discussed in the next section (section 5.3.5). All three additives – PDT, HDT and ODT with higher boiling points compared to o-DCB and will result in slower evaporation, thus yielding relatively higher phase separation compared to without additive blend. The roughness of these blend films are also obtained as 3.52 nm (NA), 6.04 nm (HDT), 7.37 nm (ODT), and 11.63 nm (PDT), showing an increasing trend with increasing phase separation in additive processed blends. The highest value of surface roughness in the PDT-added blend is consistent with the largest aggregation (which seems to be beyond the optimal), which points to a poorer morphology of the active layer. Such aggregation in the blend without any doubt will improve the photo-absorption but at the cost of exciton dissociation efficiency (due to a decrease in D/A interfaces). Moreover, strong aggregation of polymer also causes discontinuous pathways to the electrodes as shown later in schematic of **Fig 5.13**. With a lack of percolation pathways, the free charge carriers obtained from exciton dissociation are trapped in such bigger polymer aggregates. This would reduce the charge collection efficiency at the electrode, thus resulting in poor current density. Therefore, a fine balance between aggregation, phase mixing and separation are needed for improved device performance.

Figure 5.5: AFM scans of the surface topography of (a) pristine (NA), (b) HDT, (c) ODT, (d) PDT-added and (e) thermal-annealed (TA) P3HT:PCBM blend films. The scan area is $20 \times 20 \mu\text{m}^2$ for all images.

5.3.5 Solubility of the blend components: For a binary blend, the solubility of the blend components in the solvent plays a vital role in the adaptation and distribution of these components in the solution and subsequently in the blend film. A comparison of the solubility parameters of the blend components can provide a good anticipation of the degree of the intermolecular interactions, which can be estimated from their solubility parameters (δ). The values of solubility parameter for PDT, HDT, ODT, P3HT and PCBM are reported as 19.7, 19.2, 18.6, 9.1 and $7.8 \text{ J}^{1/2} \cdot \text{cm}^{3/2}$ respectively.^{147,159,160} The degree of the molecular interaction between two molecules can be correlated with their solubility parameter difference. Larger solubility parameter difference ($\Delta\delta$) often results in poor miscibility (or strong “bad” interaction), while a minimum difference in solubility parameter ($\Delta\delta \approx 0$) indicates the good miscibility (or strong “good” interaction). Although ODT, as compared to the other additives, shows the smallest $\Delta\delta$ with respect to P3HT ($\Delta\delta_{\text{ODT-P3HT}} = 9.5$), its higher boiling point causes ODT to take longer time to evaporate and hence providing ample time to interact with P3HT. The comparable value of $\Delta\delta_{\text{HDT-P3HT}}$, yet relatively lower boiling point of

HDT promotes a more balanced interaction that causes a lower amount of aggregation. On the other hand, largest solubility parameter difference of PDT with respect to P3HT ($\Delta\delta_{\text{PDT-P3HT}} = 10.6$), despite its lowest boiling point, suggests a poor interaction with P3HT and hence a more extensive aggregation. Thus, the extent of the phase separation of both donor and acceptor can be tuned by adjusting additive-donor and additive-acceptor interactions, which can in turn be achieved through proper selection of additive molecules with a balanced solubility parameter and boiling point. Next, organic solar cell devices fabricated with these alkanedithiols-processed P3HT:PCBM active layers were then characterized to be correlated with their physical measurements.

Electrical characterizations

5.3.6 Dark Characteristics: Fig 5.6 shows the plot of current–voltage ($I_{\text{dark}}-V$) measurements performed in dark for NA, TA and additive-added P3HT:PCBM solar cell devices. The dark forward biased current density of OSC is very much dependent on the charge carrier transport and recombination mechanism. For clear picture of these mechanisms, dark characteristics can be elucidated using diode equation:

$$I_{\text{dark}} = I_0 \left[\exp\left(\frac{V - JR_s}{n_{\text{dark}} kT / q}\right) - 1 \right] + \frac{V - JR_s}{R_{SH}} \quad (5.2)$$

where, I_0 represents the reverse saturation current density, n_{dark} dark ideality factor, while k , T and q are the Boltzmann constant, temperature and elementary charge, respectively. Resistance of the device refers to the series resistance (R_s) and shunt resistance (R_{SH}). The scattered points in Fig 5.6 represent the experimentally measured I_{dark} while solid lines represent the fitting curves. The value of R^2 for fitting characteristics is ~ 0.99 for all devices. Dark current fitting parameters are summarized in table 5.1. Series resistance is dropped drastically by thermal annealing as well as incorporation of the additives which could be the reason for higher current in these devices. Furthermore, the value of n_{dark} is reduced from 2.5

to 1.63 in HDT-processed while 1.42 and 1.83 in ODT and PDT-added P3HT:PCBM devices, respectively. The ideality factor of devices from dark forward current corresponds to the energetic disorder in the density of states (i.e. trap states and their distribution) controlling the charge transport.^{161,162} The presence of traps in blend film increases the energetic disorder and makes the charge transport inefficient which results in poor dark current. The lower value of n_{dark} in additive-modified OSCs as shown in **table 5.1** indicates the reduction of trap density in P3HT:PCBM. Among these additives, ODT appears to be a most effective additive which suppress the maximum amount of the trapping sites in P3HT:PCBM devices.

Table 5.1 | Dark current fitting parameters of different P3HT:PCBM OSCs.

Parameters/Devices	NA	TA	HDT	ODT	PDT
R_s ($\Omega\text{-cm}^2$)	66.99	2.99	4.48	3.00	7.07
R_{sh} ($\Omega\text{-cm}^2$)	1.27E+04	4.32E+04	1.08E+04	3.03E+03	9.81E+03
I_0 (A)	2.04E-08	1.23E-07	5.80E-09	7.74E-09	5.19E-07
n	2.5	1.94	1.63	1.42	1.83

Figure 5.6: Semi-log current –voltage characteristics in dark of NA, TA and additive-added P3HT:PCBM solar cell devices.

5.3.7 Light Characteristics: The current–voltage (J – V) characteristics of NA, TA and additive- added P3HT:PCBM solar cell devices measured under the calibrated solar simulator illumination of AM 1.5G at 100 mW cm^{-2} are shown in **Fig 5.7a**. All the relative parameters i.e., PCE, J_{sc} , V_{oc} , FF, R_s and R_{sh} extracted from the plot are summarized in **table 5.2**. Both

NA and TA devices are included for comparison. Because of the low J_{sc} , V_{oc} and FF of the NA devices, it yielded the lowest performance (1%). Overall, the TA devices exhibited the best performance⁷⁰, while PDT-added system gave the worst performance among all the additive-added devices. It should be noted that we have used glass/ITO/PEDOT/P3HT:PCBM/Al as the device structure and any of the electron transporting layer (ETL) such as LiF or Ca is not used. The absence of such ETL in all our devices would have indeed reduced the performances compared to the state-of-the-art in the field. In this work, the comparisons and correlations were made between all devices/films without introducing any ETL. Therefore, the absence of the ETL should not affect our findings on the structural-functional relationship between the additive-induced changes in morphologies with the device performance.

Figure 5.7: (a) Current density–voltage (J - V) measured at AM1.5 Sun under an intensity of 100 mW·cm⁻² and (b) Incident-photon-to-collected-electron efficiency (IPCE) for the NA, TA and additive-added P3HT:PCBM solar cell devices.

Table 5.2: Electrical performances of NA, TA and additives added P3HT:PCBM OSC devices under illumination.

Device/ Parameters	PCE (%)	J_{sc} (mA-cm ⁻²)	V_{oc} (V)	FF	R_s (Ω -cm ⁻²)	R_{sh} (Ω -cm ⁻²)
NA	1.0±0.3	7.0±0.5	0.48±0.02	0.38±0.02	23±5	129±38
TA	3.1±0.2	10.4±0.2	0.53±0.01	0.57±0.02	10±2	512±53
HDT	2.8±0.3	8.8±0.3	0.55±0.02	0.58±0.02	11±1	833±85
ODT	2.8±0.1	10.2±0.4	0.48±0.02	0.58±0.02	9±1	813±47
PDT	1.7±0.3	8.2±0.2	0.43±0.02	0.50±0.02	14±2	277±23

J_{sc} in solar cell devices is mainly determined by the absorption of light, dissociation and recombination of the charges inside the blend, and their collection at the external electrodes. The highest value of J_{sc} in the TA device can be correlated to the higher absorption in blend film (**Fig. 5.2**), and improved charge carrier mobilities, which has been previously reported.¹⁶³⁻¹⁶⁵ Among the additive-treated devices, treatment with HDT and ODT gave similar performances with PCEs of 2.8%. Higher performance of the HDT-added device results from an optimum mixing of the materials in the presence of the HDT among the all additives. The devices prepared with ODT additive shows comparable current density to the TA device but is higher than those of the NA and HDT-added devices. This is very likely to be the result of better exciton generation and polaron formation than those in HDT blend in optimized blend morphology.

In BHJ solar cells, open-circuit voltage can be estimated by calculating the energy offset between donor's highest occupied molecular orbital (HOMO) and acceptor's lowest unoccupied molecular orbital (LUMO) level.¹⁶⁶ In spite of this difference, V_{oc} is also affected by the higher recombination current in the device with poor film morphology.¹⁶⁷ The V_{oc} of PDT-added solar cell devices is only 0.43 V, the lowest among all devices, which could be due to its higher dark current near V_{oc} attributed to the higher charge recombination. According to the Double-Junction Model, the poor phase-segregated PDT-added device

shows a higher recombination current through the shunt paths between two electrodes and hence lowers the photogenerated current, even though the blend has the highest photo-absorption. **Fig. 5.7(b)** displays the incident photon-to-current (IPCE) spectra measured for all these devices. Consistent with the trend observed for the current density, TA and ODT-added blend device shows the highest IPCE, while the NA device had the lowest IPCE, in the range 350–650 nm. Both TA and ODT-processed devices exhibit a maximum IPCE of around 50–60% in the wavelength range of 450–650 nm (**Fig 5.7b**). Amongst the additive-treated devices, the PDT-processed device shows the lowest IPCE, consistent with the measured short circuit density. This indicates a higher charge recombination and a more inefficient charge collection at the electrodes in PDT-treated device. These spectra show that the presence of additive induces a more favourable ordering in the blend than NA devices, which leads to improvement in the photocurrent.

5.3.8 Open Circuit Vs Intensity Measurements: The light dependency of open circuit voltage provides completely independent information on the recombination dynamics. At open circuit voltage condition, the photogenerated current becomes zero as consequence of recombination in the devices thus the V_{oc} is very sensitive to the recombination process. To extract the recombination information, intensity-dependent V_{oc} measurements were also performed under illumination from ~0.3-1.0 Sun of AM 1.5G. **Fig. 5.8** shows the V_{oc} versus $\ln(I)$ (I is the illumination intensity) relationship for different P3HT:PCBM blend devices. The slope of this relation is described by nkT/q , (where n represents the ideality factor under illumination, k represents the Boltzmann constant, q is the elementary charge and T is the temperature) which is dependent on the recombination processes in devices¹⁶⁸. TA solar cell devices exhibit $n = 2.2$ while PDT added devices shows the maximum slope value i.e. 2.7. Assuming the value of n of the NA devices to be the benchmark for trap assisted mono molecular recombination (which is widely reported), the relatively lower values of n in HDT

($n_{\text{HDT}} = 1.6$) and ODT ($n_{\text{ODT}} = 2.1$) added systems indicate the dominance of the bimolecular recombination in these solar cell devices which is consistent with our previous measurements.¹⁶⁹

Figure 5.8: Intensity-dependent open-circuit voltage measurement for NA (black), TA (red), HDT (blue), ODT (green) and PDT (purple) additives added P3HT:PCBM solar cell devices.

On account of the physical property measurements and electrical characterizations, we infer that the optimal morphology of the blend in HDT, ODT-processed solar cell devices is the key source of the better performance while poor phase segregation between P3HT and PCBM due to the poor intermixing induced by PDT dilapidates J_{sc} , V_{oc} , and FF of the device. To gain deeper insights into the influence of the additives on the charge dynamics of P3HT:PCBM blend films, we turn to transient absorption spectroscopy (TAS).

Charge Carrier Dynamics in the Femto–microsecond Temporal Regime

5.3.9 Transient Absorption Spectra: TAS measurements were performed on NA, TA and additive-added P3HT:PCBM blend films (100 ± 5 nm thick) to investigate the effect of additives on the charge generation and recombination dynamics in these films. **Fig. 5.9** shows

the differential transmission (DT) spectra spanning from 520 nm to 1600 nm at four different delay times following the photoexcitation of these blend films. It should be noted that 500 nm was used as a pump wavelength and PCBM radical anions are optically transparent at this wavelength therefore the signals were only resulting from the excitations of P3HT. The vibronic peaks corresponding to 0-0 (~610 nm) and 0-1 (~560 nm) absorption transitions are apparent and they are also referred to as the ground state bleaching (GSB) signals.⁹² GSB signals represents the relative populations of the excited species at different times following photoexcitation.¹⁰³ From **Fig. 5.9**, it can be observed that the photo-bleaching signal for 0-0 transition is stronger for the additive-added films as compared to the NA film. In addition, 0-1 GSB peak is relatively more apparent in additive-added blend films than in NA. This increase in GSB signal comes from the higher absorption in additive-added blend films which results in larger population of photogenerated excitons and polarons formation. The negative $\Delta T/T$ signal from 630 nm to 1600 nm, also known as photo-induced absorption (PIA), arises from the absorption of excited species (*e.g.*, polarons, excitons, charge transfer excitons, *etc*).

Figure 5.9: Transient absorption spectrum of (a) NA, (b) HDT, (c) ODT (d) PDT added and (e) TA P3HT:PCBM blend film.

Fig. 5.10 shows the normalized decay dynamics of the 0-0 GSB peak for NA and compared with the various additive-added blend films. The comparable initial GSB decay dynamics (<10 ps) in the additive-added blend films indicating the presence of an equivalent amount of intermixed phases (*i.e.*, disordered/ordered P3HT and PCBM domains) in these films. In contrast, the GSB signal decay faster in the NA blend, consistent with a poorer intermixing of the D/A phases and smaller domains that resulted in more recombination. On comparing the GSB decay among the additive-added systems, the signal in the HDT and ODT-added blend films decay faster within the first 100 ps (to nearly 60% of its initial value) and remains almost invariant until 1 ns. This phenomenon is consistent with better crystallinity of these additive-added blends compared to the NA blend, in which a larger population of free carriers can persist longer in the suitably-sized P3HT aggregates. Consequently, this allows their charge carriers to be extracted before recombination, yielding a higher photocurrent than from the NA blend. However, the PDT-blend film decays at a

much faster rate continually over the measured time window of a few microseconds. Despite the fact that PDT-blend films possess the highest absorption (**Fig. 5.2**) and crystallinity (**Fig. 5.4**), the larger domain size (**Fig. 5.5**) in these blends is far from ideal for efficient charge extraction. As the carriers are transported to the electrodes, carrier recombination of trapped charges in the PDT-blend films will result in a lower photocurrent (**Fig. 5.7**).

Figure 5.10: Normalized decay dynamics of 0–0 GSB peak in different P3HT:PCBM blend films excited with $35 \text{ mJ}\cdot\text{cm}^{-2}$ pump fluence.

5.3.10 Global fitting of the PIA dynamics: To address the mechanism of the formation of excitons and polarons in different blend films, a SVD and global fitting analysis for the TA spectra was performed to separate the spectral features that have different time evolutions. **Fig. 5.11** shows the separation of the different features in all different blend films over the time range from 100 fs to 5 ns and the extracted time constants are summarized in **table 5.3**.

Figure 5.11: Pre-exponential coefficient spectrum obtained by SVD and global fitting analysis of (a) NA, (b) TA, and (c) HDT, (d) ODT, (e) PDT added P3HT:PCBM blend films.

The first two most prominent decay time constants are mainly due to singlet excitons (dominant around 1230 nm); first time constant is attributed to the excitons presents in the amorphous or intermixed phase of P3HT:PCBM; while second time constant is assigned to the delayed exciton dissociation due to the migration in larger P3HT domains. **Fig 5.11a** shows that excitons present in intermixed phase of polymers dissociate faster (<1ps) than in crystalline phase (~13.8ps) of the NA blend film. With addition of HDT in P3HT:PCBM blend film, the first decay constant is delayed, while second remains almost invariant (**Fig 5.11c**). The first delayed dissociation process can be correlated to the transition of intermixed phase to the ordered or segregated phase and enlargement of the P3HT domains (as a result of the interaction with HDT); which resulted in the migration of excitons to the interface before dissociation. While comparing the additives added blend film, all these fits show the similar decay constants of the excitons dissociation in larger domains, which could be of similar average size. The third and last decay constant in all blend films can be attributed to the long lived free polarons which persist longer than measured time window. The overall all comparison among these blend shows that the singlet excitons present in the intermixed

phase was found to be slightly slower in the TA and additive-treated blends as compared to the NA control. This lifetime increase is likely due to the increased crystallinity.

Table 5.3: Time constants from the global fitting of the different transient absorption spectra

Conditions/ Time Constants	NA	TA	HDT	ODT	PDT
τ_1 (ps)	0.8 ± 0.1	1.5 ± 0.5	1.1 ± 0.5	1.4 ± 0.4	1.3 ± 0.5
τ_2 (ps)	13 ± 2	18 ± 2.0	13 ± 5	16 ± 4	15 ± 2

* τ_3 persist longer than measured time window therefore it is not included in this table.

5.3.11 Pump fluence dependent charge dynamics in ns- μ s temporal regime: For the further understanding of the relaxation dynamics of the polarons beyond 5 ns and to elucidate the loss mechanism, the decay measurements over the ns - μ s timescale in all these blend films were also performed as a function of excitation pump fluence (from 35 - 140 $\mu\text{J}\cdot\text{cm}^{-2}$). Here, we focused on the 710 - 740 nm spectral range where the polarons are generated as a function of pump fluence dependence in crystalline P3HT domains (the governing phase) in these blend films. **Fig. 5.12** displays the normalized decay profiles of the delocalized polaron states in the NA, TA and additive-added P3HT:PCBM blend films measured under different excitation pump fluences. In the NA blend film, the polarons decay rate is independent of the excitation pump fluence. This behaviour shows that these polarons generated in the NA blend film are immobile and strongly bound. They are trapped at the interfacial traps where they undergo the Shockley-Read-Hall (SRH)-type trap-assisted recombination involving a free and opposite charge that is subsequently trapped by the same trap state. Pristine pDTS(FBTTh2)2:PDI-based solar cell devices also showed such type of intensity-independent trap-assisted recombination.¹⁷⁰ On the other hand, HDT and ODT-added P3HT:PCBM blend films (**Fig. 5.12c** and **Fig. 5.12d**) including the TA blend film (**Fig. 5.12b**) exhibited intensity-dependent polaron recombination dynamics. Such recombination

behaviour is the characteristic of a Langevin-type bimolecular recombination of free charges that is charge carrier concentration-dependent.^{171,172} To achieve high-efficiency solar cell, efficient charge carrier collection is also essential after exciton dissociation occurring at the D:A interface. The IPCE values are representative of the carrier transport in the interpenetrating network of the respective blends. The higher yield of IPCE (>55%) in ODT-added blend device represents the formation of the better charge carrier transporting pathways in additive-added devices. On the other hand, the lower values of J_{SC} and IPCE in the HDT-processed device can be attributed to the lower photoabsorption, because of their similar decay dynamics as that of the ODT-added blend (**Fig. 5.7**), which indicates comparable charge transport properties. This shows that HDT and ODT additives have a similar effect on the charge dynamics of blends as that of thermal annealing – *i.e.*, improving the crystallinity and percolation of the blend films which helps to reduce interfacial traps and increase the delocalization of charges in the system.

Figure 5.12: Normalized pump fluence dependent DT signal between 710-740 nm in (a) NA, (b) TA, (c) HDT, (d) ODT, and (e) PDT-added P3HT:PCBM blend films excited at 35-140 $\mu\text{J-cm}^{-2}$ pump fluence.

However, a different scenario is observed in PDT-added blend film (**Fig. 12e**), which exhibits intensity-independent recombination dynamics similar to that of the NA blend film (**Fig. 12a**). From PL, XRD and AFM measurements, we deduce that the inclusion of PDT as additive results in an extreme case of phase separation and aggregation. Such interaction promotes the large crystallites but isolated polymer domains with inefficient percolation with the PCBM phase. As a result, the photogenerated polarons are spatially trapped in these isolated larger domains, unable to reach the percolation network and therefore annihilate through trap-assisted recombination (**Fig. 5.13b**). Despite showing the highest photo-absorption and crystallinity among these blend films, the higher trap-assisted charge carrier recombination in the PDT-added blends caused by poor interpenetrating network is severely limiting its device performance – as evident from their lowest IPCE (<40 %), fill factor (50 %) and open circuit voltage (0.43 V). The deleterious effects of such disproportionate phase separation on solar cell performance was also previously reported for excessive ODT-added P3HT:PCBM¹⁵¹ and DIO-added PBDTTT-C:PC₇₁BM blend film.¹⁷³

Figure 5.13: Schematic of the (a) HDT or ODT-added optimized and (b) PDT-added unoptimized morphology. Red circle and cross represent the losses in blend.

5.4 Conclusions

In summary, an in-depth charge dynamics study of thiol-added P3HT:PCBM blend films by ultrafast spectroscopy is performed to reveal the influences of thiols on the charge generation and recombination dynamics in these BHJ solar cells. The use of additives certainly improves the crystallinity and hence the optical absorption of the blends. However it does not have any direct relationship with the boiling points of solvent additives. The selection of the solvent additive having balanced boiling point and solubility parameter provides the optimum intermolecular interaction in order to achieve phase segregation with the ideal aggregate size. Although the improved crystallinity (hence the optical absorption) of the blends enhances the exciton generation, the extraction of the charge carriers is still significantly affected by the final blend morphology, domain aggregation and percolation pathways. With HDT and ODT incorporation, device performance of the thermal-free processed P3HT:PCBM solar cell improves to 2.8% as compared to the 1.0% non-annealed (NA) P3HT:PCBM solar cell. Transient spectroscopy reveals a Langevin-type free carrier bimolecular recombination in the former as compared to the trap-assisted recombination of the latter. However, for the PDT-blends, the poorer device performance of 1.7% is attributed to the excessive enlargement of the polymer domains that resulted in poorer intermixing and percolation of the donor-acceptor networks. Consequently, a trap-dominated recombination prevails as the charges cannot be effectively transported to the electrodes. Therefore, to fabricate the efficient thermal-free organic solar cells by using the solvent additive, it is important to have the careful choice of solvent with balanced solubility parameter and boiling point in order to achieve higher degree of order while maintaining effective domain intermixing and percolation pathways.

Chapter 6

Uncovering the morphology assisted charge dynamics in small molecule based solar cell devices

Summary

In the preceding chapters, we have presented an in-depth understanding of the device morphology and photophysics in polymer:fullerene as a photoactive materials for bulk heterojunction solar cells using different low temperature processing approaches. Small molecules are the other category of the photoactive materials which was discarded earlier due to the expensive processing for the solar cell fabrication. However, they have garnered more interest due to feasibility in modifying their structure to make them solution processable. In this chapter, a solvent vapour thermal annealing approach as a post treatment of the active layer is presented as another low temperature processing approach to improve the efficiency in small molecule based solar cells. As a result of the post treatment, the improved crystallinity of the blend system enhances the photo-absorption. In addition, the strongly bound charge transfer states are reduced by efficient dissociation and charge carrier mobility by the presence of the interconnecting pathways.

6.1 Introduction

Since the development of the conjugated polymers, the field of the organic solar cells is dominated by them due to the ease of solution processing, as photoactive materials. With the rapid progress over recent years, PCEs over 9% have been achieved for polymer based organic solar cells with bulk-heterojunction architecture.^{126,174,175} Despite such higher performance reported by these BHJ solar cells, inconsistent PCEs have been observed due to small variation in polymer processing. A disparity in batch to batch solubility, purity and molecular weight during the synthesis process of the same structure are found to be the main source of this discrepancy. On the other hand, the progress of the photoactive materials for solar cells have slowly-slowly migrated to the development of the new small molecule donor materials¹⁷⁶⁻¹⁷⁸, that consist of well-defined molecules of intermediate dimensions which were overlooked.^{179,180} The encouraging advantage of the small molecule BHJ solar cells is the high reproducibility which was major concern in polymer counterparts. Small molecule based solar cells have shown the encouraging power conversion efficiency whether processed by vacuum deposition^{181,182} or by conventional solution processing method.¹⁸³⁻¹⁸⁵ Recently, the power conversion efficiency over 8% has been reported based on solution processed DR3TBDTT:PC71BM small molecule BHJ solar cells (SM-OSCs).^{176,186} In addition, Yang *et.al.* has also demonstrated the PCE as high as 10% in tandem solar cell structure using small molecule as photoactive material.¹⁸⁷

Apart from such higher performance, small molecules also have other benefits such as versatile chemical structures, mobility tuning, easier energy level control, and batch-to-batch performance consistency.^{188,189} It is also believed that higher performance could also be achieved from SM-OSCs by synthesizing new molecules or by tuning the properties of the existing molecules. Current research have been mainly focusing on the development of new photoactive materials (donor and acceptor) and optimization of the device structure to obtain

the higher performance of both kinds of solar cells (based on polymer and small molecules as well).¹⁷⁴ For designing the small molecule donor materials, numerous issues are considered altogether such as widespread and higher photo-absorption, dissolution, high charge carrier mobility and suitable energy levels for efficient charge extraction.¹⁹⁰ Moreover for the device optimization, controlling the morphology to obtain proper aggregate sizes of the order of tens of nanometres of donor and acceptor phases with nanoscale interpenetrating network are the other essential factor.^{39,191}

Recently, Chen *et. al.* and co-workers have developed a series of new solution processed small molecule as a photoactive materials using 2-(1,1-dicyanomethylene) rhodanine as the terminal unit for the solar cell application. Among these molecules, the compound DRCN5T (2,2'-((5Z,5'Z)-5,5'-((3,3''',3''',4'-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-quiquethiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-ethyl-4-oxothiazolidine-5,2-diylidene))dimalononitrile as shown in **Fig. 6.1** exhibited the best PCEs (~10%) for small molecule based OPV after combining both thermal and solvent vapor annealing (i.e. post-treatment).¹⁹² Undoubtedly, the photo-absorption inside the blend film was improved due to the formation of the highly crystalline donor fibrillar network in the post treated sample and hence the improved solar cell device performance. However, detailed insights into the impact of such treatment on the relationship of the morphology-carrier dynamics and device performance of small molecule based devices are still severely lacking. Thus, it becomes essential to have the in-depth understanding of the different mechanism governing the charge dynamics inside the blend and explore the possibilities to further improve the device performance.

In this chapter, a systematic investigation of the origin of the enhanced device performance from 3.3% to 10.1% after post-treatment in DRCN5T based solar cell have been carried out in a bid to investigate the structure-functional relationship by correlating the

effects of morphology with the carrier dynamics. Large amount of strongly bounded charge transfer states (CTSs) were formed in the pristine BHJ blend due to the well-miscible morphology without expedite charge transport channel, which mainly undergo Shockley-Read-Hall (SRH) type trap-assisted geminate recombination.¹¹² The enhanced device performance after post-treatment for DRCN5T is mainly ascribed to the increased effective photon absorption in the active layer, inosculate with the reduced geminate and non-geminate recombination owing to the improved charge transport channels in the crystallized fibril morphology.

6.2 Experimental Details

DRCN5T was designed by replacing the thiophene group from (5Z,5'Z)-5,5'-((3,3''',3''',3''',4',4''-hexaethyl-[2,2':5',2'':5'',2''':5''', 2''':5''',2''':5''',2''':5'''-sepithiophene]-5,5''''diyl) bis(methanyl-ylidene))bis(3-ethyl-2-thioxothiazolidin-4-one) (DERHD7T)¹⁹³ by dicyanomethylene groups as shown in **Fig. 6.1**.¹⁹⁴ The dicyanomethylene group has a strong electron accepting nature to enhance light absorption.

Figure 6.1: Chemical structure of DRCN5T.

Device fabrication and characterization: The conventional devices were fabricated with the structure: glass/ITO/PEDOT:PSS/ DRCN5T:PC₇₁BM/PFN/Al. Substrates were cleaned as mentioned in section 5.2 of chapter 5. A thin layer of PEDOT:PSS was coated on them and dried at 120 °C for 20 min. Subsequently, the active layer was spin-coated from blend ratios

(w/w, 1:0.8) of DRCN5T (10 mg mL^{-1}) and PC₇₁BM in a chloroform solution at 1700 rpm for 20 sec on the ITO/PEDOT:PSS substrate. Then thermal annealing of one set of devices was performed at 120 °C for 10 minutes followed by solvent vapor annealing in chloroform environment for 60 sec which are termed as “post-treated”. While none of the treatment was performed on second set of active layers which are termed as “as-cast” or “pristine”. A thin layer of PFN was spin coated on all these active layers and 60 nm Al layer was deposited subsequently on the 0.04 cm^2 active layer under high vacuum ($< 1.5 \times 10^{-6}$ mbar). For optical characterizations, these active layers were directly prepared on quartz substrates which were cleaned by the same procedure. The optoelectronic properties of the photovoltaic devices were measured by Keithley 2400 source-measure unit.

6.3 Results and discussions

6.3.1 Photovoltaic Performance: The device performance of structure ITO/PEDOT:PSS/DRCN5T:PC₇₁BM/PFN/Al measured in dark and under 1 sun illumination is shown in **Fig. 6.2(a)**. The measured electrical parameters are summarized in **table 6.1**. It shows that the PCE is significantly improved from 3.3% to 10.1% compared with the pristine device without any treatment. This tremendous improvement of the performance occurred mainly from improved fill factor (from 0.47 to 0.69) and current density (from 7.3 to $\sim 16 \text{ mA-cm}^{-2}$) in post treated devices. However, open circuit voltage is found to have dropped by $\sim 0.04 \text{ V}$. This drop in V_{oc} indicates the enhancement of the crystallinity of the small molecule. On the other hand, the devices fabricated with blend film subjected to the thermal and solvent annealing exhibits the significant improvement in the dark current at selected voltage and 0.15V drop of built-in-voltage which is attributed to the efficient charge transport and collection properties in these devices. **Fig. 6.2(b)** shows the IPCE spectra measured for pristine and post treated DRCN5T:PC₇₁BM devices. Consistent with the trend observed for the current density, the post treated device shows higher IPCE than device prepared with as-

casted blend film. The post-treated device exhibit a maximum IPCE of around 65–75% in the wavelength range of 450–700 nm (**Fig 6.2b**) while other device shows less that 30% IPCE. In the next part of this work, the further investigation of the origin of the enhanced performance in post-treated devices are performed and it's relationship with active layer morphology and ultrafast charge generation dynamics by analyzing detailed photo-physical processes are established.

Table 6.1: Electrical performances DRCN5T:PC₇₁BM based OSC devices under illumination.

Device/ Parameters	PCE (%)	J_{sc} (mA·cm ⁻²)	V_{oc} (V)	FF
DRCN5T:PC ₇₁ BM	3.3±0.5	7.3±0.9	0.96±0.01	0.47±0.01
DRCN5T:PC ₇₁ BM-TA-SVA	9.8±0.3 (10.1)	15.9±0.2	0.92±0.01	0.68±0.01

Figure 6.2: (a) J - V curves of the conventional device with structure of ITO/PEDOT:PSS/DRCN5T:PC₇₁BM/PFN/Al under simulated 100 mW cm⁻² (AM 1.5G) illumination and (b) IPCE spectra measured for these devices.

6.3.2 UV-Vis Absorption Spectra: **Fig. 6.3** shows the linear absorption spectra of the as cast (pristine) and post-treated DRCN5T and DRCN5T: PC₇₁BM blend films measured on the similar thicknesses of the films on quartz substrates. The pristine DRCN5T film shows the photoabsorption between 450-800 nm wavelengths (**Fig 6.3a**) which is the indication of

maximum harvesting of the solar spectrum as compared to other existing counterpart polymers like P3HT, PCPDTBT etc as shown in chapter 4. It consists of three main vibronic peaks between 550-750 nm. The vibronic peaks correspond to 580 nm and 634 nm represents the π - π interaction within molecule while peak shoulder at 695 nm corresponds to the inter-chain interaction of DRCN5T molecules.¹⁹⁵ In post treated pure film, the peak at longest wavelength is dominated which indicates the presence of stronger inter-chain interaction within molecules and hence attribute to the improved crystallinity as a result of the treatment. The absorption intensity in post treated DRCN5T is improved in entire visible wavelength range when it is mixed with PC₇₁BM as shown in **Fig. 6.3b**. The spectral profile of pristine DRCN5T was found to be narrowed upon blending with PC₇₁BM which attribute to better miscibility of DRCN5T with PC₇₁BM without post-treatment. Thus, the enhanced crystallinity of pure DRCN5T is almost retained after blended with PC₇₁BM in post-treated samples.

Figure 6.3: UV-Vis absorption spectra of (a) only DRCN5T and (b) blend DRCN5T:PC₇₁BM films before and after post-treatment.

6.3.3 Morphology analysis: To understand the reasons behind such drastic improvement and visualize the crystallinity improvement before and after post-treatment, the morphologies of different active layers were investigated by using TEM.

Figure 6.4: Morphology of blend films. TEM images of DRCN5T film before (a) and after (b) post-treatment, and DRCN5T:PC₇₁BM blend films without (c) and with (d) post-treatment. The scale bar is 200 nm.

TEM studies reveal the distinct morphology of the pure DRCN5T and DRCN5T:PC₇₁BM blend film with and without post-treatment as shown in **Fig. 6.4**. In pure DRCN5T film, the morphology is changed from very small grains to highly crystalline fibrillar-type in post-treated films, which is the evidence of the enhanced crystallinity by post-treatment. In the pristine blend film of DRCN5T:PC₇₁BM (**Fig. 6.4a**), the PC₇₁BM molecules are well dispersed in the DRCN5T matrix and very small grains of DRCN5T or PC₇₁BM are finely mixed together. Such morphology at nanoscale facilitates the formation of the inefficient charge transport channel to the electrodes and hence strongly bound CTSs which may act as recombination losses in the devices. However, an apparent nanoscale phase separation and bicontinuous network system with the “fibrillar”-like morphology were observed over the entire area for the DRCN5T blend film after post-treatment, with the domain size (fibre width) at approximately 15~20 nm. For the highly efficient devices, such type of morphology is required where higher crystallinity support to absorb higher amount of photons while fibrillar structure provides the recombination-less pathways to the charge carriers.

Transient Absorption Measurements

6.3.4 Charge Generation in DRCN5T and DRCN5T:PC71BM films: To find deeper insights the ultrafast mechanism were probed to investigate the root cause of the higher performance in post-treated devices. Transient absorption measurements were carried out on these blend films of similar thickness coated on quartz substrates. TA profiles and dynamics of the as cast (pristine) and post-treated DRCN5T films were firstly measured before probing the carrier dynamics of the DRCN5T:PC₇₁BM blends. It should be noted that DRCN5T:PC₇₁BM film without any treatment is termed as “as-cast” and thermal annealing with solvent vapour annealing films (DRCN5T:PC₇₁BM-TA-SVA) are termed as “post-treated” for the following discussion. **Fig. 6.5** shows the TA profile spanning from 520 nm to 1600 nm at varying delay times following photoexcitation by 500 nm pump wavelength. The pump beam fluence was set at 50 $\mu\text{J cm}^{-2}$ per pulse. DRCN5T film shows positive transient signals ($\Delta T/T > 0$) below ~ 770 nm with a sharp peak at ~ 710 nm corresponding to the GSB of the DRCN5T molecule due to the state-filling of the excited states. Broad and negative transient signals ($\Delta T/T < 0$) were observed in the NIR region with a peak centred at around 1190 nm are attributed to the dominating photo-induced absorption (PIA) of DRCN5T singlet excitons. The decay dynamics of this exciton peak is fitted to the multi-exponential function as listed in table **6.1**. The decay dynamics of excitons show three exponential decays: ~ 1 ps (fast), ~ 10 ps (intermediate), and ~ 100 ps (slow). The fast and intermediate part can be attributed to the exciton migration and relaxation to lower states. Exciton-exciton annihilation cannot be excluded during this time scale considering the high fluence used in TA measurements. The final or slow exponential decay (~ 100 ps) is attributed to the recombination of exciton to ground states radiatively and/or non-radiatively. In addition to that a long lived component (> 1 ns) is also obtained during the fitting of the dynamics. This

component can be attributed to the inefficient/delayed polaron generation in pristine DRCN5T, which is possibly generated via charge transfer between different DRCN5T molecules. The TA spectrum and dynamics of both pristine and post-treated only DRCN5T were found analogous.

Figure 6.5: fs-ps transient profiles for (a) as-cast and (b) post-treated DRCN5T films. The corresponding (c) GSB dynamics monitored at 710 nm and (d) exciton dynamics monitored at 1190 nm.

Table 6.1: Summary of the decay dynamics in as-cast and post-treated pure DRCN5T film.

DRCN5T	Wavelength (nm)	τ_1/ps	τ_2/ps	τ_3/ps
As-cast	710	2.7 ± 0.1 (52%)	81 ± 2 (35%)	$>1 \text{ ns}$ (13%)
	1190	5.2 ± 0.2 (37%)	41 ± 2 (42%)	329 ± 17 (21%)
Post-treated	710	2.2 ± 0.1 (56%)	39 ± 1 (29%)	$>1 \text{ ns}$ (15%)
	1190	3.0 ± 0.2 (27%)	27 ± 1 (46%)	213 ± 8 (26%)

However, the effect of the post-treatment on transient spectral profile becomes prominent when DRCN5T is blended with PC₇₁BM (**Fig. 6.6**) The as-cast DRCN5T PC₇₁BM film exhibits featureless GSB profile between 520 nm – 690 nm. The absence of sharp GSB peak at ~710 nm indicates the interruption of the DRCN5T organization by the presence of PC₇₁BM. Such featureless spectral profile attributes the dominance of the disordered phase in the as cast system as shown in TEM images (**Fig. 6.4c**). The post-treatment of the as-cast blend film alleviates the morphological interruption of DRCN5T (**Fig. 6.7** for the zoom-in GSB profiles). The presence of the sharp peak at 710 nm and reoccurrence of the vibronic structure leads to the GSB profile resembling to the pristine DRCN5T film. All the GSB profile changes after post-treatment (i.e. red-shift and appearance of vibronic shoulders) are found to be analogous to that of P3HT:PCBM after thermal annealing, reflects the well-ordered region in the film where strong interchain interaction (as observed from absorption spectrum) as well as exciton-phonon coupling occurs.^{92,196}

Figure 6.6: fs-ns transient profiles at selected delay times for the (a) as-cast and (b) post-treated DRCN5T:PC₇₁BM films. The zoom-in profiles of the TA profile at 700 - 1200 nm region showing the evolution of CT and polaron states are also presented for the (c) as-cast and (d) post-treated DRCN5T:PC₇₁BM films.

Figure 6.7: The GSB profiles in fs-ns TAS for the (a) as-cast and (b) post-treated DRCN5T:PC₇₁BM films.

In the NIR region, the PIA exciton in the as-cast DRCN5T:PC₇₁BM is found to be slightly blue-shifted to around ~1150 nm compared to that of pure DRCN5T and post-treated DRCN5T:PC₇₁BM which support the presence of the amorphous phase of DRCN5T in the as-cast blend system. Additionally, the initial exciton signal is stronger in the post-treated DRCN5T:PC₇₁BM than the as-cast DRCN5T:PC₇₁BM. This indicates that larger amount of excitons are ultrafast quenched in the as-cast DRCN5T:PC₇₁BM film due to the well miscible morphology. The lower TA signal can also be correlated to the lower amount of photogeneration as a result of relatively lower photoabsorption as seen in absorption spectrum. On the other side in post-treated blend films, excitons need to diffuse longer distance in the crystalline domains to reach at the interface where they are subsequently quenched by PC₇₁BM. Once the excitons signal disappear at ~100 ps time delay, a long-lived PIA peak centered at around 1100 nm becomes prominent. This long-lived component persists for few microseconds which is shown in **Fig. 6.6d**, is attributed to the polaron induced absorption. The PIA signal at ~3 ns represents the population of the free charges in blend films because all the excitons are either recombined or dissociated into free charges by this time. **Fig. 6.6c** and **6.6d** shows the comparison of the PIA signal at 3 ns time scale which indicates that the population of free charges in both films are similar. This shows that these excitons are fully quenched within 100 ps by PC₇₁BM in the post-treated films and provides the similar amount of the free charges to contribute for the photocurrent. The carrier dynamics at 1100 nm were further extracted to investigate the polaron generation mechanism and fitted with tri-exponential function (**Fig. 6.8a**). Apart from the two short lifetimes (i.e. <5 ps and <100 ps) which are attributed to excitons in PIA at 1100 nm (**table 6.2**), a long-lived component (that extends beyond the measurement window) with a very slow rising constant of 1020 ± 90 ps and 920 ± 80 ps was also found for the as-cast and post-treated films, respectively. As summarized in **table 6.2**, besides the first two decay constants (2.4 ps, 52 ps

in as-cast and 4.4 ps, 73 ps in post-treated blend film) which are attributed to excitons, a slow rise of TAS signals with a time constant of 934 ± 167 ps and 612 ± 84 ps is obtained in as-cast and post-treated blend films, respectively. This slow rise should be attributed to the fraction of polaron generation via charge transfer states.^{110,197} Concurrently, the PIA at around 700 nm - 950 nm region decays significantly with a time constant of about 1042 ± 43 ps which correspond to similar rise time of the polaron signals and thus we attribute this life time to the decay of the CTSs (**Fig. 6.8c, 6.8d and 6.9b**).^{92,197} This assignment is also consistent with the reported spectra position of the PIA band due to CTSs for polymer based OPVs.^{197,198} The CTSs for the post-treated film exhibit much weaker PIA signals than that of the as-cast film, which indicates that the CTSs were almost totally suppressed after post-treatment.

From the charge generation dynamics, we found a similar fraction (65 – 55 %) of CTS in DRCN5T can dissociate into free charges regardless of the processing conditions. The presence of relatively higher population of CTS but lower yield of polarons in as-cast films implies a heavy loss of CTS through recombination. In addition, the higher density of CTS in as cast films can further act as interfacial traps that accelerate the charge carrier non-geminate recombination over a longer time scale.

Table 6.2: Summary of the dynamics for DRCN5T:PC₇₁BM blend film without and with post-treatment.

DRCN5T:PC ₇₁ BM	Wavelength (nm)	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	τ_4 (ps)
As-cast	1100	2.4 ± 0.6 (18%)	73 ± 12 (27%)	933 ± 167 (17%)	Long (39%)
	750-950	1042 ± 43 (65%)	Long (35%)	-	-
Post-treated	1100	4.4 ± 1.3 (16%)	52 ± 11 (25%)	612 ± 85 (21%)	Long (38%)
	750-950	899 ± 84 (55%)	Long (45%)	-	-

Figure 6.8: fs-ns transient dynamics for the as-cast and post-treated DRCN5T:PC₇₁BM films monitored at (a) 1100 nm and (b) 750 nm - 950 nm regions.

6.3.5 Charge Recombination in the as-cast and post-treated DRCN5T:PC₇₁BM films:

To investigate the effects of the morphology on the charge recombination dynamics, we also performed TA measurements over ns-μs time regime. **Fig. 6.9a-c** shows the ns-μs TAS profiles at selected time delays (1 ns, 10 ns, 100 ns) for films with and without post-treatment. The as-cast film shows a much higher CTS (870 nm - 950 nm) magnitude than post-treated films. This indicates that the charge carriers in as-cast film are more preferable to stay in the CTS than the post-treated film, *i.e.*, more charge carriers in as-cast film are bounded charge pairs rather than spatially-free charges. This bounded charge pairs can easily recombine via the CTS. This is validated by comparing the dynamics of 870 - 950 nm and that at 1100 - 1200 nm for the as-cast films as shown in **Fig. 6.9d-e**. The charge carriers in CTS are short-lived than that in polaron states. In addition, the former wavelength range shows weak intensity-dependence decay dynamics while the latter is strongly intensity-dependent. This indicates that CTS act as interfacial traps for charge recombination. Such recombination is Shockley-Read-Hall (SRH) type trap-assisted recombination which is usually a monomolecular process.¹¹² The charges in the polaron band (*i.e.*, free charges), on the other hand, recombination via Langevin type trap-free bimolecular recombination and hence strongly intensity-dependent.¹¹⁰ The post-treated films show similar intensity

dependent behaviour in the two spectra regions, indicating the consistency of our conclusion (Fig. 6.10). Based on transient absorption results, we believe the presence of high density of CTSs and the heavy loss from geminate recombination and trap-assisted non-geminate recombination studied for the as-cast films using TAS techniques is the culprit for the low FF under operation conditions if as-cast devices. The post-treatment can recover the crystalline structures that formed in pristine DRCN5T films and lead to the phase segregation of DRCN5T and PC₇₁BM. Such benign structure with much reduced interfacial CTS can reduce the geminate loss as well as the trap-assisted non-geminate loss.

Figure 6.9: ns- μ s transient profiles for the as-cast and post-treated DRCN5T:PC₇₁BM films monitored at (a) 1 ns, (b) 10 ns and (c) 100 ns delays. Intensity-dependent charge recombination dynamics for the as-cast DRCN5T:PC₇₁BM films monitored at (d) 870 - 950 nm and (e) 1100 - 1200 nm regions.

Figure 6.10: Intensity-dependent charge recombination dynamics for the post-treated DRCN5T:PC₇₁BM films monitored at (d) 870 nm - 950 nm and (e) 1100 nm - 1200 nm regions.

6.4 Conclusions

In this chapter, we have systematically investigated the origins of higher performance of small molecule based BHJ solar cells devices fabricated with as-casted and post-treated (thermal annealing followed by solvent vapour annealing) DRCN5T:PC₇₁BM blend films. The amorphous morphology in the lack of percolated pathways promotes the formation of the strongly bounded CTSs, which predominantly undergo the geminate recombination or function as interfacial traps that facilitate the non-geminate recombination of charge carriers in as-casted blend film. On the other hand, these CTSs are almost completely diminished owing to the formation of the bi-continuous network with crystallized fibrillar morphology after post-treatment, which acts as “highways” for the effective exciton diffusion to the interfaces and subsequent dissociation which gives the higher performance in devices. The results gained in this work provide new insights to investigate the origin of different J-V behaviors for bulk-heterojunction organic solar cells from morphology aspects and excited state dynamics, which could be used to directly guide the further optimization of the performance of SM-OPVs through judicious morphology control and engineering.

Chapter 7

Conclusions and Future Works

7.1 Conclusions

It is well known that the morphology of active layer plays a crucial role in the device performance as an improved morphology promotes charge carrier transport in that particular layer. In this work, we have investigated the ultrafast photophysics in wide range of active blend systems and correlated with the nano-morphology and their optoelectronic properties for low temperature processable solar cell devices. External electric field treatment, usage of solvent additive and solvent vapour thermal annealing of the active layer are adopted as three different processing methods to tailor the morphology and hence the charge carrier dynamics in corresponding devices.

In the first part of this thesis, the benefit of ‘dipole polarization’ is advantageously used to get better morphology through external E-field treatment of the conjugated polymer films. It should be noted that the treatment is carried out during the active layer drying step prior to cathode deposition while fabricating organic solar cells. In this work we reveal the essential requirements of a conjugated polymer to have an effective interaction with external E-field to promote the efficiency of OSC. Results on pristine and E-field treated blend films fabricated with P3HT-nanofibre and other popular photovoltaic polymers viz., P3HT, P3BT, PTB7 and PCPDTBT have been presented in this thesis. Blend films of these donor molecules were made with PCBM and devices fabricated with them were also characterized. A comparative study on film morphology and electrical properties has been presented here to understand the role of electric field during the solvent drying of the active layer. E-field treatment of different conjugated polymer blend systems and their comparison with standard or untreated films/devices leads to the following conclusions:

- E-field treated films become more crystalline as confirmed by the x-ray diffractogram studies. As the electric field is applied across the blend system, the external field aligns the polar dipoles in the direction of the field leading to the improved orientation of polymer chains.
- The charge carrier mobility improves in E-field treated devices. This conclusion is based on dark J - V characteristics of solar cell devices fabricated without and with E-field treatment.
- Application of E-field during thermal annealing of P3HT blend system modify the physical and electrical peroperties of the active layer. The active surface of the P3HT:PCBM and P3BT:PCBM system become rougher by E-field treatment with significant increment in exitons/polarons population as proved by transient absorption spectroscopy.
- The improvement of the PCE under the external electric E-field treatment depends on donor system that is used to prepare the active blend sysem. PCE improves from ~1.8 % to ~2.2 % in the case of P3HT-nf:PCBM blend system while it improved by ~0.5 % and ~0.4 % in magnitude in P3HT:PCBM and P3BT:PCBM blend systems respectively where active layers were subjected to external E-field treatment.
- An investigation of individual efficiencies related to the intermediate steps of solar cell working mechanism reveals that charge transfer and collection get enhanced significantly in E-field treated blend films. The higher roughness increase the contact area between the deposited metal layer and the active layer, resulting in improved electrical contact. On the other hand, better morphology in E-field treated blend system helps in efficient charge transport by reducing bimolecular recombination losses P3HT:PCBM and trap assisted monomolecular recombination in P3BT:PCBM.

- However, amorphous blend systems *i.e.* PTB7:PCBM and PCPDTBT:PCBM remain unresponsive in 2.0-8.0 kV-cm⁻¹ E-field range. X-ray diffractometry on amorphous polymers shows similar diffraction pattern of nontreated and E-field treated amorphous donor system.
- Our study reveals that the intrinsic molecular dipole moment is not the sole criteria but self-organization ability, linear monomer molecular structure and smaller molecular size are the other essential requirements for the effective E-field and polymer interaction.
- In the second part of the thesis, “solvent additive” is introduced as another simple and effective approach in the direction of the developing high performance solar cell devices for flexible application is presented. In this method, a small fraction of the high boiling point solvent is added to the host solvent in organic blend system. Here we present a detailed study of the optoelectronic properties, morphology and charge carrier dynamics using ultrafast spectroscopy in pristine, thermally annealed and different thiol-based additive-added P3HT:PCBM blend devices. The degree of the interaction between additive and P3HT are correlated and apparent in XRD, AFM and the charge carrier recombination dynamics. The effect of different alkenedithiols as solvent additive in P3HT:PCBM system and their comparison with pristine and thermally-annealed thin films and OSC performances lead to the following conclusions:
 - The presence of the solvent additive in P3HT:PCBM precursor solution modifies the film crystallization process during the film formation at the time of solution spinning.
 - The crystallinity and phase separation of donor/acceptor is decided by the degree of the molecular interaction of the solvent additive and P3HT system which can be determined by their solubility parameter difference.

- As compared to HDT and PDT, the smallest solubility parameter difference $\Delta\delta$ with respect to P3HT ($\Delta\delta_{\text{ODT-P3HT}} = 9.5$) and its higher boiling point causes ODT to take longer time to evaporate and hence providing ample time to interact with P3HT.
- Such degree of the molecular interaction improves the crystallinity and photo-absorption in active layer to enhance the PCE to 2.8% in HDT and ODT as compared to 1.0% non-annealed (NA) P3HT:PCBM solar cell.
- On the other hand, the largest solubility parameter difference of PDT with respect to P3HT ($\Delta\delta_{\text{PDT-P3HT}} = 10.6$), despite its lowest boiling point, suggests a poor interaction with P3HT and hence a more extensive aggregation. Such aggregation indeed improved the crystallinity and photo-absorption but poorer inter-networking invites other loss mechanism and limited the efficiency increment to 1.7% only in P3HT:PCBM solar cell.
- Transient spectroscopy reveals a Langevin-type free carrier bimolecular recombination in HDT and ODT added blend film as compared to the trap-assisted recombination in PDT added system. The poorer device performance of 1.7% for the PDT-blend is attributed to the excessive enlargement of the polymer domains that resulted in poorer intermixing and percolation of the donor-acceptor networks. Thus, a trap-dominated recombination prevails as the charges cannot be effectively transported to the electrodes.
- 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, 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.

In the last part of the thesis, solution processed small molecule DRCN5T, is presented as an alternative of the photoactive conjugated polymers for the solar cell application. In this part, a solvent vapour and thermal annealing as post treatment of active layer is presented as another low temperature processing approach to improve the efficiency in small molecule based solar cells. The impact of solvent vapour thermal annealing as post treatment of DRCN5T:PCBM and their comparison with pristine thin films and devices lead to the following conclusions:

- The ultrafast dynamics is not only controlled by the distinct morphologies of conjugated polymers blend system but also determined by the morphology changes in solution processed small molecule system. The solvent vapour annealing of the pristine DRCN5T:PCBM promote the finely mixed amorphous donor/acceptor system to efficiently distributed donor and acceptor domains with fibrillar structure in blend. This in result improves the generation of the photo charge carriers and hence device performance from 3.3% in pristine device to 10% in post treated devices.
- The amorphous morphology in the lack of percolated pathways promotes the formation of the strongly bounded CTSs in pristine DRCN5T:PCBM. These CTSs predominantly undergo the geminate recombination or function as interfacial traps that facilitate the non-geminate recombination of charge carriers. On the other hand, these CTSs are almost completely diminished owing to the formation of the bi-continuous network with crystallized fibrillar morphology after solvent vapour annealing as post-treatment,

which acts as “highways” for the effective exciton diffusion to the interfaces and subsequent dissociation which gives the higher performance in devices.

7.2 Recommendation for future work:

The detailed study presented in this thesis do indicate that E-field annealing, solvent additive and solvent vapour thermal annealing are useful low processing temperature approaches to enhance the PCE. However, the work carried out in this thesis also shows the way forward to identify important issues that could be addressed in future work. Some of the possible works are as follows:

- **Role of the PCBM:** One of the main reasons for the improvement in solar cells based on different active blend systems was efficient charge transport properties. This might be because of better hole mobility and/or, improved electron mobility in PCBM. Electron only devices can be fabricated from PCBM with device structure (for example Al/PCBM/Al) in order to study the change transport properties in PCBM because of the E-field treatment. Since PCBM has very high dipole moment of 4.1Debye, it is worth to investigate the change in charge transport in this electron acceptor material.
- **Recombination and trap analysis:** None of the study is carried out in this work to determine the traps density in different blend systems. So capacitance-voltage (C-V) measurements and dark J - V at the trap-limited current region could be further analysed and correlated to the recombination dynamics measured by transient spectroscopy.
- **Use of Magnetic Field:** In this work DC electric field is used to promote the organization of the active layer. Similarly, magnetic field can also be applied across the film made of ferroelectric polymers containing magnetic responsive groups to orient them in particular direction and compare the effectiveness of the field.

- **Experiment with different systems:** This study can be further extended to other organic or hybrid systems. Newly developed small molecules such as DRCN5T and perovskite as hybrid photoactive layer are the good option to explore and investigate the effect E-field and charge dynamics. Since the higher dipole moment, self-organization ability and linear structure is the necessity for the effective interaction than judicious choice of the material is required.
- **Other solvent additives and systems:** Solvent additive study in this thesis is limited only to the alkenodithiole family and P3HT:PCBM system. It can also be extended to the other organic material systems such as PTB7:PCBM, PCDTBT:PCBM, PCPDTBT:PCBM, DRCN5T:PCBM etc. Apart from this, different solvent additive can also be used to reduce the recombination mechanism and hence to further improve the PCE.
- **Other blend system:** To further enhance the performance beyond the binary system, it is required to explore the ternary blend system. Combining different polymer systems having the counter absorption in visible range can solve the limited range absorption problem of single conjugated system. Moreover, the photophysics using TA, PL and TRPL can further help to find the best combination of the different components to minimum the charge carrier losses and maximum extraction.
- **Optical Characterizations**

Photoluminescence: Steady state PL measurement is indeed a good technique to speculate the recombination processing inside the blend system but does not provide the information about the trap density causing for the loss of charge carriers. However, measuring the PL emission on varying the excitation fluence (few tens to hundreds of $\mu\text{J}\cdot\text{cm}^{-2}$) the trap density inside the system can be monitored. Therefore, fluence dependence

steady state PL measurements can also be performed to reveal the role of traps in P3HT:PCBM system inclusion of the additives and different treatments on DRCN5T system which is still vague.

Time-resolved photoluminescence (TRPL) and Florescence Upconversion Spectroscopy: This is another useful technique to investigate the charge transfer mechanism in BHJ systems. In addition, monitoring the PL dynamics can also provide the information about the exciton diffusion length in the system and hence the estimation of the microstructure of the bulk heterojunction. Since the amorphous polymers systems are independent of the varying amplitude of the electric field, the estimation of the lifetime and exciton diffusion length will give more insights of the photo-physical phenomenon of these systems. Florescence upconvresion spectroscopy would allow one to probe the ultrafast excitonic recombination in conjugated polymers beyond the timescales of traditional time-correlated single photon counting and streak camera based approaches.”

Pump-push probe spectroscopy: This is another useful technique to investigate the excited states of organic molecules. This technique involves a more advanced pump-probe steup, comprising of three optical pulses – the pump-push probe and the pump-dump-probe. Such studies can reveal more insight into the excitonic properties and charge transfer states such as torsional relaxation and detrapping of bound charge pairs, the role and significance of exciton delocalization and dissociation in newer BHJ systems.¹⁹⁹

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