

**Impact of film morphology upon the
performance of polymer / fullerene solar cells**

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Declaration of Originality

The work presented in this thesis was performed under the supervision of Prof. James Durrant and Prof. Iain McCulloch in the Department of Chemistry at Imperial College London.

I declare that the work presented in the thesis is my own except where specific reference is made.

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Abstract

Polymer:fullerene blend microstructure has been recognised as a key, but poorly understood, factor in optimising performance of polymer:fullerene based solar cells. This thesis focuses on investigating the impact of material chemical structure upon the blend microstructure, and thereby on device efficiency and stability for polymer:fullerene solar cells.

It will be shown in the first results chapter that polymer fluorination can promote phase segregation in polymer:fullerene blend, limiting its charge generation as demonstrated using transient absorption spectroscopy. The promotion in phase segregation is shown to vary from polymer to polymer. With a careful modification of the polymer backbone, the negative impact of polymer fluorination can be avoided, resulting in an improvement in device performance.

The following chapter focuses on the impact of polymer side chain on device performance. Linear side chain for PTTV polymers is found to offer a better polymer:fullerene mixing in comparison to branched side chains, potentially due to its better ability to accommodate fullerene molecules. This subsequently addresses limitations of poor of fullerene exciton dissociation efficiency.

The next chapter provides new insights into the effects of polymer molecular weight on device performance. A high molecular weight of two DPP-containing polymers is shown to be beneficial to device performance, by offering a higher degree of material mixing in the polymer:fullerene blend.

The last results chapter compares two polymers with different crystallinity in terms of their blend microstructure and device performance upon thermal annealing. It is shown that devices employing a crystalline DPP based polymer exhibits a sharp collapse in efficiency for annealing at temperatures beyond 140 °C, which is assigned to the polymers poorer miscibility with fullerene, making it incapable to suppress fullerene clusters formation. In contrast, an amorphous IDT based polymer shows a smaller decrease in efficiency under the same condition, consistent with its greater miscibility with fullerene.

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1. "Towards optimisation of photocurrent from fullerene excitons in organic solar cells" S. D. Dimitrov, Z. Huang, F. Deledalle, C. B. Nielsen, B. C. Schroeder, R. S. Ashraf, S. Shoaee, I. McCulloch and J. R. Durrant, *Energ Environ Sci*, 2014, 1037-1043
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Abbreviations

AFM atomic force microscopy

BT benzothiadiazole

CS charge separation

CT charge transfer

DPP diketopyrrolopyrrole

DS diffraction strength

EA electron affinity

ΔE_{CS} driving energy for charge separation

EQE external quantum efficiency

FF fill factor

HOMO highest occupied molecular orbital

ICBA bis-indene-C60

IP ionisation potential

ITO indium tin oxide

J current density

J_{SC} short circuit current

LUMO lowest unoccupied molecular orbital

MDMO-PPV poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene]

MEH-PPV poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]

M_n number average molar mass

NEXAFS near edge X-ray absorption fine structure

OPV organic photovoltaic

OD optical density

P3HT poly(3-hexylthiophene)

pBTTT poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene)

PC₆₁BM [6.6]-phenyl-C61 butyric acid methyl ester

PC₇₁BM [6.6]-phenyl-C71 butyric acid methyl ester

PCDTBT poly(*N*-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole

PCE power conversion efficiency

PDI polydispersity index

PL photoluminescence

PLQ photoluminescence quenching

PTV poly(thiophene vinylene)

PTTV poly(thienothiophene vinylene)

RR regioregular

RRa regiorandom

TAS transient absorption spectroscopy

TEM transmission

UV ultraviolet

V voltage

V_{OC} open circuit voltage

WAXS wide angle X-ray scattering

Chapter 1

Introduction

1.1 Motivation

Ever since the Industrial Revolution in the 18th century, the development of human society has been heavily reliant on advances in technology. From a business standpoint, technology development allows people to generate more revenue with lower cost, resulting in higher profits. With rising global population and economic growth, energy technologies are increasingly important as they are keys to enabling advances in other technologies which improve the quality of human life.

Fossil fuels have been a primary source of energy for mankind since the 20th century, due to their relatively effective production of energy at a reasonably low cost (in terms of raw materials, processing and equipment). However, the use of fossil fuels is known to emit gases (e.g. CO₂, SO_x, NO_x) which can contribute to the greenhouse effect and air pollution. The environmental cost of utilising fossil fuels, which was once difficult to quantify, is now becoming much clearer. Recently, the Chinese Academy of Environmental Planning reported that the annual cost of environmental damage in China was approximately \$230 billion, equivalent to more than 3% of the country's gross domestic product.¹ In parallel, there is increasing evidence that cycles of extreme weather are increased by global warming, which, apart from impacting human lives, also puts noticeable numbers of animals at high risk of extinction. Rising environmental costs makes the use of fossil fuels a less profitable source of energy. As a result, a number of countries have sequentially drawn plans to increase utilisation of renewable energy in order to reduce environmental degradation. In the United Kingdom, the current target is to generate 15% of the national energy consumption using renewable energy by 2020.²

Renewable energy is energy extracted from a source that is continually restored, such as sunlight, wind and geothermal heat. The absence of pollutant gas emission makes renewable

energy of environmental and political interest. Figure 1.1 shows the estimated media attention and the potential economic impact of 12 technologies which have aroused most interest in 2013.³ The fact that renewable energy receives much media attention implies its high public expectation to help resolve environmental degradation. In contrast, renewable energy exhibits less economic impact than ‘advanced oil and gas exploration and recovery’ on the graph suggesting that it is currently difficult for renewable energy to replace the conventional way of energy sourcing in financial terms.

Media attention

Number of relevant articles in major general interest and business publications over 1 year (log scale)

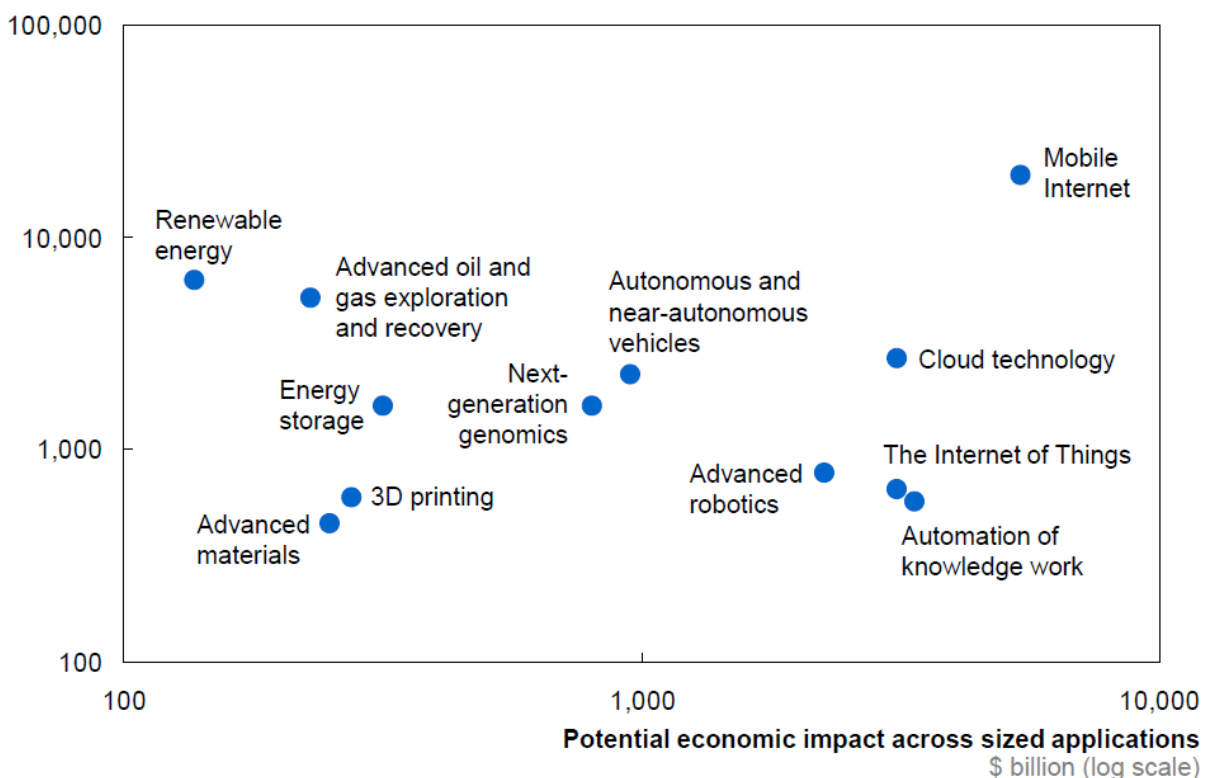


Figure 1.1 Estimated media attention and potential economic impact of 12 potentially economically disruptive technologies. [Taken from ref³]

Photovoltaics, a form of renewable energy conversion which has been predicted by McKinsey & Company to have massive economic impact (\$200 billion annually) in 2025,³ is a method to generate electricity by exciting semiconductors using sunlight. One of the difficulties that photovoltaics have in replacing fossil fuel is their high cost of production. Nowadays commercialised solar cells are mostly based on crystalline silicon, which is an inorganic semiconductor. Despite an 80% reduction in cost over the last decade,⁴ silicon based solar cells are still not competitive against fossil fuels. Recently, significant attention in scientific research has been focusing on organic photovoltaics, a potentially more cost-

effective solar cell. The most promising organic solar cells are based on semiconductor polymers which may only require low production costs once successfully scaled up. They are soluble in organic solvents making roll-to-roll manufacturing possible for higher throughput. In addition, these polymers generally have high molar extinction coefficients such that only a small amount of material is required to harvest a large number of photons. All these factors make polymer based solar cells a potentially more cost effective approach to harness solar energy. However, the cost effectiveness of state-of-the-art polymer based solar cells is currently insufficient for commercial application. They generally suffer heavily from low power conversion efficiency and poor stability which hamper their commercialisation. With regards to the former, the efficiency of polymer based solar cells has been experiencing a rapid growth, reaching 12 % in 2013.⁵ This figure is still lower than the best efficiency recorded so far for inorganic solar cells.⁶ In terms of stability, the lifetime of a typical polymer solar cell with excellent encapsulation has been estimated to reach 7 years under controlled conditions.⁷⁻⁹ This is still not comparable to that of silicon based solar cells which is on the scale of 25 years. The lower efficiency and poorer stability of polymer solar cells is a result of several issues. This thesis primarily addresses how the morphology of the photoactive layer of such solar cells contributes to their efficiency and stability.

1.2 Polymer semiconductors

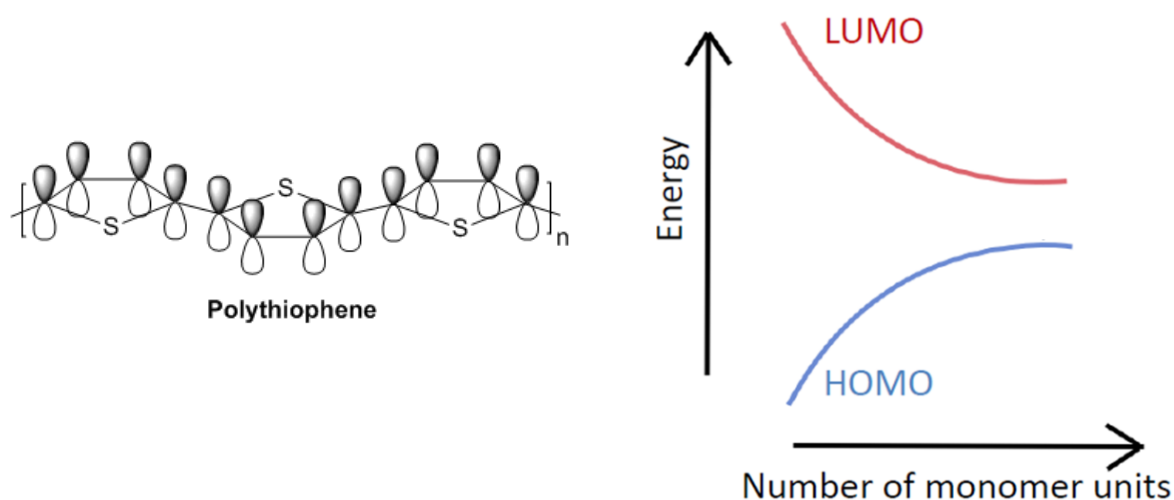


Figure 1.2: (Left) π -conjugation of extended p_z orbital overlapping along polythiophene backbone; (right) Energy levels of the LUMO and HOMO of polythiophene as functions of monomer units in the polymer. [This image has been reproduced with the permission of the rights holder, The Royal Society of Chemistry¹⁰]

The electronic properties of polymer semiconductors, such as the magnitude of their band gap, are determined by their π -conjugation. Carbon atoms in the conjugation along a polymer backbone are sp^2 hybridised, resulting from mixing between one 2s orbital and two 2p orbitals.^{11, 12} This allows the carbon atom to form three σ -bonds to adjacent atoms. The remaining p_z orbital of each carbon along the conjugated chain interact with each other in a side-to-side manner, forming a relatively delocalised and extended π -bond as illustrated in Figure 1.2 (left). This extended π -bond is called the π -conjugation. In this case, the π -bonding is the highest occupied molecular orbital (HOMO) while the π -antibonding orbital is the lowest unoccupied molecular orbital (LUMO). The energy difference between these two energy levels is the band gap (E_g) of the polymer semiconductor. Extending the backbone of the polymer allows more p_z orbitals to overlap with each other, increasing the length of the π -conjugation. This results in an increase in the energy of the HOMO and a decrease in the energy of the LUMO leading to a smaller band gap for the polymer. However, as the backbone is extended, the length of effective conjugation may not scale up accordingly due to chemical defects, presence of end groups or bends in the polymer backbone, which may limit the length of π -conjugation.^{13, 14}

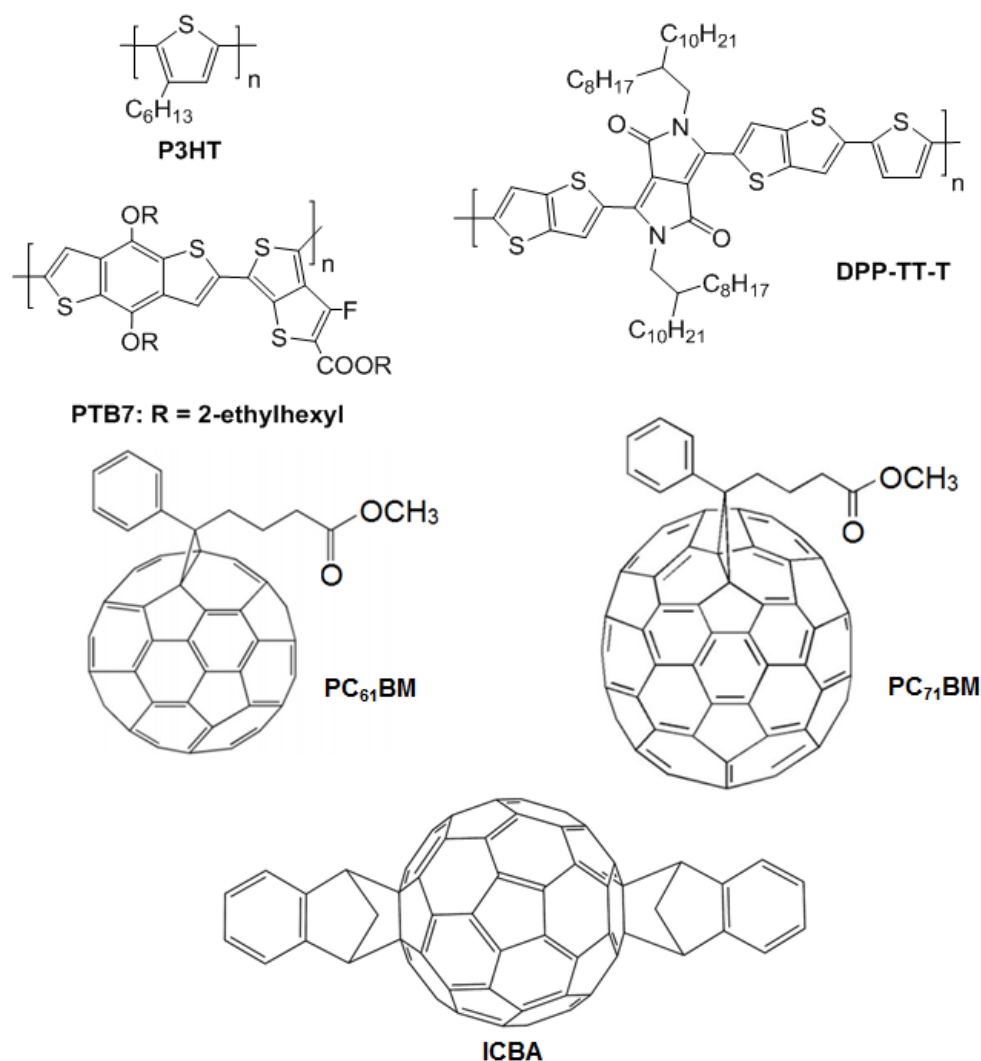


Figure 1.3: Chemical structures of the polymer semiconductors and fullerenes mentioned in the Introduction.

1.3 Operating principle for polymer:fullerene solar cells

Polymer semiconductors require other components to generate photocurrent. The polymer based solar cells focused on in this thesis are polymer:fullerene bulk heterojunction solar cells, which have a sandwich architecture of ITO/PEDOT:PSS/polymer:fullerene/aluminium (Figure 1.4). The polymer:fullerene layer, also called the active layer, is a blend layer containing polymer and fullerene phases. Most of the key photocurrent generation mechanisms occur within the active layer while the other layers mainly act as transporting media to deliver negative or positive charges to the external circuit.

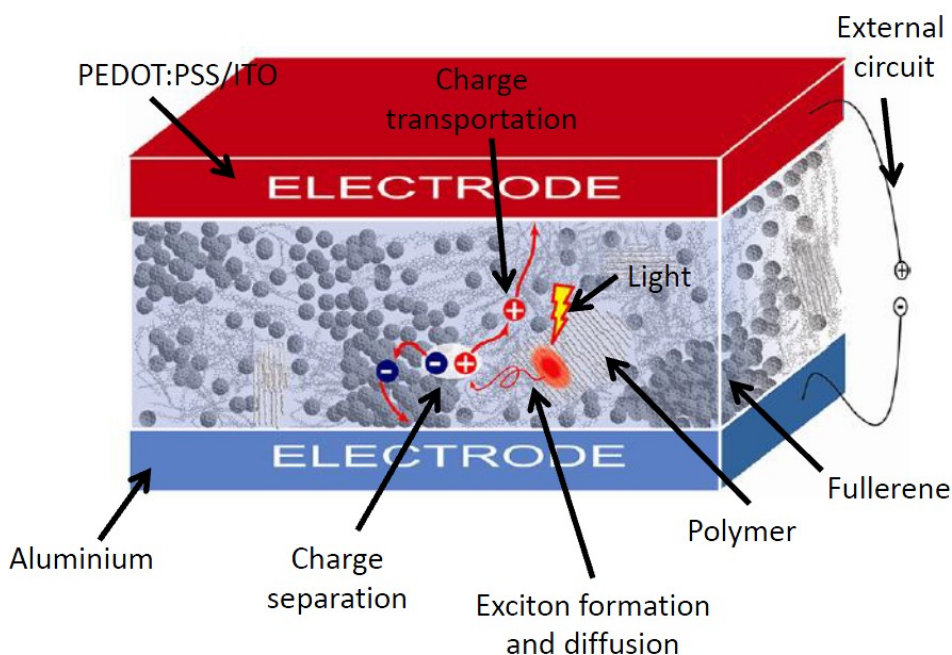


Figure 1.4: Illustration of photocurrent generation in a polymer:fullerene solar cell. [This image has been reproduced with the permission of the rights holder, American Chemical Society¹⁵]

The photocurrent generation in bulk heterojunction solar cells is widely believed to consist most simply of three consecutive steps, namely photon absorption, dissociation of exciton into separated charges and charge collection.¹⁶ These processes can be most simply described as detail below, although it should be noted that much of this thesis will be concerned with the limitations of this relatively simplistic description. It starts from the interaction between a photon and the polymer in the active layer. A photon with energy greater than the band gap of the polymer can be absorbed, promoting an electron from the HOMO of the polymer to the LUMO, leaving a positive hole at where the electron was originally positioned. The electron and hole are still attracted to each other by their Coulomb attraction, resulting in a characteristic bound but mobile state called an exciton. The exciton then diffuses within the polymer domains via energy transfer mechanism until it reaches the polymer:fullerene interface to undergo dissociation. This takes place when the electron in the LUMO of the polymer is transferred to the LUMO of the fullerene, driven by the downhill energy offset between the LUMOs of the two materials. Although the electron and the hole reside on different molecules at this stage, some studies suggest that they can still be attracted to each other by their Coulomb attraction, potentially resulting in the formation of a state called a ‘charge transfer’ (CT) or bound polaron pair state. Some electron-hole pairs can escape from their Coulomb attraction giving rise to relatively free positive and negative

charges (referred to as ‘polarons’). They can eventually be collected by the electrodes contributing to the photocurrent in the external circuit.

The photocurrent generation mechanism at short circuit condition can be summarised by equation 1,

$$J_{sc} = q \int N_{ph}(\lambda) EQE(\lambda) d\lambda \quad (1)$$

where J_{sc} is the photocurrent generated from the device under short circuit condition, $N_{ph}(\lambda)$ is the flux of photon with wavelength λ per unit area, q is the elementary charge and EQE is the external quantum efficiency defined as the probability of an incident photon resulting in a charge flowing in the external circuit as determined by

$$EQE(\lambda) = \eta_{ABS} \times \eta_{CS} \times \eta_{COLL} \quad (2)$$

where η_{ABS} stands for the efficiency of photon(λ) absorption, η_{CS} is the probability that an exciton will lead to separated charges, and finally η_{COLL} is the efficiency of collecting the free charges at the electrodes.^{16, 17} Fullerenes like Phenyl-C71-butyric acid methyl ester (PC₇₁BM, see figure 1.3) can also harvest visible-light photon and give rise to photocurrent in the external circuit. In this case, the exciton dissociation is based on a hole transfer where the hole is transferred from the HOMO of the fullerene to the HOMO of the polymer. Equation 2 implies that not all the absorbed photons result in photocurrent generation in organic solar cells. This is because there are other loss mechanisms that can compete with photocurrent generation. In the next section, the mechanism of charge generation and the associated loss pathways are discussed in more detail, particularly focusing on the step of dissociation of exciton into separated charges.

1.4 Fate of exciton

1.4.1 Formation and recombination of exciton

The photophysics of polymers semiconductors discussed in this section covers the fate of the exciton including information such as exciton formation, recombination and exciton binding energy.

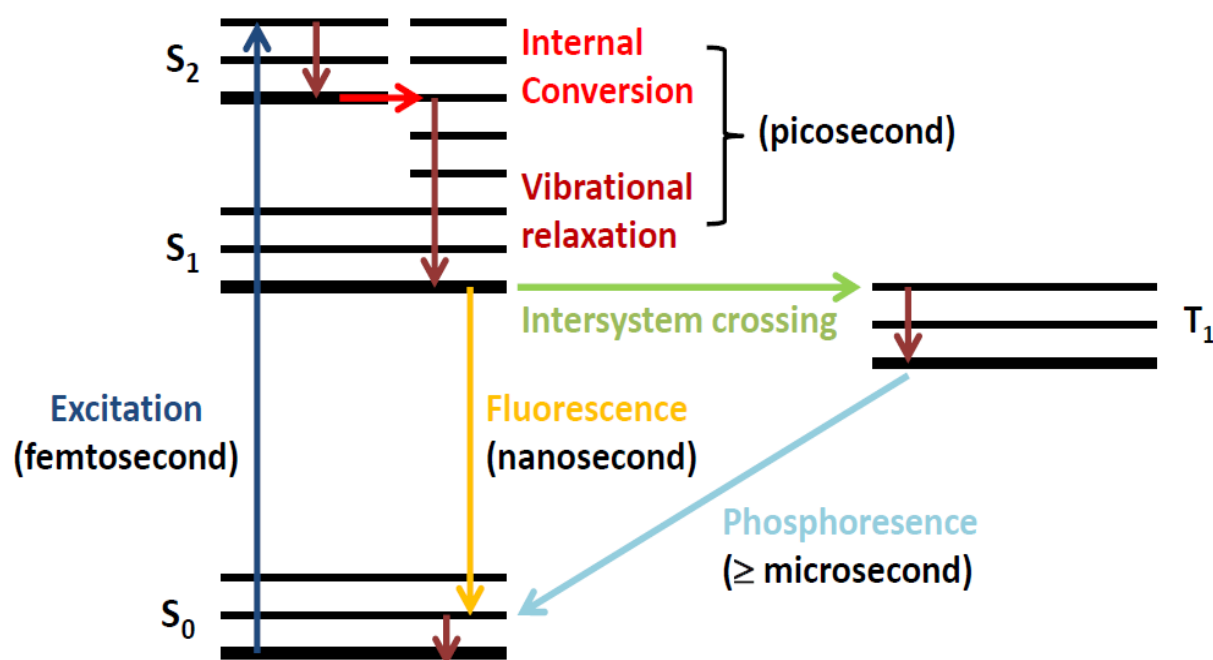


Figure 1.5: A Jablonski diagram, showing electronic states of organic molecules and the associated electronic transitions. Note that relaxation to ground state (S_0) can also occur via internal conversion from S_1 and intersystem crossing from T_1 . [This image has been reproduced with the permission of the rights holder, Nature Publishing Group¹⁸]

As mentioned above, formation of exciton requires absorption of a photon with energy greater than the bandgap of a molecule.¹⁹ During this process, an electron in the HOMO of the molecule is promoted to higher electronic levels; equivalent to excitation of molecule singlet ground state (S_0) to higher excited states (S_n), with n depending on the energy of the photon (figure 1.5).²⁰ Subsequently, the excited electron undergoes fast decay via internal conversion and vibrational relaxation (on femto or picosecond timescales²¹) to the LUMO of the molecule (or described as $S_n \rightarrow S_1$), giving rise to the formation of an exciton. Following this, the exciton can undergo recombination via fluorescence according to Kasha's rule,²² with the excited electron returning to the HOMO ($S_1 \rightarrow S_0$).

1.4.2 Exciton binding energy

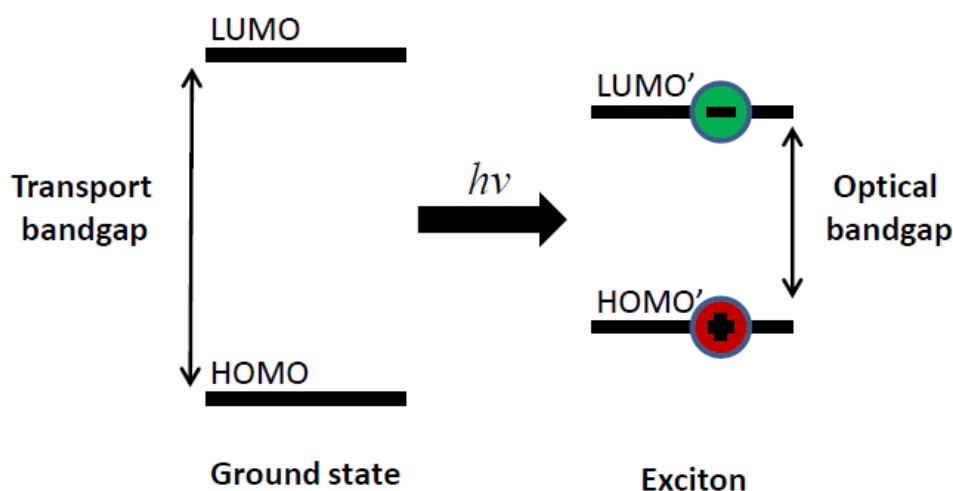


Figure 1.6: A diagram showing the change in bandgap upon formation of exciton.

Upon formation of the exciton, the bandgap of the molecule can be different from the bandgap in the ground state. The attraction between the positive hole and the negative electron in the exciton can be calculated using Coulomb's Law:

$$\text{Coulomb attraction} = \frac{q_1 q_2}{4\pi r \epsilon_0 \epsilon_r} \quad (3)$$

where q_1 and q_2 are elemental charges of the hole and the electron. r is the separation between the two charges, ϵ_0 is the permittivity of free space while ϵ_r is dielectric constant of a material. The attraction results in an increase in energy of the HOMO and a decrease in energy of the LUMO, leading to a smaller bandgap for the excited state compared to the band gap at ground state. The resultant bandgap is referred as the 'optical bandgap' compared to 'transport bandgap' for the ground state (figure 1.6).²³ The difference in bandgaps before and after excitation is referred to as the exciton binding energy, which reflects how easily the hole and electron can escape from each other. Depending on the magnitude of exciton binding energy, excitons can be classified into Wannier-Mott exciton or Frenkel exciton.^{24, 25} The electron and hole in a Wannier-Mott exciton exhibits weak Coulomb attraction (~ 10 meV) and are separated by a distance greater than the lattice constant. This occurs in materials with a relatively large ϵ_r as exhibited by many inorganic materials (e.g. 10.68 for Silicon). The bound electron-hole pair can easily be overcome by thermal energy at room temperature (~ 25 meV) giving rise to free charges.²⁶ In comparison, Frenkel excitons exhibit strong Coulomb attraction ($\sim 0.1 - 1$ eV) with the electron and hole separated on the order of the lattice

constant. This is usually found in materials which display a small dielectric constant, such as polymer semiconductors which are of interest in this thesis ($\epsilon_r \sim 2-4$).²⁷ As a result, Frenkel excitons more readily undergo recombination and are more difficult to be separated into free charges.

1.5 Photocurrent generation

1.5.1 Exciton dissociation at polymer:fullerene interface

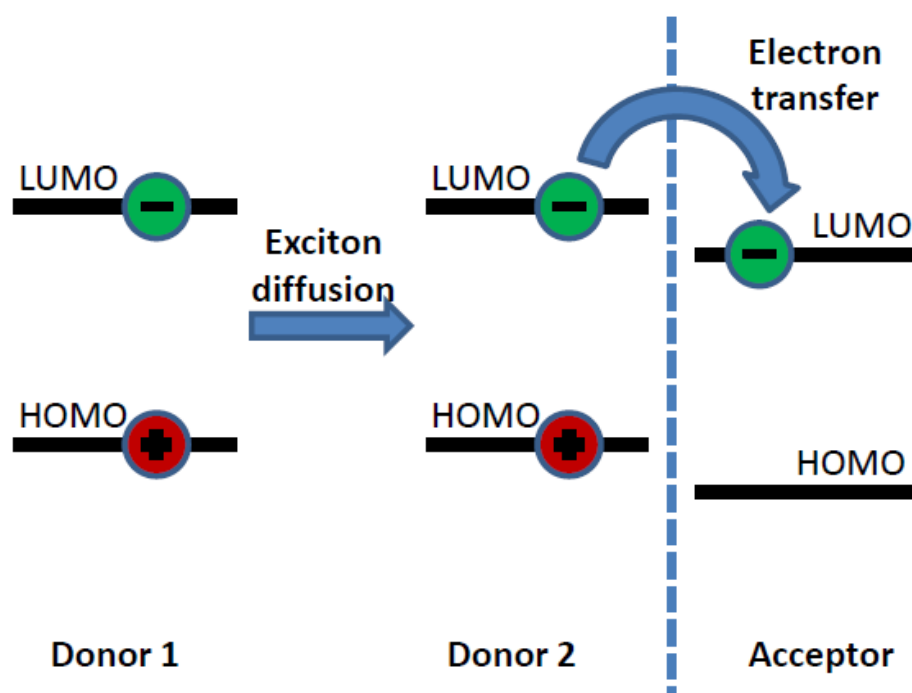


Figure 1.7: Illustration of exciton diffusion to donor/acceptor interface followed by exciton dissociation. [This image has been reproduced with the permission of the rights holder, American Chemical Society²⁷]

Dissociation of the relatively strongly bound excitons of polymer semiconductors into free charges is one of the major challenges for organic photovoltaics in order to achieve high device performance. A general approach to resolve this problem is to use an electron acceptor material, which provides a $\text{LUMO}_{\text{polymer}}\text{-LUMO}_{\text{acceptor}}$ offset greater than the exciton binding energy to split the electron-hole pair formed on the polymer (figure 1.7).^{28, 29} The electron accepting materials for this thesis are fullerene derivatives such as phenyl-C61-butyric acid methyl ester (PC₆₁BM) or PC₇₁BM (figure 1.3). Exciton dissociation is an electron transfer process in which the electron on the LUMO of the polymer is transferred to the LUMO of the

fullerene while the positive hole on the HOMO of the polymer remains at the same position.^{28,}
³⁰ This process happens only at the polymer:fullerene interface.

Excitons which are formed at a certain distance from the interface will need to diffuse to the interface to trigger the dissociation (figure 1.7). Diffusion of excitons only happens over a limited average distance before recombination takes place. This distance is referred to as the exciton diffusion length, which varies between materials (typically 5-10 nm for organic semiconductors).^{31, 32} As a result, some excitons fail to reach an interface, due to their limited diffusion length, causing a loss in photocurrent.¹⁶ This issue may be resolved by optimising the morphology of polymer:fullerene layer to ensure the majority of excitons are formed near the interface. The details about the active layer morphology are collectively discussed in section 1.6.

1.5.2 Charge transfer state and charge separation

The exact mechanism of charge separation is still under an active debate. One proposed model to describe charge separation is presented in this section and applied for data interpretation in Chapter 3-6. For more consideration of this topic, the reader is referred to recent reviews on this subject.^{15, 16, 27, 33, 34}

There is increasing evidence suggesting that exciton dissociation does not necessarily lead to the generation of free charges.³⁵⁻³⁸ For example, P3HT:PCBM devices displayed a reduced polymer photoluminescence quenching upon thermal annealing, indicative of a loss in the efficiency of exciton dissociation.³⁹ However, the formation of free charges, as measured by transient absorption spectroscopy, was increased considerably. The mismatch between exciton dissociation and free charge formation can be explained by a model described in this section, which is based on the existence of an intermediate state between these two processes^{35, 40-43} (Figure 1.8). Exciton dissociation happens at the polymer:fullerene interface, where the polymer and fullerene are in close proximity. The attraction between the electron and hole after exciton dissociation at the interface can be roughly estimated to be 0.1-0.5 eV using Coulomb's law, which is larger than the thermal energy at room temperature (0.025eV).²⁷ This clearly suggests that the electron and hole can still be bound to each other, despite residing on different molecules (Figure 1.8). Such a configuration is called a 'charge transfer'(CT) state or sometimes a 'bound polaron pair' or 'geminate pair' depending on

nomenclature. The CT state may undergo rapid spin mixing to change between singlet and triplet configuration.

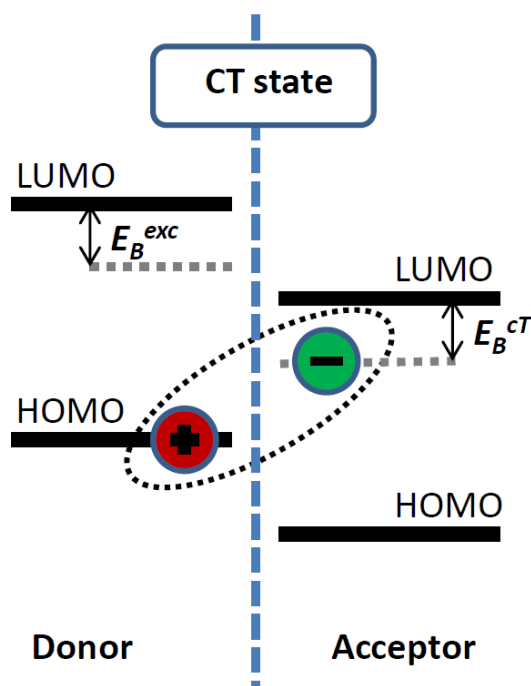


Figure 1.8: Illustration of charge transfer state in which the electron and hole are bound by Coulombic attraction. [This image has been reproduced with the permission of the rights holder, American Chemical Society²⁷]

In order to form free charges, the attraction between the hole and electron in the charge transfer state must be overcome. Successful dissociation of CT state has been suggested to be essential for efficient charge separation,^{35, 44-47} but the exact mechanism of the CT state dissociation and associated governing factors are still under active debate.^{34, 35, 48-51} A model based on Onsager theory describing the separation of CT state is shown in Figure 1.9.^{15, 27, 52} This model suggests that the efficiency of charge separation depends upon a competition between spatial charge separation and energetic relaxation of CT state. An exciton with higher energy is more likely to generate a CT state with more thermal or electronic energy (sometimes referred to as a ‘hot’ CT state), helping spatial charge separation exceed the Coulomb capture radius for free charge formation. Otherwise, with smaller exciton energies, energetic relaxation of the CT state, and eventually CT state recombination, will be more likely to happen.

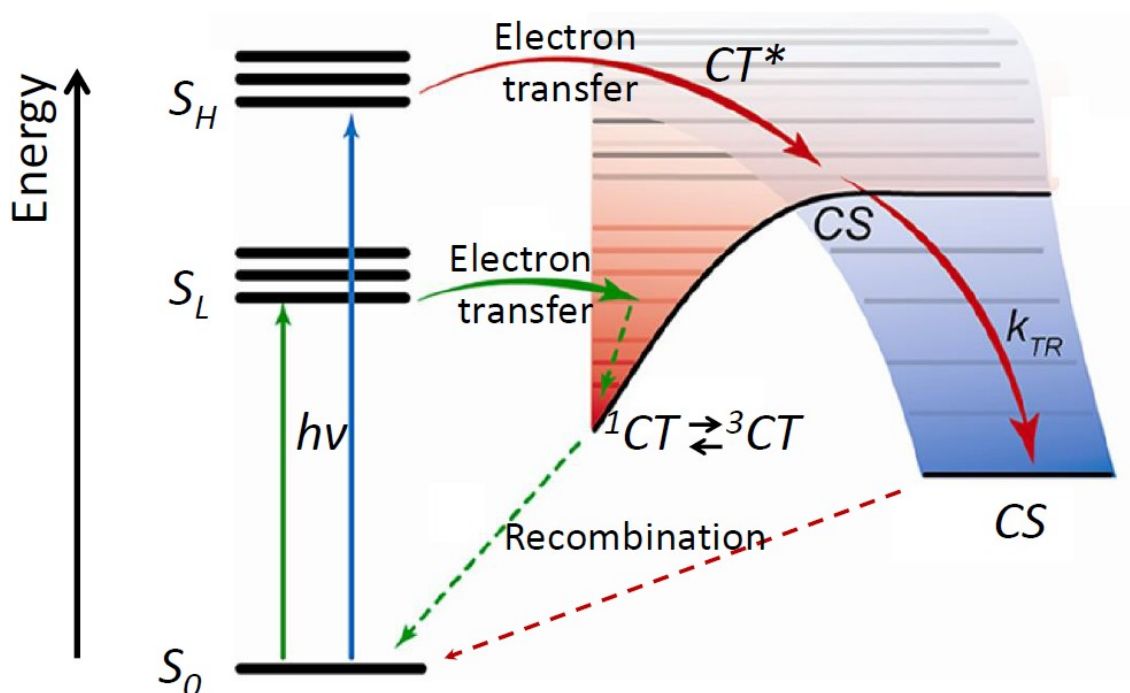


Figure 1.9: An energy diagram describing separation of CT state using two scenarios as examples. An exciton with higher energy (S_H) is more likely to generate ‘hot’ charge transfer state (CT^*), eventually leading to formation of free charges. On the other hand, exciton with lower energy (S_L) gives rise to a CT state with less thermal energy after exciton dissociation and therefore may not be enough to overcome the Coulombic attraction to generate free charges (or undergo charge separation (CS)). [This image has been reproduced with the permission of the rights holder, American Chemical Society¹⁵]

1.5.3 Charge recombination and transport

There are two different mechanisms by which charges can undergo recombination to compete with photocurrent generation, namely geminate recombination and bimolecular recombination. Geminate recombination describes the recombination of electrons with the originally paired-up hole, for example in exciton or CT states. There are two ways for this type of recombination to happen. Firstly, if the electron-hole pair in CT state fails to overcome the Coulomb attraction during its lifetime, they recombine geminately. Alternatively, if the electron and hole are able to overcome the Coulomb attraction but physically confined within isolated domains, they will not be collected by electrodes and can only recombine with each other. Geminate recombination is a monomolecular process which decays exponentially on a timescale of picoseconds to nanoseconds.^{27, 30, 53, 54}

On the other hand, bimolecular recombination, by definition, is the recombination between charges that are not originally from the same exciton and have diffused away from each other. As charge diffusion takes place before recombination happens, bimolecular recombination is a relatively slow process in comparison to geminate recombination. The rate of recombination follows a second order kinetic as the process requires collision between two free charges. The typical timescale of bimolecular recombination is from nanoseconds to milliseconds.^{42, 55, 56}

As mentioned previously, charge transport takes place after formation of separated charges, in parallel to bimolecular recombination. Charge collection efficiency can be considered as a result of competition between charge transport and charge recombination.^{17, 57} In the solar cells of interest to this thesis, polymers and fullerenes act as hole and electron conducting media respectively to deliver charges to the corresponding electrodes. Due to the high degree of disorder in organic semiconductors, charge transport takes place via thermally activated or tunnelling charge hopping between localised states.^{17, 58-60} This is typically slower than the band transport which is often found in inorganic crystalline materials.

The efficiency of charge generation depends on kinetic competition between the consecutive charge generation steps and the potential loss pathways. This means that in order to maximise the efficiency of charge generation, we need to improve the efficiency of photon absorption, exciton dissociation and charge separation and suppress the loss mechanisms such as exciton recombination, geminate recombination as well as bimolecular recombination. There are a substantial number of studies investigating these mechanisms in terms of energetics.^{15-17, 27, 28} Over the last decade, an increasing amount of research indicates that the morphology of the polymer:fullerene active layer is also playing a crucial role in determining the efficiency of charge generation, and thereby the power conversion efficiency.^{10, 61-65} In the next section, the active layer morphology and its impact upon device efficiency are discussed.

1.6 Morphology

1.6.1 Bilayer architecture active layer

As mentioned previously, polymer excitons generally have high binding energy due to low material dielectric constants. As such, formation of separated charges in polymer based solar cells relies on a LUMO-LUMO energy offset offered by introducing a secondary material. This strategy was firstly used by Tang and co-workers who invented heterojunction organic

solar cells with bilayer architecture⁶⁶ (figure 1.10 top) in 1986. The active layer of the device consists of two layers made from two organic materials with electron donor and electron acceptor nature respectively. Excitons can undergo dissociation if they reach the interface between the two materials. However, the power conversion efficiency of such device was only about 1% at the time. One reason for such poor power conversion efficiency is believed to be poor exciton dissociation efficiency associated with the bilayer device. Although organic materials generally have high absorption coefficient, in order to absorb most of the incident photons the layer of organic material need to be ~ 100 nm thick.¹⁰ This is much greater than the exciton diffusion length of organic materials which is on the order of 10 nm.³² As a result, only excitons formed near the interface can undergo dissociation, limiting the efficiency of photocurrent generation.

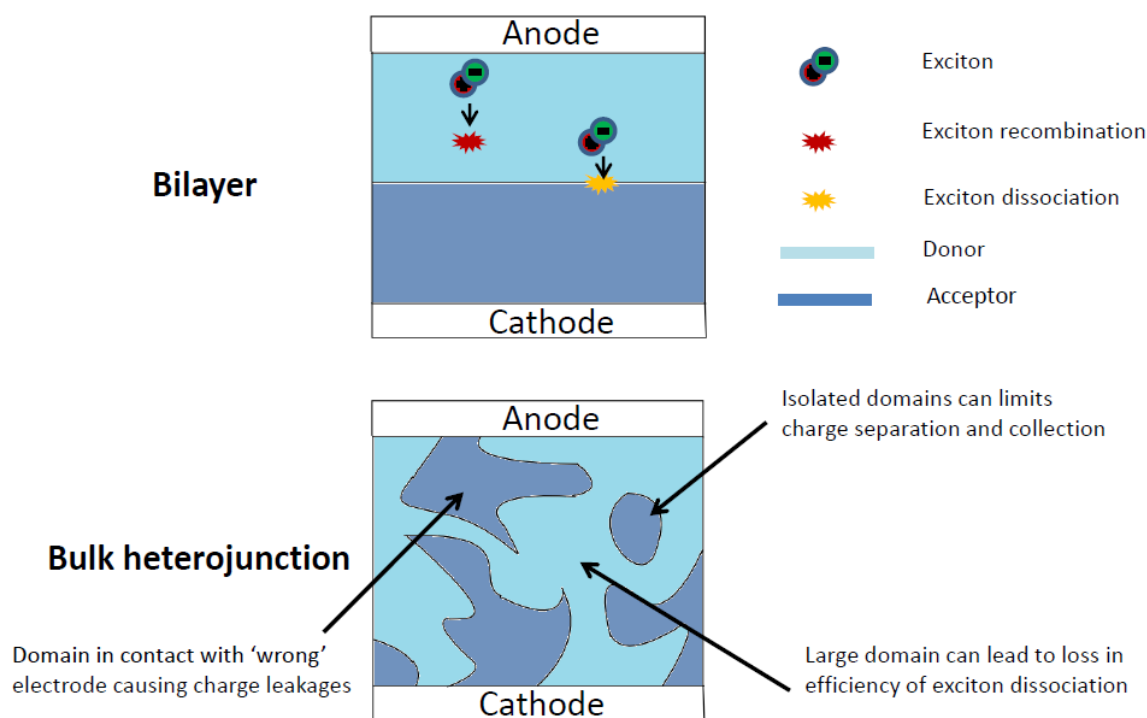


Figure 1.10: (Top) Schematic of a bilayer architecture organic solar cell. The poor exciton dissociation efficiency is demonstrated by showing the fate of two excitons formed at different distances from the donor/acceptor interface. (Bottom) Schematic of a bulk heterojunction solar cell with some features highlighted, which are detrimental to device performance. [This image has been reproduced with the permission of the rights holder, The Royal Society of Chemistry¹⁰]

1.6.2 Bulk heterojunction architecture active layer

One strategy to avoid the limitation of the bilayer architecture is to employ a bulk heterojunction architecture (figure 1.10 (bottom)).⁶⁷ In such a device, the electron donor and acceptor materials are blended together, offering phase segregation on the nanometre scale. As such, the efficiency of exciton dissociation can be drastically improved as excitons are formed at shorter distances from the interface as compared to in the bilayer structure. A traditional model for understanding morphology describes the blend as a two-phase structure consisting of a donor phase (polymer) and an acceptor (phase) which are bicontinuous and interpenetrating.^{10, 15, 64, 68} The phases or domains of each material are assumed implicitly to be pure. The model describes that exciton dissociation happens at the interface between the polymer phase and the fullerene phase. This results in the formation of free charges which will then be collected at electrodes through the two phases. Under such a model, the following features of morphology are highlighted:

Domain size

The model of blend morphology considers exciton dissociation as an interfacial process. It is suggested that the material domain size (or phase segregation) needs to be on a comparable scale to the exciton diffusion length, namely ~ 10 nm, in order to achieve high exciton dissociation efficiency. While the formation of small domains can favour the process of exciton dissociation, it may also lead to a corresponding increase in charge recombination which limits photocurrent generation. As mentioned before, hole and electron polarons are confined in polymer and fullerene domains respectively. Previous studies have demonstrated that an active layer with over-finely mixed domains could encourage geminate as well as bimolecular recombination, limiting charge generation and collection.⁶⁹⁻⁷¹

Thickness

Optimising thickness of active layer in order to achieve better power conversion efficiency can be considered as a trade-off between photon absorption and charge collection. As mentioned before, the active layer thickness of organic solar cells generally needs to be ~ 200 nm in order to harvest most of the photon from the incident light.¹⁰ However, at such thicknesses, charge collection efficiency may be limited in comparison to thinner active layer, due to an increase in recombination resulting from the longer distance charges need to travel.⁷²⁻⁷⁴

Percolation and vertical segregation

After free charges are formed, they are delivered through the corresponding phases and eventually collected by the correct electrodes. One basic requirement for efficient charge collection is that the phases need to be continuous. This ensures that the charges are not physically blocked by any isolated phases while on their way towards the correct electrodes, otherwise the likelihood of undergoing geminate or bimolecular recombination is increased.^{75, 76} Similar to this idea, phase segregation in the vertical direction is also important for charge collection. This considers the possibility of electrode blocking by the wrong phase (figure 1.10). For example, the blocking of cathode by polymer domains has been suggested to result in charge leakage limiting the photocurrent generation.^{10, 77}

Crystallinity

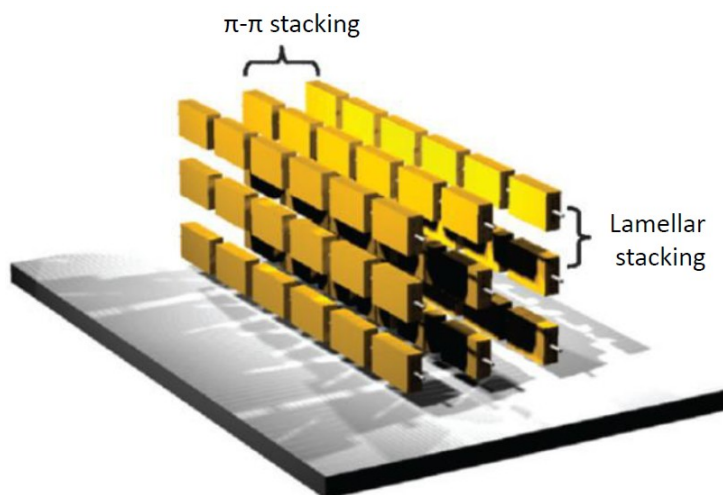


Figure 1.11: A diagram showing spatial arrangements of lamellar stacking and π - π stacking of conjugated polymers. The yellow plane represents the plane of chemical bonds involved in π -conjugation (which is perpendicular to p_z orbital). [This image has been reproduced with the permission of the rights holder, The Royal Society of Chemistry⁷⁸]

Crystallinity refers to the degree of order in spatial arrangement of molecules. Polymer semiconductors, due to their high molecular weight, are polycrystalline and consist of amorphous and crystalline regions with different sizes. Studies based on poly(3-hexylthiophene-2,5-diyl) (P3HT, see figure 1.3 for the chemical structure), which is a benchmark material for polymer based solar cells, have suggested that a change in polymer crystallinity can influence material energetics, mobility as well as active layer morphology, thereby impacting device performance.

Previous studies on P3HT have shown that polymers in the crystalline regions have different energy levels from those in amorphous regions. The optical absorption of semicrystalline P3HT was found to have red-shifted bands in comparison to amorphous P3HT. This observation is believed to be caused by the π - π interchain interactions (figure 1.11) between adjacent polymers in the 2-dimensional lamellae, leading to HOMO destabilisation and LUMO stabilisation.⁷⁹⁻⁸¹ The red shift in P3HT absorption has been suggested to improve the photon absorption efficiency, and hence be beneficial for device performance.⁸²

On the other hand, polymer crystallinity is also believed to influence the domain size in the active layer. Crystalline polymer regions are suggested to be free of fullerene molecules.^{83, 84} (note that there are some exceptions such as poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene) (pBTTT) which can form a co-crystalline structure with fullerene. More details are included in section 1.6.2). As such, formation of crystalline polymer was suggested to exclude fullerene molecules into the rest of the active layer, promoting phase segregation.^{39, 63} The effect of the increase in domain size by improving crystallinity has been discussed before. It could lead to a loss in exciton dissociation efficiency while also potentially reduces recombination for devices.

Lastly, there are also studies investigating the correlation between charge mobility and polymer crystallinity. Depending on the orientation of polymer packing, there are two types of spatial arrangements for polymer semiconductor: lamellar packing and π - π stacking (figure 1.11). The latter allows p_z orbitals on adjacent polymer backbones to overlap in a head-to-head manner and is believed to facilitate charge transport for polymer semiconductors. This can be attributed to the better delocalisation of charge carriers between adjacent chains, in comparison to the charges for amorphous polymers which are more confined to individual chains.^{80, 85, 86}

1.6.3 Mixed/pure phase model for bulk heterojunction morphology

The traditional model is based on phase segregation into polymer and fullerene domains which are assumed to be pure. The correlation between device performance and morphology under such a model is often interpreted in terms of changes in domain size, phase percolation and vertical segregation. The model emphasises that exciton dissociation happens at the interface between polymer phase and fullerene phase, and therefore the size of the pure domains is compared to the exciton diffusion length to estimate the efficiency of the exciton dissociation. However, recent structural models for blend microstructures suggest that there exist some regions in the active layer where polymer and fullerene are intimately mixed to a degree which is underestimated in the traditional model.^{15, 62, 63, 87-89} Such regions are commonly called the ‘mixed phase’.

1.6.3a Existence of ‘mixed phase’

The existence of the mixed phase has been shown in many studies.^{63, 83, 84, 87-96} For example, McGehee and co-workers have demonstrated that a range of semicrystalline polymer semiconductors, such as pBTTT, are molecularly mixed with fullerenes by a spatial arrangement called ‘fullerene intercalation’.^{71, 87, 97-99} This term refers to fullerene molecules being accommodated between side chains of the polymers, forming a crystalline region containing both polymer and fullerene referred to as a ‘co-crystal’ structure. The existence of such a structure could be directly proven using X-ray diffraction (XRD) techniques which show an increase in backbone separation of lamellar stacking upon blending the polymers with fullerene, without loss of diffraction strength. As both materials are mixed on a molecular lengthscale in this structure, exciton dissociation was found to be highly efficient, as demonstrated using photoluminescence spectroscopy. Fullerene intercalation can also exist in amorphous polymers, but it is more difficult to study since the signal intensities obtained from amorphous polymers using XRD will be weak.^{87, 94, 100} For example, fullerene intercalation by the amorphous polymer poly[2-methoxy-5-(3’,7’-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) was indirectly proven by McGehee and co-workers using a combination of techniques including photoluminescence spectroscopy and space charge limited current measurement.⁹⁴ They attributed the improvement in MDMO-PPV mobility upon blending with PCBM to fullerene intercalation which unfolded the polymer backbone, but only limited proof of conformational structure was given. This suggestion was later complemented by the work by Grey and co-workers, who used Raman spectroscopy to

demonstrate that PCBM preferentially interact with the vinylene group along the MDMO-PPV backbone.¹⁰⁰

For polymers such as P3HT and 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]] (PTB7), in which fullerene intercalation is less clear, a range of techniques have been employed to study the polymer:fullerene mixed phase.^{83, 84, 91-93, 96, 101, 102} For instance, Treat and co-workers employed dynamic secondary ion mass spectrometry and grazing incidence wide angle X-ray scattering (GIWAXS) to study the interdiffusion of PCBM in P3HT:PCBM bilayer films.⁸³ They found that the fullerenes rapidly diffuse into the P3HT layer and reached 40% in the polymer layer within 30 seconds when the film was annealed at 150 °C, a temperature at which P3HT:PCBM blend is normally annealed to achieve an optimised morphology. Meanwhile, the size of P3HT crystals was found to be independent of PCBM diffusion and therefore concluded to be free of PCBM. This suggests that fullerene is much more compatible with amorphous P3HT rather than crystalline P3HT, leading to the concept of a mixed amorphous P3HT:PCBM phase and a pure crystalline P3HT phase.

In parallel, another work on the mixed phase is from Jamieson and co-workers who have found that a range of amorphous polymer:PCBM exhibited exceptionally high polymer photoluminescence quenching (> 95%).⁹⁶ This suggests that polymer exciton dissociation is highly efficient and polymer and fullerene are intimately mixed on a molecular scale in the polymer phase. The quenching is less efficient in a more crystalline polymer such as P3HT, consistent with the discussion above that crystallisation promotes phase segregation. In the case of the fullerene phase, fullerene photoluminescence quenching in polymer:PCBM blends is often less efficient compared to polymer photoluminescence quenching, suggesting PCBM phase is relatively pure in comparison to the polymer phase. This is potentially also associated with the tendency of PCBM to form aggregates.¹⁰³⁻¹⁰⁵

Whilst the work mentioned above were based on qualitative measurements, more quantitative measurements to reveal the existence of a mixed phase have also been performed using techniques based on soft X-ray.^{63, 91, 101, 102, 106} For example, near edge X-ray absorption fine structure studies (NEXAFS) were employed to study the composition of polymer:fullerene blends with a resolution of 50 nm.^{63, 102} The resolution was later improved using resonant soft X-ray scattering (R-SoXS) which showed that the material separation in binary blend system could be on the order of 10 nm.¹⁰⁶

Recent work on blend morphology as discussed above have painted a new picture of the morphology of active layer blends, which consists of mixed and pure phases, compared to the traditional morphology based on two pure phases. In the new model, crystalline polymer domains are generally considered to be free of fullerene in comparison to amorphous polymer which can more intimately mixed with fullerene, unless a co-crystal is present. On the other hand, fullerenes were suggested to be dispersed in the polymer matrix but also able to form relatively pure domains because of their ability to form aggregates.

1.6.3b A new model to correlate photocurrent generation with blend microstructure

With the new understanding on polymer:fullerene blend microstructure, a new model to understand the correlation between photocurrent generation and blend microstructure is needed. There are a few works which have attempted to address how the mixed phase (or polymer:fullerene miscibility) contribute to device performance.^{88, 89, 98, 107-112} For this thesis, a new model developed by Dr. Jamieson and co-workers from Prof. James Durrant's group is described (figure 1.12), as it is employed to investigate correlation between device performance and blend microstructure in the Chapter 3-6.^{88, 96}

The model considers the mixed phase to function as an exciton quenching centre.^{99, 107, 110} Due to the high degree of mixing in such phase, most excitons formed in this region are able to undergo dissociation.^{84, 94, 98, 110, 113} However, separated charges may also undergo rapid recombination as the opposite charges are also intimately mixed in this region. This problem is resolved by incorporating the mixed phase with the pure fullerene phase which helps photocurrent generation in two ways. Firstly, the pure fullerene phase may provide a downhill energy to favour the charge separation. A previous study has found that the LUMO of neat PCBM film is 100 meV lower than that of a polymer:PCBM blend film.⁹⁶ This implies that the fullerene in the pure phase should also have a lower LUMO in comparison to the fullerene in the mixed phase, which helps the electron escape from the mixed phase to the pure phase. A similar effect is also possible with pure crystalline polymer domains, whose ionisation potential may be smaller than polymer in more amorphous mixed domains.¹¹⁴ Secondly, once the electrons reach the pure phase, it becomes less likely to undergo charge recombination as the pure phase may provide a clear pathway for their transport towards the electrode.^{10, 89, 107, 110} This model implies that a correct combination between the mixed phase and the pure phase is the key to efficient photocurrent generation.

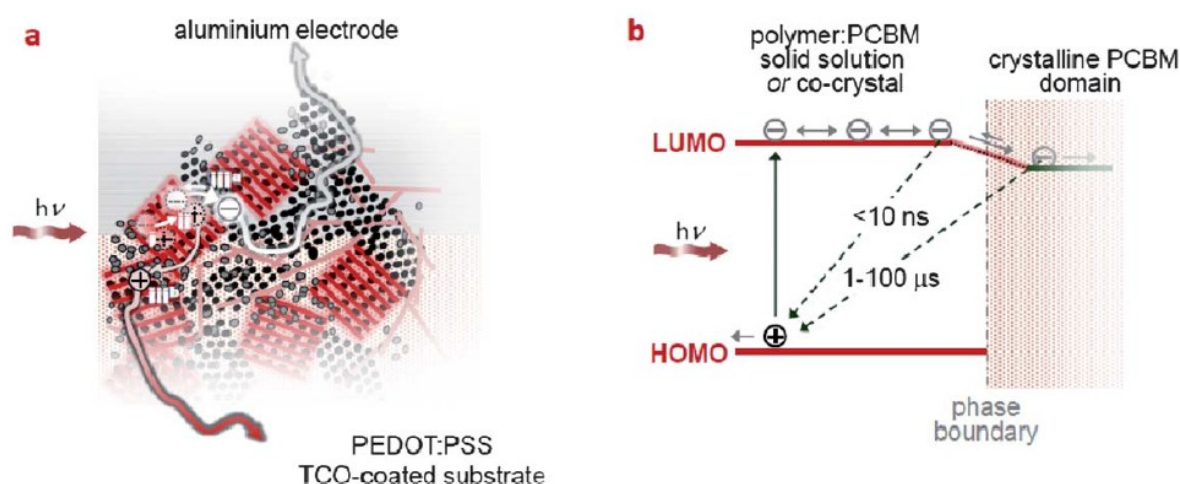


Figure 1.12: Illustration of the mixed/pure phase model. (a) The picture of blend morphology in which exciton is dissociated in the mixed phase followed by the negative polaron delivered through the pure PCBM domain towards electrodes. (b) Energy diagram to show the downhill energy in LUMO between the PCBM in the mixed phase and in the pure phase, which facilitates charge separation. [This image has been reproduced with the permission of the rights holder, The Royal Society of Chemistry⁹⁶]

In summary, two models to describe the correlation between device performance and active layer morphology have been discussed. Each of the steps in charge generation and associated loss pathways are linked to different aspect of active layer morphology. With advancements in probing techniques and better understanding of device working mechanisms, a better model can be developed to assist us in more accurately predicting the optimised morphology for a polymer:fullerene system. This is particularly useful in providing information to control morphology in order to achieve better device performance.

1.7 Device characterisation

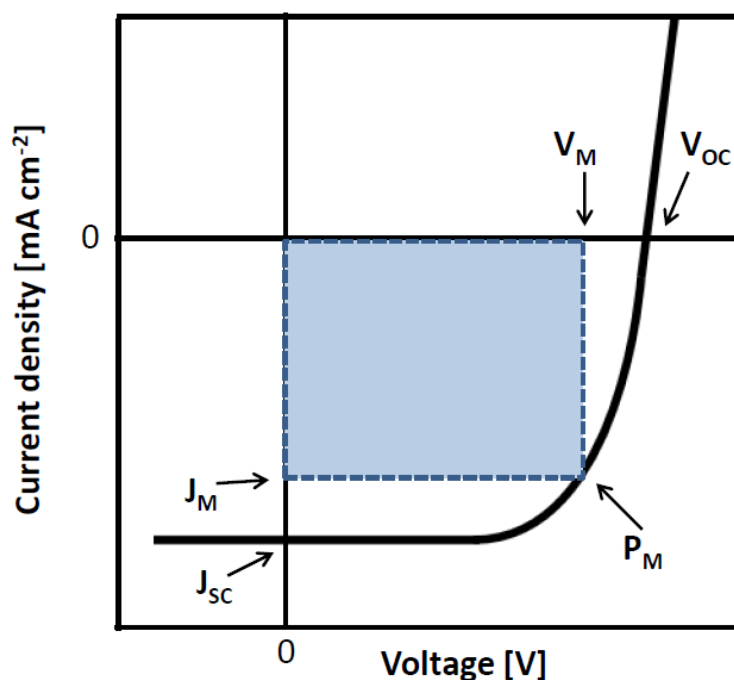


Figure 1.13: A typical J-V measurement for polymer:fullerene solar cells in order to examine maximum power conversion efficiency of the devices.

In order to measure the efficiency of polymer based bulk heterojunction solar cell, an external electric field is applied to the device. The current density across the device is measured as a function of the voltage applied when the device is exposed to a light source which simulates air mass (AM) 1.5. This generates a J-V curve for a device which has a similar shape to that of a photodiode (Figure 1.13). Several parameters which are associated with device performance are highlighted.¹¹⁵ The voltage at the intercept on V-axis is referred to the open circuit voltage (V_{OC}) of the device. It is the potential difference across the device when there is zero net current through the device. In polymer:fullerene based device, the V_{OC} is roughly proportional to the difference between the HOMO of the polymer and the LUMO of the fullerene.^{116, 117} On the other hand, the current at zero voltage is called the short circuit current which to some extent reflects the highest photocurrent that can be generated from the device. The maximum power conversion efficiency (P_m) is somewhere in the region between the V_{OC} and J_{SC} . The exact position varies from system to system and depends on a parameter called fill factor which is defined as:

$$FF = \frac{V_m \times J_m}{V_{oc} \times J_{sc}} \quad (4)$$

where V_m and J_m are the voltage and current respectively when the device is at maximum power conversion efficiency. Rearranging equation 4 results in another equation shown below:

$$P_m = V_m \times J_m = V_{oc} \times J_{sc} \times FF \quad (5)$$

This equation suggests that V_{oc} , J_{sc} as well as FF are important parameters in determining the maximum power conversion efficiency of a device.

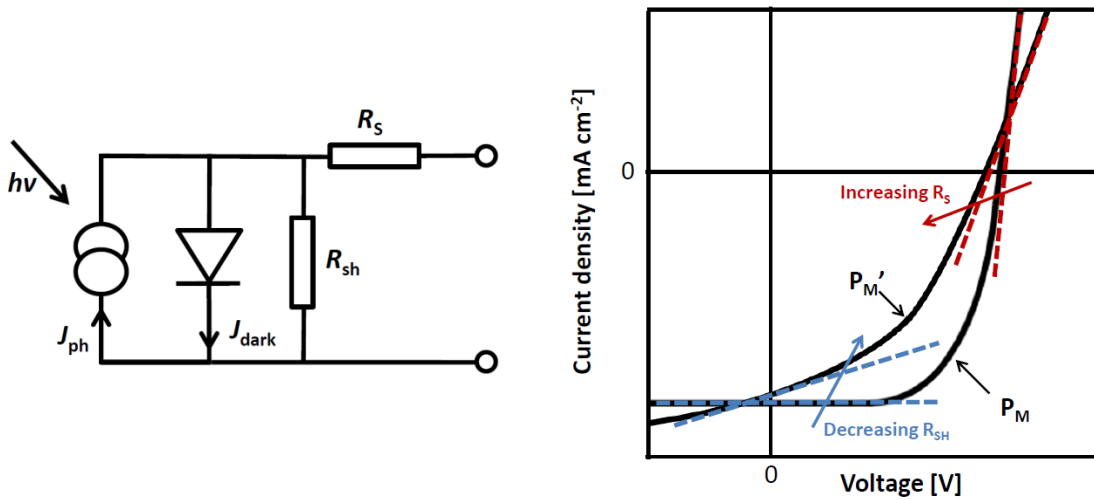


Figure 1.14: (Left) A simplified electronic circuit for a polymer:fullerene bulk heterojunction solar cell. (Right) Two J-V curves showing the impact of series and shunt resistances on fill factor and maximum power conversion efficiency.

The origin of fill factor is still under debate. One simplified way to analyse the fill factor is to consider two resistances associated with a bulk heterojunction solar cell as shown in Figure 1.14. The device is considered to be a current source and a photodiode connected in parallel.^{17, 115, 118} Both of these components are then connected to two resistances in series and in parallel respectively. An applied voltage source is added to complete the circuit. Studies suggested that the series resistance (R_s) depends on the intrinsic resistance of materials from the active layer as well as the injection barrier between the active layer and electrode. The value of the R_s can be extracted from the J-V curve by taking the inverse slope in the first quadrant when the curve becomes approximately linear. On the other hand, the shunt

resistance (R_{SH}) is the resistance connected in parallel to the current source and photodiode. It is the resistance to additional pathways for charges to bypass the diode resulting in current leakage. It is related to impurities present in the active layer or defects in blend microstructure. The value of the R_{SH} can be estimated as the inverse slope of the J-V curve near the position of the short circuit current. Figure 1.13 shows that a high R_S and a low R_{SH} can push the position of P_m towards the origin in the plot, resulting in a smaller value of FF. Conversely, a system with a low R_S and a high R_{SH} is beneficial for achieving high power conversion efficiency by offering a high FF.

1.8 Stability of polymer:fullerene solar cells

1.8.1 Overview

Over the last 5 years, power conversion efficiency of polymer based solar cells has been experiencing a rapid increase with the highest record being as 12%. With the promising achievement in terms of power conversion efficiency, there is an increasing research interest in stability of polymer-based solar cells (figure 1.15), which is a problem that need to be addressed in order to make the solar cells economically viable.^{7, 119}

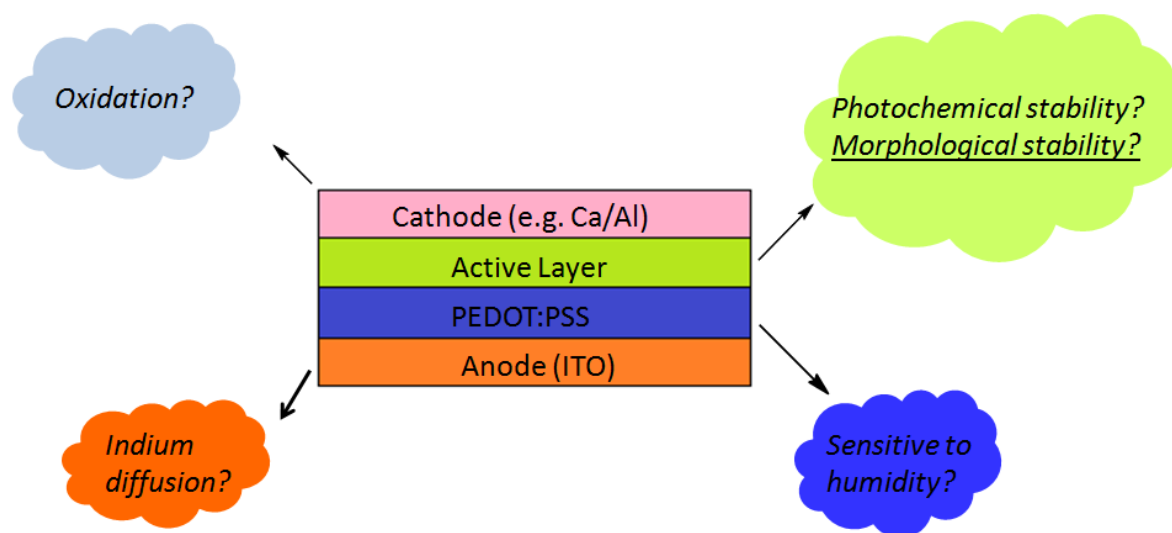


Figure 1.15: A diagram showing the structure of a conventional polymer:fullerene solar cell with potential degradation pathways highlighted.

The typical architecture of polymer-based solar cells consist of ITO/PEDOT:PSS/active layer/Ca/Al. The limited stability of polymer based solar cells is derived from several problems associated with each component in the device structure under operating condition. Degradation of solar cells can be classified as chemical degradation and physical degradation.¹¹⁹ The former refers to chemical reaction of the materials induced by light, oxygen as well as water. This causes loss in electronic properties of the materials and subsequently impacts device performance. For example, PEDOT:PSS, which is a hole transporting layer, was reported to react with O₂ or H₂O from air due to its acidic nature, reducing its conductivity.^{120, 121} Polymers such as PPV were found to be prone to oxidation when exposed to oxygen and light, damaging their π -conjugation.¹²² On the other hand, physical degradation considers the possibility of evolution of the active layer morphology and structure under thermal stress which impacts device performance negatively.¹²³ This is discussed in more detail in the next section.

1.8.2 Morphological degradation

As discussed before, the morphology of the active layer is a key determinant of device performance. It influences the photocurrent generation mechanism (e.g. absorption, charge separation and charge collection) as well as potential loss pathways (geminate and non-geminate recombination). However, numerous studies have suggested that the active layer cannot retain its optimised morphology over time, causing device performance degradation (figure 1.16).¹²³⁻¹³⁰

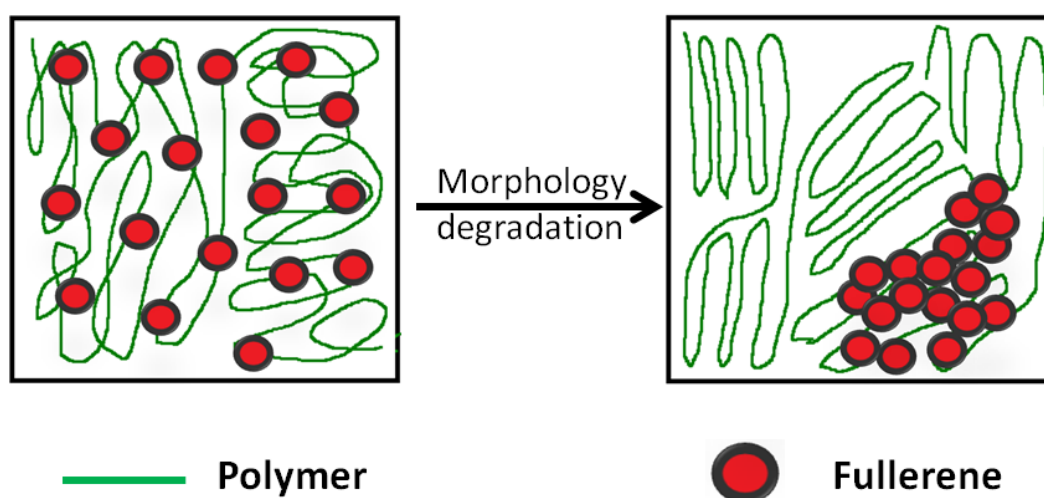


Figure 1.16: Schematic of morphological degradation upon thermal aging.

Blend morphology for optimised device performance is usually obtained by spin-casting, an approach that allows the two materials to mix with each other on a molecular level in solid form by quickly evaporating solvent from the blend solution. In other words, the optimised active layer is formed using a kinetic approach, resulting in a blend microstructure that is not thermodynamically stable. As such, it has been suggested that the optimised morphology should evolve, especially at high temperatures, to achieve a thermodynamically stable state, causing loss in device performance.^{63, 123} This is particularly a concern for solar cells, as the temperature of a solar cell under operating condition can reach as high as 85 °C.

Previous studies on benchmark materials such as P3HT and MDMO-PPV suggest that the evolution of morphology is particularly driven by fast fullerene diffusion, accompanied by slow spatial rearrangement of polymers.^{128, 131, 132} This is due to the small size as well as weak intermolecular interaction which allow for fullerenes to move relatively freely through the polymer matrix. As the morphology evolves, features such as growth in domains or reduction in phase percolation were observed to lower the efficiencies of exciton dissociation and charge collection (Figure 1.15).^{128, 133, 134} This process is more severe at higher temperatures, resulting for example in the formation of micron-sized fullerene clusters.^{124, 128, 135} This is indicative of heavily degraded morphology and could be observed by optical microscopy.

System used	Device architecture	Solvent	Degradation conditions	Time for 10% drop [min]
P3HT:PC ₆₁ BM ¹³⁶	ITO/PEDOT/Active layer/Al	ODCB	150 °C	110
P3HT:PC ₆₁ BM ¹³⁷	ITO/PEDOT/Active layer/Yb/Al	ODCB	45 °C	240
P3HT:PC ₆₁ BM ¹³⁸	ITO/PEDOT/Active layer/LiF/Al	CB	60 °C	120
P3HT:PC ₆₁ BM ¹³⁸	ITO/PEDOT/Active layer/Ca/Ag	CB	60 °C	120
P3HT:PC ₆₁ BM ¹³⁹	ITO/PEDOT/Active layer/Ca/Al	ODCB	110 °C	90
P3HT:PC ₆₁ BM ¹³⁶	ITO/PEDOT/Active layer/Al	CB	150 °C	150
MDMO-PPV:PC ₆₁ BM ¹⁴⁰	ITO/PEDOT/Active layer/Al	CB	110 °C	10
MDMO-PPV:PC ₆₁ BM ¹²⁸	ITO/PEDOT/Active layer/Al	CB	110 °C	20
P3HT:PC ₇₁ BM ¹²⁹	ITO/PEDOT/Active layer/TiOx/Al	CB	80 °C	4500
PCDTBT:PC ₇₁ BM ¹²⁹	ITO/PEDOT/Active layer/TiOx/Al	DCB:CB	80 °C	9000
PCDTBT:PC ₇₁ BM ¹⁴¹	ITO/PEDOT/Active layer/Ca/Al	DCB	37 °C	3000

Table 1.1: Decay times of different polymer:fullerene solar cells measured under different degradation conditions. [Data extracted from ref^{129, 136-142}]

The thermal stability stabilities of a range of polymer-based solar cells are summarised in Table 1.1. The decay times, defined as time taken for 10% loss in power conversion efficiency, range from 10 minutes to over 9000 minutes. The large variation in thermal

stability is probably derived from its dependency on multiple parameters. For instance, Bertho and co-worker reported a modified version of MDMO-PPV with high glass transition temperature (T_g) could limit the fullerene diffusion to suppress morphological degradation.¹²⁸ Nguyen and co-workers found that devices using polythiophenes with various side chains shows different thermal stability, with longer side chains exhibiting a shorter device lifetime.¹⁴³ Another work reported by Swinnen and co-workers discovered that fullerene loading, annealing time and annealing temperature correlated with the degree of fullerene clusters formation in P3HT:PC₆₁BM system.¹²⁴ Morphological degradation also depends on fabrication condition and device operation condition. For example, Wang and co-workers demonstrated an exceptional long decay times (9000 minutes for 10% in PCE, see table 1.1) for poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) based devices.¹²⁹ However, this study did not include device performance degradation from the first initial 10 minute pre-annealing at 70 °C, which has been reported to be approximately 10% in PCE at 80 °C for the same duration by Li and co-worker.¹²⁶ In addition, it was shown that active layers cast from a high boiling solvent exhibited worse morphological stability, possibly due to trapped solvent molecules in the active layer facilitating the fullerene diffusion.¹⁴⁴ Recently, a study from our group also has demonstrated that thermal stability could be enhanced when the device was exposed to even modest light irradiance.^{126, 127} A key concern is that results obtained from different studies are not comparable unless consistent conditions were used across different studies.

On the other hand, attempts were also made in order to address this issue of unstable morphology for polymer:fullerene solar cells. For example, one approach involves using a block-copolymer in which the polymer donor and fullerene acceptor are joined by chemical bonds in an alternating manner, leading to better control of miscibility between donor and acceptor.¹⁴⁵⁻¹⁴⁷ However, this approach has not been very successful, not least since the synthesis of the block-copolymer is complicated. In addition, there is an increasing interest in utilising cross-linkers to achieve stable morphology.^{148, 149} In this approach, a small amount of cross-linkers are incorporated to the blend solution between polymers and fullerenes. After casting the active layer, the film is exposed to UV light or annealed thermally in order to trigger a reaction forming covalent bonds between the cross-linkers and polymers. This resulted in a rigid polymer matrix which immobilised both the polymers and fullerenes, giving rise to improved morphological stability. However, there are also a couple of drawbacks associated with this approach. Firstly, polymers generally need to be modified by

incorporating a functional group to act as a cross-linking reaction centre. This would complicate the process of polymer synthesis. Secondly, cross-linking reactions from previous studies were not highly selective, which potentially results in degradation of π -conjugation, negatively impacting the optical properties, mobility and crystallinity of the polymers.¹⁴⁹ As such, there is still a need to develop a new approach which can achieve better stability without having any detrimental effects on polymer:fullerene solar cell efficiency.

1.9 Materials design and device performance

Advance in organic photovoltaics has been relying heavily on the development of electron donor materials. Efforts in material design have particularly been focused on the energy level requirement to achieve better photon absorption, open circuit voltage and charge separation for better device performance.^{61, 82, 150}

Polymers with lower bandgap result in better absorption, as they absorb into the near IR region where the intensity of the solar emission is maximum.⁸² A low bandgap is achieved by either lifting the HOMO or lowering the LUMO of polymers. The most common way to achieve this is to use a donor-acceptor structure.^{151, 152} Such polymers have an electron donor and acceptor in its repeating unit, which lead to a low bandgap by a ‘push-pull’ effect. For instance, the donor-acceptor polymer poly-thieno[3,2*b*]thiophene-diketopyrrolopyrrole-co-thiophene (DPP-TT-T, see figure 1.3) has an absorption maximum at ~ 800 nm, compared to P3HT which absorbs below 650 nm.^{61, 153}

The open circuit voltage (V_{OC}) is also one of the parameters that influence device performance. It is widely believed that the V_{OC} of organic solar cells is roughly proportional to the energy difference between the HOMO of polymer and the LUMO of fullerene.^{103, 104} For a higher V_{OC} , the energy level of polymer HOMO may be lowered by, for instance, introducing fluorine atoms to the backbone, since they have strong electron withdrawing nature.¹⁵⁴ On the fullerene side, the energy levels can be tuned by modifying the adduct attached to the fullerene cage. For example, bis-indene-C60 (ICBA) has a higher LUMO than PCBM and therefore greatly improves the V_{OC} for P3HT-based devices.¹⁵⁵ On the other hand, the efficiency of charge separation has been reported to depend on $LUMO_{Polymer} - LUMO_{Fullerene}$ offset, with the larger offset favouring formation of free charges.^{22, 23} In this regard, a high polymer LUMO or low fullerene LUMO is beneficial. However, obtaining a

low bandgap for better light absorption by raising the HOMO or lowering the LUMO inevitably reduces the V_{OC} or efficiency of charge separation from an energetic standpoint. A trade-off must thus be made between these three parameters when tuning the energy levels in order to optimise device performance.

On the other hand, active layer morphology also play an important role in determining device performance, with features such as polymer:fullerene miscibility, crystallinity, domain size and percolation highlighted in section 1.6. There are increasing numbers of studies investigating the correlation between material chemical structure and active layer morphology. For instance, studies on benchmark materials have suggested that polymers with higher molecular weight are more beneficial to device performance as they offer better charge mobility and phase percolation in the active layer.^{88, 156} The morphology of high regioregularity (RR) P3HT:PCBM has been reported to have more severe phase segregation in comparison to P3HT with low regioregularity, and has a better charge mobility which benefits device performance.^{157, 158} Side chains attached to polymer have been recently found to influence crystallinity and polymer:fullerene miscibility, although they were once considered to impact primarily polymer solubility.^{100, 159, 160} The chemical structure of materials also affects morphological stability. As mentioned in section 1.8.2, the rigidity of polymer network can limit fullerene diffusion, and hence impact upon morphology degradation.¹¹⁹ The rigidity could be tuned by parameters such as side chain, backbone stiffness etc.

1.10 Objectives

There is an increasing number of studies suggesting blend morphology is playing a critical role in deciding the performance of polymer:fullerene solar cells in terms of both efficiency and stability. While tuning material chemical structure to fulfil energetic requirements is important for optimised device performance, one must consider any potential accompanying impacts upon blend morphology. Controlling both energy levels and morphology simultaneously by modification of material chemical structure is non-trivial. In particular, the correlation between material chemical structure and blend morphology is less well understood. In this thesis, a range of novel materials (see Chapter 2 for chemical structures) are investigated focusing on the impact of change in material chemical structures upon blend

morphology, and thereby device performance. The ultimate purpose of this thesis is to provide a guideline for material design to achieve optimised device performance by controlling blend morphology.

Charge generation is studied using transient absorption spectroscopy while photoluminescence spectroscopy, atomic force microscopy (AFM), transmission electron microscopy (TEM), wide angle X-ray scattering (WAXS) and optical microscopy are used for blend morphology studies. The data obtained from these measurements are analysed to establish correlations between morphology and device performance. The details of these techniques are described in Chapter 2.

Chapter 3-5 demonstrate the impacts of polymer chemical structures upon blend microstructure and device efficiency. More specifically, Chapter 3 demonstrates how polymer fluorination, which was suggested to improve the V_{OC} and PCE for polymer based solar cell,^{161, 162} can sometimes lead to device performance deterioration. Fluorination is applied to two polymers backbones, SiIDT-BT and SiIDT-DTBT, leading to deterioration and improvement respectively for the performance of corresponding solar cells. The blend microstructures of the devices are compared using AFM, TEM and PL spectroscopy, and correlated with free charge formation measured by TAS. It is shown that fluorination of SiIDT-BT can increase the polymer crystallinity, promoting phase segregation which subsequently reduces the charge formation. However, it is also shown that such effects on blend microstructure varies between different polymer backbones and therefore sometimes can be beneficial for device performance.

Chapter 4 presents the studies on how alkyl side chain can influence the degree of polymer:fullerene mixing in blend microstructure. Two alkyl side chains (linear vs branched) on poly(thienothiophene vinylene) (PTTV) backbone are compared. The polymer with the linear side chain (C16-PTTV) is demonstrated to have better miscibility with PC₇₁BM, potentially due to its better ability in intercalating fullerene molecules. It is found that the improved morphology offered by the linear side chain particularly addresses the poor exciton dissociation efficiency of fullerene, which has been reported to be the key factor limiting the photocurrent contribution from fullerene excitons. This in turn improves the charge generation from fullerene absorption, giving rise to a better device performance for the linear side chains in comparison to the branched side chain. The studies also highlight that charge

generation from polymer and fullerene excitons may require separate considerations when correlating with blend microstructure.

In Chapter 5, the dependence of device performance on polymer molecular weight for two DPP-containing polymers is investigated. It is shown that polymers with higher molecular weight can offer a better blend microstructure, which is the key to its better device performance. This is discussed with regard to earlier studies which suggested polymers with higher molecular weight benefited device performance by providing better photon absorption and charge mobility. The correlation between polymer molecular weight and blend microstructure is studied using WAXS, AFM, TEM and PL spectroscopy. Longer polymers are potentially more miscible with fullerene due to their higher volume fraction of amorphous region, which favours the charge generation for device performance.

Chapter 6 focuses on the influence of blend microstructure on the thermal stability of polymer-based devices. The stability is evaluated under thermal aging conditions with different temperatures. PL spectroscopy is employed in this study to assay the domain evolution on the lengthscale of exciton diffusion length while optical microscopy is used to probe the formation of micron sized fullerene clusters in the polymer:fullerene blends. The semicrystalline polymer DPP-TT-T and the amorphous polymer SiIDT-BT are compared in terms of their morphological stability. At temperatures below 140 °C, DPP-TT-T exhibits better device stability owing to its initial morphological evolution which is beneficial for device performance. However, when temperature is above 140°C, the crystalline polymer based device exhibits a severer degradation compared to the amorphous system. Further analysis shows that the severe degradation at high temperature may be associated with ‘thermodynamic polymer:fullerene miscibility’, measured using near edge soft X-ray absorption fine structure (NEXAFS). A similar study is carried out to compare PC₆₁BM with PC₇₁BM in DPP-TT-T devices. It is shown that PC₇₁BM exhibits better morphological stability, potentially due to its less diffusive nature. Lastly, it is also demonstrated that photo-induced fullerene transformation can be applied to DPP-TT-T:PC₆₁BM to increase its morphological stability.

Finally, the findings on the correlation between blend microstructure on device efficiency and stability are summarised in Chapter 7. Suggestions are also made for potential research in the future.

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Chapter 2

Experimental techniques

2.1 Materials

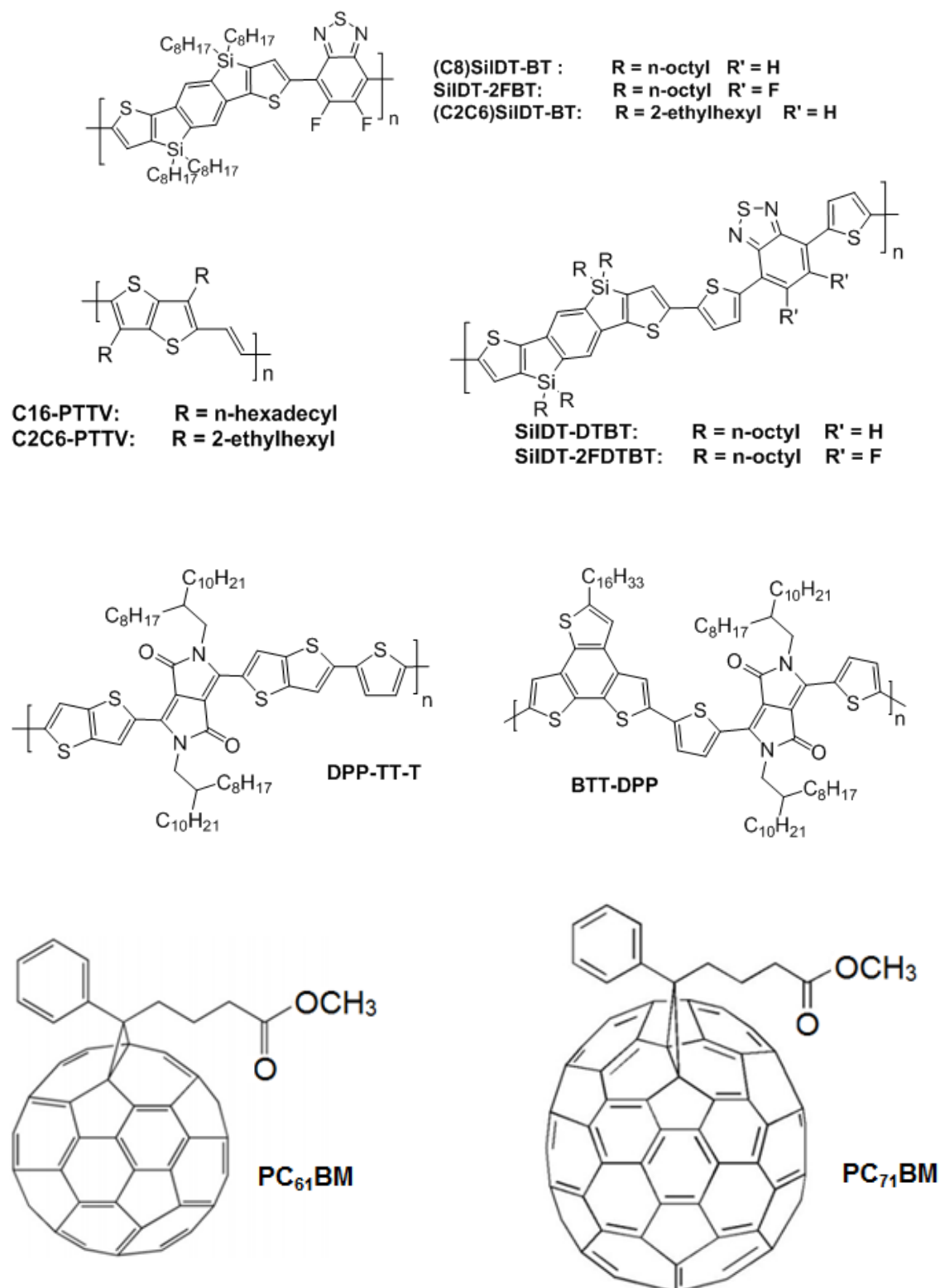


Figure 2.1: Chemical structure of the materials used in this thesis.

Materials for this thesis were used as received without further purification. All the polymers were synthesised at Imperial College London, with the chemical structures presented in Figure 2.1. Polymers with SiIDT-BT and SiIDT-DTBT backbones were synthesised by Dr. Bob Schroeder and Dr. Shahid Ashraf from Professor Iain McCulloch's group and used for Chapter 3 and 6. PTTV polymers were synthesised by Dr. Dickson Koroma from Dr. Martin Heeney's group and used for Chapter 4. DPP-TT-T and BTT-DPP polymers were synthesised respectively by Dr. Hugo Bronstein and Dr. Christian Nielsen from Professor Iain McCulloch's group. PC₆₁BM was purchased from Nano-C while PC₇₁BM was purchased from Solenne.

Polymer	M _n (kDa)	PDI	Chapter
(C8)SiIDT-BT	30	2.0	3
SiIDT-2FBT	22	1.7	3
SiIDT-DTBT	21	2.5	3
SiIDT-2FDTBT	26	2.7	3
C16-PTTV	16	1.8	4
C2C6-PTTV	16	2.4	4
BTT-DPP (22 kDa)	22	1.5	5
BTT-DPP (73 kDa)	73	2.1	5
BTT-DPP (90 kDa)	90	2.1	5
DPP-TT-T (14 kDa)	14	1.9	5
DPP-TT-T (34 kDa)	34	1.8	5
DPP-TT-T (62 kDa)	62	1.9	5
DPP-TT-T	35	4.3	6
(C2C6)SiIDT-BT	28	1.3	6

Table 2.1: Molecular weight (M_n) and polydispersity index (PDI) of the polymers used for this thesis.

2.2 Device fabrication

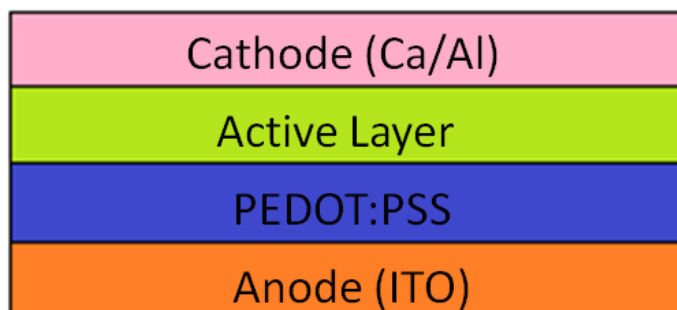


Figure 2.2: Architecture of the conventional device used for this thesis.

The polymer:fullerene solar cells investigated in this thesis have a conventional sandwich structure of ITO/PEDOT:PSS/polymer:fullerene/Ca/Al, as shown in figure 2.2.

The ITO layers are 12 mm × 12 mm glass substrates pre-coated by 110 nm thick 8 mm × 12 mm ITO. The substrates were washed by sonication in detergent, distilled water, acetone and isopropanol consecutively for 15 minutes respectively. They were then dried by nitrogen gun and were taken to undergo ultraviolet ozone plasma treatment for 7 minutes. PEDOT:PSS layers of 30 nm thick were then spin-casted onto the substrates and then annealed at 150°C for 20 minutes. For the active layer, a blend ratio solution of polymer and fullerene was made and spin coated onto the PEDOT:PSS layer, with the details of solution preparation specified in the experimental section of each results chapter. Lastly, a 25 nm thick calcium layer and 150 nm thick aluminium layer were deposited on the active layer sequentially by evaporation deposition under high vacuum (2×10^{-6} mbar). This resulted in 6 working pixels of 0.045 cm² on each substrate. They were kept in the dark in a nitrogen filled glovebox to minimise potential device performance degradation.

Optimised procedure was obtained by changing parameters such as solvent for blend solution, blend ratio, blend concentration, solvent additive and active layer thickness for device fabrication until optimised device performance was achieved.

2.3 J-V curve measurement

In this experiment, current passing through a light-exposed device was measured while an applied bias voltage across the device was changed from -1.5 V to 1.5V. This helped to determine power conversion efficiency (PCE) and other important device parameters such as open circuit voltage, short circuit current and fill factor. The error of PCE for this thesis was estimated using standard deviation from the mean.

The light source used for this experiment was a solar simulator of LOT-QuantumDesign fitted with a 150 W Xenon lamp filtered to simulate AM 1.5. A silicon photodiode was used as a reference for calibrating the intensity of the light. The short circuit current and PCE presented in this thesis have been corrected by taking the spectral mismatch between AM 1.5 and the Xenon lamp into account. The device was in a nitrogen filled chambers during the measurement. A Keithley(2400) source meter was used to measure the current as well as control the bias voltage across the device.

2.4 External quantum efficiency measurement

External quantum efficiency (EQE) is defined as the probability of generating a charge in external circuit by exposing the device to a photon at a certain wavelength (λ). $EQE(\lambda)$ depends on the efficiencies of the photon absorption, charge separation and collection, as mentioned in Chapter 1. This value was typically used to allow comparison in efficiency of photocurrent generation from photon with different energy or from absorption of different materials (e.g. polymer vs fullerene for this thesis).

The light source for this experiment was a tungsten halogen lamp (100 W). The incident light was filtered by a monochromator equipped with computer-controlled stepper motor to allow photons with selected wavelength to reach a solar cell. For photon with wavelength longer than 620 nm, an additional 590-nm long pass filter was used to block the light from second order diffraction. Prior to the measurement, the intensity of the lamp was calibrated using a photodiode. Keithley(2400) source meter was used to measure the current of the device under short circuit condition. The EQE measurements made for this thesis typically ranges from 350 nm to 900 nm with a 10 nm wavelength interval.

2.5 Film Preparation

Apart from samples for wide angle X-ray scattering, film preparations for all measurements involved in this thesis were based on spin casting. Preparation procedure for blend solution varies from polymer to polymer and was obtained from device fabrication with the details outlined in section 2.2. In general, solvent used for blend solution includes chloroform(CF), chlorobenzene(CB), dichlorobenzene (DCB) or a mixture of CF:DCB (4:1). The blend ratio as well as solution concentration are specified in Chapter 4-6.

The substrates where thin films were deposited were VWR glass slides of 1.3 cm $\times$ 1.3 cm. Prior to spin casting, the substrates were cleaned in acetone and isopropanol sequentially for 15 minutes respectively. They were then dried using nitrogen gun. Thin films were spun onto the substrates at 1500-4000 rpm for 1 minute using a spin coater (WS400A-6NPP Lite, Laurell Technologies Corporation). For thermal aging experiment, the thin films were stored in a chamber under vacuum of -2 mbar before subjected to annealing. For transmission electron microscopy (TEM) measurement, polymer:fullerene blend was deposited on a glass substrate coated with 10 nm PEDOT:PSS. The sample was then submerged in deionised water to dissolve the PEDOT:PSS and peel off the blend layer. The blend layer was transferred to a copper grid and stained by RuO₄ or iodine vapour prior to the TEM measurement.

Drop casting was used to prepare samples for wide angle X-ray scattering experiment. This allowed formation of thick films on the order of micrometre in order to yield better diffraction signal from the experiment. Details of solution for deposition are included in each result chapter. The (0.3 ml) solution was used to completely wet a glass slide of 1.0 cm $\times$ 2.0 cm. The sample was allowed to dry at room temperature overnight.

2.6 Steady state UV/visible absorption spectroscopy

Steady state UV/visible absorption spectroscopy was used to measure the optical absorption of a sample. The optical absorption can yield energetic information such as the optical bandgap of the sample. For materials such as polymers, the optical bandgap is also influenced by molecular packing as mentioned in Chapter 1. As such, this technique can also be employed as a preliminary investigation on material crystallinity. The absorption of a material is measured as absorbance defined according to Beer-Lambert's law as:

$$A(\lambda) = -\log_{10}\left(\frac{I}{I_0}\right) \quad (2.2)$$

, where $A(\lambda)$ is the absorbance at wavelength λ , I is the intensity of light that is transmitted through the material and I_0 is the intensity of the light before hitting the material. This value was often converted to calculate the fraction of photons absorbed by the sample using:

$$1 - \text{transmission} = 1 - 10^{-A(\lambda)} = 1 - \frac{I}{I_0} \quad (2.3)$$

The absorption spectra of the materials investigated in this thesis were measured in air using a UV/visible spectrometer (UV-1601 Shimadzu). A neat glass substrate was used as the background reference.

2.7 Transient absorption spectroscopy

Transient absorption spectroscopy is a technique to investigate short-lived excited species induced by a transient laser excitation on a neat or blend thin films. After exposing the sample to an excitation pulse, change in absorption of the films (or optical density which is preferentially used for TAS) at a specific delayed time was monitored as a function of wavelength. This allows identification of existence of photo-induced transient species, which generally have characteristic shape of absorption different from ground state species.

Alternatively, the absorption of the excited species at a specified wavelength could be measured as a function of time to yield information on the dynamic of the excited species, from micro to millisecond timescales for the setup employed for this thesis. Exciton¹⁻³ and geminate charge pairs^{4,5} dissociations have been reported to occur on timescale ranging from femtosecond to nanosecond. As such, the technique employed in this thesis measured the

longer lived charges which had escaped from geminate recombination. The change in optical density (ΔOD) of the excited species at $\sim 1\mu s$ was interpreted as yield of dissociated charge formation and has been reported to scale up with J_{SC} measured from the corresponding devices.^{4, 6} Moreover, from a standpoint of energetic, the yield of free charge formation has also been reported to correlate with driving energy (ΔE_{CS})^{4, 6} defined as:

$$\Delta E_{CS} = E_g - (IP - EA) \quad (2.4)$$

Where E_g is the bandgap of the material absorbing the photon; IP is the ionisation potential of the electron donor and EA is the electron affinity of the electron acceptor. For this thesis, E_g was estimated using the optical bandgap obtained from the onset of polymer absorption, while the bandgap of fullerene was assumed to be 1.9 eV according to ref^{7, 8}. IP was measured using cyclic voltammetry (CV) or ultraviolet photoelectron spectroscopy (UPS), whilst the EA was taken from ref^{7, 8}.

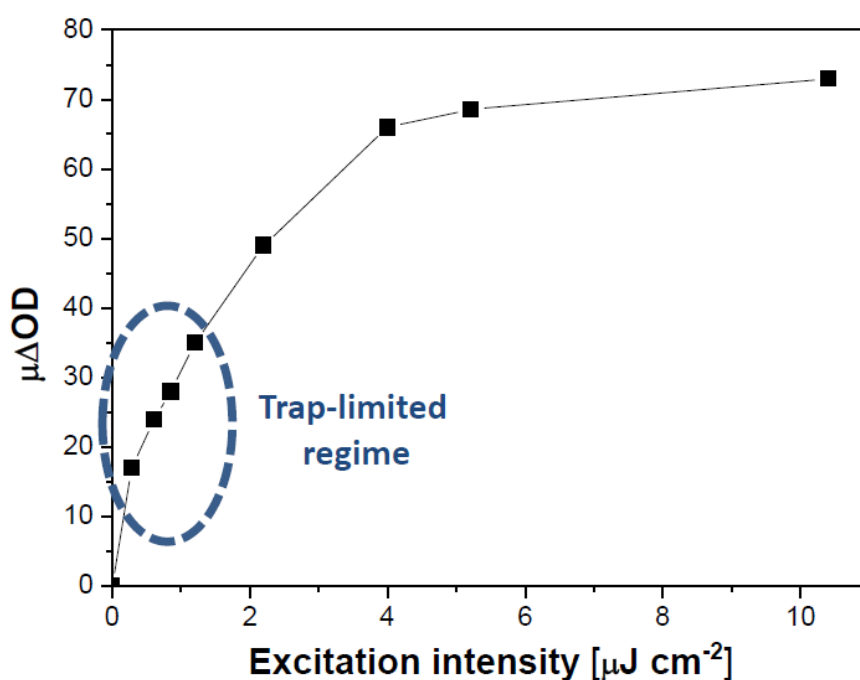


Figure 2.3: Plot of ΔOD amplitude (at $\sim 1\mu s$) versus excitation intensity. The regime of trap-limited is highlighted in blue.

The charge carrier dynamics observed in these experiments typically exhibit power law decay dynamics, characteristic of bimolecular recombination. As such, they appear linear on a log/log plot and fit to power law of $\Delta OD \sim time^{-\alpha}$, with a lower α suggesting a higher degree of energetic traps present in the system.^{9, 10} Moreover, the signal amplitude of 1-2 μs

exhibited sub-linear excitation intensity dependence¹⁰ as shown in figure 2.3, assigned to an increasing proportion of bimolecular recombination before 1 μ s at higher intensities. The initial region where the amplitude appears to scale up linearly with excitation intensity is used in this thesis to evaluate the yield of charge generation.^{10, 11}

The sample of interest is placed in a quartz cuvette fitted with nitrogen flow. The source of excitation pulse was a Nd:YAG laser equipped with an optical parametric oscillator. The excitation wavelength was typically the absorption maxima of a component (polymer or fullerene) in a blend sample at a repetition frequency of 20 Hz and a pulse width of 20 ns. The pump intensity in this setup could be tuned using neutral density filters and had a range from 0.3 μ J cm⁻² to 19 μ J cm⁻² for this thesis. The probe light source was a halogen lamp (100 W, Bentham, IL 1) equipped with a stabilised power supply (Bentham, 605), and typically probed at the absorption maximum of the excited species of interest if known. The probe wavelength was selected by a monochromator located between the sample and the probe light source. The probe light was filtered after passing the samples by a second monochromator to reduce noise of signals. A silicon photodiode (Hamamatsu Photonics, S1722-01) was used to collect the probe light, which generated a signal recorded by an oscilloscope (Tektronics, TDS220) and then sent to a computer.

The femtosecond TAS measurement for Chapter 5 was carried by Dr. Stoichko Dimitrov, with the results and details of experimental setup included in ref³.

2.8 Photoluminescence spectroscopy

Photoluminescence(PL) spectroscopy was used to measure intensity of photon emission associated with a decay from an excited state to ground state. This technique is particularly useful for polymer:fullerene solar cells when comparing the intensities of emission from neat and blend samples, yielding a value called PL quenching (PLQ) (Equation 2.5).

$$PLQ = \left(1 - \left(\frac{PL_{Blend}}{PL_{Neat}} \right) \right) \times 100\% \quad (2.5)$$

This value indicates the increase in percentage of excitons that have undergone non-radiative decay in the blend film compared to neat films, reflecting the efficiency of exciton dissociation at the polymer:fullerene interfaces. Efficient exciton dissociation requires the

domain size of a component in the blend system to be comparable to or smaller than the length of exciton diffusion. As such, PL spectroscopy can be used to probe information on the blend morphology.^{3, 12} In this regard, the PLQ can be used to estimate the average length that an exciton can diffuse before undergoing dissociation (L) according to Equation 2.6.¹³ This, to some extent quantitatively, reflects the degree of phase segregation on the scale of exciton diffusion. (5-10 nm for polymer exciton¹⁴ and 5 nm for fullerene exciton¹⁵)

$$L = L_{ex} \times (1 - PLQ)^{1/2}$$

where L_{ex} is the length of exciton diffusion.

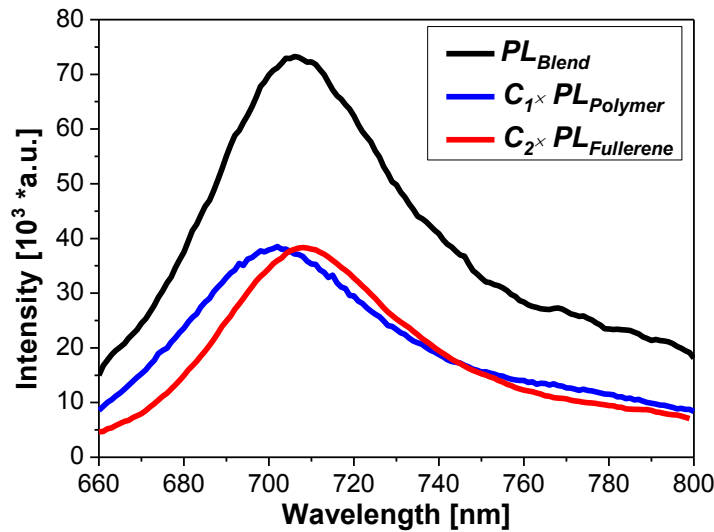


Figure 2.4: Photoluminescence of a blend sample obtained from experiment. The peak composition was analysed using deconvolution, showing the blend emission comprises of two peaks from polymer (blue) and fullerene (red).

In some blend systems, the emission of polymer may strongly overlaps with that of fullerene (e.g. Chapter 4). In this case, deconvolution was performed to analyse the peak composition (figure 2.4) based on the following assumption:

$$PL_{Blend} = C_1 \times PL_{Polymer} + C_2 \times PL_{Fullerene} \quad (2.6)$$

where $PL_{Polymer}$ and $PL_{Fullerene}$ are emission from neat polymer and fullerene respectively and C_1 and C_2 are constants.

2.9 Wide angle X-ray scattering

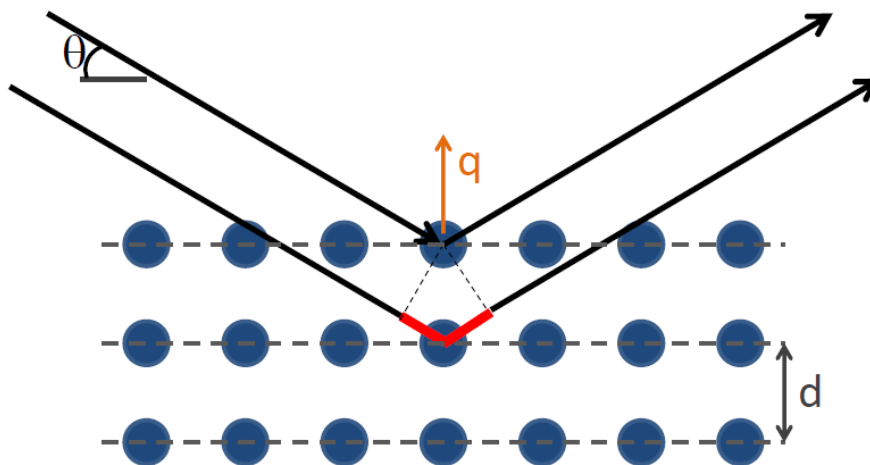


Figure 2.5: Diagram showing Bragg's Law for X-ray scattering, with the pathway difference between the two beams highlighted in red.

Wide angle X-ray scattering is a technique which was used to assess information (e.g. molecular separation and degree of molecular ordering) on crystalline structure of a solid. In this technique, incident monochromatic X-ray beams were directed to a sample, producing a scattering pattern which depends upon sample structure and can be described by Bragg's Law. Figure 2.5 shows the diffraction of two incident beams on a lattice. A detector was used to collect any diffracted photons that have undergone constructive interferences. Bragg's Law states that the constructive interference can only happen if the pathways of these photons differ by an integer multiple of λ (highlighted in figure 2.5), where λ is the wavelength of the photon. This can be represented mathematically using equation 2.6.

$$n\lambda = 2d\sin\theta \quad (2.7)$$

Where n is an integer, λ is the wavelength of the monochromatic X-ray, d is the spacing between the adjacent lattice planes (or called d -spacing) and θ is the angle between the incident beam and the scattering lattice planes. In this thesis, θ was converted into scatter vector q defined as:

$$q = \left(\frac{4\pi}{\lambda}\right) \sin\theta \quad (2.8)$$

The results obtained from WAXS are presented in plots of signal intensity against q . With the setup of the wide angle X-ray scattering employed for this thesis, only the information on

out-of-plane scattering can be probed (i.e.: perpendicular to the substrate) – for example corresponding to out of plane stacking illustrated in Figure 2.6. This setup probably is particularly relevant to OPV, with reports of efficient polymer semiconductors exhibiting signals from out-of-plane π - π stacking.¹⁶⁻¹⁸ In addition, for relatively amorphous polymers (such as most of those studied in this thesis), dropping casting typically results in non-orientated films, such that the WAXS measurement is a reasonable assay of film crystallinity.

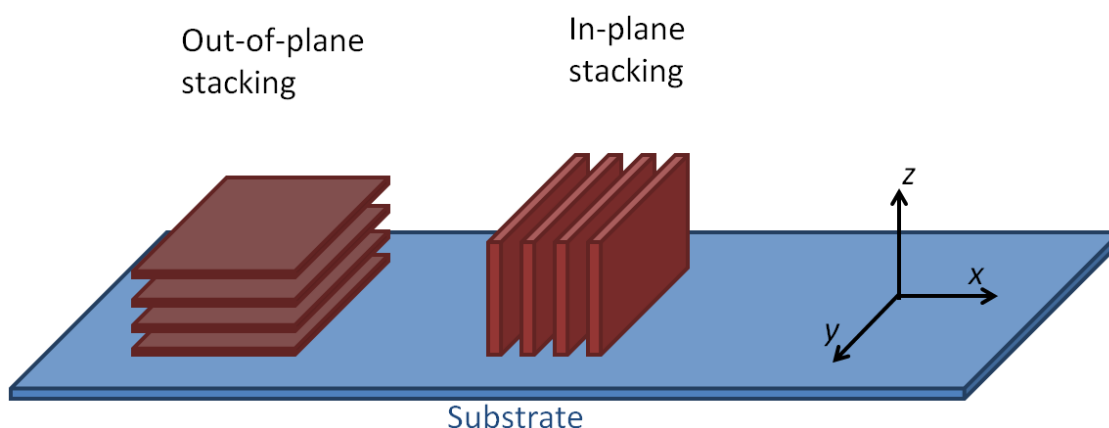


Figure 2.6: Diagram showing crystalline with different orientations (out-of-plane vs in-plane) with respect to the substrate. Only the crystalline in out-of-plane direction can be probed by WAXS.

This technique allows comparison on the degree of crystallinity between different materials by extracting a parameter called diffraction strength. This is defined as the area of the associated signals divided by the sample thickness, which has been suggested to scale up with the volume fraction of crystalline domains.¹⁹ In addition, the full width half maximum (FWHM) of the signals can be extracted to calculate the average size of the associated crystalline domains (τ) according to Scherrer equation^{20, 21}:

$$\tau = \frac{K\lambda}{\beta \cos\theta} \quad (2.9)$$

where K is a shape factor with a typical value of 0.89 and β is the FWHM. Lastly, the technique can also be used to probe the existence of fullerene intercalation in polymer crystals, as have been suggested by McGehee and co-workers²² (see Chapter 1 or 4 for the details). With the fullerene intercalated between polymer side chains, the d-spacing of polymers lamellar stacking was expected to increase, causing a shift in the position of associated signals.²²

Samples for WAXS measurement were prepared by drop casting, as described in section 2.5. A PANALYTICAL X'PERT-PRO Materials Research Diffractometers (MRD), which has a nickel-filter Cu $K_{\alpha 1}$ beam (wavelength = 1.54 Å) and a X' CELERATOR detector, was used for the measurement. The current and accelerating voltage used were 40 mA and 40 kV respectively.

2.10 Atomic force microscopy

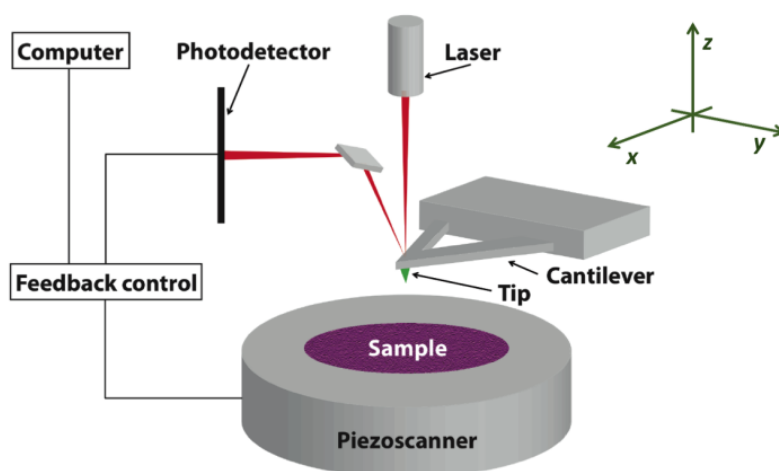


Figure 2.7: Diagram showing the setup of typical atomic force microscope.²³

Atomic force microscopy is a technique used to probe surface topography of polymer:fullerene thin films with resolution on the order of nanometre. The topography information is extracted based on interaction between an oscillating mechanical probe and the surface of a sample. The AFM used for this thesis is in non-contacting mode with its setup illustrated in figure 2.7.

The sample was located on a piezoscanner which allows the sample to move in the Z direction. The mechanical probe used for AFM was a sharp tip (radius < 7 nm) placed at the free oscillating end of a micron size cantilever, which was made of silicon or silicon nitride. In non-contacting mode, the probe was allowed to move above the sample and oscillate with high frequencies of ~300 kHz and a resonance amplitude. The movement of the probe was monitored by a beam deflection method, in which a laser was reflected from the top of the cantilever into a detector. When the probe was brought to a very close proximity to the sample (but not touching it), interactions arose, such as van de Waals force, and caused the

amplitude of the oscillating probe to deviate from its standard resonance amplitude. The change in amplitude was detected giving rise to an electronic feedback, which adjusted the probe-to-sample distance by the piezoelectric effect in order to maintain the standard resonance amplitude. The change in probe-to-sample distance was recorded, producing a topography image of the sample.

2.11 Transmission electron microscopy

Transmission electron microscopy (a high-resolution JEOL 20110 TEM (80-200 kV)) was employed to assay active layer morphology with assistance of Dr. Mahmoud Ardakani for Chapter 3 and by Dr. Safa Shoaee for Chapter 5. This is an image probing technique based on the interaction between materials and an incident electron beam. Material contrast derives from deflection of the beam of electron passing through the sample, with a higher electron density of the material leading to higher degree of deflection. More information regarding the fundamental operating principle of TEM can be found in ref²⁴. For probing the morphology of the active layer for OPV, the contrast between polymer and fullerene is generally poor because both materials consist predominantly of carbon atoms. This problem can be solved by staining the samples with RuO₄ or Iodine vapour prior to the measurements, which have been reported to improve the material contrast in binary systems comprised of organic materials.^{25, 26} With the aid of other measurements such as PL spectroscopy, the darker or brighter regions in the TEM images in this thesis could be assigned to fullerene rich or polymer rich regions. The samples for TEM measurement was prepared as described in section 2.5.

2.12 Optical microscopy

Optical microscopy was employed with the assistance of Mr Paul Westacott and Dr. Him Cheng Wong at Imperial College London. This technique probed the formation of micron sized fullerene clusters in the polymer:fullerene blend on glass substrates, which had been subjected to extreme thermal aging conditions prior to the measurement. The optical microscope is an Olympus BX 51 in transmission mode.

2.13 Near edge Soft X-ray absorption fine structure

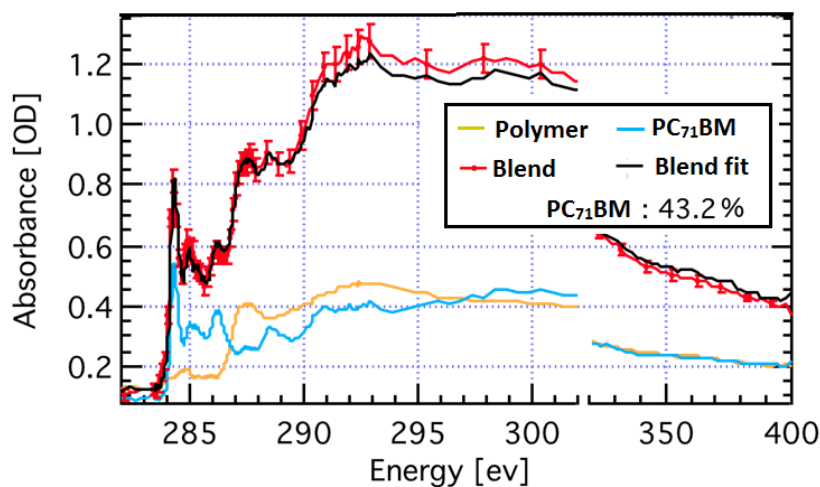


Figure 2.8: An example showing fits of NEXAFS obtained in fullerene-depleted region of a polymer:fullerene blend films.

This measurement was undertaken by Dr. Wei Ma from Professor Harald Ade's group in the University of North Carolina to test the 'thermodynamic' miscibility of polymer and fullerene²⁷. Some of the fundamental information is described here while more detailed information can be found in ref^{28, 29}. This technique allows material composition analysis based on absorption of X-ray photons which, in this case, can promote an electron in 1s orbital to unoccupied electronic orbitals. The X-ray photon absorption spectra are sensitive to the molecular structure of materials and hence produce chemical contrast between materials. Figure 2.8 shows an example of composition analysis of a polymer:fullerene blend. The spectrum obtained from the blend sample was fit by the signals from the neat polymer and neat fullerene to calculate the composition. This can be converted into weight percentage of fullerenes. The setup for this thesis has a resolution of ~ 40 nm.²⁹ For miscibility measurement, the blend was annealed at high temperature (140 °C or 170 °C for Chapter 6) for 100 hours prior to the measurement, to trigger the formation of micron sized fullerene clusters. Following this, NEXAFS was employed to measure the weight percentage of fullerene in the fullerene-depleted regions, and defined as the thermodynamic polymer:fullerene miscibility.²⁸ This parameter has been used to predict the morphological stability of a blend at a specific temperature.^{27, 28}

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Chapter 3

Influence of polymer fluorination on device performance and blend microstructure

Abstract

This chapter explores the effects of fluorination of two polymers silaindacenodithiophene-benzo[c][1,2,5]thiadiazole (SiIDT-BT) and silaindacenodithiophene-4,7-dis(thiophen-2-yl)-benzo[c][1,2,5]thiadiazole (SiIDT-DTBT) on their device performance. From device characterisation, after fluorination SiIDT-BT exhibits reductions in both short circuit current and power conversion efficiency. In contrast, fluorination of SiIDT-DTBT leads to an improvement in device performance, and in particular a higher fill factor. In both cases, fluorination is found to increase the phase segregation of the blend microstructure demonstrated using atomic force microscopy (AFM) and photoluminescence (PL) spectroscopy, consistent with WAXS data which shows a higher crystallinity for the fluorinated polymers. This is an effect of fluorination that has been significantly less explored in the OPV literature. For SiIDT-BT, it is demonstrated that the reduced device performance upon fluorination is derived from reduced charge generation, which can be in part attributed to the severe phase segregation. On the other hand, the better performance of SiIDT-DTBT after fluorination is probably due to the less severe phase segregation of the blend microstructure and a better out-of-plane π - π stacking of the polymer. Our results suggest that the impact of fluorination on device performance depends on the nature of the backbone. With the additional thiophene units present in the backbone, fluorinated SiIDT-DTBT can adopt a conformation to favour device performance and also potentially compensate the phase segregation resulted from fluorination.

3.1 Introduction

Fluorinated molecules have attracted significant interest for a range of applications including pharmaceuticals, OLEDs, OFETs and, of particular interest in this thesis, organic photovoltaics.¹⁻⁶ Fluorine is the most electronegative element in the periodic table and the smallest in the halogen group. In general, replacing C-H with C-F allows the tuning of molecular properties with only a small change in steric hinderance.¹ Such replacement has been suggested to lower both the HOMO and the LUMO of a molecule because of the electron withdrawing nature of fluorine atom.⁷ On the other hand, adding fluorine atoms could alter the charge density distribution within the molecule and subsequently alter intermolecular interactions.^{1, 8-10} In some cases, fluorinated molecules were found to have improved π - π stacking, potentially leading to a positive effect on charge mobility.^{1, 11}

Fluorinated polymers are particularly of interest to organic photovoltaics primarily because they are expected to improve open circuit voltage (V_{oc}) for devices.¹²⁻¹⁷ In general, V_{oc} for organic photovoltaic devices is believed to be primarily dependent on the difference between the HOMO of donor polymer and the LUMO of fullerene (see chapter 1).^{18, 19} If there is no negative impacts on J_{sc} and FF, lowering the HOMO of polymer by introducing fluorine should, in principle, lead to an increase in V_{oc} and hence an improved PCE. This idea has been successfully applied for several polymer series including the well-known PTB7 resulting in devices with over 7% power conversion efficiency.²⁰

Due to the early successful examples, fluorinated polymers are attracting extensive research interest and are considered to be one of the most promising methods to improve device performance. However, as more effort has been put in this area, some other features of fluorinated polymers have been revealed which, in some cases, have had negative impacts on device efficiency.^{16, 21-25} In particular, fluorinated polymers were found to promote phase segregation within the active layer in some organic solar cells. In poly[2,6-(4,4-bis(2-ethylhexyl)-4h-cyclopenta[2,1-b;3,4-b']dithiophene)-alt-4,7-(2,1,3-benzo-thiadiazole)] (PCPDTBT) systems, using transmission electron microscopy, Albrecht and co-workers showed that fluorination could encourage the polymer aggregation leading to larger domains in active layers.¹⁶ In parallel, Tumbleston and co-workers reported that polybenzodithiophene-benzotriazole (PBnDT-FTAZ) after fluorination exhibited a lower thermodynamic miscibility with fullerene (see Chapter 6 for the definition of thermodynamic miscibility of polymer:fullerene) based on the measurements of near edge X-ray absorption

fine structure (NEXAFS).²² In these examples, the fluorine introduction was found to increase the polymer crystallinity, potentially accounting for the promotion in phase segregation. On the other hand, given that fluorine is the element with the highest electronegativity, a couple of recently reports primarily from Yu and co-workers also suggested that introduction of fluorine to PTB analogue polymers could change the intramolecular dipole, which potentially in turn could impact on charge separation efficiency.^{25, 26}

In order to correctly apply fluorinated polymers to achieve better organic solar cells performance, the advantages and disadvantages of fluorination must be thoroughly understood. In this chapter, fluorine atoms are introduced to SiIDT-BT and SiIDT-DTBT polymers (figure 3.1) to explore the effects of fluorination on device performance for these two polymers.²¹ The SiIDT-BT contains a thiophene-phenylene-thiophene donor unit which is a fused aromatic system. The fused aromaticity has been suggested to give higher rigidity and better planarity for the polymers and hence improves the hole mobility.²⁷⁻²⁹ Compared to SiIDT-BT, SiIDT-DTBT has an additional electron rich thiophene unit which has been suggested to raise the HOMO and improve the planarity of the polymer.^{30, 31} The PCE of the solar cells based on these two polymers have been reported to be over 3.5%.²⁹ In this chapter, fluorine atoms are introduced by replacing two hydrogen atoms in each benzothiadiazole (BT) unit to give SiIDT-2FBT and SiIDT-2FDTBT (figure 3.1). Two opposite effects of fluorination upon device performance are observed. In the case of SiIDT-BT, it is shown that introducing fluorine can have negative effects on the active layer morphology and device efficiency. The work demonstrates that fluorination in this polymer enlarges the fullerene domains and lowers the efficiency of fullerene exciton dissociation and charge generation from fullerene absorption. However, such effect is not seen in SiIDT-DTBT in terms of device performance, which differs from SiIDT-BT by having an additional thiophene unit. The reasons for the different fluorination effects on device performance are discussed.

3.2 Experimental

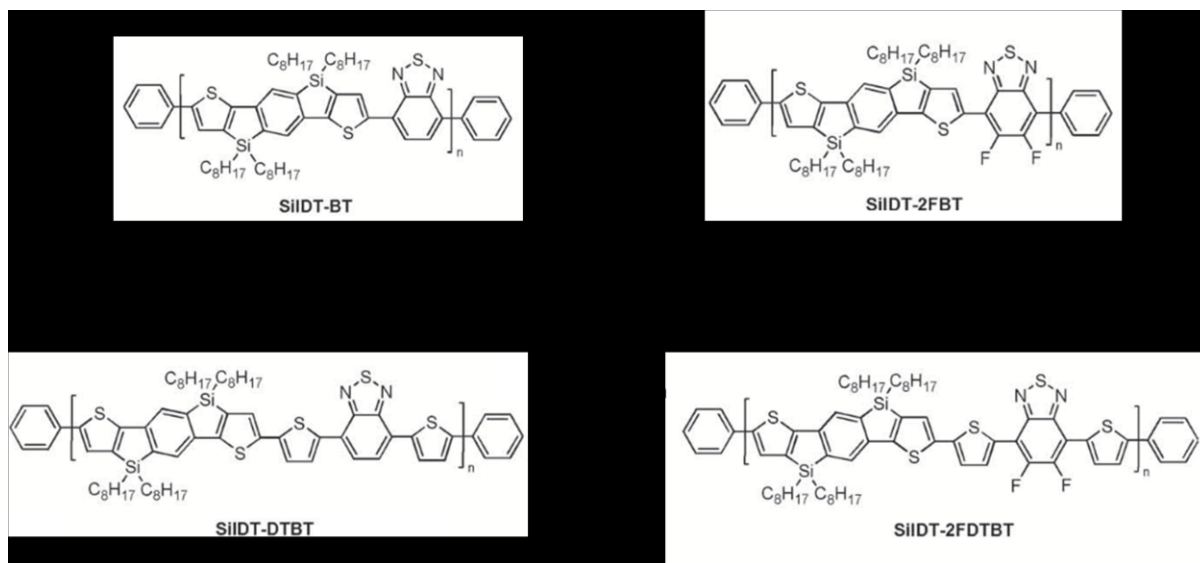


Figure 3.1 Chemical structures of SiIDT-BT, SiIDT-2FBT, SiIDT-DTBT and Si-IDT-2FDTBT. The arrows indicate the difference between neighbour polymers.

Polymer	M_n [kDa] ^{a)}	PDI ^{a)}
SiIDT-BT	30.0	2.0
SiIDT-2FBT	22.3	1.7
SiIDT-DTBT	21.0	2.5
SiIDT-2FDTBT	26.4	2.7

Table 3.1: Molecular weight and polydispersity index (PDI) of the four polymers, which were measured using gel permeation chromatography. Polystyrene was used as the standard while chlorobenzene was used as the solvent.

Materials - SiIDT-BT and SiIDT-DTBT are polymers synthesised by Dr. Shahid Ashraf and Dr. Bob Schroeder from Prof. Iain McCulloch's group (figure 3.1). The details of the polymer preparation are presented in the literature.²¹ The molecular weight and PDI of each polymer was measured by GPC using polystyrene as the standard and chlorobenzene as the eluent, with the data showing in table 3.1.

Device fabrication – the devices for this study have a conventional architecture consist of ITO/PEDOT:PSS/polymer:PC₇₁BM/Ca/Al. The general device fabrication procedure is outlined in Chapter 2. The optimised fabrication procedure was obtained by tuning parameters including blend solvent, blend ratio, spin rate for film deposition and usage of solvent additive. The optimised blend ratio was found to be 1:3.5 (polymer:PC₇₁BM) for

SiIDT-BT and 1:2 for SiIDT-2FBT, with an overall concentration of 30 mg/ml in dichlorobenzene solvent. The procedure of SiIDT-BT was applied to SiIDT-DTBT and SiIDT-2FDTBT, as this has been found to be the optimised procedure for a couple of IDT-BT analogue polymers.^{29, 32}

Sample preparation - Most films for this study were prepared using the spin coating method which is described in Chapter 2. For wide angle X-ray scattering (WAXS) measurement, the films were prepared using drop casting in order to give a better signal. For TEM measurement, the films were stained with iodine vapour prior to the measurement in order to improve the material contrast.

Experimental techniques - The details of UV/visble absorption spectroscopy, WAXS, photoluminescence (PL) spectroscopy, transient absorption spectroscopy (TAS), atomic force microscopy (AFM) and transmission electron microscopy (TEM) are described in Chapter 2. The topography image of SiIDT-BT:PC₇₁BM was obtained by Dr. Dong-Seok Leem. The TEM was carried out with the assistance of Dr. Mahmoud Ardakani.

Thermal annealing - the films were baked at 180°C on a hotplate for 10 minutes in a nitrogen filled glovebox for WAXS measurement.

3.3 Results

The result section starts with analysing the fundamental properties, such as energy levels, absorption and crystallinity, of the four polymers present in figure 3.1. Studies on the impact of fluorination on blend microstructure and device are then presented separately for the SiIDT-BT backbone and SiIDT-DTBT backbone. More specifically, the active layer morphology was probed using WAXS, AFM as well as TEM. For polymers with SiIDT-BT backbone for which material amounts were sufficient, photoluminescence and transient absorption spectroscopy was also employed to analyse charge generation of the samples, in order to better understand the correlation between device performance and blend microstructure.

3.3.1 Material properties

Energy levels

Polymer	HOMO [eV]	LUMO [eV]
SiIDT-BT	-5.4	-3.6
SiIDT-2FBT	-5.4	-3.6
SiIDT-DTBT	-5.0	-3.3
SiIDT-2FDTBT	-5.1	-3.4

Table 3.2: Energy levels of HOMO and LUMO for the four SiIDT polymers. Energy levels of the HOMOs were determined using ultraviolet photoelectron spectroscopy in air (UV-PESA) while LUMOs were estimated by adding polymer absorption onsets to the HOMOs.

Ultraviolet photoelectron spectroscopy in air (UV-PESA) was performed by Dr Scott Watkins from the Commonwealth Scientific and Industrial Research Organisation (CSIRO) in Australia in order to measure the energy levels of the HOMOs for the four polymers (table 3.2). The energy levels of the LUMOs were calculated by adding the estimated bandgap using the onset of UV-vis absorption (figure 3.2) to the energy levels of the HOMOs. As shown in table 3.2, in the case of SiIDT-BT, the HOMO and LUMO are unchanged after introducing fluorine to the SiIDT-BT, suggesting there is negligible impact on the energy levels from fluorination in this particular polymer. In contrast, it can be seen that fluorination reduces the energy levels of both the LUMO and the HOMO for SiIDT-2FDTBT, as expected.

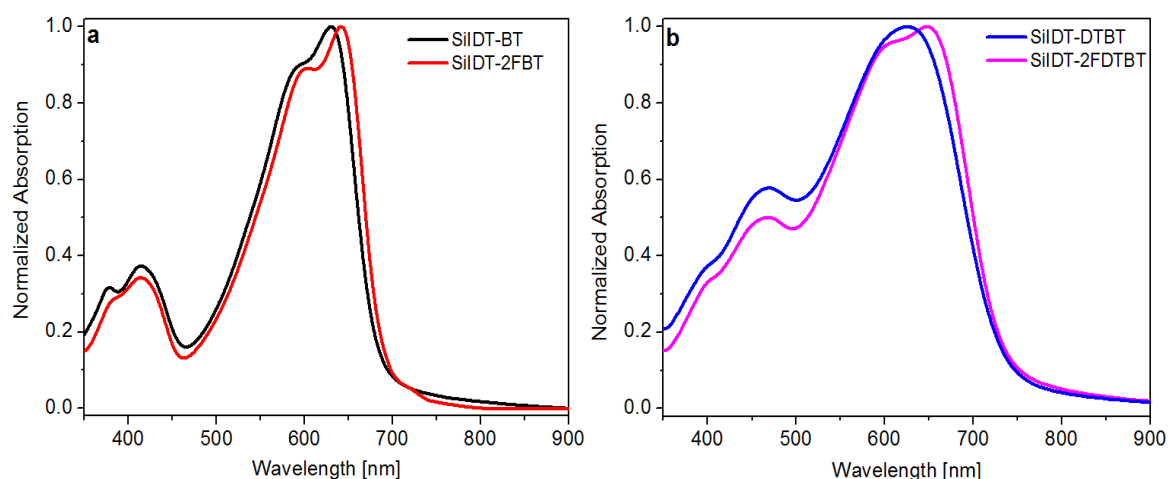


Figure 3.2 Normalised UV/visible absorption spectra of SiIDT-BT (a, black), SiIDT-2FBT (a, red), SiIDT-DTBT (b, blue) and SiIDT-2FDTBT (b, pink) thin films, prepared using spin casting from chlorobenzene.

The thin film absorption spectra of all the four polymers were measured and are presented in figure 3.2. All the samples were prepared by spin casting using chlorobenzene as the solvent. Overall, all polymer shows two peaks in their absorption spectra, with the lower energy one (circa 600 nm) assigned to internal charge transfer where the transition is from the donor part of the polymers to the acceptor part.³³ The absorption of the SiIDT-2FBT thin film exhibits a peak at ~ 640 nm, which is 10 nm longer than the peak observed from SiIDT-BT sample. However, both spectra display an onset ~ 688 nm, implying an optical bandgap of 1.8 eV for these polymers. Similarly, a red shift in absorption maxima was also observed in SiIDT-DTBT from 620 nm to 650 nm upon fluorination. The bandgap of SiIDT-DTBT analogue was estimated to be 1.7 eV using the absorption onset. The red shifts observed in SiIDT-BT and SiIDT-DTBT absorption upon fluorination are potentially resulted from a change in molecular packing. This is verified using wide angle X-ray scattering (WAXS) in following section.

Wide angle X-ray scattering

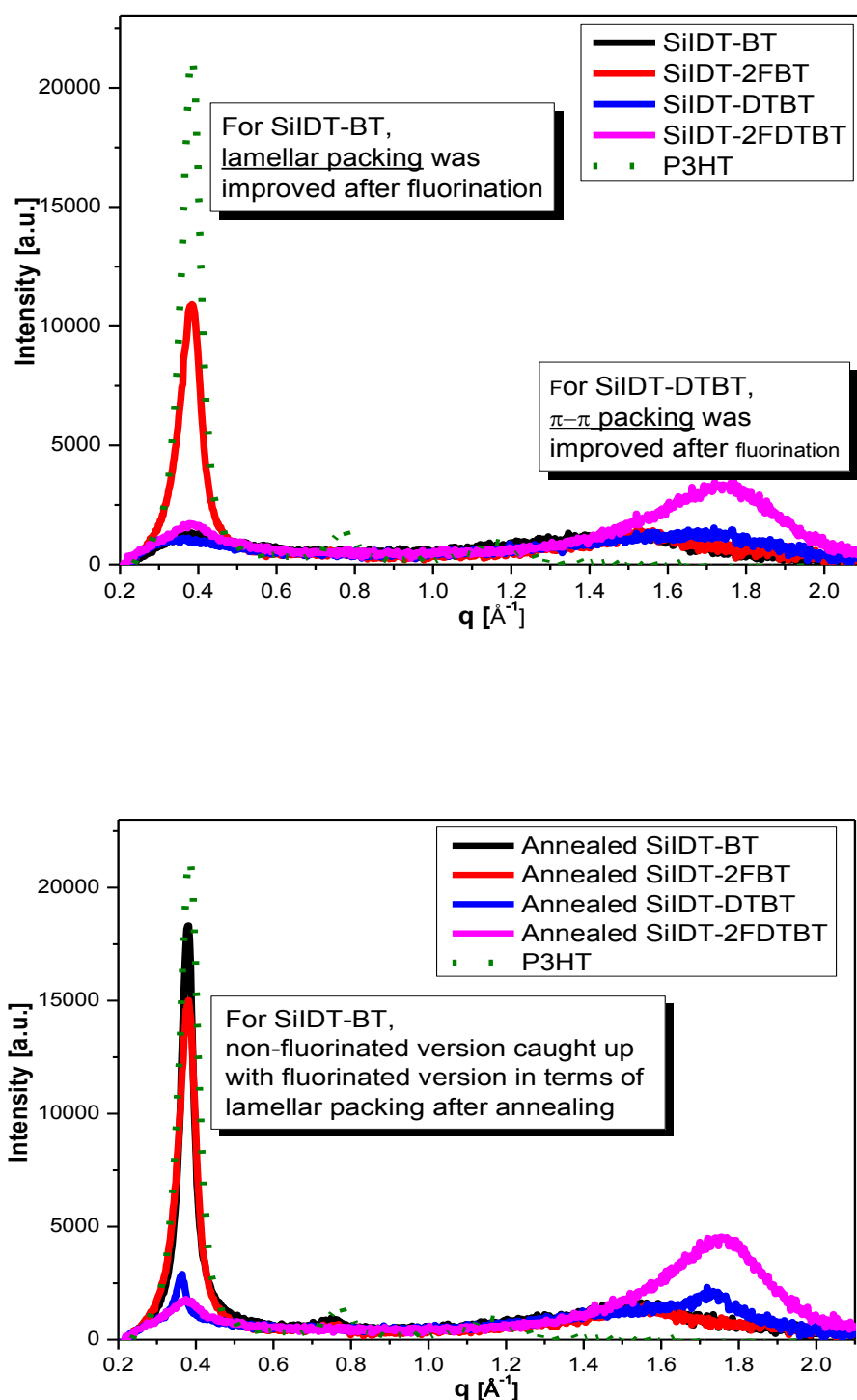


Figure 3.3 Wide angle X-ray scattering signals of the four polymers in drop-cast pristine films before (top) and after (bottom) annealing at 180 °C for 10 minutes on a hotplate in a nitrogen glovebox. Signal of drop-cast pristine P3HT film is used as comparison.

Polymer	DS of lamellar packing (a.u.)		DS of π - π stacking (a.u.)	
	Pristine	Annealed	Pristine	Annealed
SiIDT-BT	66	292	159	191
SiIDT-2FBT	270	312	130	183
SiIDT-DTBT	74	91	224	278
SiIDT-2FDTBT	103	90	477	568
P3HT	1042	-	-	-

Table 3.3: Diffraction strength (DS) of lamellar stacking and π - π stacking of the four polymers before or after annealing at 180 °C for 10 minutes. The DS were estimated by integration of the peak area and corrected by the film thickness.

Wide angle X-ray scattering was used to assay the crystallinity in out-of-plane direction for these polymers, with the details of the technique outlined in chapter 2. Figure 3.3 displays the results measured using wide angle X-ray (WAXS) scattering on drop-casted samples. Diffraction strength (table 3.3) of the WAXS signals was estimated as the peak area over thickness, which is a parameter scaling up with volume fraction of crystalline region in the film.³⁴ Note that the background signals from glass substrate could not be completely removed. As such, diffraction strength for signals with poor intensity could be overestimated.

Both SiIDT-BT and SiIDT-2FBT shows two broad peaks at $q \sim 0.4 \text{ \AA}^{-1}$ and $1.5 \text{ \AA}^{-1}$, assigned to lamellar packing and π - π stacking respectively. The diffraction strengths (DS) of SiIDT-BT signals are low (table 3.3), compared to P3HT which is known to be semicrystalline, suggesting that this polymer is relatively amorphous. After thermal annealing at 180 °C for 10 minutes, the DS of the signals, particularly the lamellar peak (DS ~ 292 a.u.), becomes more comparable to that of P3HT, indicating the polymer crystallinity is significantly increased. Such observation suggests that the ability of SiIDT-BT to crystallise is restrained by a thermal barrier and SiIDT-BT preferentially adopted lamellar packing over π - π stacking along the out-of-plane direction. Upon fluorination, SiIDT-2FBT exhibits a pronounced lamellar peak with diffraction strength of 270 a.u. and a weak π - π stacking peak, with the former signals indicating its more semicrystalline nature in comparison to pristine SiIDT-BT.

On the other hand, two signals with $q \sim 0.37 \text{ \AA}^{-1}$ and $1.75 \text{ \AA}^{-1}$ are observed from both pristine SiIDT-DTBT and SiIDT-2FDTBT, which can be assigned to lamellar packing and π - π stacking. Similar to SiIDT-BT, the signals of pristine SiIDT-DTBT are weak, indicating an amorphous nature. After thermal annealing treatment, both of the signals are improved, with

the enhancement in π - π stacking being slightly higher than the lamellar packing. Introducing fluorine atoms to this polymer primarily increases the out-of-plane π - π DS, with the associated DS increased by a factor of approximately 2. This is different to SiIDT-BT, in which the lamellar diffraction is increased instead upon fluorination. This difference may at least in part be associated with changes in backbone orientation, although in both cases fluorination increases the overall diffraction intensity. Note that the d-spacing of π - π stacking for SiIDT-DTBT is 0.6 Å shorter than that in SiIDT-BT, implying the π - π stacking is favoured by a stronger interaction or more planarity of the SiIDT-DTBT backbone.

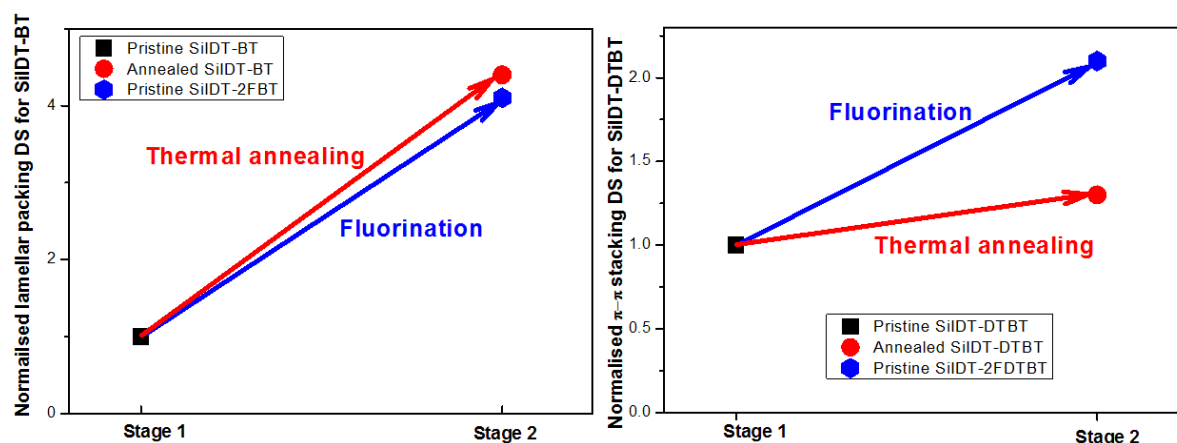


Figure 3.4: Demonstrate the impacts of thermal annealing and fluorination on lamellar packing for SiIDT-BT (left) and on π - π stacking for SiIDT-DTBT (right).

To sum up, both SiIDT-BT and SiIDT-DTBT exhibit an increase in the degree of crystallinity upon fluorination, similar to what has been reported previously for some other polymers.^{12, 23, 35} Interestingly, fluorination preferentially improved the lamellar packing for SiIDT-BT compared to the π - π stacking which is increased for SiIDT-DTBT. The increase in polymer crystallinity by fluorination for both of these polymer backbones are similar to the increase resulting from thermal annealing. To illustrate this trend better, the lamellar packing DS of pristine SiIDT-BT, annealed SiIDT-BT and SiIDT-2FBT are present in figure 3.4 (left). The signals were normalised by the DS of pristine SiIDT-BT. It can be clearly seen that both annealing and fluorination improve the lamellar DS by a factor of approximately 4. Similar analysis was repeated on the π - π stacking for the polymers with SiIDT-DTBT backbone, which also shows a qualitative agreement between the effects on crystallinity by thermal treatment and by fluorination. These results suggest that SiIDT-BT and SiIDT-DTBT have different preferred crystal structures which are hindered by a thermal barrier. It is speculated that fluorination could encourage the polymer to adopt their preferred crystal structure by

offering fluorine-hydrogen bond, fluorine-sulphur interaction or charge density redistribution within the molecule.^{1, 35}

3.3.2 Fluorination effects on SiIDT-BT

Device characterisation

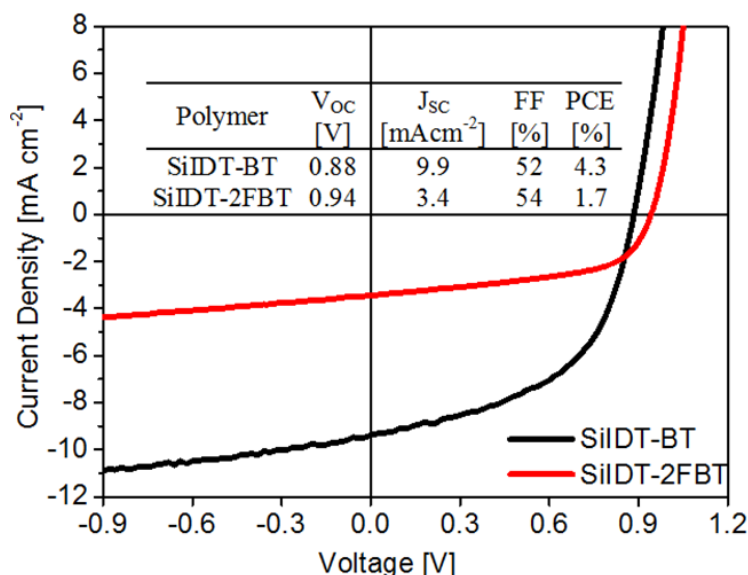


Figure 3.5: J-V curves of the devices made by SiIDT-BT:PC₇₁BM (1:3.5) and SiIDT-2FBT:PC₇₁BM (1:2) respectively. The insert shows the device parameters for the two polymers.

Studies on fluorination effects on SiIDT-BT and on SiIDT-DTBT in terms of morphology and device performance are presented in section 3.3.2 and 3.3.3 separately. All the devices made for this chapter consist of a conventional device architecture of ITO/PEDOT:PSS/polymer:PC₇₁BM/Ca/Al. By tuning the fullerene loading for the active layer, it has been found that the optimised blend ratio for SiIDT-2FBT is 1:2 ratio (polymer:PC₇₁BM) while the optimised blend ratio used for all other polymers is 1:3.5. The J-V curves of the devices made of SiIDT-BT and SiIDT-2FBT are presented in figure 3.5, with the inserted table showing the device parameters. The optimised SiIDT-BT device exhibits a PCE of 4.3% ($\pm 0.1\%$). Introducing fluorine atoms to the polymer reduces the PCE to 1.7% ($\pm 0.1\%$). This drop primarily results from a 60% reduction in the short circuit current. On the other hand, an improvement of 60 mV is observed in the open circuit voltage, although this is not enough to compensate the reduction in short circuit current.

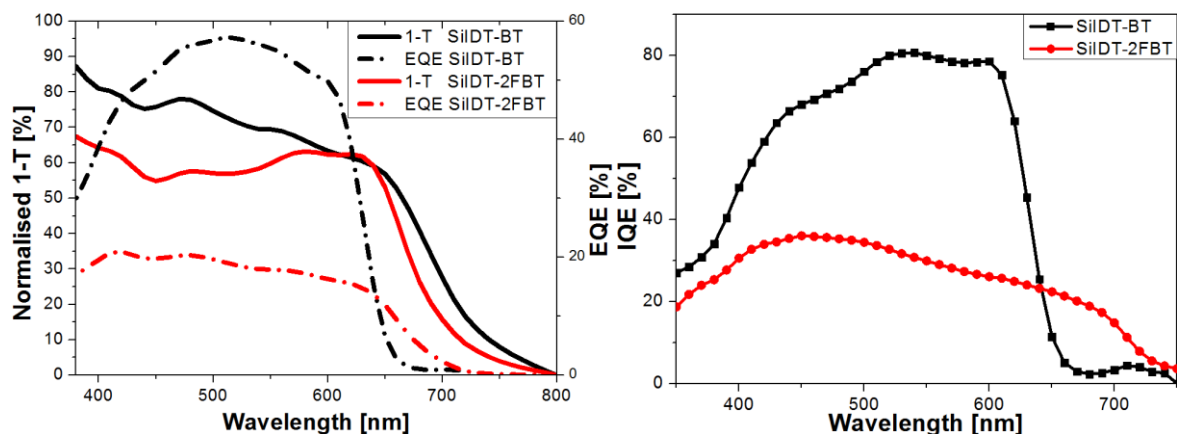


Figure 3.6: (left) Normalised 1-transmission spectra of SiIDT-BT:PC₇₁BM (1:3.5) and SiIDT-2FBT:PC₇₁BM (1:2) thin films and external quantum efficiency spectra of corresponding devices; (right) Internal quantum efficiency spectra of SiIDT-BT:PC₇₁BM and SiIDT-2FBT:PC₇₁BM based devices estimated by correcting the EQE spectra with 1-T spectra.

The smaller short circuit of SiIDT-2FBT devices may be partially derived from its lower absorption since its fullerene loading is lower. The absorption spectra of SiIDT-BT:PC₇₁BM (1:3.5) and SiIDT-2FBT:PC₇₁BM (1:2) thin films are presented in figure 3.6 (left), normalised at 640 nm where the polymers primarily absorb. It can be clearly seen that SiIDT-2FBT:PC₇₁BM displays a poorer absorption at wavelengths below 550 nm, owing to the lower fullerene composition in the blend. To further analyse the short circuit current, the external quantum efficiency of SiIDT-BT and SiIDT-2FBT devices were measured and overlaid with the 1-Transmission spectrum of SiIDT-2FBT:PC₇₁BM blend, as shown in figure 3.6 (left). Internal quantum efficiency spectra (IQE) of the devices were estimated by correcting the EQE spectra with the 1-T spectra and shown in figure 3.6 (right). It is apparent that SiIDT:PC₇₁BM device exhibits stronger IQE at wavelength < 640 nm, compared with SiIDT-2FBT:PC₇₁BM. Integration of IQE spectra of SiIDT:PC₇₁BM is approximately twice as big as that of SiIDT:PC₇₁BM, qualitatively matching the trend in short circuit current. As such, it can be concluded that the stronger fullerene absorption in SiIDT-BT:PC₇₁BM (1:3.5) cannot account for the difference in the short circuit current. Rather, the difference in device performances appears to be derived from charge generation and collection indicative of the IQE spectra.

Other than the difference in absorption, UV-PESA measurements indicate that the two polymers have similar HOMO and LUMO levels, implying that the differences in photocurrent and open circuit voltage may not be due to differences in the energetics of the

two polymers. Therefore, it is expected that there could be differences in terms of morphology which potentially explain the changes observed in both J_{sc} and V_{oc} , as will be discussed in the following section.

Wide angle scattering X-ray

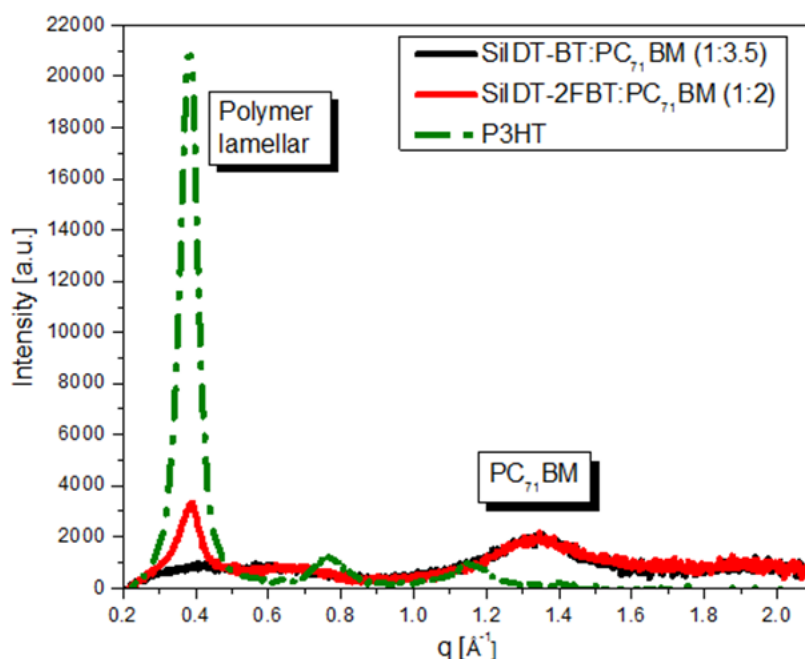


Figure 3.7 Wide angle X-ray scattering signals of SiIDT-BT:PC₇₁BM (1:3.5) and SiIDT-2FBT:PC₇₁BM (1:2) films prepared by drop-casting.

The neat polymers exhibit different degrees of crystallinity, as demonstrated by the WAXS data detailed in section 3.2 above. This technique was applied again to examine if differences in crystallinity can be preserved upon the presence of PC₇₁BM. As shown in figure 3.7, upon blending with PC₇₁BM, an additional peak is observed at $q \sim 1.3 \text{ \AA}^{-1}$ assigned to PC₇₁BM.³⁷ SiIDT-BT remains amorphous after blending while the lamellar stacking diffraction strength of Si-IDT-2FBT drops from 270 a.u. for the neat polymer films to 91 a.u. for the blend (table 3.3). Overall the SiIDT-2FBT is still more crystalline than SiIDT-BT after blending with PC₇₁BM. The WAXS data suggests that SiIDT-2FBT blend contains some polymer crystallites, which are likely to be free of fullerene.³⁸ Formation of polymer crystallites has been suggested to push fullerene into the rest of the film, promoting phase segregation.^{39, 40} This possibility is tested using atomic force microscopy, transmission electron microscopy and photoluminescence spectroscopy in the following sections.

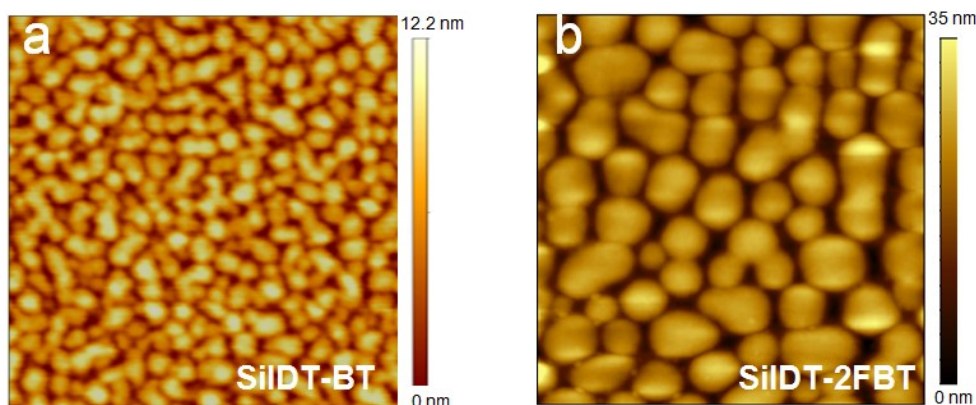


Figure 3.8: Topography images ($2\ \mu\text{m} \times 2\ \mu\text{m}$) of SiIDT-BT:PC₇₁BM (a) and SiIDT-2FBT:PC₇₁BM (b) measured by atomic force microscopy. [This image has been reproduced with the permission of the rights holder, Wiley-VCH²¹]

The blend morphology was studied using atomic force microscopy in tapping mode. From the topography images shown in Figure 3.8, clearly these two films have distinctly different morphologies. In SiIDT-BT:PC₇₁BM, a relatively fine blend microstructure can be seen from the topography images with phase segregation smaller than 50 nm. This is compared with the topography from SiIDT-2FBT which shows phase segregation on the scale of 50 nm–200 nm. It is apparent that the domain size is far greater than the diffusion length of excitons (5–10 nm for polymer exciton⁴¹ and 5 nm for fullerene exciton⁴²), especially for SiIDT-2FBT:PC₇₁BM. Therefore, poorer exciton quenching was expected in SiIDT-2FBT:PC₇₁BM, which was investigated further using photoluminescence spectroscopy below.

Photoluminescence

Photoluminescence (PL) spectroscopy was employed to estimate the exciton dissociation efficiency within these blend films. By comparing the signals obtained from a blend film with that from a neat film, the percentage of excitons that have undergone dissociation can be estimated. This provides us with information on the domain size compared with the exciton diffusion length and also on the upper limit of charge generation. For donor polymers, exciton diffusion lengths are typically measured to be between 5 and 10 nm,⁴¹ for PC₆₁BM, a diffusion length of 5 nm has been reported.⁴¹ In this experiment, the polymer or fullerene were excited selectively so that the polymer exciton or fullerene excitons can be investigated separately.

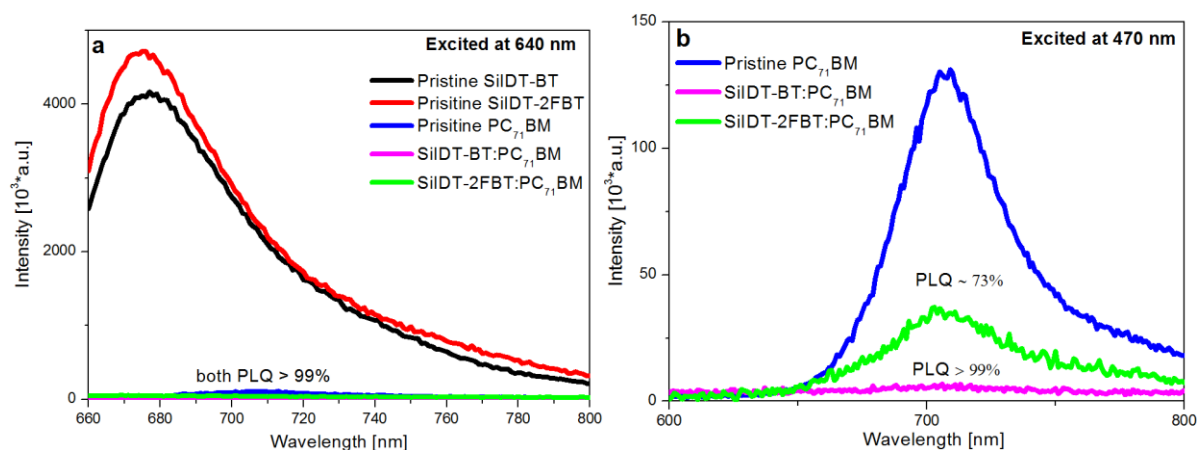


Figure 3.9: Photoluminescence of SiIDT-BT, SiIDT-2FBT, PC₇₁BM films, 1:3.5 SiIDT-BT:PC₇₁BM and 1:2 SiIDT-2FBT:PC₇₁BM thin films excited at 640 nm (a) or 470 nm (b). [This image has been reproduced with the permission of the rights holder, Wiley-VCH²¹]

As shown in figure 3.9, neat SiIDT-BT and SiIDT-2FBT both exhibit a broad PL peak at ~ 675 nm, which strongly overlaps with the emission from PC₇₁BM at ~ 707 nm.⁴³ The neat and blend samples were firstly excited at 640 nm in an attempt to selectively excite the polymers, with the photoluminescence spectra shown in figure 3.9 (a). It is apparent that emissions from both SiIDT-BT:PC₇₁BM and SiIDT-2FBT:PC₇₁BM blend films are weak in comparison to the neat polymer emission, showing more than 99% photoluminescence quenching (PLQ). Such high PLQ suggests most polymer in the blend is intimately mixed with fullerenes on a lengthscale of ~ 1.0 nm (calculated using $L = L_{\text{ex}}(1-\text{PLQ})^{1/2}$ as outlined in Chapter 2 and assuming polymer exciton diffusion length of 10 nm) and therefore leading to a high efficiency of polymer exciton dissociation.⁴⁴

The experiment was repeated by exciting the fullerene at 470 nm, which is a minimum in polymer absorption. As shown in figure 3.9 (b), SiIDT-BT:PC₇₁BM once again displays a high PLQ ($> 99\%$), indicative of fine mixing feature of blend microstructure on the 0.5 nm lengthscale (assuming PC₇₁BM exciton diffusion length of 5 nm). On the other hand, SiIDT-BT:PC₇₁BM is found to exhibit a pronounced peak at 707 nm. Such emission is most likely to primarily comprise of fullerene photoluminescence, since the polymer PLQ in this system is more than 99%. As such, comparing this photoluminescence with neat fullerene photoluminescence results in a 73% PLQ ($L \sim 2.6$ nm), suggesting 27% loss in efficiency of fullerene exciton dissociation. The relatively poor fullerene exciton dissociation is indicative of a significant fraction of the PCBM in the film being in domains larger than the PCBM exciton diffusion length (5 nm).^{42, 45, 46} This interpretation is in agreement with the results

obtained from AFM data shown previously which show larger domains for SiIDT-2FBT:PC₇₁BM than for SiIDT-BT:PC₇₁BM. In addition, note that the phase segregation on the scale of 50-200 nm by AFM for SiIDT-2FBT:PC₇₁BM is substantially longer than the fullerene exciton diffusion length. The observation of significant (73%) fullerene PLQ, and efficient polymer PLQ, even for this blend, suggests that the domains observed in AFM images are likely not to be chemically pure polymer and pure fullerene, but rather include some degree of molecular mixing.^{39, 44, 47}

Transient absorption spectroscopy

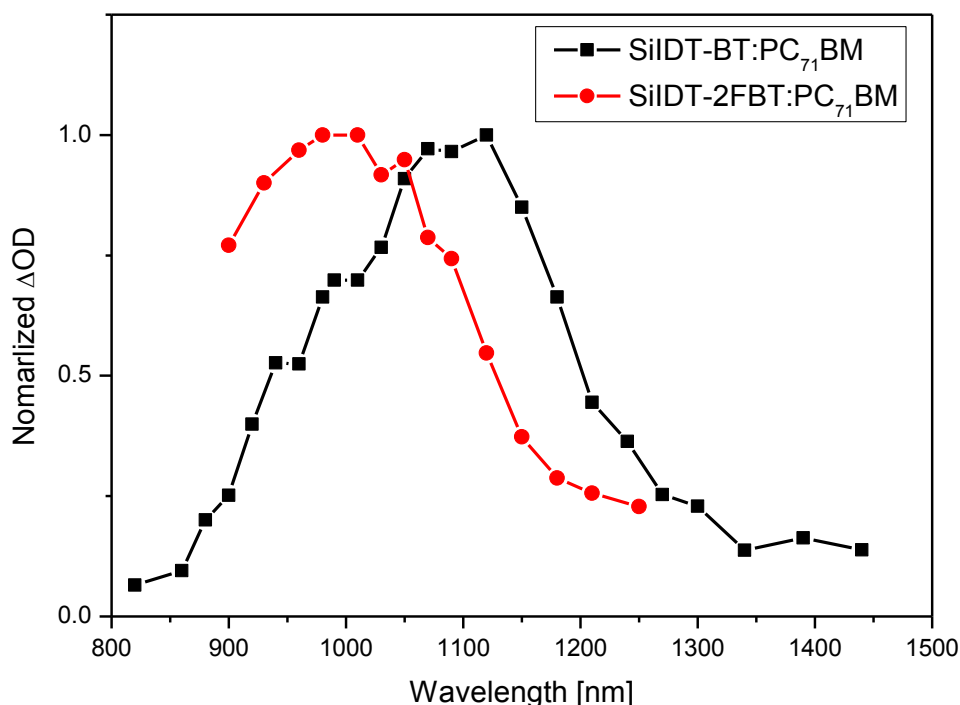


Figure 3.10: Transient data collected from SiIDT-BT:PC₇₁BM (1:3.5) and SiIDT-2FBT:PC₇₁BM (1:2) films with various probing wavelength. The signals were determined at 1 μs following excitation at 640 nm with an excitation intensity of 11 μJcm⁻² under a nitrogen atmosphere.

To further explore the difference in device performance, transient absorption spectroscopy was applied to assess the charge generation from these blends. Figure 3.10 shows the signal amplitude at 1 μs as a function of probe wavelength for SiIDT-BT:PC₇₁BM (black) and SiIDT-2FBT:PC₇₁BM (red) blends. It can be seen that the absorption of SiIDT-BT:PC₇₁BM covers from 800 nm to 1300 nm with a peak at 1100 nm. This peak can be assigned to SiIDT-

BT^{•+} polaron. After fluorination, the spectrum is slightly blue shifted and peaked at 980 nm, assigned to SiIDT-2FBT^{•+}.

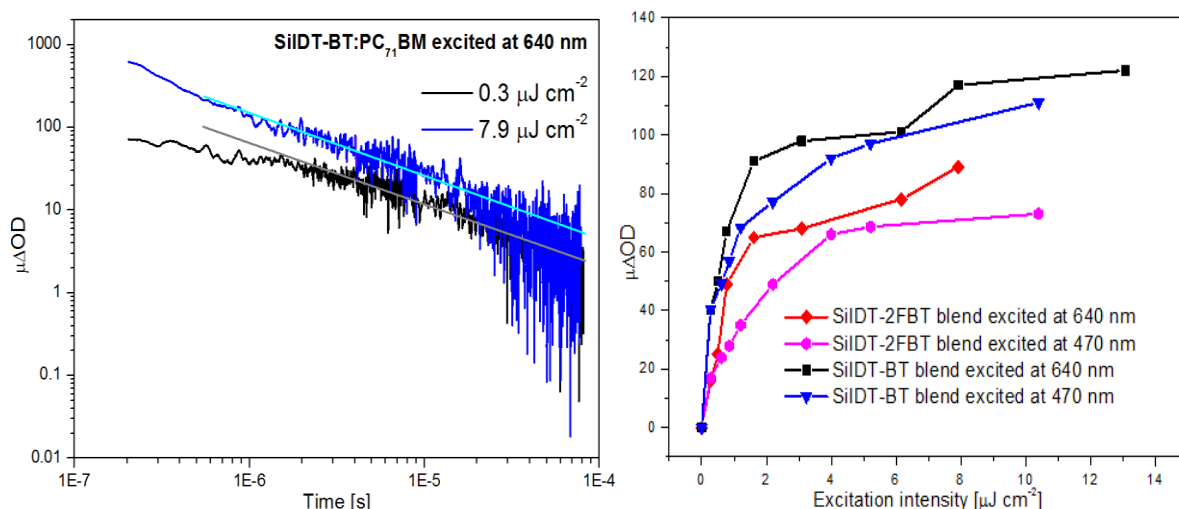


Figure 3.11: (left) Transient decay kinetics obtained from SiIDT-BT:PC₇₁BM (1:3.5) by exciting at 640 nm and probing at 1050 nm with excitation intensity of 0.3 μJcm^{-2} (black) and 7.9 μJcm^{-2} (blue) respectively; (right) The plots of decay amplitude at 1 μs versus excitation intensity obtained from SiIDT-BT:PC₇₁BM (1:3.5) and SiIDT-2FBT:PC₇₁BM (1:2) by exciting at 640 nm or 470 nm and probing at 1050 nm.

Figure 3.11(left) shows the transient decay of SiIDT-BT:PC₇₁BM sample probing at 1050 nm excited at 640 nm with two different excitation intensities. 1050 nm corresponds to the wavelength at which the two normalised polaron absorption band have similar intensities, so facilitating comparison of signal intensities between the two polarons. The decay at 7.9 μJcm^{-2} can be fit to power law of $\Delta\text{OD} \sim t^{-\alpha}$ with $\alpha = 0.74$, corresponding to a linear decay on the log/log plot. This is consistent with bimolecular recombination kinetics in the presence of charge trapping, which typically are observed on this timescale.⁴⁸ As the excitation intensity is lowered to 0.3 μJcm^{-2} , a plateau appears around ~0.7 to 1 microsecond, which deviates from the linear fitting shown, consistent with bimolecular recombination kinetics. A similar plateau is also observed in the SiIDT-2FBT:PC₇₁BM sample. As such, the amplitude at 1 microsecond of the decays from these samples could be assigned to the yield of polymer polarons. The presence of bimolecular recombination can be further evidenced by plotting the amplitude of decay at 1 microsecond with various excitation intensities, as displayed in figure 3.11 (right). It can be seen that all the four dependencies exhibit a biphasic trend, with the amplitudes being roughly linear with excitation intensity up to 0.8 μJcm^{-2} and then start to saturate with further increase in excitation intensity. The biphasic trend has also been

reported previously in other polymer systems, and is also characteristic of bimolecular recombination in the presence of charge trapping.⁴⁹

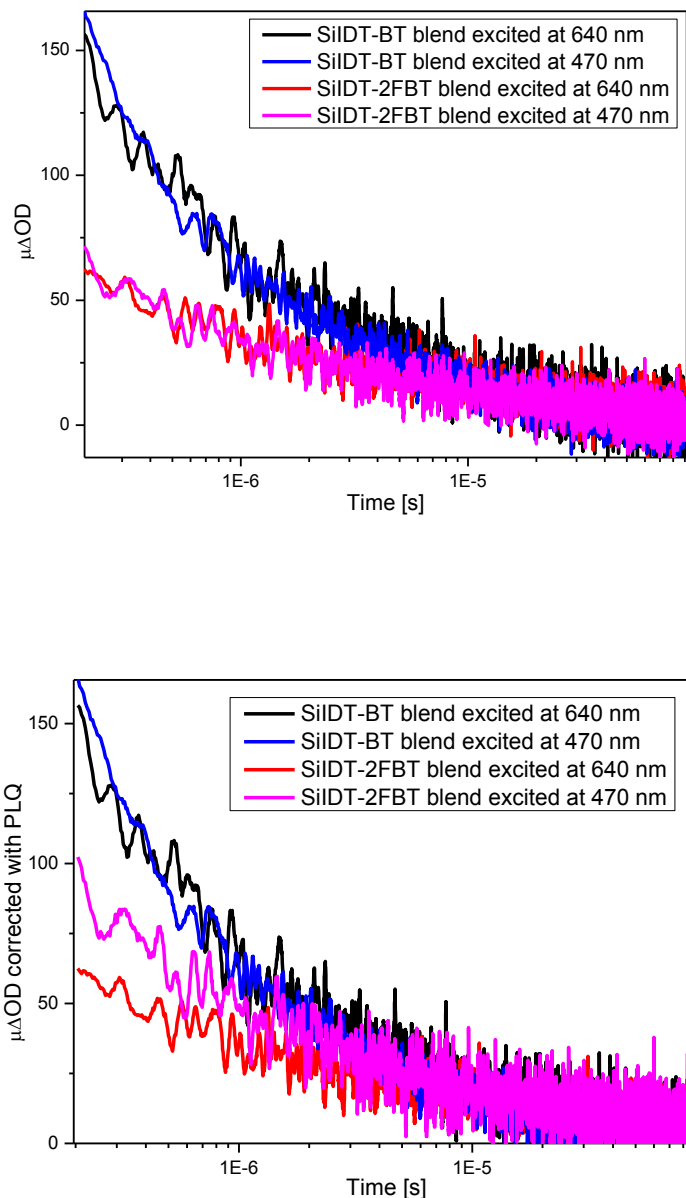


Figure 3.12: (Top) Transient decay kinetics obtained from SiIDT-BT:PC₇₁BM (1:3.5) SiIDT-2FBT:PC₇₁BM (1:2) probing at 1050 nm by exciting at 640 nm with excitation intensity of $0.5 \mu\text{Jcm}^{-2}$ or exciting at 470 nm with excitation intensity of $0.9 \mu\text{Jcm}^{-2}$; These data have been corrected to normalise for differences in the density of absorbed photons. (bottom) these decays were further corrected with PLQ. All the decays were corrected for blend absorption and number of incident photons.

Polymer	ΔOD (1 μs) excited at 640 nm	ΔOD (1 μs) excited at 470 nm	Driving energy for e-transfer [eV]	Driving energy for h-transfer [eV]
SiIDT-BT	73×10^{-6}	68×10^{-6}	0.6	0.7
SiIDT-2FBT	33×10^{-6}	47×10^{-6}	0.6	0.7

Table 3.4: The yield of polaron extracted at 1 μs from figure 3.12 (estimated by fitting the decays to power law of $\Delta OD \sim t^{-\alpha}$, followed by extracting the amplitudes at 1 μs of the fits); (bottom) and the associated driving energy for charge separation. For estimating the driving energy, the energy levels for PC₇₁BM was used from ref.^{50, 51}

To assay the yield of polaron formation of the two blends induced by polymer absorption and fullerene absorption, four decays obtained from these two blends by exciting at 640 and 470 nm respectively, as presented in figure 3.12 (top). These decays have been corrected by blend absorption and the number of incident photons, with the later taking the difference in number of photon at different excitation wavelength into account.⁴³ In each blends, the decay excited at 640 nm is similar to that at 470 nm, suggesting the decay dynamics of polarons formed by polymer absorption is comparable to those formed by fullerene absorption. Both decays obtained from SiIDT-BT samples display stronger signals than the two from SiIDT-2FBT, with the amplitude at 1 μs of SiIDT-BT being approximately 2-fold bigger than that of SiIDT-2FBT (estimated by fitting the decays to power law of $\Delta OD \sim t^{-\alpha}$, followed by extracting the amplitudes at 1 μs of the fits). This is qualitatively consistent with the trend in the short circuit current, indicating the loss in device performance for SiIDT-2FBT is, at least partially, due to the reduced yield of polaron formation.

The stonger amplitude of SiIDT-BT indicates an increase in yield of long-lived polymer polarons, which could be due to the difference in efficiency of exciton quenching or driving energy for charge separation.⁴⁸ To futher explore this, the four decays were corrected with the PLQ obtained previously and are shown in figure 3.12 (bottom). After correcting with PLQ, the signals obtained from SiIDT-2FBT by exciting the fullerene is improved, closing the gap between the yields of polaron in these two systems. This suggest that the severer phase segregation of SiIDT-2FBT:PC₇₁BM is one of the reasons for the poor polaron formation in this system. However, overall the signals obtained from SiIDT-BT are still stronger than those from SiIDT-2FBT. The difference in polaron formation between these systems is unlikely to be due to difference in energetics, as the estimated driving energy for charge separation is similar in both cases (table 3.4). Recently, Yu and co-workers have reported a

correlation between charge separation and dipole moment of exciton. As such, it is speculated that fluorination of SiIDT-BT changes the dipole moment in a way that disfavours the charge separation, and thereby giving rise to poor amplitude for SiIDT-2FBT. In addition, note that the amplitude of the decays induced by fullerene absorption in SiIDT-2FBT is better than that from polymer absorption. This is potentially due to a better driving energy for the hole transfer (table 3.4) as well as potentially different nature of fullerene excitons.³⁶ The latter is discussed in more details in Chapter 4.

3.3.3 Fluorination effects on SiIDT-DTBT

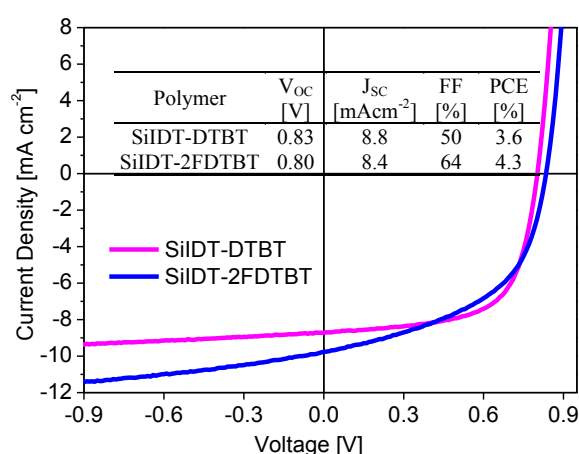


Figure 3.13: J-V curves of the devices made by SiIDT-DTBT:PC₇₁BM (1:3.5) and SiIDT-2FDTBT:PC₇₁BM (1:3.5) respectively. The insert shows the device parameters for the two polymers.

The device architecture and fabrication procedure for SiIDT-DTBT was the same as that for SiIDT-BT polymers, with a blend ratio of 1:3.5 (polymer:PC₇₁BM). As shown in figure 3.13, the SiIDT-DTBT:PC₇₁BM blend solar cell shows a PCE of 3.6% ($\pm 0.1\%$). After fluorination, despite a slight decrease in the short circuit current and open circuit voltage, the PCE is increased to 4.3% ($\pm 0.2\%$) primarily because of the improvement in the fill factor. To investigate the fluorination further, atomic force microscopy was once again employed to investigate their blend morphology.

As shown in figure 3.14 (a and b), SiIDT-DTBT shows a similar trend in terms of phase segregation to SiIDT-BT upon fluorination. Specifically, SiIDT-DTBT:PC₇₁BM has a phase segregation on the scale of approximately 50 nm compared to that in SiIDT-2FDTBT blend which is on the scale of more than 200 nm. However, the domains in topography appear to be less defined than those for SiIDT-BT & SiIDT-2FBT. To further confirm this observation,

transmission electron microscopy was employed to assess the morphology of SiIDT-2FBT:PC₇₁BM and SiIDT-2FDTBT:PC₇₁BM blends. In this measurement, iodine was used as a stainer which has been suggested to be preferentially absorbed by one component over the other in a binary system,⁵² yielding the darker areas in the TEM images. As shown in figure 3.14 (c and d), the TEM images of both SiIDT-2FBT:PC₇₁BM and SiIDT-2FDTBT:PC₇₁BM display some dark regions with similar domain sizes to those observed in the AFM measurements. Since the fullerene exciton quenching in SiIDT-2FBT:PC₇₁BM is lower than the polymer exciton quenching, the dark regions in the TEM images are assigned to fullerene rich regions. It can be seen that the domain contrast for SiIDT-2FDTBT is much less clear than that for SiIDT-2FBT, implying the domains are likely to be more impure, with more mixing of polymer and fullerene. The presence of intimately mixed polymer and fullerene has been observed for several other donor polymers exhibiting high device efficiencies, and could be the reason for the positive effect of fluorination on SiIDT-DTBT compared to SiIDT-BT.^{44, 53, 54} In addition, the better performance offered by fluorination for SiIDT-DTBT could also be due to enhancement in out-of-plane π - π stacking. Indeed, efficient performance of a couple of polymer based devices has been attributed to the presence of such polymer arrangement in the active layer.^{20, 55, 56}

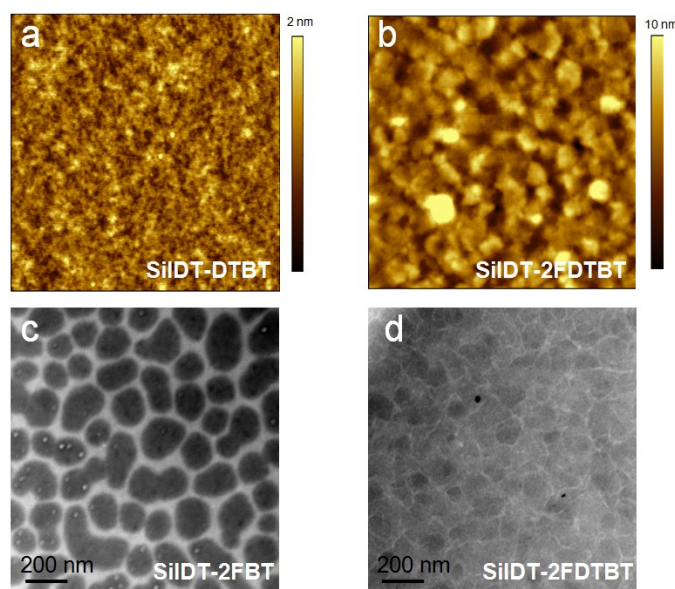


Figure 3.14: (Top row) Topography images (2 $\mu\text{m} \times 2 \mu\text{m}$) of SiIDT-DTBT:PC₇₁BM (a) and SiIDT-2FBT:PC₇₁BM (b) measured by atomic force microscopy. (Bottom row) TEM images of SiIDT-2FBT:PC₇₁BM (c) and SiIDT-2FDTBT:PC₇₁BM (d). The samples for TEM measurement was stained using iodine vapour prior to the measurement. [This image has been reproduced with the permission of the rights holder, Wiley-VCH²¹]

3.4 Discussion

Based on the results presented in the last section, two pairs of polymers have been used to demonstrate that the effects of fluorination on blend morphology and device performance vary from system to system. In both cases, it has been observed that fluorine introduction could lead to improvement in polymer packing, phase segregation in blend morphology but that the impacts on device performance are different.

In the neat polymer samples, fluorination was found to considerably improve the degree of crystallinity for both SiIDT-BT and SiIDT-DTBT. This improvement is consistent with the properties of fluorination which has been well known traditionally – it can potentially alter the charge density distribution within the molecule and potentially lead to better crystallinity.¹ Similar observations have also been reported in some of other conjugated polymers in the literature.^{13, 24, 28} In our case, fluorination appears to reduce the thermal barrier to facilitate the polymers adopting their preferential spatial arrangement. Our WAXS measurements suggest these two polymers tend to adopt different arrangements, with SiIDT-BT preferring out-of-plane lamellar packing over π - π stacking and SiIDT-DTBT preferring the opposite way. This is potentially associated with the additional thiophene units present in SiIDT-DTBT backbone,^{30, 31} which reduces the steric hindrance between the IDT and BT units. This should in turn offer a better planarity for the SiIDT-DTBT backbone and hence encourage the backbone to adopt π - π stacking. This interpretation is also supported by the smaller d-spacing of π - π stacking for SiIDT-DTBT backbone, implying the better planarity allows adjacent polymers to interact with each other at a closer distance.

Upon blending with fullerenes, it has been shown that fluorination consistently promotes phase segregation for both polymer backbones. This is likely due to the higher volume % of crystals for the fluorinated polymers which disfavours the mixing with fullerene molecules.^{39, 40} However, despite having very similar phase segregation, SiIDT-2FDTBT appears to have less defined domain as demonstrated by TEM. This implies that the domains observed in SiIDT-2FDTBT are probably relatively impure, with polymer and fullerene being intimately mixed on a much smaller scale. The ability of the polymer to intimately mix with fullerene potentially compensates the phase segregation induced by fluorination. While phase segregation was reported to be governed by several parameters such as polymer crystallinity⁴⁰, intrinsic polymer:fullerene miscibility³⁹ and fabrication condition⁵⁷, one plausible reason for the better mixing of SiIDT-2FDTBT is its potential better ability to intercalate fullerene. This

refers to the capability of a polymer to accommodate the fullerene between the side chains to allow polymer and fullerene mixed on molecular level.^{58, 59} This ability has been suggested to depend on polymer:fullerene interaction as well as the available space between the side chains for intercalation.⁶⁰ With the two additional thiophene units present in SiIDT-DTBT in comparison to SiIDT-BT, in principle the larger space between side chains should offer a better ability for SiIDT-DTBT to intercalate fullerene and hence a more finely mixed feature.

Lastly in terms of device performance, the effect of fluorination on open circuit voltage is minimal in comparison to the reduction in short circuit current for SiIDT-BT or to the improvement in fill factor for SiIDT-DTBT. For SiIDT-DTBT, the better device performance is attributed to the less severe phase segregation and the improved out-of-plane π - π stacking after fluorination. In the case of SiIDT-BT, the devices exhibit an approximately 60% loss in the short circuit current upon fluorination. This appears to be, at least in part, due to the weaker absorption of the fullerene in SiIDT-2FBT:PC₇₁BM thin film, since the fullerene loading was low. On the other hand, our TAS measurements show a poorer polaron formation comparing SiIDT-2FBT:PC₇₁BM with SiIDT-BT:PC₇₁BM, indicating a lower yield of long-lived polaron in this system. This is unlikely to be due to difference in driving energy for charge separation, as both SiIDT-BT and SiIDT-2FBT have similar HOMO and LUMO. While it has been shown that this should partially be derived from the severe phase segregation of SiIDT-2FBT:PC₇₁BM blend, a potential change in dipole moment of polymer exciton could also account for the loss in the yield of long-lived polaron upon fluorination. It has also been reported that an exciton with higher polarity could lower the energy requirement to overcome coulombic attraction associated with the charge transfer state, and therefore be beneficial for charge separation.²⁶ Several studies have shown that replacing hydrogen with fluorine, which is the most electronegative element, could alter the polarity of the polymer exciton.^{25, 35} However, a change in polarity is difficult to predict as it seems to depend on a number of parameters such as original backbone polarity, the number of added fluorine atoms and the position of fluorination.²⁵ Based on these studies, it is speculated that fluorination of SiIDT-BT potentially changes the polymer exciton polarity in a way that disfavours the charge separation, and hence gave rise to a lower yield of long-lived polaron. This hypothesis requires further experiments to verify. In addition to polaron formation, SiIDT-2FBT was reported to have a lower mobility than SiIDT-BT measured in an organic field-effect transistor configuration,²¹ which could also account for the poorer current observed in SiIDT-2FBT devices.

3.5 Conclusions

Introduction of fluorine has been shown to have different effects on device performance, with a negative effect for SiIDT-BT and a positive effect for SiIDT-DTBT. In both cases, adding fluorine can increase polymer crystallinity and promote blend phase segregation, but the subsequent impact on device performance seems to also depend on the nature of the polymer backbone. The positive effect of adding fluorine on SiIDT-DTBT is potentially due to the additional thiophene units. Firstly, they offer better planarity to encourage the polymer to adopt out-of-plane π - π stacking, favouring charge transportation. Secondly, the larger space between polymer side chains with the presence of thiophene could potentially result in better polymer:fullerene mixing, compensating the demixing caused by fluorination. Note that the change in morphology for SiIDT-BT upon fluorination could not fully explain the difference in device performance. This appears to be associated with a potential change in polymer polarity after adding fluorine, which requires further research effort to verify.

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Chapter 4

The effect of alkyl side chains on the performance of poly(thienothiophene vinylene)based solar cells

Abstract

In this chapter, two different alkyl side chains, attached to two poly(thienothiophene vinylene) polymers, are compared (namely linear vs. branched) in terms of their impact on the active layer's morphology, as well as photovoltaic device performance. It is found that poly(thienothiophene vinylene) with a linear side chain (C16-PTTV) offers a better PCE as a result of a higher short circuit current compared to the branched version (C2C6-PTTV). Photoluminescence studies show that both the polymer exciton quenching and fullerene exciton quenching are more efficient in C16-PTTV, suggesting a finer mixing of the active layer's morphology. This higher degree of mixing gives rise to a better charge carrier formation particularly from fullerene exciton, as confirmed using transient absorption spectroscopy. The better mixing of C16-PTTV and PC₇₁BM is potentially due to the linear side chain, which is better at accommodating fullerene molecules, in comparison to the branched side chain.

4.1 Introduction

Alkyl side chains attached to a polymer can be modified in order to adjust the power conversion efficiency of polymer solar cells. Originally, alkyl side chains were added to polymer semiconductors as solubilising groups in order to make the material solution-processable.¹⁻³ Polythiophene, a bench mark material for polymer solar cells, was reported to follow this trend.^{4, 5} As the electronegativity of alkyl side chain is rather neutral, the impact of side chain on device performance was assumed to be negligible.⁶⁻⁸ However, this assumption has been shown to be incorrect, with increasing research finding that a range of polymer properties which can influence device performance, including mobility, glass transition temperature, and photoluminescence, all of which depend on the side chain attached to a polymer.^{4, 5, 9-13}

There is a considerable amount of evidence showing that side chains attached to the polymer backbone can impact upon the miscibility of polymers and fullerenes^{4, 11, 14-18}, which can subsequently impact upon photocurrent generation. However, effects of side chain on polymer:fullerene miscibility appear to be rather complicated and vary from study to study, as they have been shown to depend upon a number of parameters including chain length, branching point, side chain position and polymer backbone structure. Recent novel donor materials (e.g. PTB7) generally have complex chemical structure in comparison to the conventional polymers (e.g. P3AT), making the effect of side chains more complicated to analyse.¹⁷ The following paragraphs focus on the effects of side chain by tuning the length and shape (branched vs linear).

Fullerenes can mix with polymers by fullerene intercalation¹⁹ or by simply dispersing in the polymer matrix.¹⁹⁻²¹ In the former case, fullerene intercalation refers to accommodating fullerene molecules between the side chains attached to a polymer, resulting in a molecular separation between polymer and fullerenes.¹⁹ Some semicrystalline polymers can intercalate fullerene, forming a co-crystal structure with an increase in the d-spacing of polymer lamellar stacking that can be probed by X-ray diffraction.^{19, 22-24} Fullerene intercalation can also occur in amorphous polymers blends, but the associated structures are more difficult to analyse.^{19, 25, 26} Previous studies suggest that the ability of a polymer to intercalate fullerene depends on the available space between side chains, as demonstrated by a comparative study between PC₇₁BM and bisPC₇₁BM shown in figure 1.7.²⁴ In terms of shape of side chains, previous studies also suggest that linear alkyl side chains generally tend to intercalate fullerene

molecule better than bulky, branched side chain, since the linear side chain provides more space to accommodate the fullerene molecules.¹⁹ In this regard, polymers with linear side chains should be more miscible with fullerene in comparison to branched side chains.

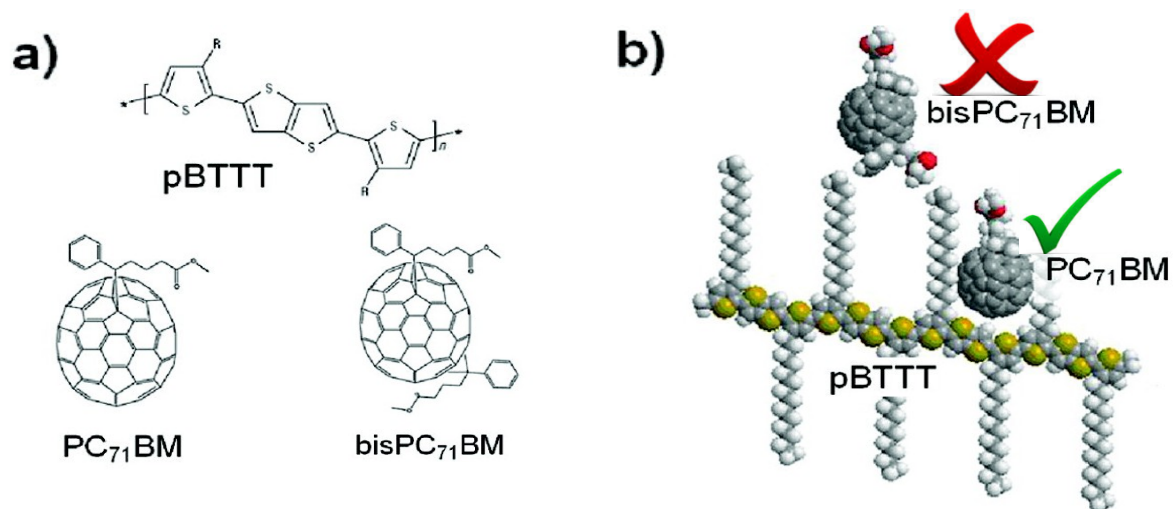


Figure 4.1: The concept of fullerene intercalation in a polymer matrix using pBTTT:PC₇₁BM and pBTTT:bisPC₇₁BM systems as examples. (a) Chemical structures of pBTTT, PC₇₁BM and bisPC₇₁BM. (b) Demonstrate that pBTTT can only intercalate PC₇₁BM but not bisPC₇₁BM because of the bulkier size bisPC₇₁BM has. [This image has been reproduced with the permission of the rights holder, American Chemical Society²⁴]

On the other hand, fullerenes can mix with polymers by simple dispersion in the polymer matrix.^{20, 21, 27, 28} There are several studies investigating the correlation between polymer side chain and phase segregation.^{4, 11, 14-18} For example, there are studies considering the correlation between domain size and torsion energy given by different side chains.¹⁸ Long or branched side chain was found to give higher torsion energies in comparison to short linear side chains, resulting in a more rigid polymer matrix; that has been suggested to promote phase segregation. A study given by Ngugen and co-workers showed that P3AT with longer linear side chain could promote phase segregation by enabling faster fullerene diffusion through the polymer matrix.¹⁵ Other studies have suggested that side chains can have an impact on the relative solubility between polymer and fullerene and thereby on phase segregation.^{16, 29} Last but not least, a number of studies reported that tuning side chain can change polymer crystallinity,^{4, 30, 31} which should in turn lead to different phase segregation³² as discussed in Chapter 3.

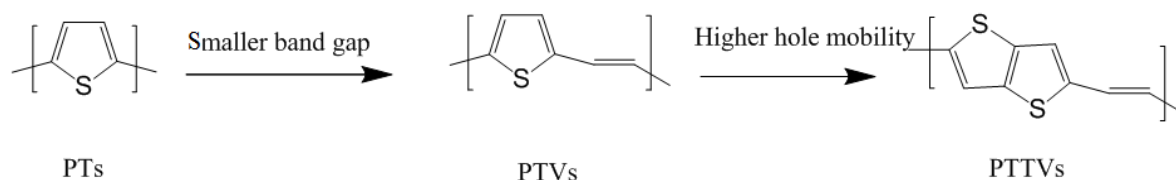


Figure 4.2: Chemical structure design of poly(thienothiophene vinylene)

Charge separation from PC_{71}BM exciton has been reported to be an efficient process in some polymer systems.^{33, 34} However, it has been reported that dissociation of fullerene exciton can be less efficient in comparison to polymer excitons, limiting its contribution to device photocurrent.³⁵⁻⁴⁰ This is likely to be a blend microstructure issue,^{34, 37} since fullerenes tend to aggregate forming large domains.^{35, 41} In this chapter, the impact of polymer side chain upon blend microstructure is investigated in an attempt to address the issue of relatively less efficient dissociation of fullerene excitons. Two poly(thienothiophene vinylenes) PTTV polymers with different side chains were used. The PTTV backbone was designed based on the structure of P3HT. (figure 4.2) The additional double bond and thiophene unit were added to P3HT backbone, which was reported to lower the bandgap and ensure a reasonable hole mobility for the polymers.^{42, 43} Charge generation from polymer excitons and fullerene absorption is measured using transient absorption spectroscopy, while information on polymer:fullerene microstructure is obtained by employing photoluminescence spectroscopy. The data are analysed to correlate charge generation from polymer and fullerene absorption respectively with blend microstructure.

4.2 Experimental

Materials - C2C6-PTTV and C16-PTTV were synthesised by Dr. Koroma from Dr. Martin Heeney's group, with the details of synthesis included in ref⁴⁴. ~20 mg was obtained for each polymers but the majority amount of the materials was used to optimise device performance, leaving ~6 mg available for further analysis and measurement.

Sample preparation - The samples for UV/visible, PL and TAS measurements were prepared using spin casting approach. The blend solutions had an overall concentration of 30 mg ml⁻¹ with a blend ratio ranging from 1:1 to 1:4 (polymer:PC₇₁BM) in dichlorobenzene solvent. All the solutions were stirred in nitrogen on a hotplate at 150 °C overnight before spin casting to allow the polymers to fully dissolve in the solvent. Prior to spin casting, the substrates were kept at 150 °C on a hotplate. Dynamic spin casting was used in which the solution deposition was performed while the substrates were spinning.

For WAXS measurement, samples of the neat polymers were prepared using drop casting approach resulting in relatively thick films. ~0.30 ml of solutions with a concentration of 10 mg/ml were poured onto 2 x 1 cm² glass substrates and allowed to dry at room temperature overnight.

Transient absorption spectroscopy - The experiment was carried out using the same samples from photoluminescence experiment. Excitations at 410 nm and 640 nm were used for selective fullerene and polymers excitation respectively. Probe wavelength 980 nm was used for both polymers.⁴⁵

Device fabrication - The devices for this study have a conventional structure of ITO/PEDOT:PSS/polymer:PC₇₁BM/Ca/Al. The general procedure of device fabrication is described in Chapter 2. The active layers were prepared using the same approach as those for TAS and photoluminescence experiments. J-V curve measurement was done using the light source which simulates 1 sun AM 1.5, as also described in Chapter 2. Both polymers were difficult to dissolve in most common organic solvent for OPV device fabrication. Most of materials were used to find out a correct procedure to ensure an optimised and reproducible device performance. This resulted in lack of materials for later analysis and measurements.

4.3 Results

4.3.1 Fundamental material properties

In this chapter, the effects of side chains attached to PTTV upon polymer:PC₇₁BM blend microstructure and charge generation are investigated. The polymers (C16-PTTV and C2C6-PTTV) used for this chapter have a PTTV backbone with two different alkyl side chains (see Chapter 2 for the chemical structure). The ground state absorption spectra - taken on neat thin films of C16-PTTV and C2C6-PTTV prepared from spin casting onto glass substrate - are shown in Figure 4.3.

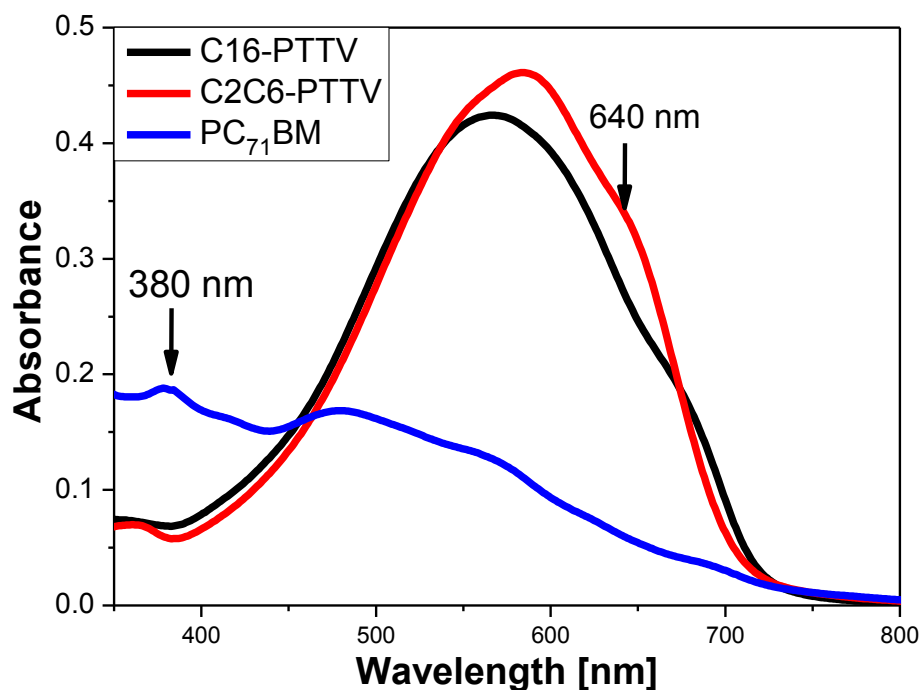


Figure 4.3: 380 nm and 640 nm are highlighted wavelength used to excite fullerene and polymer selectively respectively for photoluminescence experiment. Neat glass was used as the reference for these measurements.

Polymer	HOMO [eV] ^{a)}	LUMO [eV] ^{a)}	Bandgap [eV]	M _n [kDa] ^{b)}	Abs onset [nm]
C16-PTTV	-5.1	-3.3	1.8	16	701
C2C6-PTTV	-5.1	-3.3	1.8	16.3	707
PC ₇₁ BM ^{c)}	-6.1	-4.2	1.9	-	-

Table 4.1: Energy levels and molecular weights of C16-PTTV and C2C6-PTTV. a) Energy levels of the HOMOs were determined using cyclic voltammetry while LUMOs were estimated by adding polymer absorption onsets to the HOMOs. b) Measured using gel permeation chromatography. Polystyrene was used as the standard while chlorobenzene was used as the solvent. c) Energy levels for PC₇₁BM are taken from ref⁴⁶, assuming it is the same as PC₆₁BM.

Table 4.1 shows the material properties of these two polymers, including their energy levels, molecular weights and onsets of their ground state absorption. C16-PTTV and C2C6-PTTV have molecular weights of 16 kDa and 16.3 kDa respectively which are comparable to each other. The energy levels of the HOMOs were measured using cyclic voltammetry by Dr. Koroma from Dr. Martin Heeney's group while the LUMOs were estimated using the onsets of UV/visible absorption. It can be seen that these two polymers have very similar HOMO and optical bandgap of 1.8 eV, leading to a similar LUMO. The bandgaps are smaller than the bandgap (1.9 eV taken from literature)⁴⁷ of P3HT, matching well the prediction from the chemical structure design.^{42, 43}

Material crystallinity (Wide angle X-ray scattering)

In previous studies on pBTTT (figure 4.1) by McGehee and co-workers, X-ray diffraction was employed to investigate the existence of PC₇₁BM intercalations.^{19, 24, 25} It has been reported that intercalating PC₇₁BM by alkyl side chain of pBTTT increases the separation of pBTTT backbone in a lamellar packing arrangement, leading to a shift in the position of the polymer lamellar peak.¹⁹ Such an approach requires a higher degree of polymer crystallinity. However, both of the polymers studied in this chapter are rather amorphous, as demonstrated by WAXS data. As shown in figure 4.3, P3HT displays a relatively high diffraction strength of lamellar packing, consistent with this polymer exhibiting a high degree of crystallinity. In contrast, it is apparent that both C16-PTTV and C2C6-PTTV have a rather amorphous nature, indicated by their weak diffraction strength of their lamellar packing. C2C6-PTTV displays a broad lamellar peak at $q \sim 0.42 \text{ \AA}^{-1}$ (d-spacing $\sim 14.7 \text{ \AA}$), while the lamellar peak of C16-PTTV is slightly stronger and appears at a smaller angle at $q \sim 0.22 \text{ \AA}^{-1}$ (d-spacing $\sim 28.5 \text{ \AA}$),

consistent with its longer side chain. The amorphous nature exhibited by both of the polymers suggests the absence of polymer:fullerene ‘co-crystal’ in either of the blend films.^{19, 25}

The correlations between alkyl side chains and energy levels have been interpreted in terms of side chain influences on polymer crystallinity and backbone planarity, leading to changes in energy levels.^{4, 30, 31} As demonstrated in table 4.1, both polymers have similar optical bandgaps and HOMOs energy levels, which is consistent with the similar amorphous nature of the two PTTV polymers. The similar bandgaps are also in agreement with predicted similar electron-donating ability of the two alkyl side chains.

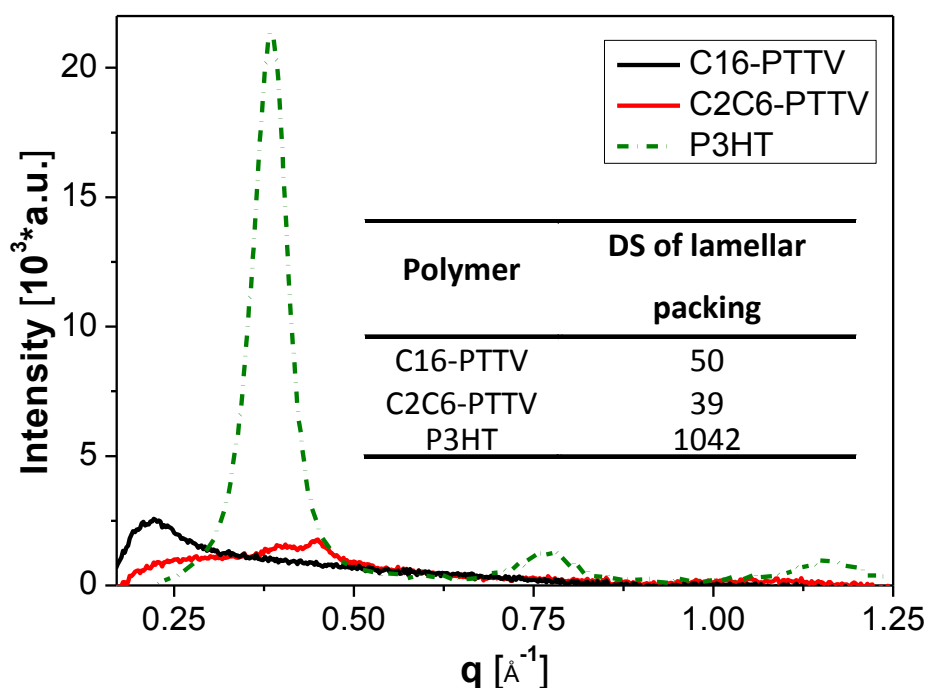


Figure 4.4: Wide angle X-ray scattering signals of C16-PTTV, C2C6-PTTV and P3HT from their drop-cast neat films. Inserted table shows diffraction strength (DS) of lamellar packing estimated by the area of lamellar peaks corrected with film thickness. The signals displayed have been corrected using the signals of the substrate.

4.3.2 Blend ratio optimisation for device performance

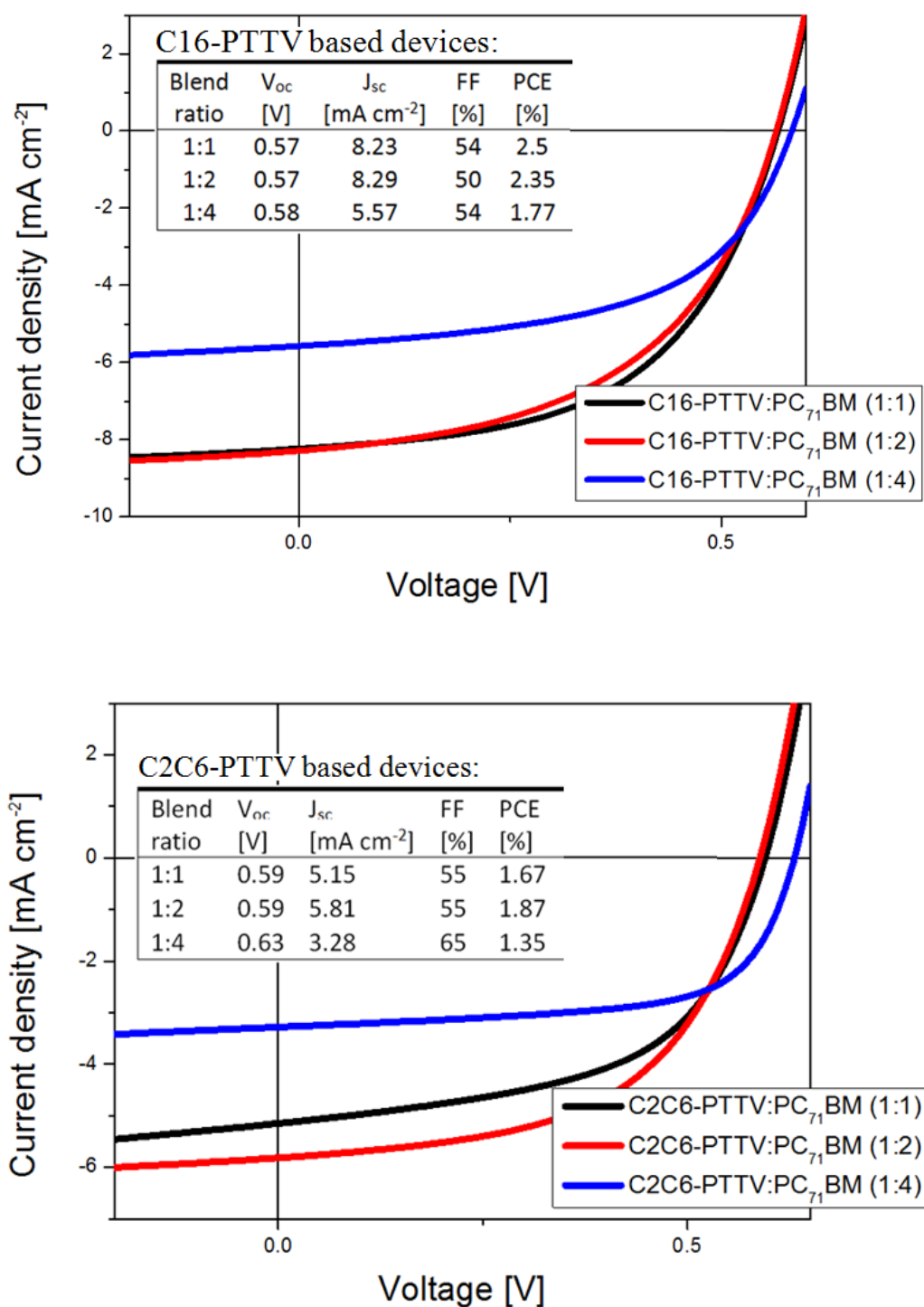


Figure 4.5: J-V curves of C16-PTTV (top) and C2C6-PTTV (bottom) based devices as a function of blend ratio. The inserted tables show the device parameters for different blend ratio.

A composition study on device fabrication was carried out in order to determine a procedure for optimised device performance. The details of device fabrication are described in 4.2. It is worth noting that both polymers were quite insoluble in most common organic solvents. C16-PTTV was only fully dissolved in DCB by heating the solution at 150 °C overnight, while C2C6-PTTV appeared to be slightly more soluble as it only required 100 °C of thermal heating.

The J-V curves and device parameters with varied blend ratio are presented in figure 4.5. In the case of C16-PTTV based devices, there is a decrease in PCE as the fullerene loading is increased. The PCE drops from 2.5 % to 2.35 % as the blend ratio is changed from 1:1 to 1:2 (polymer:PC₇₁BM), followed by a more rapid drop to 1.77 % as the blend ratio reaches 1:4. The short circuit current also exhibits a considerable decrease as the blend ratio switched from 1:2 to 1:4, resembling the rapid loss in PCE. On the other hand, the changes in open circuit voltage as well as fill factor are relatively small and therefore less influential to the changes in PCE.

In the case of C2C6-PTTV, the PCE starts at 1.67 % at 1:1 (polymer:fullerene) blend ratio and peaks to 1.87% when the blend ratio reaches 1:2. Similar to C16-PTTV, the lowest PCE (1.35%) is observed at a blend ratio of 1:4. Once again, the drop in PCE matches well with the trend observed for short circuit current. It should be noted that at 1:4 blend ratio, the open circuit voltage and fill factor are improved in comparison to the 1:1 and 1:2 ratios, which slightly compensate the decreasing short circuit current.

Further analysis focuses on the changes in the short circuit currents as they dominate the trend in power conversion efficiency in both cases. The difference in short circuit currents between different fullerene loadings could not be fully explained by differences in photon absorption. This is evident by overlaying the external quantum efficiency of C2C6-PTTV by the 1-Transmission (T) spectra of the C2C6-PTTV:PC₇₁BM blends (figure 4.6). The spectra are normalised at 640 nm, where the polymer primarily absorbs. At 1:1(polymer:fullerene) blend ratio, it can be seen that the 1-T of PC₇₁BM (wavelengths < 500 nm) is weaker than that of the polymers (wavelengths > 500 nm), but the EQE in the PC₇₁BM absorption region is higher than that from polymer absorption. This suggests that the charge generation from the fullerene exciton is more efficient than that of the polymer exciton at 1:1 blend ratio. As the blend ratio is changed to 1:4, the 1-T of PC₇₁BM becomes stronger than that of polymers, consistent with the increased loading of fullerenes. However, the EQE in the PC₇₁BM

absorption region is reduced in comparison to that at 1:1 blend ratio. As such, it can be concluded that the difference in absorption upon changing blend ratio cannot account for the changes in the short circuit current. The observation appears to agree with a previous study on BTT-DPP system by Dimitrov and co-workers from our group, in which the author has reported that the charge generation from fullerene absorption is limited by the tendency of fullerene to form aggregates, preventing fullerene excitons reaching polymer;fullerene interface to undergo dissociation.^{33, 39} To examine whether PTTV behaves similarly to BTT-DPP, photoluminescence spectroscopy and transient absorption spectroscopy was employed, with the data showing in the following sections. (Note that further study on BTT-DPP is also included in Chapter 4)

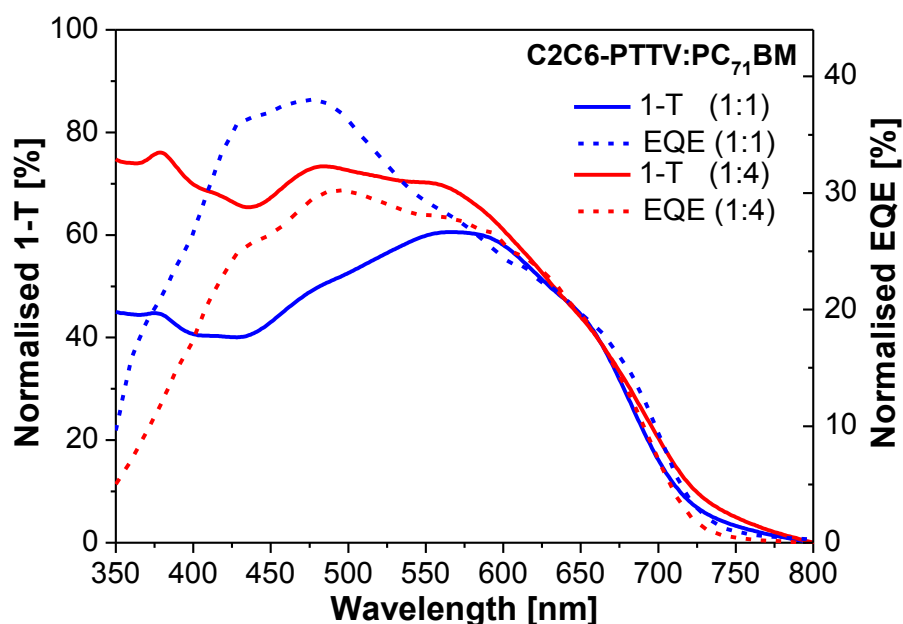


Figure 4.6: External quantum efficiency of C2C6-PTTV:PC₇₁BM (1:1 in blue solid line and 1:4 in red solid line) based device as a function of wavelength. (1-Transmission) spectra (dash lines) of C2C6-PTTV:PC₇₁BM thin films are also provided.

4.3.3 Photoluminescence spectroscopy to probe degree of phase segregation

Blend morphology as a function of blend ratio is generally known to influence phase segregation between the polymer and the fullerene, leading to different exciton dissociation efficiencies.

Photoluminescence spectroscopy was applied to C16-PTTV:PC₇₁BM and C2C6-PTTV:PC₇₁BM blend films, with the details of the measurements covered in section 4.2. The blend films were excited at 640 nm or 380 nm in order to extract the photoluminescence quenching of polymer and fullerene excitons respectively. Note that neat C16-PTTV and C2C6-PTTV emit at 697 nm and 702 nm respectively which strongly overlap with the emission of pristine PC₇₁BM film at 707 nm. As such, deconvolution was performed (see Chapter 2 for the detail of deconvolution) to analysis the peak composition from the photoluminescence of the blend films in order to estimate the PLQ.

As shown in figure 4.7, changing the blend ratio in the C16-PTTV system results in minimal changes in the quenching of polymer photoluminescence (87-89%). In contrast however, the quenching of fullerene photoluminescence remains at ~ 82% for blend ratio of 1:1 and 1:2 (polymer:fullerene) and sharply drops to 37% as the blend ratio is further changed to 1:4. These changes correlates qualitatively with the changes in the short circuit current from the corresponding devices, suggesting the loss in short circuit is primarily as a result of the lower fullerene photoluminescence quenching at high fullerene compositions. A reason for this loss can be understood by the potential large fullerene domains which can be present at high fullerene composition.^{23, 48-50}

In the case of C2C6-PTTV (figure 4.8), polymer photoluminescence quenching increases moderately from 73% to 85% while fullerene photoluminescence quenching decreases gradually from 58% to 48% when the blend ratio changed from 1:1 to 1:4. The increase in polymer photoluminescence quenching could be due to an increase in polymer:fullerene interface as more fullerenes are added.^{40, 47-49} Note that a sharp drop in the quenching of fullerene photoluminescence was not observed at 1:4 blend ratio in this case, unlike that of C16-PTTV. The more gentle decrease in C2C6-PTTV could be resulted from the better solubility of the polymer, encouraging formation of morphologies with better mixing between the polymer and fullerene.²⁹ The decreasing efficiency of fullerene dissociation is once again qualitatively consistent with the trend in the short circuit current, and also with decreasing EQE in the fullerene region (figure 4.7) as the blend ratio is changed from 1:1 to 1:4. As such,

the results suggest that the device efficiencies for both PTTV polymers are limited by the relatively large fullerene domains in the blend microstructure, hindering fullerene exciton undergoing dissociation. Decreasing fullerene loading is one way to optimise device efficiency by offering higher degree of polymer:fullerene mixing to favour the fullerene dissociation.

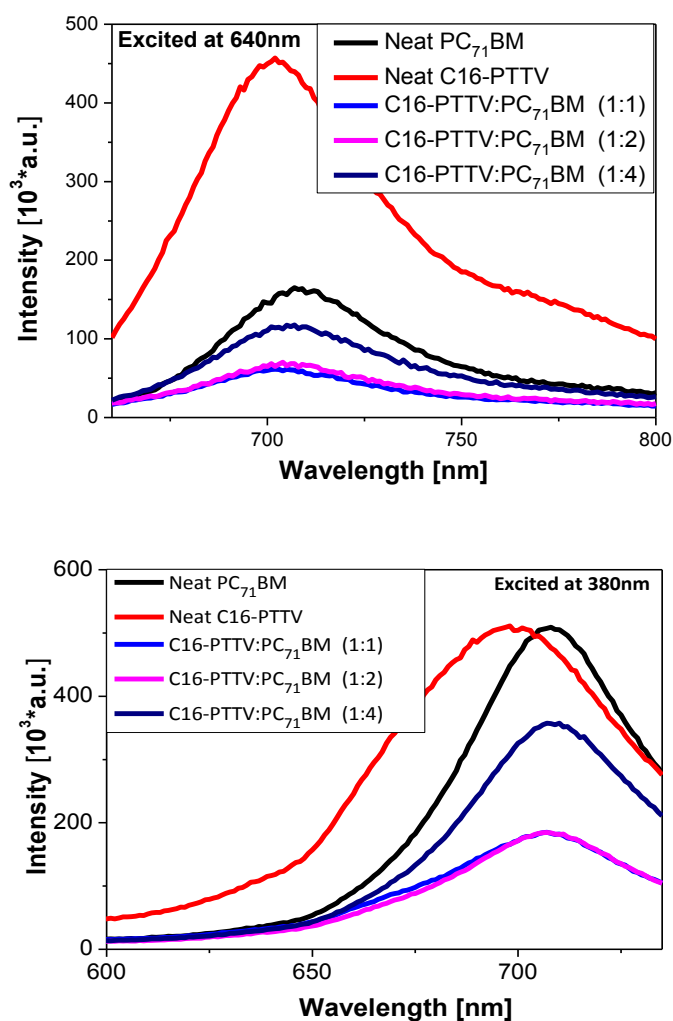
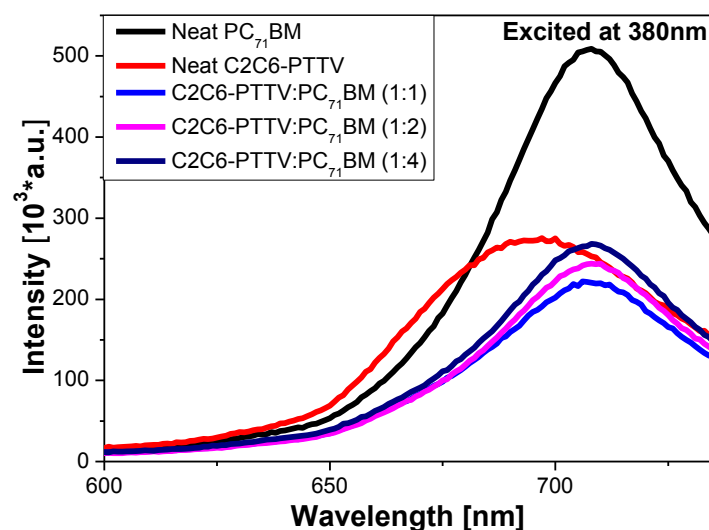
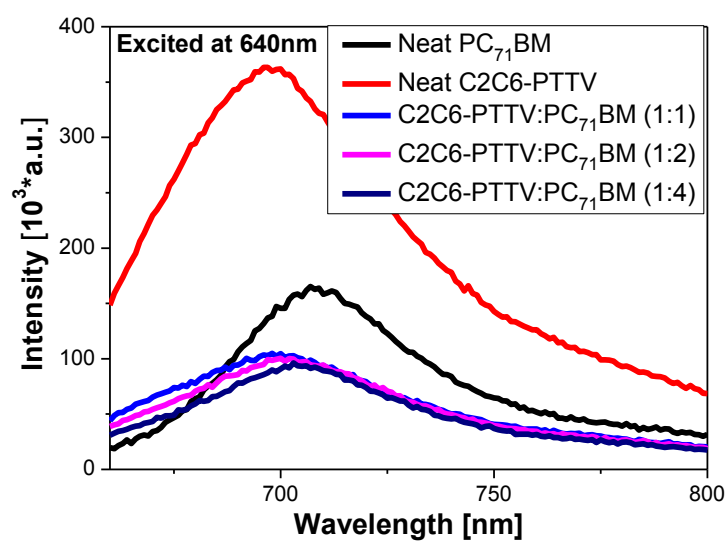


Figure 4.7: Photoluminescence of neat PC₇₁BM, neat C16-PTTV and C16-PTTV:PC₇₁BM films excited at 640 nm (top left) or at 380 nm (top right). The bottom table shows the quenching of polymer and fullerene photoluminescence in the blend films, estimated by the deconvolution described in section 4.2.



Blend ratio	Quenching of polymer PL (excited at 640 nm)	Quenching of PC ₇₁ BM PL (excited at 380 nm)
1:1	73%	58%
1:2	79%	53%
1:4	85%	48%

Figure 4.8: Photoluminescence of neat PC₇₁BM, neat C2C6-PTTV and C2C6-PTTV:PC₇₁BM films excited at 640 nm (top left) or at 380 nm (top right). The bottom table shows the quenching of polymer and fullerene photoluminescence in the blend films, estimated by the deconvolution described in section 4.2.

On the other hand, both the quenching of the polymer and fullerene photoluminescence are higher in C16-PTTV system in comparison to C2C6-PTTV at the same ratio (apart from 1:4 blend ratio), qualitatively consistent with the better short circuit current observed in the C16-PTTV based devices. This suggests the degree of polymer:fullerene mixing can be further improved to boost up the device performance by changing the side chain from branched to linear.

In addition, it is worth noting that the fullerene PLQ is lower than the polymer PLQ for C2C6-PTTV, even though the majority of the current was derived from the fullerene absorption. This may imply a better charge separation efficiency following fullerene absorption, which is discussed in more detail in the following section.

4.3.4 Charge separation in optimised C16-PTTV and C2C6-PTTV based devices

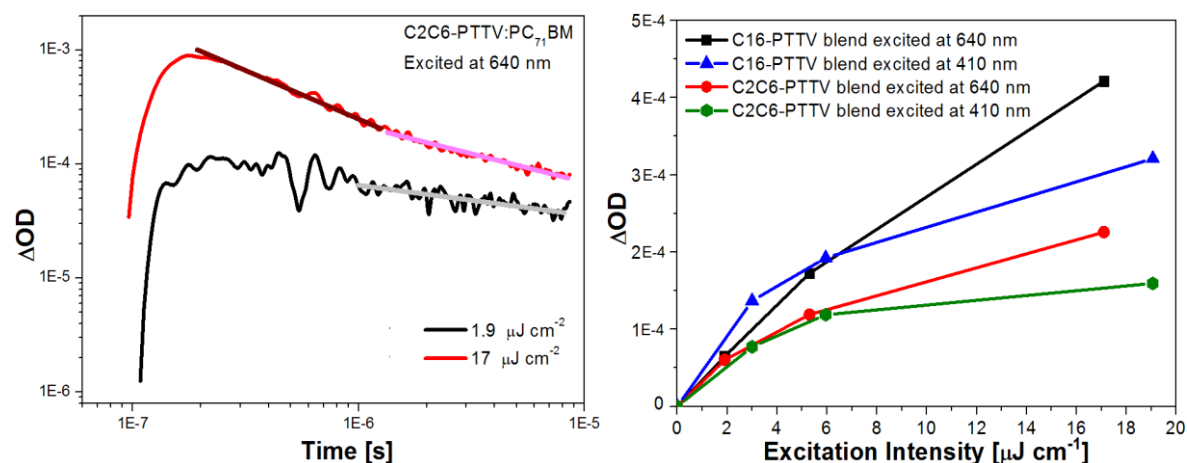


Figure 4.9: (Left) Transient absorption decay obtained from C2C6-PTTV:PC₇₁BM (1:2) thin films by exciting at 640 and probing at 980 nm, with excitation intensities of 1.9 $\mu\text{J cm}^{-2}$ and 17 $\mu\text{J cm}^{-2}$ (Right) The plots of decay amplitude at 1 μs versus excitation intensity obtained from C16-PTTV:PC₇₁BM (1:1) and C2C6-PTTV:PC₇₁BM (1:2) by exciting at 640 nm or 410 nm and probing at 980 nm.

The performance of devices made from these two polymers are now compared at their optimised blend ratio, namely 1:1 (polymer:fullerene) for C16-PTTV and 1:2 for C2C6-PTTV. Although C2C6-PTTV exhibits a higher open circuit voltage and fill factor, its power conversion efficiency is still lower than that of C16-PTTV based device due to its lower short circuit current. From the photoluminescence study shown above, both polymer exciton quenching and fullerene exciton quenching are more efficient in C16-PTTV system,

suggesting a more finely mixing morphology in the C16-PTTV:PC₇₁BM blend. Therefore it was hypothesised that the better exciton dissociation should further lead to a more efficient charge formation in C16-PTTV:PC₇₁BM, which was verified using transient absorption spectroscopy.

By applying transient absorption spectroscopy, the yields of polaron formation and the decay dynamics were investigated (see section 4.2 for the details of the experiment). The optical absorptions of the polarons were monitored at 980 nm as a function of time. The films were excited at 410 nm and 640 nm in order to probe the charge generation from fullerene absorption and polymer absorption respectively. TAS decays were obtained with a range of excitation intensities (1.9-19 $\mu\text{J cm}^{-2}$). Figure 4.9 (left) shows two TAS decays obtained from C2C6-PTTV blends by exciting at 640 nm with two different excitation intensities. The decay at 1.9 $\mu\text{J cm}^{-2}$ is fit to power law of $\Delta\text{OD} \sim t^{-\alpha}$ with $\alpha = 0.26$, which is consistent with trap-limited bi-molecular recombination kinetics typically observed on this timescale.⁵¹ The α has been reported to associate with the level of the deep charge trapping in the system, with a smaller α reflecting a higher level of the deep traps.⁵¹⁻⁵³ A plateau is also observed at early times ($< 1 \mu\text{s}$), consistent with observation of the onset of bimolecular recombination. At higher excitation intensity (17 $\mu\text{J cm}^{-2}$), an additional fast decay phase is observed on sub-microsecond timescales (figure 4.9 (left)), while the ΔOD amplitude observed at 1 μs starts to saturate (figure 4.9 (right)). This has been reported to be characteristic of trap-limited bimolecular recombination.^{52, 53} Similar observations were also made when exciting C2C6-PTTV or C16-PTTV blends at 410 nm. In addition, the amplitude appears to be rather linear with excitation intensity for C16-PTTV blend excited at 640 nm. The α associated with the decays in this sample ranges from 0.06 to 0.24, lower than the 0.4 that has been reported previously for MDMO-PPV,⁵² suggesting a high level of deep traps in this system. As such, the traps in this system probably are far from completely filled within the excitation intensity range employed in this study, preventing the amplitude from saturation.

As previously, the initial amplitude ($\sim 1 \mu\text{s}$) of the power law decay, measured under low excitation conditions so as to be as close as possible to the onset of bimolecular recombination losses, has been employed as a quantification of the yield of dissociated polarons in polymer:fullerene blend films.^{35, 51, 54} The amplitude at $\sim 1 \mu\text{s}$ has also been reported to exhibit a good correlation with short circuit current.³⁵ As such, similar analysis was applied to compare the charge generation in the PTTV blends. The decays when the

samples were excited at 640 nm ($1.9 \mu\text{J cm}^{-2}$) or 410 nm ($3 \mu\text{J cm}^{-2}$) from C16-PTTV:PC₇₁BM and C2C6-PTTV:PC₇₁BM thin films are presented in figure 4.9, which have been corrected by the density of absorbed incident photons. The polaron yields were extracted by extracting the amplitude of the signal at 1 μs (estimated by fitting the decays to power law of $\Delta\text{OD} \sim t^{-\alpha}$, followed by extracting the amplitudes at 1 μs of the fits), as shown in the inserted table in figure 4.10 (top). It can be clearly seen that the polaron yields in C16-PTTV blends, particularly from fullerene absorption, are stronger than those from C2C6-PTTV, consistent with the higher short circuit of C16-PTTV based device. This suggests the better short circuit current of C16-PTTV based device is primarily derived from the more efficient charge generation from fullerene absorption.

The difference in charge generation has been previously reported to be associated with the differences in driving energy for charge separation as well as the efficiency of exciton quenching.⁵¹ In the case of energetics, the driving energy (ΔE_{CS}) was calculated using $\Delta E_{\text{CS}} = E_{\text{g}} - (\text{IP} - \text{EA})$, as detailed in Chapter 2. In this case, the optical bandgaps estimated are used for E_{g} of the polymers, whilst the energy levels of fullerenes are taken from ref⁴⁶. The results are presented in the inserted table in figure 4.10 (bottom). It can be seen that the ΔE_{CS} for the hole-transfer in both blends are similar, which suggests that the difference in yield of polaron from fullerene absorptions is unlikely to be due to differences in energetics. To further explore this, the decays and the amplitude at 1 μs are corrected with the PLQ obtained above, as presented in figure 4.10 (bottom). After PLQ correction, the amplitude from the fullerene absorption in C16-PTTV becomes comparable to that in C2C6-PTTV. A similar result was also observed from analysis of data following polymer excitation. These observations suggest that the better charge generation in C16-PTTV is primarily due to its higher degree of polymer:fullerene mixing, rather than differences in energetics, consistent with the discussion above.

The charge generation from polymer absorption is now compared with that from fullerene absorption. As shown in figure 4.10 (bottom), after accounting for differences in light absorption and exciton quenching, the ΔOD amplitudes from fullerene absorption are approximately twice as big as those from polymer absorption. The ΔE_{CS} for the hole-transfer from fullerene excitons is 0.1 eV higher than that for electron-transfer from polymer excitons. This correlation is consistent with previous studies on polythiophene based

polymers,⁵⁴ suggesting the better charge generation from fullerene absorption is partially due to higher driving energy for the associated charge separation via hole transfer.

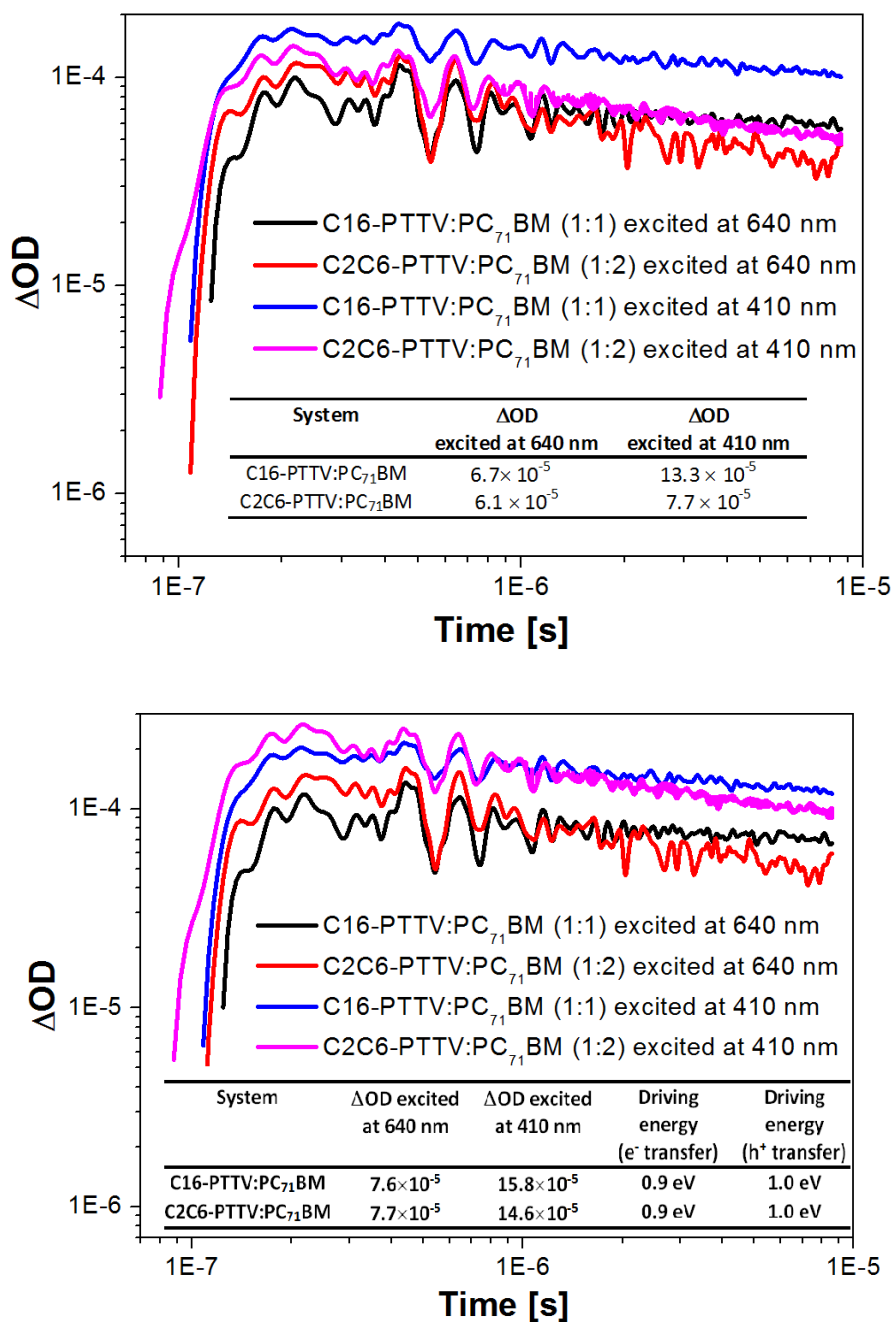


Figure 4.10: (Top) Transient absorption decay on C16-PTTV:PC₇₁BM and C2C6-PTTV:PC₇₁BM thin films probed at 980 nm. The excitation wavelength was 640 nm or 410 nm with excitation intensities of 1.9 μJ cm⁻² or 3 μJ cm⁻² respectively. These data have been corrected to normalise for differences in the density of absorbed photons. (bottom) The four decays were further corrected with the corresponding PLQ obtained in section 4.3.3. The insets show the amplitude extracted at 1 μs and driving energies for charge separation.

4.4 Discussion

In the last section, it has been demonstrated that the blend microstructure of PTTV:PC₇₁BM blend can be improved by tuning polymer:fullerene blend ratio or alkyl side chain, leading to better device performance. More specifically, it has been found that both of these approaches particularly improve the fullerene PLQ to favour the charge generation from fullerene absorption. This section primarily focuses on discussing the correlation between blend microstructure and charge generation from fullerene absorption, followed by a brief discussion on comparing generation following fullerene absorption with that following polymer absorption.

Previous studies have found that charge generation following fullerene absorption could be important to photocurrent generation,^{37, 38, 55, 56} but may be limited by the relatively poor efficiency of fullerene exciton dissociation.^{36, 37, 55} For example, McGehee and co-workers demonstrated that the fullerene PLQ was only 41% in comparison to the polymer PLQ of ~95% in P3HT:PC₆₁BM (1:1) blends.³⁶ In parallel, Janssen and co-workers reported a fullerene PLQ of 30% in MDMO-PPV:PC₇₁BM (1:4) system, accompanied with a complete quenching of polymer photoluminescence.⁵⁵ The asymmetric PLQ pattern between polymer and fullerene is similar to what has been observed in C2C6-PTTV blends, with PLQ of ~50% and ~80% for fullerene and polymer respectively depending on blend ratio. This suggests that the microstructure of C2C6-PTTV blends should contain a relatively impure polymer phase and relatively pure fullerene phase, consistent with the amorphous nature of the polymers and the known tendency of fullerene to form aggregates.^{35, 41} In this regard, intimately mixed phase in blend microstructure is particularly important for fullerene excitons to undergo dissociation.

This blend microstructure issue was previously addressed by increasing polymer molecular weight or using alternative blend solvent.^{34, 37, 55} In our study, a more fundamental approach by tuning polymer:fullerene blend ratio was employed initially to address this issue.^{33, 37} It has been shown that as the fullerene loading is reduced, the fullerene PLQ is improved in C2C6-PTTV blends, leading to better device performance. This is consistent with previous studies which have shown that reducing fullerene loading can lead to smaller domains in PTV:fullerene blends.⁵⁷ In addition to reducing fullerene loadings, our study has also shown that the fullerene PLQ in PTTV blends can be further improved by changing the side chain from branched to linear. The fullerene PLQ for C16-PTTV is over 80% at blend ratio of 1:1 or 1:2 (polymer:fullerene), indicative of a better mixing of polymer and fullerene, compared

with the fullerene PLQ of ~55% at similar blend ratio for C2C6-PTTV.⁴¹ It is speculated that the better miscibility resulted from potentially better fullerene intercalation offered by C16-PTTV in the amorphous regions. Based on previous studies, polymers with longer and slimmer side chains could provide more space to accommodate fullerene molecules, hence allowing polymer and fullerene to intimately mix together on molecular level.¹⁹ Note that the slightly higher crystallinity^{27, 32, 58} and poorer solubility^{16, 29} of C16-PTTV should reduce the degree of polymer:fullerene mixing according to other previous studies, which is the opposite to what was observed in this study. Presumably, the effect of fullerene intercalation is dominant and therefore gives a better material mixing for C16-PTTV:PC₇₁BM blend.

The charge separation via hole-transfer is now compared to that via electron transfer. As have been discussed in last section, the better charge generation from fullerene absorption should be at least partially derived from a difference in energetics, as the driving energy for hole transfer is 0.1 eV higher than that for electron transfer. This interpretation is in agreement with a previous study by Bakulin and co-workers.⁵⁹ The authors compared the charge separation via hole transfer with that via electron transfer on a couple of benchmark materials including MDMO-PPTV and PCDTBT. It has been suggested that, the charge separation via hole transfer, if exhibiting a higher driving energy than electron transfer, can suppress the formation of bound charge transfer state to facilitate free charge generation.

There are of course other possibilities which may also explain the difference in efficiency of charge separation when comparing polymer absorption with fullerene absorption. For examples, charge pairs in charge transfer states formed following dissociation of fullerene excitons could be separated by a longer spatial distance, in comparison to that from dissociation of polymer excitons.⁶⁰ In addition, the efficiency of charge separation has been found to depend on the conformational structure of the donor and acceptor at the interface, potentially also contributing to the difference in charge separation between these two excitons.⁶¹ Together with our findings, all of these studies suggest that charge generation following fullerene absorption and that following polymer absorption are both important to device performance, and may need to be considered separately in order to optimise the efficiency.

4.5 Conclusions

In this chapter, it has been demonstrated that tuning blend ratio and the side chain attached to PTTV polymers impact the blend microstructure, and thereby the device performance. The better miscibility of C16-PTTV:PC₇₁BM in comparison to C2C6-PTTV:PC₇₁BM is attributed to its better ability to intercalate fullerene molecules, which results from the longer and slimmer side chain. It has been highlighted that charge generation from fullerene absorption is also important to device performance for PTTV systems but suffer from poor efficiency of exciton dissociation for C2C6-PTTV in comparison to that from the polymer absorption. This reveals that nature of charge generation following fullerene absorption can be different from that following polymer absorption, suggesting these two different charge generation mechanisms should be considered separately when optimising device performance.

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Chapter 5

Effects of molecular weight on performance of diketopyrrolopyrrole-containing polymer based devices

Abstract

In this chapter, device optimisation by tuning the polymer molecular weight is applied to two diketopyrrolopyrrole(DPP)-containing polymers, which are comparable to P3HT in terms of degree of crystallinity. This study demonstrates that the device performance of these polymers is improved owing to a better blend microstructure at high molecular weight. More specifically, based on data from AFM, TEM, TAS and PL spectroscopy, these polymers are suggested to suffer heavily from severe phase segregation resulting in poor exciton dissociation and charge generation. At higher molecular weight, this problem can be addressed as the blend microstructure becomes more finely mixed. The correlations between molecular weight and blend microstructure are also discussed. This study highlights the importance of the improved blend microstructure given by high polymer molecular weight, different from the improved light absorption or charge transport highlighted in previous literature.

5.1 Introduction

The molecular weight of polymers is another parameter that can be adjusted in order to optimise device performance, alongside other parameters such as fluorination and alkyl side chain discussed in Chapter 3 and 4. According to the classic polymer science, polymer molecular weight can impact upon material microstructure, leading to changes to various properties of polymer films, such as Young modulus and melting temperature.¹⁻⁶ As molecular weight increases, the morphology of polymers can be most simply considered to evolve from chain-extended crystals to a mixture of interconnected crystals and amorphous matrix (figure 5.1), which can lead to large changes in some polymer properties.¹⁻⁶ One reason for the appearance of the amorphous matrix is chain folding. This happens at a transitional molecular weight, which varies from polymer to polymer.

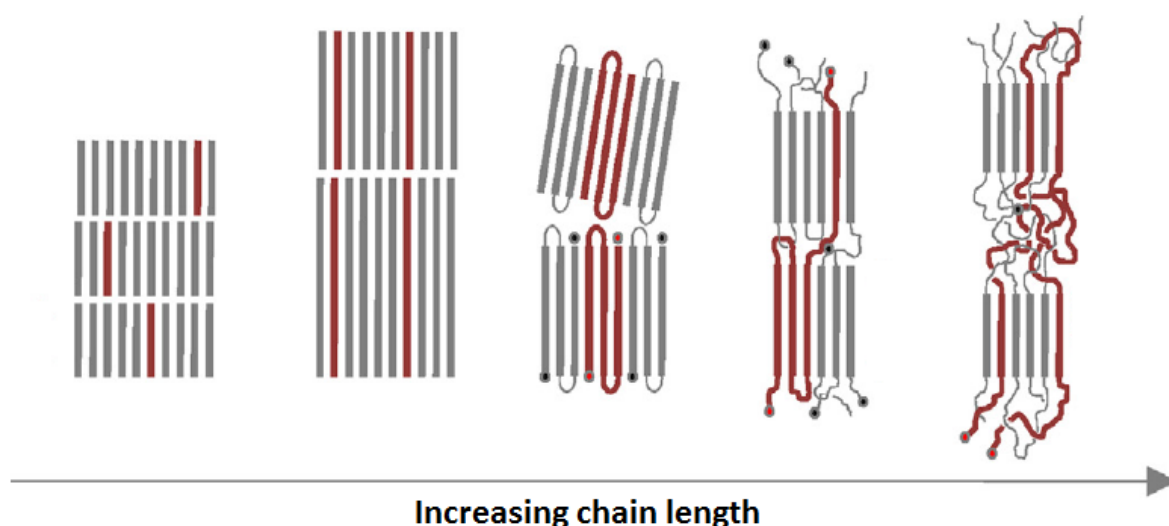


Figure 5.1: Morphological evolution of classic polymers or P3HT with increasing chain length. [This image has been reproduced with the permission of the rights holder, Elsevier⁶]

Organic photovoltaics utilise conjugated polymer semiconductors (e.g. P3HT and PTB7) which have significantly different chemical structures to classic polymers such as polyethylene, being for example typically more rigid. This raises questions on whether the morphology of the polymer semiconductors follows the morphological evolution with molecular weight of classical polymers and how this impacts upon polymer electronic properties and solar cells performance. In this regard, P3HT, which has wide applications in OFET and OPV, has been widely investigated.⁶⁻¹⁵ Previous studies have suggested that P3HT adopts a similar morphological evolution pattern to classic polymers, with the transition molecular weight

reported to be (M_w) ~ 7.3 kDa.⁷⁻⁹ Numerous studies were carried out looking into the correlation between molecular weight of P3HT and its OFET mobility.¹⁰⁻¹³ It was observed that with increasing molecular weight, the mobility of P3HT increased initially until it became saturated when certain degree of chain entanglement was reached ($M_n > 25$ kDa).^{6, 16, 17} It was suggested that the increase in mobility was derived from the better interconnectivity between crystallites at high molecular weight. This biphasic change in mobility with molecular weight was shown to match with the evolution of P3HT morphology.⁶

A number of studies have been reported that polymers with high molecular weight can give rise to better performance by offering higher J_{SC} and FF.^{14, 15, 18-25} The improvement in PCE could be more than 2-fold as the molecule was changed from the oligomer regime to macromolecule regime. While this clearly gives guidance for polymer synthesis for OPV, the origins of the performance improvement are not well understood. Early studies on the benchmark materials, including P3HT and PCDTPT, are inconclusive. Some studies suggested the improvements in J_{SC} and FF were due to improved charge mobility of the polymers with higher molecular weights^{13, 15, 18, 19, 23}, whilst others suggested the improvement was due to better material absorption.^{20, 22}

The origins of the molecular weight upon device performance are likely to be multifold and vary from system to system. There are an increasing number of studies suggesting molecular weight can impact on blend microstructure^{15, 23-26}, in addition to mobility and absorption, and thereby on device performance. For examples, Schilinsky and co-workers reported that performance of P3HT based device was improved as the polymer molecular weight M_n was increased from 2.2 kDa to 19 kDa, with the improvement attributed to the better polymer mobility at higher M_n .¹³ A further study was carried out by Nicolet and co-workers, who found that the improvement in P3HT device performance did not reach a plateau until $M_n > 60$ kDa.²⁷ This was much greater than the molecular weight (25 kDa) at which OFET mobility started to saturate as mentioned above. The authors attributed the device improvement to the blend microstructure which was more finely mixed, with better interconnectivity at high M_n but became molecular weight independent when $M_n > 60$ kDa. In parallel, Janssen and co-workers have reported a study of diketopyrrolopyrrole(DPP)-containing polymer-based solar cells, with higher molecular weight polymers gave rise to better device performance (M_n was varied from 10 kDa to 54 kDa), although the OFET mobility was found to be independent of molecular weight.²⁴ In another study, they found that the device could be further improved as the M_n was increased to 147 kDa, attributed to

the smaller phase segregation in blend microstructure.²⁵ Note that comparing these studies to the studies on P3HT, it is clear that other polymers may not follow the exact same trend as P3HT and the M_n at which device performance becomes saturated varies from case to case.

There are a limited number of studies attempting to explain the correlation between molecular weight and blend microstructure. Recently, a more in-depth work by Westacott and co-workers proposed a model for explaining the finely mixed characteristic of blend microstructure at high M_n for P3HT.²⁶ They suggested that at high molecular weight, there were more amorphous regions of the polymer to mix with fullerene, due to the increased chain entanglement and higher susceptibility of polymer crystals to be broken up by the presence of fullerene. This leads to a higher composition of the polymer:fullerene mixed phase in the film with higher polymer M_n , resulting in better charge generation measured by transient absorption spectroscopy. The impact of molecular weight on blend morphology has also been interpreted in terms of solubility.^{15, 23} Contradictory observations to those for P3HT and the DPP-containing polymers mentioned above have also been reported, where some polymers with high M_n were found to show more severe phase segregation. The authors attributed this to the lower solubility²⁸ of the polymer, which is often found at high molecular weights.

While it is now clear that polymer molecular weight is critical to device performance, understanding of the origins that govern the performance improvement of high molecular weight polymers is currently based on a rather limited number of studied materials. As such, a study of the molecular weight dependence of two diketopyrrolopyrrole(DPP)-containing polymers, DPP-TT-T and BTT-DPP was carried (The chemical structure is included in Chapter 2). Diketopyrrolopyrrole(DPP) is a component for donor-acceptor co-polymers which has been increasingly attracting research interest due to the low optical band gaps and high hole mobilities reported for DPP based polymers.^{29, 30} DPP-TT-T is one of the best performing polymers from this family, initially giving over a 5% power conversion efficiency.³¹ The latest reported efficiencies with this polymer exceed 7%, achieved by modification of the polymer side chain, thus making it one of the top tier polymers for organic solar cells.³² Another DPP-based polymer that has recently drawn attention due to its high current generation yields from the fullerene excitons is BTT-DPP. PCE of this polymer are however more modest, being only 3%.^{33, 34} While polymer crystallinity is one of the key parameters when correlating molecular weight with polymer microstructure for P3HT and the classic polymers, most of the efficient donor-acceptor polymers for OPV reported to date

have rather amorphous characters.^{35, 36} In this regard, both of these DPP-containing polymers, as will be demonstrated later in this chapter, are comparable to P3HT in terms of crystallinity and therefore potentially could exhibit similar trends with molecular weight to those observed for P3HT and classical polymers. In this chapter, the correlation between molecular weight and device performance is explored for DPP-TT-T and BTT-DPP based blends. A correlation between polymer crystallinity and polymer:fullerene miscibility is established using WAXS, PL, AFM and TEM. In addition to this, transient absorption studies of polymer:PCBM films gives evidence that improvements in device performance is driven by the impact of molecular weight on blend microstructure.

5.2 Experimental

Material preparation - DPP-TT-T and BTT-DPP were synthesised by Dr. Hugo Bronstein and Dr. Christian Nielsen from Prof. Iain McCulloch's group, with the details of synthesis outlined elsewhere.^{31, 33, 37} The polymers were fractionated using recycling gel permeation chromatography as described in a previous study.³⁸ The details of each fraction are presented in table 5.1. A small amount of materials were obtained (~6 mg for each fraction). Most of the materials were consumed in device performance optimisation, leaving limited amount of material for analysis measurements.

Polymer	Mn	PDI
DPP-TT-T	14 kDa	1.9
	34 kDa	1.8
	62 kDa	1.9
BTT-DPP	22 kDa	1.5
	73 kDa	2.1
	90 kDa	2.1

Table 5.1: Molecular weight and polydispersity index of fractionated DPP-TT-T and BTT-DPP.

Experimental techniques - The details of WAXS, steady state UV/visible absorption and photoluminescence spectroscopy, TAS, AFM, TEM, J-V measurement and EQE measurements used in this chapter are outlined in Chapter 2. The femtosecond TAS and TEM

experiments were carried out by Dr. Stoichko Dimitrov and Dr. Safa Shoaee from Prof. James Durrant's group, with the experiment details described in ref³⁹.

Sample preparation – the same solutions were used for all measurements and device fabrication. The details of the device fabrication are included in Chapter 2. The solutions had an overall concentration of 15 mg/ml at 1:2 blend ratio (polymer:fullerene) in a chloroform:dichlorobenzene (4:1) solvent. The concentration of the DPP-TT-T (62 kDa) films was 7.5 mg/ml due to the poor solubility of the polymer. Blend solutions were spin-coated onto substrates at 2500-3500 rpm for 1 minute. Same solution was used to prepare the drop casting samples for WAXS measurement, with the details of preparation outlined in Chapter 2. All devices were fabricated in the conventional device architecture: ITO/PEDOT:PSS/polymer:PC₇₁BM/Ca/Al.

5.3 Results

5.3.1 Material properties

5.3.1a Energy levels for non-fractionated polymers

Polymer	HOMO [eV]	LUMO [eV]	E _g [eV]	ΔG for e-transfer [eV]	ΔG for h-transfer [eV]
DPP-TT-T	-5.06	-3.64	1.42	0.56	1.04
BTT-DPP	-5.20	-3.85	1.35	0.34	0.90
PC ₇₁ BM	-6.10	-4.20	1.90	-	-

Table 5.2: Energy levels of the HOMOs were determined using ultraviolet photoelectron spectroscopy in air (UV-PESA) while LUMOs were estimated by adding polymer absorption onsets to the HOMOs. Energy levels of PC₇₁BM are taken from ref^{40, 41}, assuming it is the same as PC₆₁BM. ΔG is the driving energy estimated as described in Chapter 1.

The energy levels of the HOMOs for the two unfractionated polymers were measured using ultraviolet photoelectron spectroscopy in air (UV-PESA) by Dr Scott Watkins from the Commonwealth Scientific and Industrial Research Organisation (CSIRO) in Australia (table 5.2). LUMOs were estimated by adding the bandgap calculated from the onset of absorption to the HOMOs. Both polymers are low band gap polymers with an absorption maximum over 700 nm.^{31, 33} The driving energies for electron transfer and hole transfer were estimated using $\Delta E_{CS} = E_g - (IP-EA)$ (see Chapter 2 for details) and are used for the analysis in section 5.3.2b.

5.3.1b Wide angle X-ray scattering

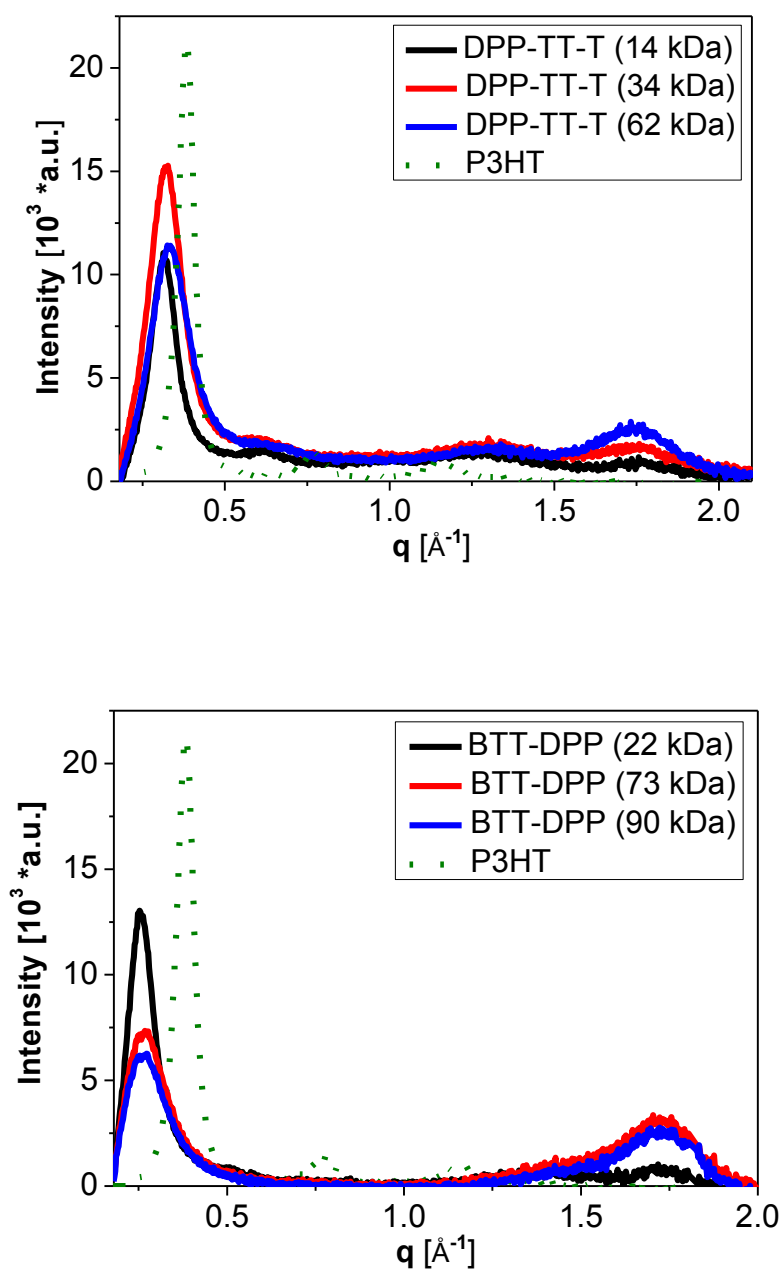


Figure 5.2: Signals obtained from wide angle X-ray scattering of neat DPP-TT-T (top) and BTT-DPP (bottom) films with various molecular weights. The samples were prepared using drop casting, with details outlined in section 5.2. *[This image has been reproduced with the permission of the rights holder, The Royal Society of Chemistry³⁹]*

The crystallinity of DPP-TT-T and BTT-DPP was estimated by wide angle X-ray scattering using neat P3HT as the reference (figure 5.2). Diffraction strengths were calculated for each signal included in figure 5.2 to assay the degree of crystallinity (or volume ratio of crystal

region over amorphous region) using the procedure described in Chapter 2. Note that this technique only reveals the information in out-of-plane direction as mentioned earlier. As shown in figure 5.2, both of the DPP-containing polymers exhibit two signals at $q \sim 0.3 \text{ \AA}^{-1}$ and $1.7 \text{ \AA}^{-1}$ assigned to lamellar packing and π - π stacking respectively according to a previous study⁴². The diffraction strength of the lamellar packing is stronger than the strength of the π - π stacking in all cases (table 5.3). The diffraction strengths of the lamellar packing ($q \sim 0.3 \text{ \AA}^{-1}$) are also on comparable scale to P3HT, indicating the semicrystalline nature of these polymers.³⁶

Both polymers exhibit an increase in diffraction strength of the π - π stacking for the larger M_n fractions, with the opposite trend observed in lamellar stacking. However, it could be misleading to conclude whether or not both DPP-containing polymers follow the same morphological evolution as classic polymers or P3HT. Firstly WAXS cannot provide conformational information along the in-plane direction. Secondly, as reported for P3HT, the evolution of polymer microstructure varies from case to case depending on a number of parameters, such as casting solvent and regioregularity.^{10, 17, 43} Nevertheless, our results suggest an improvement in π - π stacking along the out-of-plane direction, which could be beneficial to device performance by improving charge transport.¹³

Polymer	Diffraction strength of Lamellar packing	Diffraction strength of π - π stacking
DPP-TT-T (14 kDa)	272	68
DPP-TT-T (34 kDa)	225	66
DPP-TT-T (62 kDa)	203	99
BTT-DPP (22 kDa)	435	100
BTT-DPP (73 kDa)	341	305
BTT-DPP (90 kDa)	319	248
P3HT	1042	-

Table 5.3: The estimated diffraction strength associated with each peak shown in figure 5.1 to represent the degree of crystallinity of the polymers. The diffraction strength was calculated by integrating the peak area and corrected with the sample thickness, similar to the procedure reported in ref⁴⁴.

5.3.1c UV/visible absorption spectroscopy

Steady state absorption spectra of DPP-TT-T:PC₇₁BM (1:2) and BTT-DPP:PC₇₁BM (1:2) thin films with varying polymer molecular weight are shown in figure 5.3. Samples were prepared following the same procedure used for device fabrication, as outlined in section 5.2.

Figure 5.3 (left) shows that DPP-TT-T films exhibit an absorption band at approximately 730 nm with a shoulder at ~810 nm, consistent with that observed in a previous study.³¹ The absorption spectra of the three blends were normalised at 730 nm. The intensity of the 810 nm shoulder increases with polymer MW, indicating possible changes in the polymer structure/packing causing changes in polymer conjugation length and optical transitions.

The absorption spectrum of BTT-DPP is broader and exhibits two peaks at ~690 nm and ~770 nm, as shown in figure 5.3 (right). The absorption of the blends was normalised at the ~690 nm. Similar to DPP-TT-T, BTT-DPP with higher M_n shows a more intense optical transition at the longer wavelength (~770 nm). Note that, PC₇₁BM displays a negligible absorption above 700 nm and therefore cannot contribute to the increase in intensity of polymer absorption at longer wavelengths (810 nm and 770 nm for DPP-TT-T and BTT-DPP respectively).

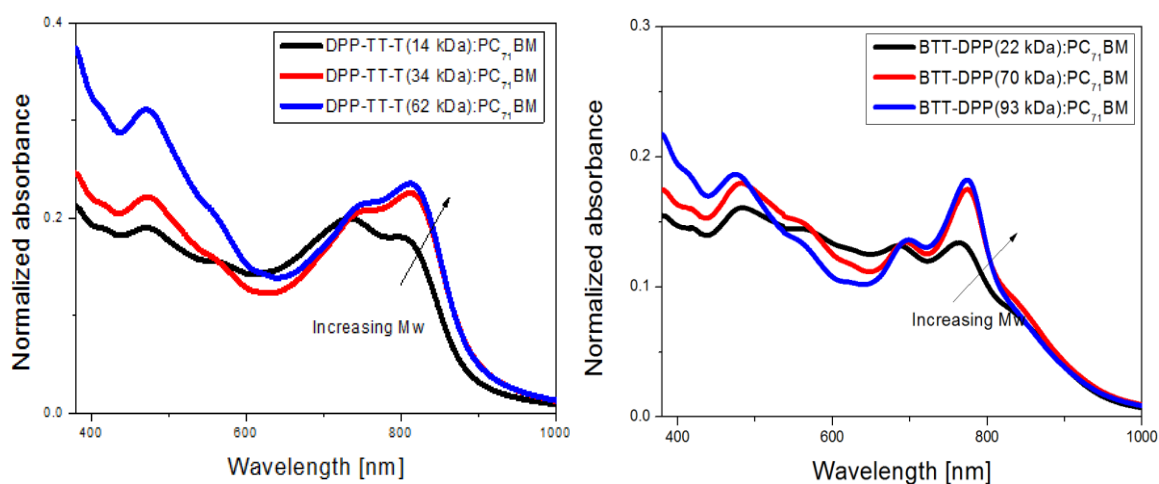


Figure 5.3: UV/visible absorption spectra of DPP-TT-T:PC₇₁BM (left) and BTT-DPP:PC₇₁BM (right) with various polymer molecular weight.

Analogous bathochromic shifts at high molecule weights have been reported for a couple of polymers^{20, 22} and in some cases were suggested to associate with an improved π - π stacking of polymers.^{13, 26, 45-47} This is consistent with what was observed from the WAXS measurements. The increasing intensities of the longer wavelength absorption at high

molecular weight could give better spectral match with solar emission to enhance the light absorption for device performance.^{20, 22}

5.3.2 Device performance and charge generation analysis

5.3.2a Device performance

Photovoltaic performance of DPP-TT-T and BTT-DPP was evaluated based on a conventional device architecture consisted of ITO/PEDOT:PSS/polymer:PC₇₁BM/Ca/Al. The active layers were prepared using a solution of polymer:fullerene (1:2) in a chloroform:dichlorobenzene (4:1) mixed solvent. The procedures for optimised DPP-TT-T and BTT-DPP devices were developed by Dr. Pabitra Tuladhar and myself respectively, with the general optimisation approach described in Chapter 2.

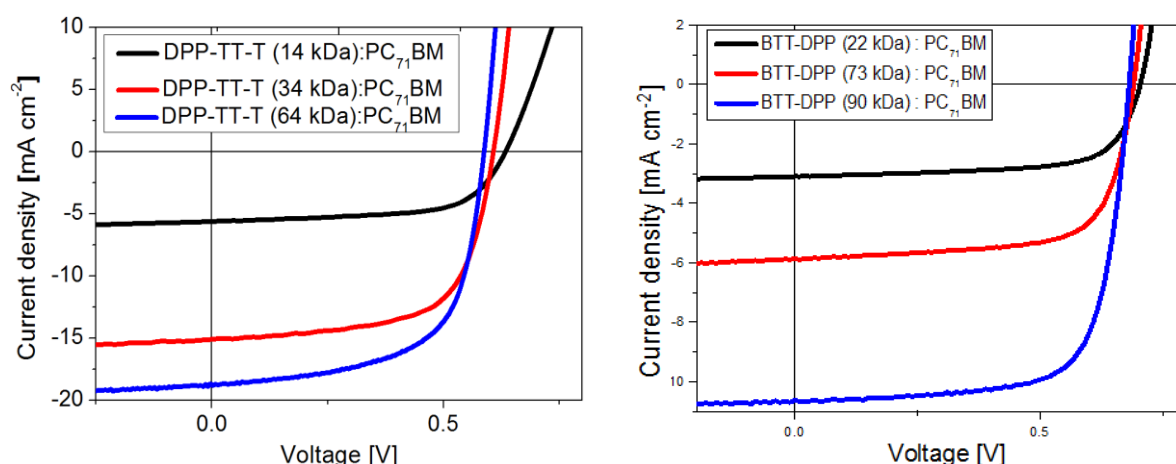


Figure 5.4: J-V curves of DPP-TT-T (left) and BTT-DPP (right) devices with various molecular weights. [This image has been reproduced with the permission of the rights holder, The Royal Society of Chemistry³⁹]

Molecular weight (DPP-TT-T)	V _{oc} [V]	J _{sc} [mA cm ⁻²]	FF [%]	PCE [%]	Active layer thickness [nm]
14 kDa	0.63	5.3	64	2.2	90
34 kDa	0.60	13.9	65	5.4	86
62 kDa	0.60	16.0	56	5.4	101

Molecular weight (BTT-DPP)	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]	Active layer thickness [nm]
22 kDa	0.70	2.9	69	1.4	50
73 kDa	0.69	5.7	70	2.8	80
90 kDa	0.68	10.5	72	5.2	100

Table 5.4: Device parameters and active layer thickness of DPP-TT-T (top) and BTT-DPP (bottom) extracted from the J-V curves in figure 5.4

For both polymers, better power conversion efficiency is observed at higher polymer molecular weight (table 5.4), consistent with other polymers reported previously.^{23, 24, 27} Almost 4-fold increases in PCE are observed across the molecular weight range examined. In the case of DPP-TT-T, despite the reductions in both open circuit voltage and fill factor there is a 3-fold increase in short circuit current with increasing polymer molecular weight, resulting in an increase in power conversion efficiency from 2.2% ($\pm 0.1\%$) to 5.4% ($\pm 0.2\%$). In the case of BTT-DPP, both open circuit voltage and fill factor appear to be independent of polymer molecular weight. As molecular weight is increased, short circuit current increases by approximately 3.6 times, boosting the power conversion efficiency from 1.4% ($\pm 0.1\%$) to 5.2% ($\pm 0.1\%$). Note that the thickness of the active layer also increases as the molecular weight is increased (table 5.4). According to the models correlating optical absorption and short circuit current reported previously in MDMO-PPV and P3HT systems,^{48, 49} the increase in thickness in this regime (from 50 nm to 100 nm) cannot result in more than 3-fold increase in the short circuit current. As such, the substantial increase in short circuit current for both DPP-containing polymers may only be partially explained by the difference in active layer thickness.

Previous studies on MEH-PPV and PCDTPT reported that a substantially improved fill factor was observed for polymers with high molecular weight, attributed to better charge transport.^{13, 18, 19, 22} However, in the current study the BTT-DPP based devices show no changes in fill factor, while the DPP-TT-T devices with the high M_n polymer (62 kDa) had their FF decreased by $\sim 15\%$. This implies that the improved PCE observed in our case may not be due to better charge transport. As the substantially improved PCE at high molecular weight for both polymers is primarily derived from the increases in the short circuit current, the following sections focus on analysis of the short circuit currents.

5.3.2b External quantum efficiency

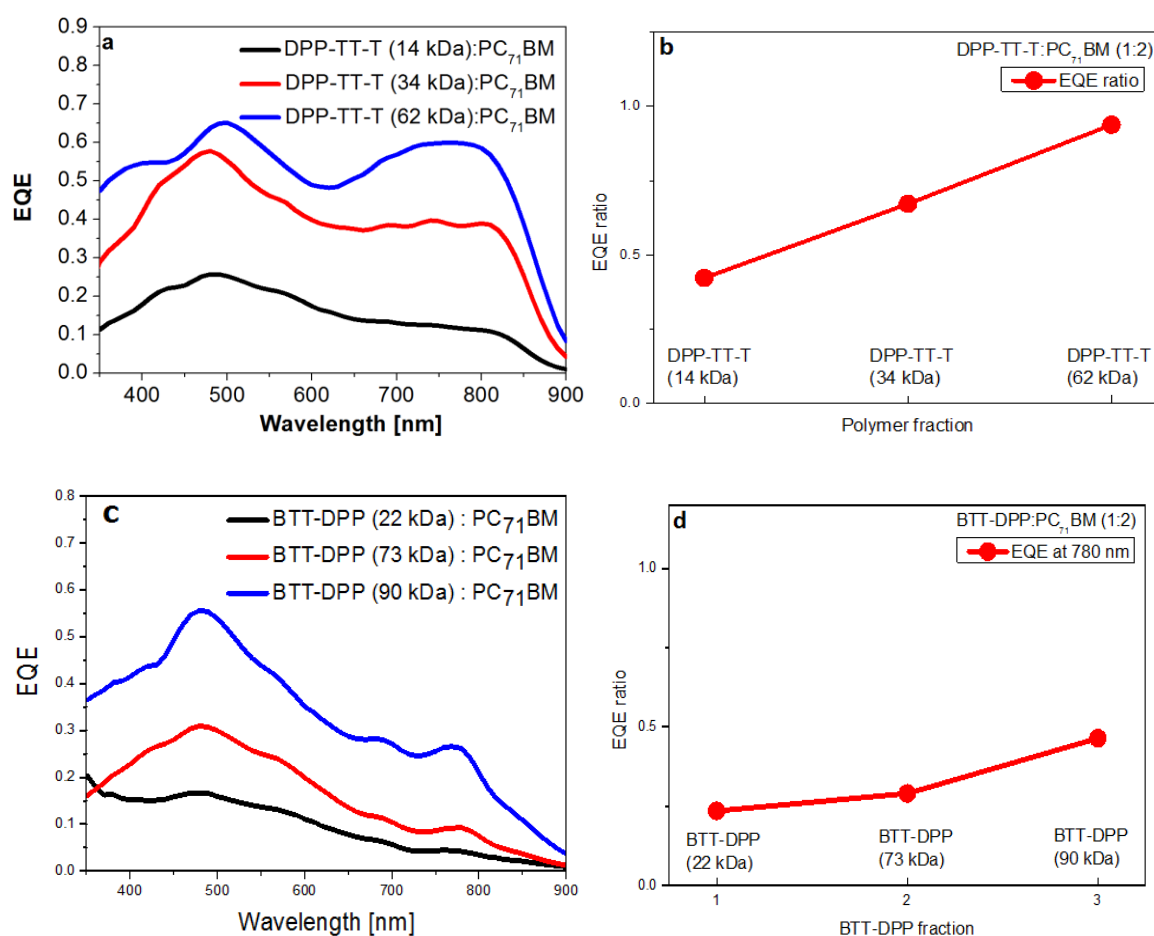


Figure 5.5: External quantum efficiencies as a function of wavelength for DPP-TT-T (a) and BTT-DPP (c) devices with various molecular weights. (b, d) The estimated ratio of polymer EQE to fullerene EQE extracted from each of the EQE spectrum in (a) and (c). Polymer EQE was estimated using the EQE at 800 nm and 780 nm for DPP-TT-T and BTT-DPP respectively, while the EQE at 480 nm was taken as the fullerene EQE. [This image has been reproduced with the permission of the rights holder, The Royal Society of Chemistry³⁹]

The external quantum efficiencies (EQE) of the devices were measured as a function of wavelength and are included in Figure 5.5 (a, c). As the molecular weight is increased, the devices exhibit increases in EQE across the whole wavelength range from 350 nm to 900 nm, consistent with the short circuit currents extracted from the J-V curve measurements. The EQE spectra of the DPP-TT-T devices exhibit a shape resembling that of the UV/visible absorptions of the two constituent materials. There are two peaks at 480 nm and 800 nm in the EQE spectra which correspond to the wavelength where PC₇₁BM and DPP-TT-T primarily absorbs respectively. However, the BTT-DPP devices show EQE spectra

dominated by fullerene absorption, with only a relatively small contribution from polymer absorption (apparent as the small peak at 780 nm).

As the polymer molecular weight is increased, it can be seen that the EQE from the polymer absorption becomes more pronounced in comparison to the fullerene absorption. This suggests the improvement in photocurrent generation from polymer absorption is greater than that from fullerene absorption with increasing molecular weight. To confirm this trend, the ratio of the EQE from polymer absorption to the EQE from fullerene absorption for each spectrum was estimated and included in figure 5.5 (b, d). More specifically, the EQE from polymer absorption was estimated using the EQE at 800 nm or 780 nm for DPP-TT-T and BTT-DPP respectively, while the EQE from the fullerene absorption was estimated using the EQE at 480 nm.

For DPP-TT-T, it can be seen that the photocurrents from polymer absorption are lower compared to the photocurrents at the fullerene absorption maximum, with the estimated EQE ratio increasing from 0.42 to 0.94 as the molecular weight is changed from 14 kDa to 62 kDa. In the case of BTT-DPP, the EQE ratio raises from 0.24 to 0.46 when the molecular weight is increased to 90 kDa. Note that the low EQE ratio for BTT-DPP suggests that only approximately 20%-30% photocurrent is derived from the polymer absorption, consistent to what has been reported previous studies.^{33, 39} This has been suggested to be associated with poor efficiency of charge separation from polymer excitons, resulting from the smaller driving energy for electron transfer in comparison to hole transfer. To demonstrate this idea, the driving energies ($\Delta E_{CS} = E_g - (IP - EA)$, with details outlined in Chapter 2) for hole and electron transfer were calculated (table 5.2). It is apparent that the driving energy for hole transfer is 0.56 eV higher than the electron transfer for BTT-DPP, which should at least partially explain the small contribution to photocurrent from the polymer absorption. In contrast, the contribution to photocurrent by DPP-TT-T absorption is greater (30%-48%), consistent with the smaller difference in driving energy between the electron and hole transfer in this system.

In summary, photocurrent generated by polymer absorption is shown to experience a greater improvement than that by fullerene absorption as polymer molecular weight is increased for DPP-TT-T and BTT-DPP. Similar observations have also been reported in other polymer systems.^{22, 24}

5.3.2c Transient absorption spectroscopy

It has been reported that the better device performance for P3HT with higher M_n is associated with the more efficient charge generation.²⁶ In this section, transient absorption spectroscopy was applied to assay charge generation efficiency for DPP-TT-T and BTT-DPP devices.

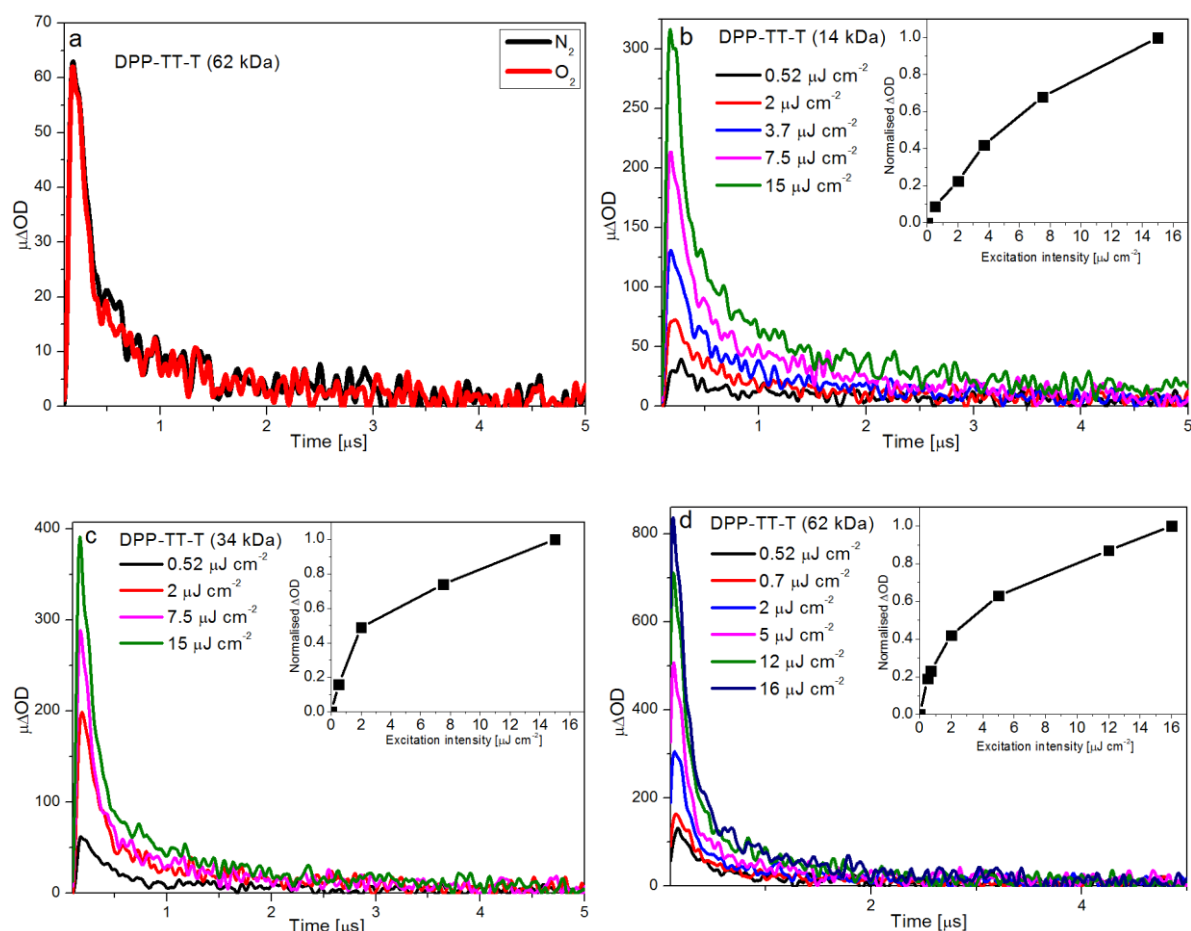


Figure 5.6: Transient photon absorptions as functions of time obtained from DPP-TT-T:PC₇₁BM, pumped at 800 nm and probed at 1200 nm. a) Demonstrates the absence of polymer triplet signals using DPP-TT-T (62 kDa). The decays were run under nitrogen and oxygen atmosphere with excitation intensity of 2 $\mu J cm^{-2}$; (b, c and d) Excitation intensity dependence of transient decays obtained from the polymer:fullerene blends with various polymer weight. Inserts show the amplitudes at 0.17 μs as functions of excitation intensity (estimated by fitting the decays to power law of $\Delta OD \sim t^{-\alpha}$, followed by extracting the amplitudes at 0.17 μs of the fits).

Nano to microsecond transient absorption spectroscopy was applied to DPP-TT-T:PC₇₁BM blends in order to resolve the charge generation yields and dynamics in the devices with the assistance of Ms Elisa Collado-Fregoso. The polaron of DPP-TT-T has been previously reported to have an absorption maximum at 1200 nm.⁵⁰ Figure 5.6 (a) shows transient decays

from pumping DPP-TT-T (62 kDa):PC₇₁BM (1:2) blend at 800 nm with an excitation intensity of 2 $\mu\text{J cm}^{-2}$ under nitrogen and oxygen atmosphere. The similarity in the decays under these different atmospheres suggests that there was an absence of triplet polymer excitons in this system. Decays of the other two fractions, which are not shown, are also insensitive to oxygen. The transient decays of the fractionated DPP-TT-T:PC₇₁BM films recorded at the polymer polaron absorption maximum using different excitation densities, are presented in figure 5.6 (b, c and d). A plot of the transient absorption (TA) amplitude at 0.17 μs as a function of excitation intensity shows a gradual increase in the polaron yield with excitation density, which starts to saturate for intensities $> 2 \mu\text{J cm}^{-2}$. Such dependence has previously been related to a trap-limited bimolecular recombination of free polarons.⁵¹

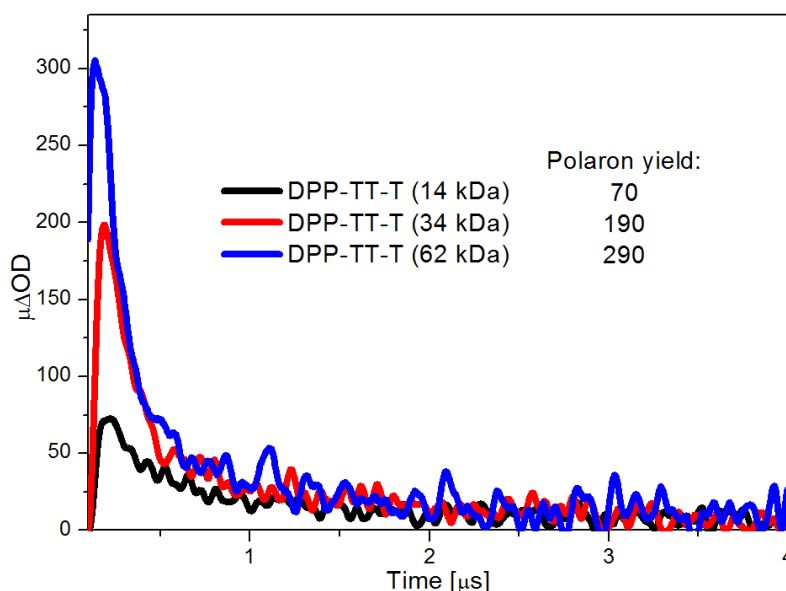


Figure 5.7: Transient decay kinetics obtained by exciting the samples DPP-TT-T :PC₇₁BM with different molecular weight, pumped at 800 nm of 2 $\mu\text{J cm}^{-2}$ excitation intensity and probed at 1200 nm. These data have been corrected to normalise for differences in the density of absorbed photons. Polaron yield was estimated using the signal amplitude at 0.17 μs (estimated by fitting the decays to power law of $\Delta\text{OD} \sim t^{-\alpha}$, followed by extracting the amplitudes at 0.17 μs of the fits).

Figure 5.7 shows the decays of the three DPP-TT-T:PC₇₁BM blends with different molecular weight, probed at 1200 nm and pumped at 800 nm with an excitation intensity of 2 $\mu\text{J cm}^{-2}$. Each of these decays can be fitted to a power law decay $\Delta\text{OD} \sim A t^{-\alpha}$. The amplitude of the transient absorption at $\sim 0.17 \mu\text{s}$ has been previously reported to be a representative for photo-induced charge generation for analogous DPP polymers, showing good correlation with short circuit current.⁵⁰ The yield of DPP-TT-T polaron at 0.17 μs , as represented by the amplitude

of these decays, is increased by roughly a factor of four when the molecular weight is increased by a factor of 4 (14 kDa to 62 kDa). It is noticeable that there is a qualitative match between the observed trends in changes in polaron yields and device short circuit currents, which suggests that the increase in charge generation is one of the major reasons for the improved short circuit current for the devices with higher polymer molecular weight.

For BTT-DPP, femtosecond transient absorption spectroscopy was applied by Dr. Stoichko Dimitrov and the results have been published.³⁹ This technique is able to trace transient absorption at femtosecond – nanosecond timescales and therefore any species formed on early time scales, including excitons, can be investigated. Since most current is derived from fullerene absorption, the samples for femtosecond TAS were excited at 470 nm where PC₇₁BM primarily absorbs (470 nm). The signals at 1200 nm were monitored as a function of time and normalised at 0.25 ps. Although both polymer singlet exciton and polymer polaron absorb at 1200 nm, they can still be distinguished as the signals of the polymer exciton have been found to diminish by 15 ps while at later time the signals are mainly contributed by the polymer polarons which have longer lifetime.³⁹ As shown in figure 5.8, fullerene excitons generated more polarons at a faster rate in the blends with higher molecular weight of BTT-DPP. The signals at 3 ns, when polymer polaron absorption is at its maximum, were extracted and show a qualitative match with the short circuit current from the devices (figure 5.3).

The better charge generation from polymer excitons observed for high molecular weight DPP-TT-T and BT-DPP can be associated with either changes in material energetics or blend microstructure. However, note that the small differences are observed in optical bandgap of the polymer with differing molecular weight (figure 5.3). The HOMO energy levels of a couple of other polymers have been reported to be invariant in a similar molecular weight regime to that this study.^{20, 22, 24} As such, the energy levels of the DPP-TT-T HOMOs are also assumed to be independent of molecular weight. This therefore suggests that the driving energy for the electron transfer should be similar across the molecular weights, and hence cannot account for the drastic changes in charge generation yields from the polymers. Such interpretation implies that the difference in charge generation should be substantially derived from the blend microstructure.

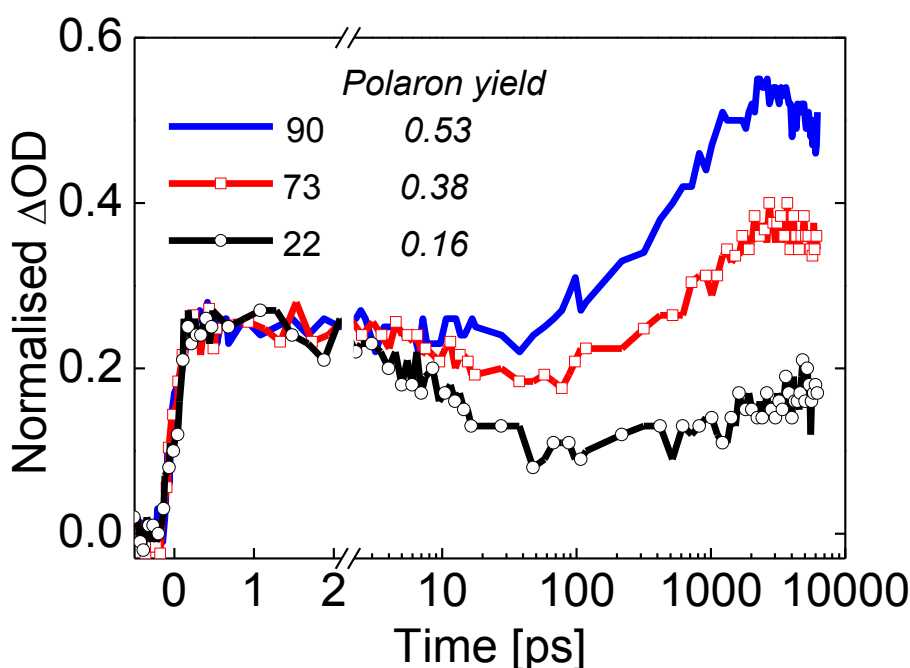


Figure 5.8: Transient photon absorption as function of time obtained by exciting the samples made of different molecular weight BTT-DPP and PC₇₁BM at 470 nm at 7.5 $\mu\text{J cm}^{-2}$ probing at 1200 nm. The polaron yield was estimated using the amplitude at 3 ns. [This image has been reproduced with the permission of the rights holder, The Royal Society of Chemistry³⁹]

5.3.3 Study on DPP-TT-T:PC₇₁BM and BTT-DPP:PC₇₁BM blend morphology

5.3.3a Photoluminescence spectroscopy

Photoluminescence spectroscopy (PL) was used for probing the exciton dissociation yields in the studied here systems. As discussed previously, the PL quenching is also an excellent indicator for the degree of mixing between the polymer and fullerene in blends. In the current experiment, fullerene was excited at 520 nm and 470 nm for DPP-TT-T:PC₇₁BM and BTT-DPP:PC₇₁BM thin films, respectively. The fluorescence of PC₇₁BM centred at 707 nm³⁹ is poorly quenched in most polymer:fullerene blends studied here (figure 5.9). However, an increased fullerene quenching was consistently observed with increasing polymer molecular weight. More specifically, as the molecular weight is increased, the quenching of fullerene photoluminescence increases from 19% to 68% for DPP-TT-T (figure 5.9 (left)) and from 32% to 50% for BTT-DPP (figure 5.9 (right)), qualitatively consistent with the trend observed in both the short circuit current and TAS. This result suggests that the BTT-DPP and DPP-TT-T

blends with PC₇₁BM suffer from poor polymer:fullerene miscibility or/and severe phase segregation, both limiting exciton dissociation as well as charge generation yields in these blends.⁵³⁻⁵⁶ In order to confirm this trend, TEM and AFM were applied to BTT-DPP and DPP-TT-T respectively.

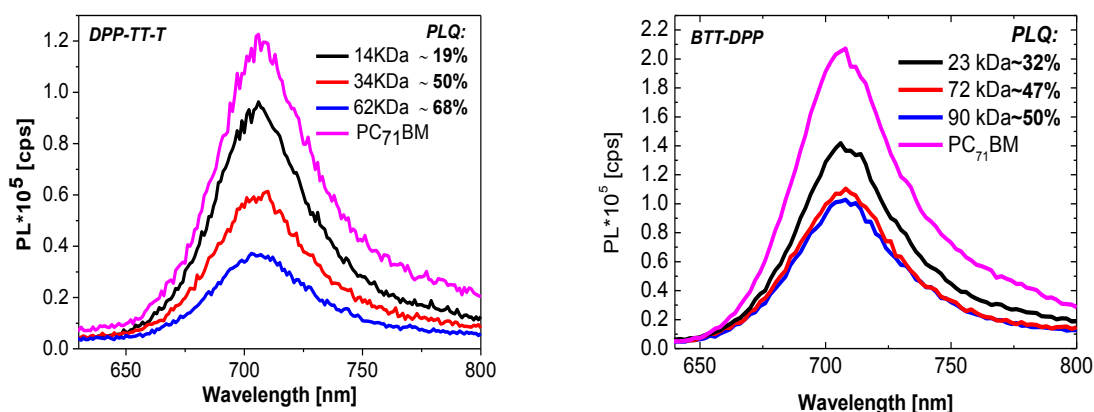


Figure 5.9: Photoluminescence of neat PC₇₁BM, DPP-TT-T:PC₇₁BM (Left) and BTT-DPP:PC₇₁BM (right) thin films with varying polymer molecular weight, with the samples excited at 520nm.

5.3.3b Atomic force microscopy

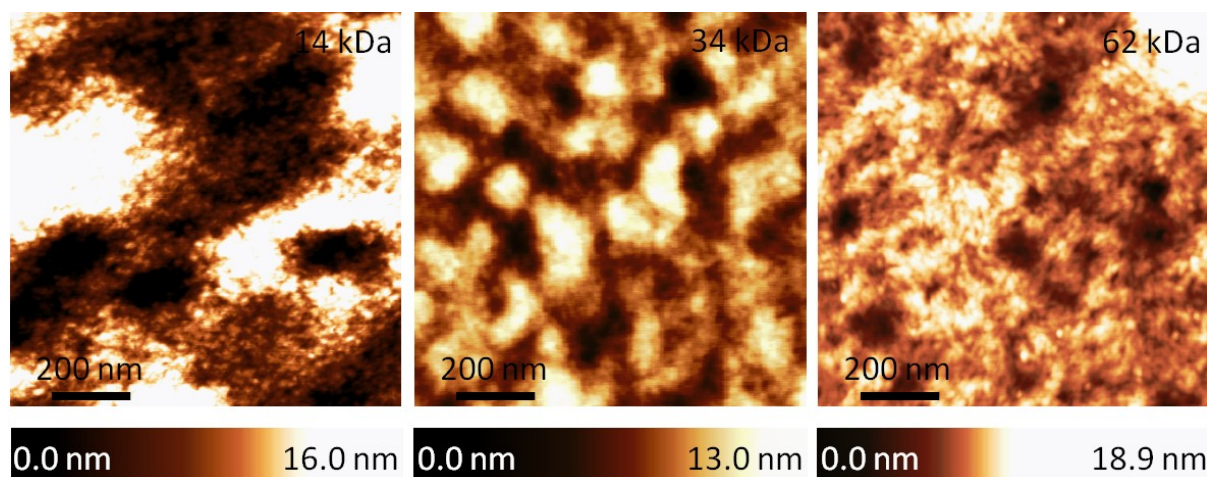


Figure 5.10: Topography images of DPP-TT-T:PC₇₁BM films with different polymer molecular weights measured by atomic force microscopy.

Atomic force microscopy was employed (See Chapter 2 for the experimental setup) to obtain the topography images of DPP-TT-T:PC₇₁BM thin films with different polymer molecular weight, as shown in Figure 5.10. DPP-TT-T (14 kDa):PC₇₁BM blend exhibits phase

segregation (defined by the contrast between the bright and dark regions) on the order of ~ 200 nm (extracted from the topography profile). Note that the domains observed in Figure 5.10 cannot be directly assigned to pure polymer or fullerene, given that the blend still exhibits a moderate fullerene exciton quenching (figure 5.9). Nevertheless, it is clear that the phase segregation becomes less severe as the polymer molecular is increased to 34 kDa and 62 kDa, implying an increase in the degree of material mixing.

5.3.3c Transmission electron microscopy

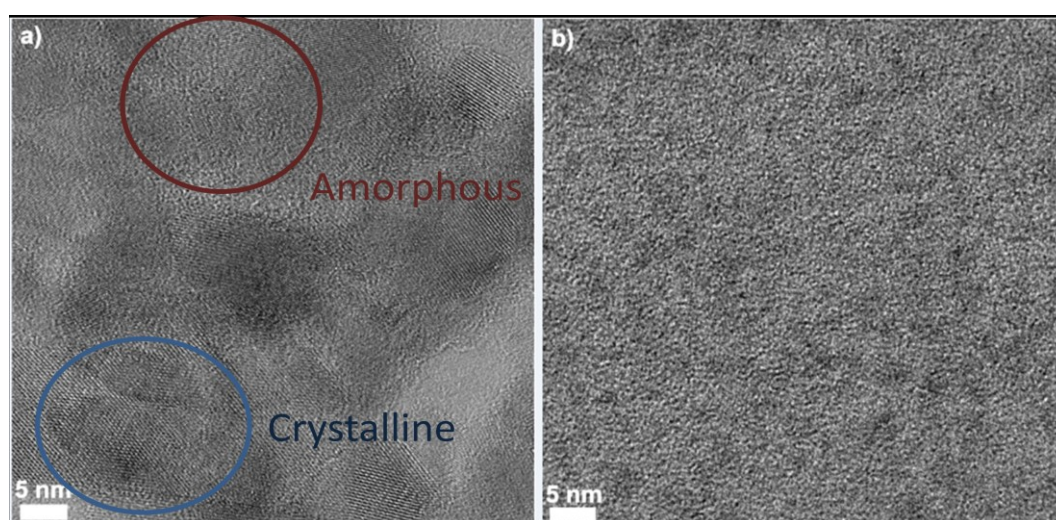


Figure 5.11: TEM images of BTT-DPP(23 kDa):PC₇₁BM and BTT-DPP(90 kDa):PC₇₁BM thin films. The samples were stained with RuO₄. [This image has been reproduced with the permission of the rights holder, The Royal Society of Chemistry³⁹]

The TEM measurements were carried out by Dr Safa Shoaee. The samples were stained by RuO₄ vapour prior to the TEM measurement in order to improve the contrast between the polymers and fullerenes. Figure 5.11 shows the TEM images obtained from BTT-DPP:PC₇₁BM samples. In the case of BTT-DPP (23 kDa), the TEM images displays observable lattice fringes, with the lattice spacing being approximately 3.5 Å. This is similar to the d spacing of π - π stacking of BTT-DPP determined by WAXS in section 5.3.1b ($q \sim 1.7 \text{ Å}^{-1}$, d spacing $\sim 3.7 \text{ Å}$). As such, the dark regions are assigned to the polymers. It can be clearly seen that BTT-DPP(23 kDa):PC₇₁BM displays a coarser domain structure consisting of crystalline and amorphous regions, with the polymer crystalline region being greater than 5 nm. In contrast, the bright and dark regions become more evenly dispersed over the whole

images for BTT-DPP(90kDa), suggesting a more finely mixed morphology. This trend matches well with the conclusion from the WAXS and photoluminescence measurements.

Although both TEM and AFM on their own provide limited information on domain composition, the agreement among TEM, AFM and PL suggests that phase segregation is reduced at higher polymer molecular weights, an observation which contrasts previous reports for other polymers.²³ This suggests that the better device performance obtained at high polymer molecular weight is a result of improved blend microstructure. The correlation between chain length and blend microstructure is discussed in section 5.4.

5.4 Discussion

Previous studies on molecular weight dependence of device performance for various conjugated polymers generally attributed the better performance achieved at high molecular weight to either better charge transport, light absorption or blend microstructure.^{13, 15, 18, 19, 22-26} In this study, the improvement in power conversion efficiency is believed to be primarily derived from blend microstructure. In the following section, the impact of molecular weight on charge transport, light absorption and blend microstructure are discussed sequentially, with a focus particularly on blend microstructure.

First of all, previous studies on a couple of polymers including benchmark materials P3HT and PCDTPT suggested that increasing polymer molecular weight could improve the polymer hole mobility, and hence raising the fill factor of the device.^{13, 18, 19, 22, 23} In our case, it is clear that the improvement in device performance cannot be derived from the same reason as those mentioned in the previous studies, since the fill factors of both DPP-containing polymers are either invariant or decreases with increasing molecular weight. Our results appear to be consistent to a study on another DPP-containing polymer from Janssen and co-workers, who have reported that the OFET hole mobility as well as device fill factor are independent of the polymer molecular weight ($M_n \sim$ from 10 kDa to 54 kDa).

Secondly, in terms of light absorption, an increase in intensity of the longer wavelength absorption (810 nm and 770 nm for DPP-TT-T and BTT-DPP respectively) is observed for both polymers with increasing molecular weight. This should reduce the spectral mismatch between active layer absorption and solar emission, leading to an improvement in photon

harvesting.^{20, 22} According to previous studies from P3HT,^{13, 26, 45-47} the red shift in our case implies a better π - π stacking of polymers, consistent with our WAXS results. In addition, the better light absorption is also partially derived from active layer thickness, with the highest molecular weight resulting in the thickest films for both polymers. The thickness of the active layer can depend upon material processability and material ordering.²² Nevertheless, it is clear that the changes in absorption cannot explain most of the increase in the short circuit current with molecular weight based on previous model correlating optical absorption and active layer thickness.^{48, 49} This is also evident by the TAS signals in section (5.3.2c) which have been corrected by photon absorption, showing qualitative match with the short circuit current.

Finally, in the case of blend microstructure, the agreement between photoluminescence measurements and AFM or TEM measurements in section 5.3 suggests that blend microstructure with increased polymer:fullerene mixing is obtained at high polymer weights. This correlates well with our TAS and short circuit currents measurements, highlighting the importance of the higher degree of polymer:fullerene mixing offered by the higher polymer molecular weight to device performance, especially for semicrystalline polymer:fullerene blends which generally exhibits more severe phase segregation than amorphous polymers.⁵³ In addition, for BTT-DPP, saturation in device performance is not observed as the molecular weight is increased from 22 kDa to 90 kDa, compared to P3HT which exhibited saturated device performance when the molecular weight exceeded $M_n \sim 60$ kDa.²⁷ This suggests other polymers may not follow the exact same evolution observed in P3HT and P3HT is likely not to be a perfect prototype for novel polymer semiconductor for OPV.

There are a limited number of studies investigating the correlation between polymer chain length and blend microstructure.^{15, 23-26} In one of them, Westacott and co-workers attributed the better P3HT:fullerene mixing to the increase in volume fraction of amorphous P3HT, which is more compatible to fullerene and induced by higher degree of chain entanglements.²⁶ In agreement with this, the increase in material mixing with increasing molecular weight observed in this study is consistent with the lower diffraction strength of lamellar packing, indicative of higher volume fraction of amorphous DPP-containing polymers.⁴⁴ However, note that the morphological evolution with molecular weight does not agree with the increased diffraction strength of π - π stacking. As such, correlation between polymer:fullerene mixing and polymer crystallinity requires further confirmation using other

techniques such as grazing-incidence X-ray diffraction which can provide 3-dimension information of material crystallinity. In addition, polymer crystals with high molecular weight have been found to be easier to breakdown by the presence of fullerenes, which is an alternative explanation for our observation of reduced film crystallinity, increased PL quenching and high charge generation yields.²⁶ In contrast, these conclusions are in contradiction with studies (with similar ranges of molecular weight) showing that some polymer with high molecular weights have reduced solubility and as a result of that severe phase segregation.^{15, 23} However, this is not the case for both of our polymers, suggesting more research effort is required to fully understand the correlation between blend microstructure and chain length of conjugated polymers.

5.5 Conclusions

Tuning molecular weight has been demonstrated to be another way, in addition to fluorination and side chains mentioned in Chapter 3 and 4, to manipulate blend microstructure for two DPP-containing polymers, leading to approximately 2 to 4-fold increase in power conversion efficiency. This study highlights the importance of the improved blend microstructure to device performance at high molecular weight, different from the improved light absorption or charge transport highlighted by previous literature. The improved device performance is likely due to more efficient exciton dissociation, offered by the better polymer:fullerene mixing. The correlation found between DPP polymer crystallinity and phase segregation seems to follow that reported by Westacott and co-workers, but required further experiment for confirmation. While there are few studies on correlating chain length with blend morphology, the substantial increase in PCE observed in our case clearly suggests more research effort should be made in this area.

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Chapter 6

Morphological stability of polymer:fullerene blends and solar cells under thermal stress

Abstract

This chapter investigates the polymer:fullerene device stability upon thermal annealing. The chapter starts with comparing a semicrystalline polymer DPP-TT-T with a relatively amorphous polymer SiIDT-BT. DPP-TT-T is shown to exhibit faster device performance degradation at annealing temperature above 140 °C for period of 10 minutes, consistent with its poorer ability to inhibit the formation of fullerene crystal clusters revealed by optical microscopy. This ability is associated with the thermodynamic polymer:fullerene miscibility, measured using near edge X-ray absorption fine structure (NEXAFS). In addition, PC₇₁BM is demonstrated to display better morphological stability than PC₆₁BM when blending with DPP-TT-T, potentially due to its less diffusive nature. Lastly, photo-induced transformation of fullerene is applied to DPP-TT-T:PC₆₁BM blend, which successfully improves the device stability upon thermal annealing.

6.1 Introduction

In Chapters 3, 4 and 5, the correlation between blend microstructure and device power conversion efficiency has been demonstrated for several polymer:fullerene systems. In this chapter, the influence of blend morphology on device stability is investigated. As mentioned in Chapter 1, the blend microstructure obtained by spin casting is a kinetic trapped morphology due to the fast timescale of film drying.^{1, 2} Therefore, it has been suggested that this blend microstructure may not be stable from a thermodynamic standpoint and may therefore evolve, particularly at high temperatures, causing loss in device performance.¹⁻⁵

Studies on the morphological stability for polymer based solar cells have been reported in the literature, but only on a relatively small library of benchmark polymers such as P3HT and MDMO-PPV.^{2, 5-9} Upon thermal annealing, the blend morphology has been found to change over time for these systems.^{2, 5, 10, 11} Morphological degradation is generally interpreted as a process consisting of fast fullerene diffusion and relatively slow rearrangement of polymer microstructure.^{4, 7, 11} In particular, the relatively fast diffusion of fullerenes, due to their small size and weak intermolecular interactions, is suggested to be the key cause of morphological degradation.¹²⁻¹⁴ It has been shown in some systems that fullerene diffusion can happen at temperatures as low as 50 °C,⁴ compared to 85 °C which the solar cells are likely to reach under operating conditions. At elevated temperatures for a sufficient annealing period, micron size fullerene clusters, surrounded by fullerene-depleted regions, are formed in the polymer:fullerene blends and can be observed using optical microscopy.^{2, 5, 7, 11, 12, 15-17} The fullerene clusters has been reported to be rich of fullerene crystalline,^{2, 5} with the growth in size following biphasic kinetics.^{15, 18} The resultant degraded morphology has been associated with the formation of such large discrete domains which could deteriorate device performance by potentially inhibiting exciton dissociation or charges collection.^{2, 7, 19, 20}

In the first part of this chapter, the impact of polymer crystallinity on blend morphological stability is investigated. Morphology stability has been suggested to be improved with increased viscosity of the polymer:fullerene blend, which has been reported to be influenced by a number of parameters including glass transition temperature, side chain structure and blend ratio, as has been outlined in Chapter 1.^{1-3, 7, 21-27} Recently, such studies have been extended to comparisons of morphological stability between blends with the semicrystalline polymer P3HT to other, more amorphous, polymers.^{7, 8, 21} P3HT is the semicrystalline benchmark material for OPV studies when blended with PCBM, and displays an improved

device performance when subjected to thermal treatments for short periods of time (typically 140 °C for 10 minutes). This improved performance has been associated with a greater material crystallinity and enhanced domain structure, facilitating charge separation and transport with causing excessive loss in exciton dissociation efficiency.^{17, 22-24}

In contrast, such thermal annealing has not been successful in improving the performance of OPV devices employing alternative donor polymers such as MDMO-PPV and PCDTBT, which are mostly with amorphous nature.²⁵⁻²⁷ For example, short term annealing (90-150 °C for 10 min) has been shown to degrade the performance of MDMO-PPV:PCBM devices.⁷ This was attributed to 1) growth in material domain size, leading to a less efficient exciton dissociation;⁷ 2) loss in fullerene intercalation into MDMO-PPV causing reduced polymer hole mobility.²⁶ For PCDTBT, short term annealing (140 °C for 10 minutes) did not result in any loss in exciton dissociation.²⁵ Rather, the negative impact of such annealing on PCDTBT device performance was attributed to a subtle reduction in ordering of the weak polymer π - π stacking which lowered the hole mobility of the polymer.^{11, 25} These studies implied that improving polymer crystallinity is probably one key requirement to ensure a positive effect on device performance upon short term annealing. In addition, it is worth noting that morphological degradation is not limited to the growth in domain size or loss in percolation. The studies on the two amorphous polymers highlighted that loss in molecular structure ordering is also critical to morphological degradation.^{11, 25, 26}

In terms of longer term thermal annealing, there are a rather limited number of studies comparing the morphological stability of P3HT blends with other amorphous polymers.^{7, 8, 11, 21} As mentioned in Chapter 1, morphological stability has been found to be dependent upon the thermal annealing condition as well as device fabrication procedure. As the conditions under which morphological stability was evaluated are different between studies reported to date in the literature, cross-comparison on morphological stability between these studies is non-trivial. For examples, Wang and co-workers reported that PCDTBT displayed better morphological stability than P3HT under a thermal cycle with temperatures varied between 25 °C and 80 °C for period of 300 hours, although this study did not include any degradation occurring during an initial 10 minute pre-annealing at 70 °C.⁸ Later, Lizy and co-workers demonstrated that formation of micron sized fullerene clusters in PCDTBT:PC₇₁BM blend were only observed after annealing at 155 °C for 2100 seconds, compared to P3HT:PC₆₁BM which required only 1000 seconds at a similar temperature. The authors suggested this

comparison reflected the greater polymer:fullerene miscibility for PCDTBT, which was believed to account for its more stable blend microstructure than P3HT.¹¹ Ebadian and co-workers demonstrated that less crystalline P3HT, obtained by reducing its regioregularity (RR), showed better device stability at 140 °C temperature in comparison to the more crystalline P3HT (high RR). Similar to the work by Lizy and co-workers, the authors also attributed the better stability of the low RR P3HT device to the better ability of the polymer to suppress fullerene clusters formation at high temperature (150 °C).²¹ The relative stability of these two P3HTs remained the same at low temperature, with the low RR P3HT exhibiting a better device stability at room temperature for a period up to 140 days. Contradicting this observation, Bertho and co-workers reported that the relative stability between two systems might not be the same at different temperatures. In their study, devices of P3HT and MDMO-PPV were compared in terms of their thermal stability for period of 25 hours.⁷ Despite having a higher T_g , MDMO-PPV devices exhibited a poorer stability at temperatures below 110 °C. This was suggested to be partially due to an initial buffer region in the performance decay of P3HT devices, in which the initial evolution of P3HT:PC₆₁BM morphology was believed to be beneficial for the device performance as mentioned above.^{17, 22, 28} At 150 °C, the opposite trend was observed, with the performance of P3HT device exhibiting a severer degradation in comparison to MDMO-PPV under the same condition. As such, the current literature remains ambiguous over whether semicrystalline polymers are more stable than amorphous polymers under thermal annealing.

Two of the studies referred to above^{8, 21} suggested that higher polymer:fullerene miscibility is an indicator of the better morphological stability observed for the low RR P3HT and amorphous PCDTBT at high temperature (~150 °C). Such miscibility can be measured quantitatively using near edge X-ray absorption fine structure (NEXAFS).^{4, 12, 29} In this experiment, a polymer:fullerene blend is annealed at certain temperature for sufficient period (~100 hours) to allow the blend to achieve a thermal equilibrium state. The weight percentage of fullerene in the fullerene-depleted region is measured using NEXAFS and defined as the thermodynamic polymer:fullerene miscibility. This miscibility study has been used to predict the film morphological stability from a thermodynamic standpoint.^{4, 29} Based on such measurements, there have been studies which show PC₇₁BM has a better miscibility with polymers than PC₆₁BM, implying a better morphological and device stability for PC₇₁BM based devices.

The second part of this chapter focuses on improving morphological stability for polymer solar cells. In this regard, most traditional strategies involve the introduction of crosslinkers which could limit fullerene diffusion by enhancing rigidity of the polymer matrix.^{1, 3} However, these approaches often require synthesis of complex materials or potential sacrifices in device performance.^{30, 31} Recently, our group have developed a convenient strategy using fullerene light transformation to enhance the morphological stability of PCDTBT:PCBM devices.^{32, 33} This approach is based on the formation of fullerene oligomers via a [2+2] cycloaddition upon light exposure (figure 6.1), which potentially are less diffusive than the monomer form, and inhibit PCBM crystal/cluster formation.³⁴⁻³⁶

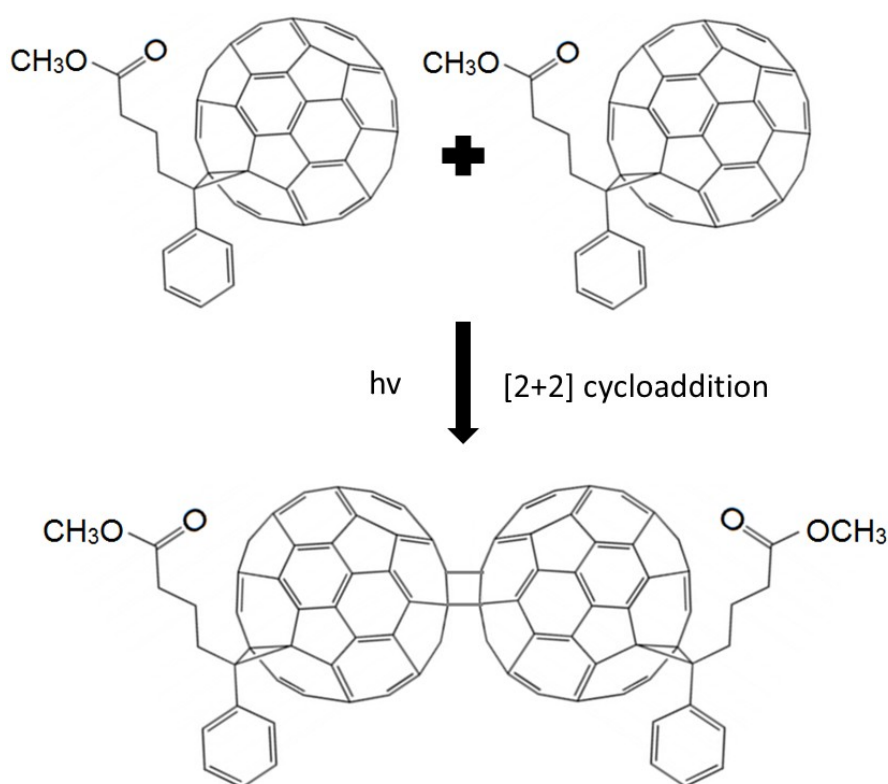


Figure 6.1: Dimerisation of PC₆₁BM via photo-induced transformation.

In this chapter, the difference between semicrystalline and amorphous polymers is explored in terms of blend morphological and device thermal stability. A comparative study under short term thermal stress conditions (10 minutes at each temperature) is carried out on two donor-acceptor polymers, DPP-TT-T and SiIDT-BT, which have different crystallinity.^{37, 38} Both of the polymers have efficiencies of over 4% in OPV devices, with details provided in Chapter 3 and 5. A range of techniques including WAXS, PL spectroscopy and optical microscopy are employed to evaluate the impact of thermal annealing upon device performance and blend microstructure. More specifically, PL spectroscopy is used to provide

information on domain evolution on the scale of exciton diffusion length ($\sim 5\text{-}10$ nm for polymer excitons³⁹ and ~ 5 nm for fullerene excitons as reported previously⁴⁰), whilst optical microscopy can probe blend images on micrometer lengthscale to investigate the formation of micron sized, fullerene crystal clusters. In addition, NEXAFS studies is used to measure the miscibilities of these two polymers with PC₇₁BM, in order to establish a correlation between such parameter and morphological stability. In addition, the thermal stability of blends with PC₆₁BM and PC₇₁BM are compared. A preliminary experiment is carried out to look at the effects of cathode composition on device stability. Lastly, fullerene light transformation is also introduced to the DPP-TT-T system, which shows improvements in both morphological stability and device thermal stability.

6.2 Experimental

Materials – DPP-TT-T was synthesized by Dr. Hugo Bronstein from Prof. Iain McCulloch at Imperial College, with a Mn of 35 kDa and PDI of 4.3. SiIDT-BT (C2C6) was synthesized by Dr. Bob Shroeder from Prof. Iain McCulloch at Imperial College, with Mn of 28 kDa and PDI of 1.3. The details of synthesis for these two polymers can be found in ref.^{37, 38} The chemical structures of the two polymers are included in Chapter 2.

Technique information - The general information of device fabrication and the techniques involved in this chapter, such as WAXS, photoluminescence spectroscopy is outlined in Chapter 2. Details of the setup of NEXAFS can be found in ref^{12, 29}. NEXAFS measurements were carried out by Dr. Wei Ma from University of North Carolina. Optical microscopy experiment was carried with the assistance of Mr Paul Westacott and Dr. Him Cheng Wong from the Departments of Materials and Chemical Engineering at Imperial College London.

Samples preparation – Spin-cast films were used for photoluminescence spectroscopy, NEXAFS, optical microscopy measurement and device fabrication. The details of DPP-TT-T solution preparation are included in Chapter 5. For SiIDT-BT, a dichlorobenzene solution of 54 mg/ml SiIDT-BT:PC₇₁BM (1:3.5) was used. Drop-cast films were used for the WAXS measurement with the preparation details described in Chapter 2. Device fabrication was undertaken as detailed also in Chapter 2. Apart from device fabrication, polymer:fullerene blend was deposited on glass substrates.

Thermal annealing – Thermal annealing was carried out on a hotplate under nitrogen atmosphere. Apart from for section 6.3.3 and for the NEXAFS measurements, the same thermal aging approach was used as described below:

The samples were treated with a thermal cycle as shown in figure 6.1. The samples were kept in the dark and annealed on a hot plate in nitrogen at a temperature for 10 minutes and then allowed to place on a metal block for 15 minutes to cool down to room temperature. A Kane-May KM330 temperature sensor was used to calibrate the temperature. The samples were then transferred to undergo different experiments such as WAXS, photoluminescence spectroscopy and optical microscopy. Finally, they were put back onto the hot plate and annealed at a higher temperature and this loop of experiments was kept repeated.

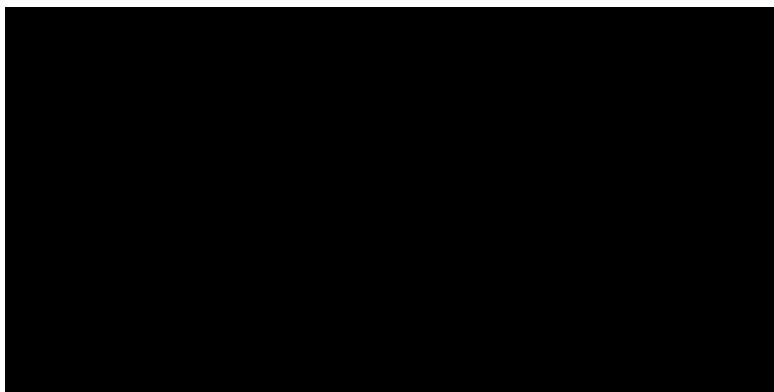


Figure 6.2: Flow chart of the thermal aging experiment.

Light treatment – samples subjected to light treatment for fullerene phototransformation were exposed to a standard low-intensity ($\sim 10 \text{ mW cm}^{-2}$) fluorescence lamp for 4 hours. The emission spectrum of the lamp is shown in figure 6.3.

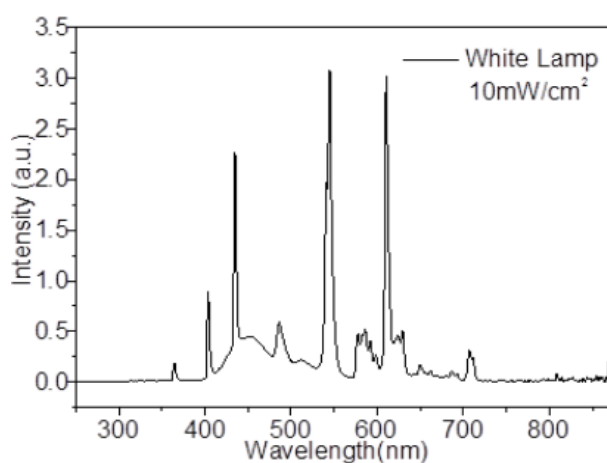


Figure 6.3: Emission spectra of the white fluorescent lamp.

6.3 Results

6.3.1 DPP-TT-T:PC₇₁BM vs SiIDT-BT:PC₇₁BM

6.3.1a Polymer crystallinity

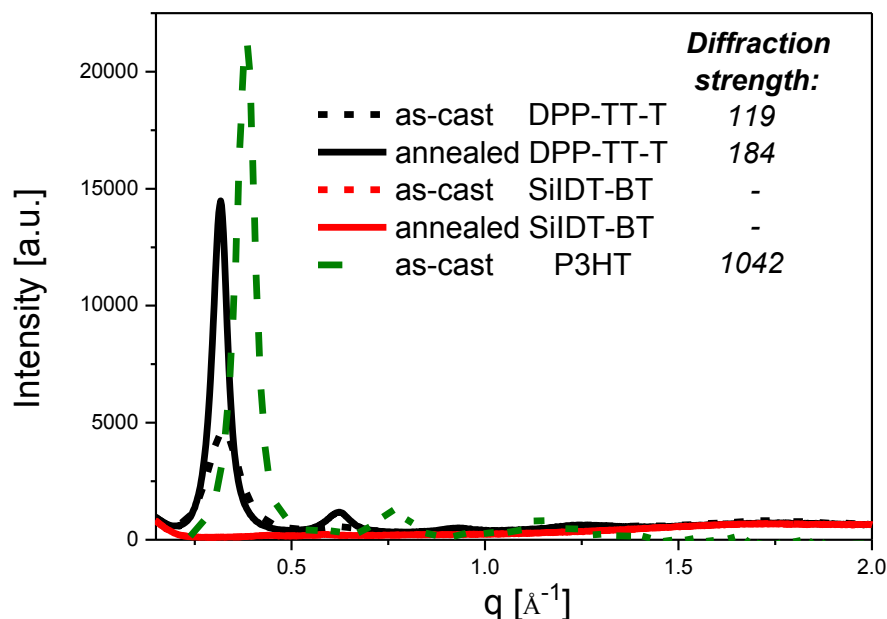


Figure 6.4: Wide angle X-ray scattering (WAXS) on DPP-TT-T (black), SiIDT-BT (red) and P3HT (green) films. Signals of as-cast and annealed (170°C for 10 minutes) films are presented with dashed lines and solid line respectively. All the samples were prepared using drop casting. The diffraction strength is the area of the WAXS signals divided by the film thickness.

The two polymers studied in this chapter are DPP-TT-T and SiIDT-BT, which are semicrystalline and amorphous as demonstrated by WAXS in figure 6.4. WAXS signals were obtained from as-cast and annealed neat polymer films deposited on glass substrates, with the details of the measurements described in Chapter 2. As shown in figure 6.4, DPP-TT-T and SiIDT-BT exhibit lamellar packing signals at $q \sim 0.3 \text{ \AA}^{-1}$ and $0.5 \text{ \AA}^{-1}$ respectively. Note that the signals of SiIDT-BT are weak and therefore appear to be featureless with the scale of the plot in figure 6.4. It has been demonstrated in chapter 5 that as-cast DPP-TT-T is a semicrystalline polymer, although it is less crystalline than P3HT (green line in figure 6.4). Annealing the polymer at 170 °C for 10 minutes in nitrogen results in a 55% increase in lamellar diffraction strength (DS), indicative of an increased degree of crystallinity. In comparison, the weak signals of as-cast SiIDT-BT remain unchanged after annealing,

suggesting the amorphous nature of this polymer is independent of the thermal aging condition employed.

6.3.1b Annealing study of polymer:PC₇₁BM blends

Thermodynamic polymer:fullerene miscibility

Temperature [°C]	Miscibility	Miscibility	Miscibility
	DPP-TT-T:PC ₇₁ BM (wt % of PC ₇₁ BM)	SiIDT-BT:PC ₇₁ BM (wt % of PC ₇₁ BM)	DPP-TT-T:PC ₆₁ BM (wt % of PC ₆₁ BM)
140	6.6	40.1	3.6
170	7.5	10.5	5.8

Table 6.1: The degree of polymer:fullerene miscibility (weight percentage of fullerene remain in the homogenous region) measured using NEXAFS on DPP-TT-T:PC₇₁BM, SiIDT-BT:PC₇₁BM and DPP-TT-T:PC₆₁BM thin films. The films had been annealed at 140 °C or 170 °C for 100 hours prior to the measurements.

Near edge X-ray absorption fine structure (NEXAFS) was employed by Dr. Wei Ma from University of North Carolina to quantitatively measure the thermodynamic polymer:fullerene miscibility for these two polymers. As mentioned in section 6.1, blend thin films on glass substrates, with polymer:fullerene blend ratios of 1:2 and 1:3.5 for DPP-TT-T and SiIDT-BT respectively, were prepared in the same manner as those for device active layers. They were annealed at a fixed temperature for 100 hours to achieve a thermodynamically equilibrium state, after which the size of the micron sized fullerene crystal clusters is saturated.^{4, 29} The weight percentage of fullerene in the fullerene-depleted region was then measured using NEXAFS, and is defined as the polymer:fullerene miscibility. (More experimental details can be found in Chapter 2) This miscibility has been reported to be independent of the initial polymer:fullerene blend ratio.⁴¹

As shown in table 6.1, SiIDT-BT is more miscible with PC₇₁BM in comparison to DPP-TT-T. At 140°C, the miscibility for SiIDT-BT was 40% wt, which is considerably higher than the fullerene miscibility with P3HT (~5% wt) and MDMO-PPV (~8% wt) measured in previous studies.⁴¹ In comparison, DPP-TT-T is very immiscible with PC₇₁BM, with a fullerene miscibility of 6.6%, similar to that with P3HT. As the temperature increases to 170 °C, the

fullerene miscibility with SiIDT-BT drops to 10.5% wt. In contrast, the fullerene miscibility with DPP-TT-T increases slightly to 7.5%, closing the gap between these two systems.

Formation of fullerene crystal clusters

In this section, short term annealing conditions are applied to study the evolution of blend microstructure and device degradation for the two polymers. The morphology of polymer:fullerene blend is investigated as a function of annealing temperature. The period for annealing at each temperature is fixed at 10 minutes unless otherwise specified. The details of thermal aging can be found in section 6.2.

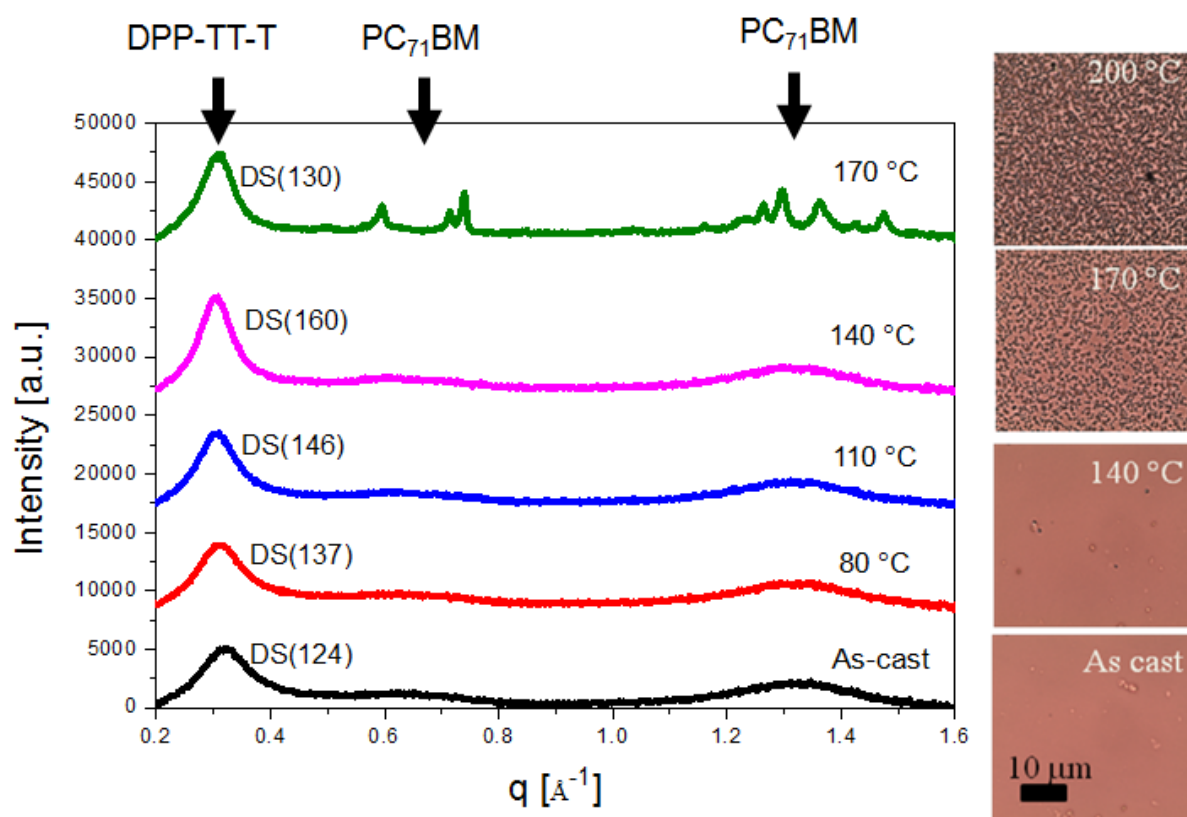


Figure 6.5: WAXS signals (left) and optical images (right) obtained from DPP-TT-T:PC₇₁BM blend films on glass substrates under different thermal aging condition. Drop cast films were used for WAXS while spin cast films were used for optical microscopy.

The morphological evolution of DPP-TT-T:PC₇₁BM (1:2) and SiIDT-BT:PC₇₁BM (1:3.5) films on glass substrates were firstly investigated using WAXS and optical microscopy in order to monitor changes in molecular packing and appearance of micron size fullerenes. Note that the drop-cast films were used for WAXS while spin-cast thin films were used for optical microscopy.

In the case of DPP-TT-T, the WAXS signals obtained from drop-cast DPP-TT-T:PC₇₁BM films under different annealing conditions are shown in figure 6.5. In addition to the lamellar peaks of the polymers demonstrated earlier, there are two additional peaks at $q \sim 0.65 \text{ \AA}^{-1}$ and $1.3 \text{ \AA}^{-1}$ in the blend films, assigned to PC₇₁BM according to a previous study.⁴² The position of the DPP-TT-T lamellar peak remains unchanged in comparison to its neat film (figure 6.2), suggesting the polymer crystals are pure and free of fullerene.^{43, 44} The mean size of polymer crystal can be estimated by Scherrer equation (outlined in Chapter 2), resulting in a magnitude of approximately 5 nm for pristine blend film. It can be seen that the DS of the DPP-TT-T lamellar peak increases with annealing temperature up to 140 °C, suggesting there is an increase in the degree of polymer crystallinity. This most probably is associated with a reduction in the volume fraction of the amorphous polymer regions, potentially promoting phase segregation. At 170°C, the DS is slightly reduced. Meanwhile there is a drastic change in fullerene crystallinity, as the broad fullerene peaks at $q \sim 0.65 \text{ \AA}^{-1}$ and $1.3 \text{ \AA}^{-1}$ are turned into well defined multiple narrow peaks.

Optical microscopy was applied to spin-cast DPP-TT-T:PC₇₁BM films under the same thermal annealing condition. As shown in figure 6.5, optical images of DPP-TT-T:PC₇₁BM films are featureless until the annealing temperature reaches 170 °C, at which temperature numerous dark areas start appearing in the blend film. This coincides with the appearance of fullerene spikes in the WAXS measurement, suggesting that the dark areas can be assigned to clusters of fullerene crystalline domains. Note that each fullerene cluster is surrounded by a bright halo, which is assigned to the fullerene-depleted region.¹²

Similar experiments were repeated on SiIDT-BT:PC₇₁BM (figure 6.6). From WAXS measurement, both polymer and fullerenes signals remain almost unchanged after annealing the films at 170 °C, suggesting the crystallisation of fullerene is significantly hampered. This was further confirmed using optical microscopy, which shows that the number of dark areas formed in SiIDT-BT:PC₇₁BM is substantially fewer than that for DPP-TT-T:PC₇₁BM at the same temperature, indicative of inhibition of fullerene crystallisation (Figure 6.6). Note that a previous study has suggested that high fullerene loading should increase the formation of the fullerene crystal clusters.⁴⁵ Since the wt % of fullerene in as the cast blends is higher for SiIDT-BT, this further confirms that SiIDT-BT inhibits fullerene crystallisation more than DPP-TT-T.

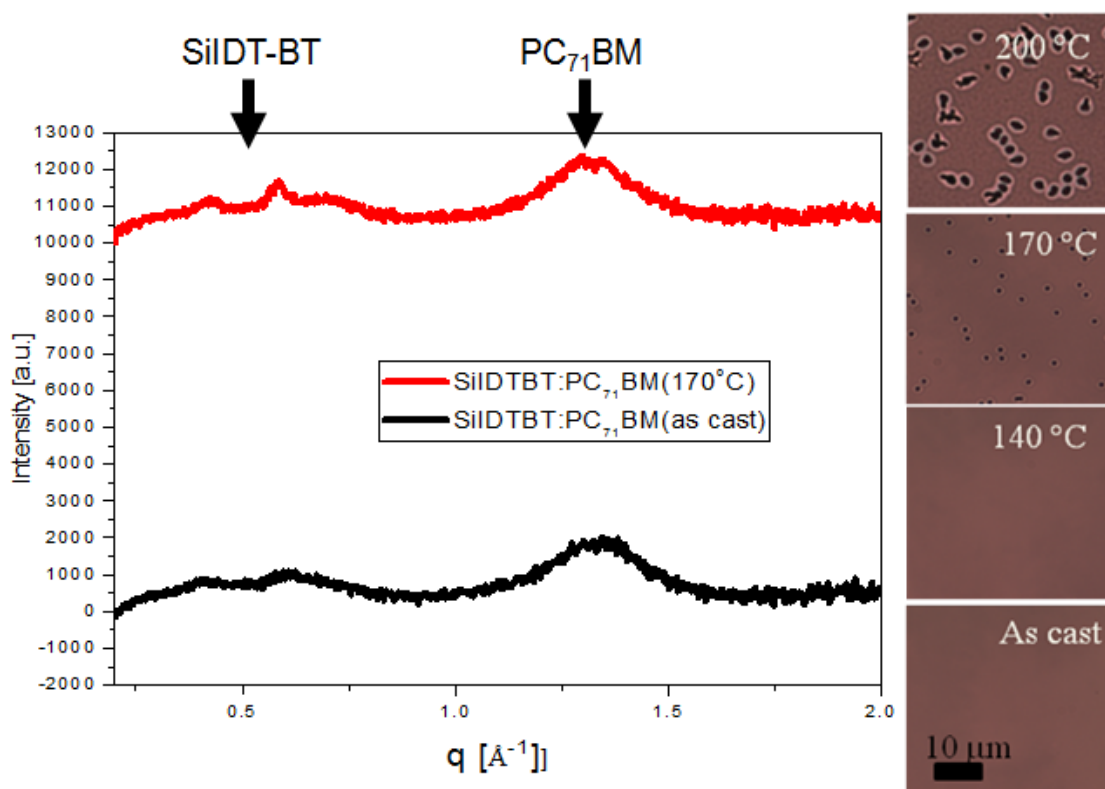


Figure 6.6: WAXS signals (left) and optical images (right) obtained from SiIDT-BT:PC₇₁BM blend films on glass substrates under different thermal aging condition. Drop cast films were used for WAXS while spin cast films were used for optical microscopy.

Evolution of phase segregation

It has been reported that the formation of fullerene crystal rich clusters results in depletion of fullerene from surrounding areas of the blend films.^{12, 17} This process should promote phase segregation by expanding the fullerene domains.⁷ As such, the WAXS and optical images above suggest a more considerable change in fullerene domain size in the DPP-TT-T based blend compared to SiIDT-BT, which was verified using PL. The details of the experiment are included in Chapter 2. In this experiment, the polymers and fullerene were excited separately to investigate how the photoluminescence varied as annealing conditions were changed.

For DPP-TT-T:PC₇₁BM blend films, 520 nm excitation was used to excite the PC₇₁BM, resulting in a photoluminescence maximum at ~ 707 nm, assigned to fullerene singlet exciton emission.⁴⁶ Photoluminescence of DPP-TT-T was not probed, as its emission is outside the wavelength range of our detector at the time of this study. As shown in figure 6.7 (b), the as-cast film exhibits rather modest fullerene photoluminescence quenching (PLQ), consistent with that reported for other semicrystalline polymers reported previously.^{46, 47} This suggests

that the blend microstructure is associated with a certain degree of phase segregation in the as-cast film. The PLQ drops from approximately 70% to 30% as the annealing temperature is increased, with this drop primarily occurring for temperatures above 140 °C. The PLQ can be used to calculate L , the distance at which an exciton diffuses before dissociation, and therefore corresponding to the fullerene domain size according to $L = L_{ex}(1-PLQ)^{1/2}$ outlined in Chapter 2.⁴⁷ This in turn means a change in PLQ from 70% to 30% corresponds to a change in L from 2.6 nm to 4.2 nm.

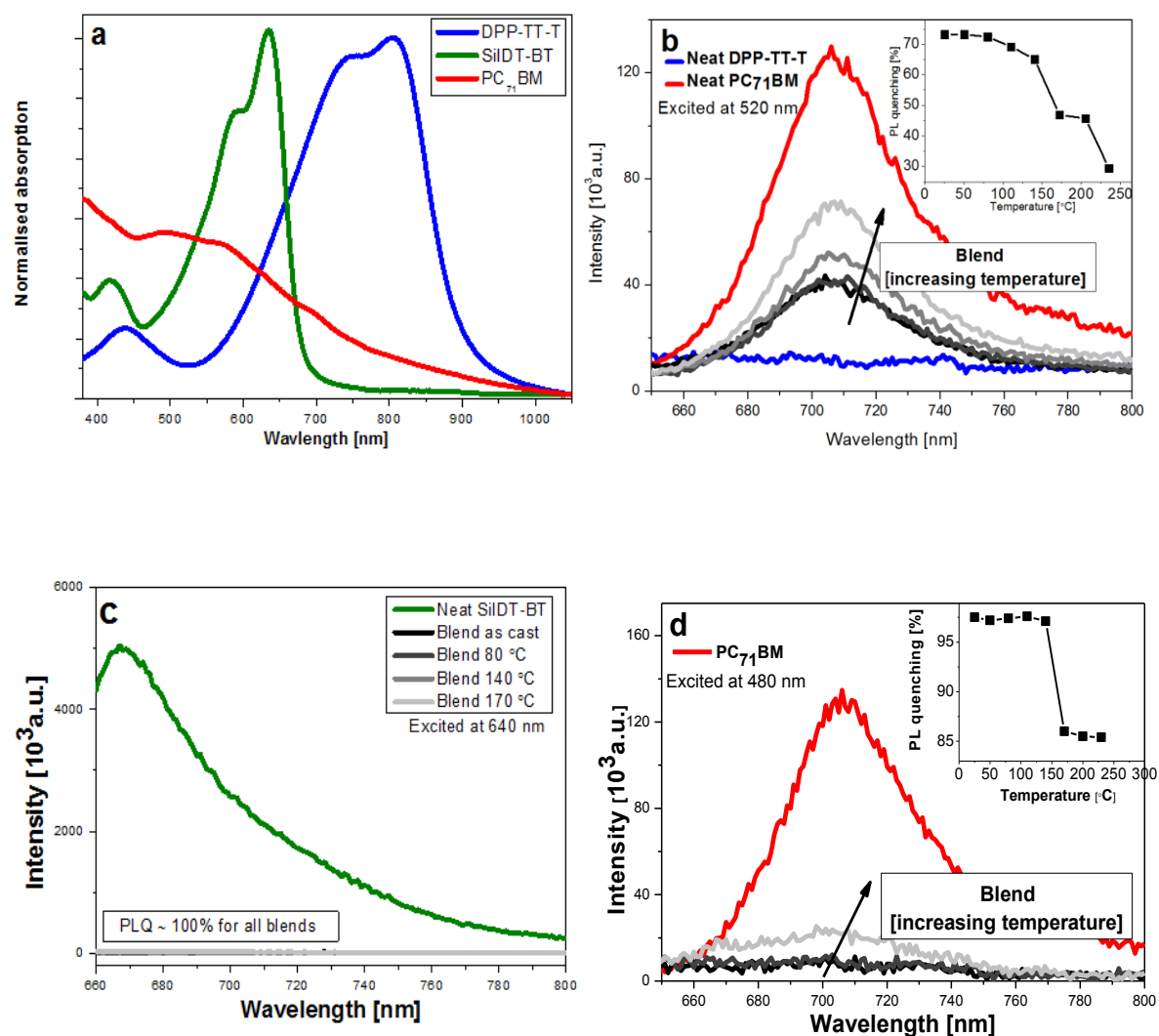


Figure 6.7: Photoluminescence of DPP-TT-T:PC₇₁BM (top left) and SiIDT-BT:PC₇₁BM (bottom left) thin films on glass substrates prepared with different thermal aging condition. The associated photoluminescence quenching as a function of annealing temperature are shown on the right. The excitation wavelength were 520 nm and 480 nm for DPP-TT-T and SiIDT-BT respectively.

On the other hand, exciton quenching in SiIDT-BT:PC₇₁BM was slightly more difficult to probe, as SiIDT-BT emits at 670 nm which strongly overlaps with fullerene emission. Figure

6.7 (c) shows the photoluminescence of these blend films by exciting the polymer at 640 nm. The polymer quenching of the blend is greater than 99% ($L \sim 0.6$ nm, assuming polymer exciton diffusion length is 10 nm) for the as-cast blend films and remains unchanged as the annealing temperature increases. The experiment was repeated by exciting the fullerene at 470 nm, giving rise to a peak at around 707 nm (figure 6.7 (d)). Given that the quenching of the polymer photoluminescence is always >99%, the peaks from the blend samples in figure 6.7 (d) should contain fullerene exciton emission exclusively, which means peak deconvolution is not required to calculate the photoluminescence quenching for fullerene emission. The fullerene emission quenching remains steady at ~97% ($L \sim 1.6$ nm) at temperature below 140 °C, followed by reduction to 86% ($L \sim 3.7$ nm) as temperature increases from 140°C to 170°C.

The results shown above suggest that these two polymers exhibit very different initial blend microstructures with PC₇₁BM on the <10 nm lengthscale (estimated exciton diffusion length from ref^{45, 46}). The semicrystalline DPP-TT-T shows poor PLQ in the as-cast film, suggesting the blend morphology is likely to be consisted substantially of a relatively pure fullerene phase and pure polymer phase (as demonstrated using WAXS). On the other hand, the as cast SiIDT-BT:PC₇₁BM blend exhibits high PLQ of both polymer (> 99%) and fullerene emission (> 97%), indicative of a more finely mixed morphology.

As the temperature increases, DPP-TT-T exhibits a larger reduction in PLQ (or larger increase in the average length of exciton diffusion), suggesting a greater evolution of fullerene domain size in comparison to SiIDT-BT. In both cases, the biggest reduction happens at temperature above 140 °C, which is associated with the formation of micron sized fullerene clusters. For SiIDT-BT, the polymer PLQ exhibits almost no change across the full temperature range, indicating the polymer remains finely mixed with fullerene molecules.

6.3.1c Device stability

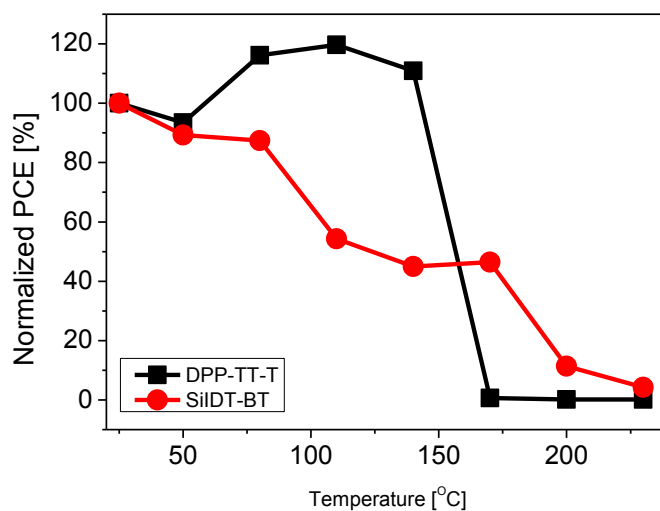


Figure 6.8: (top) Normalised PCE as a function of annealing temperature from DPP-TT-T (black) and SiIDT-BT (red) devices. The duration for each annealing temperature was 10 minutes. Annealing was undertaken prior to metal electrode deposition. The error of the normalised PCE is within $\pm 4\%$ for both devices, calculated as standard deviation of the mean.

DPP-TT-T

T [°C]	V _{oc} [V]	J _{sc} [mAcm ⁻²]	FF [%]	PCE [%]
25	0.60	17.3	52	5.3
80	0.61	18.8	54	6.2
110	0.62	18.0	57	6.4
140	0.61	16.8	58	5.91
170	0.62	0.3	20	0.04
200	0.65	0.1	14	0.01
230	0.67	0.1	15	0.01

SiIDT-BT

T [°C]	V _{oc} [V]	J _{sc} [mAcm ⁻²]	FF [%]	PCE [%]
25	0.88	9.7	55	4.7
80	0.88	9.1	50	4.08
110	0.69	8.5	43	2.5
140	0.72	6.5	44	2.1
170	0.72	5.2	50	2.2
200	0.77	1.6	42	0.5
230	0.76	0.8	32	0.2

Table 6.2: Parameters of DPP-TT-T (Top) and SiIDT-BT (bottom) devices subjected to different thermal aging conditions.

This section focuses on the impact of the thermal annealing upon device performance. All the devices involved in this chapter have a conventional architecture consisted of ITO/PEDOT:PSS/polymer:PC₇₁BM/Ca/Al. The details of general device preparation are presented in Chapter 2. Prior to Ca/Al deposition, the active layer was subjected to the thermal annealing (referred to herein as ‘pre-annealing’ to distinguish it from annealing after electrode deposition) loop as described in section 6.2.

Figure 6.8 shows the normalised power conversion efficiency (PCE) as a function of annealing temperature for both DPP-TT-T and SiIDT-BT devices. It is apparent that these two devices behave differently upon thermal annealing in our experiment. In the case of the DPP-TT-T devices, the power conversion efficiency is increased by ~ 20% at 80°C and then remains almost the same as the temperature further increases to 140°C. The PCE drops substantially to almost 0% as the temperature is raised from 140 °C to 170 °C. The trend in PCE of DPP-TT-T devices is mainly contributed from the variations in short circuit current as well as fill factor (table 6.2 (top)). As can be seen from table 6.2 (top), both parameters experience a slight improvement at moderate annealing (< 140 °C) temperature followed by a steep loss from 140 °C to 170 °C. The open circuit voltage, on the other hand, increases slowly from 0.60 V to 0.67 V with increasing annealing temperature. In the case of SiIDT-BT based devices, the PCE declines by over 95% as the temperature reached 200 °C, with two pronounced drops of ~35% happening from 80 °C to 110 °C and from 170 °C to 200 °C respectively. As shown in table 6.2 (bottom), the former reduction is attributed to loss in V_{OC} , J_{SC} and FF while the later reduction is primarily driven by the loss in J_{SC} .

To further analyse the performance degradation, the EQE of each device was measured, as shown in figure 6.9. In both cases, the whole EQE from 350 nm to 800 nm decreases with increasing temperature, consistent with the trend observed in corresponding J_{SC} . The loss in photocurrent generation following fullerene absorption is now compared to that following polymer absorption. This can be done by estimating the ratio of the EQE at which the polymer primarily absorbs to the EQE at which the fullerene absorbs from the same device, namely EQE at 800 nm for DPP-TT-T, 640 nm for SiIDT-BT, and 470 nm for PC₇₁BM. As shown in figure 6.9, for DPP-TT-T devices, the ratio remains almost unchanged with increasing annealing temperature, suggesting that photocurrent from polymer absorption decays at a similar rate to that from fullerene absorption. For SiIDT-BT, the ratio declines as temperature increases, indicative of a severer degradation in photocurrent generated by

fullerene absorption. This is qualitatively consistent with the conclusion from the PL study at temperature above 140 °C (figure 6.7 (c and d)).

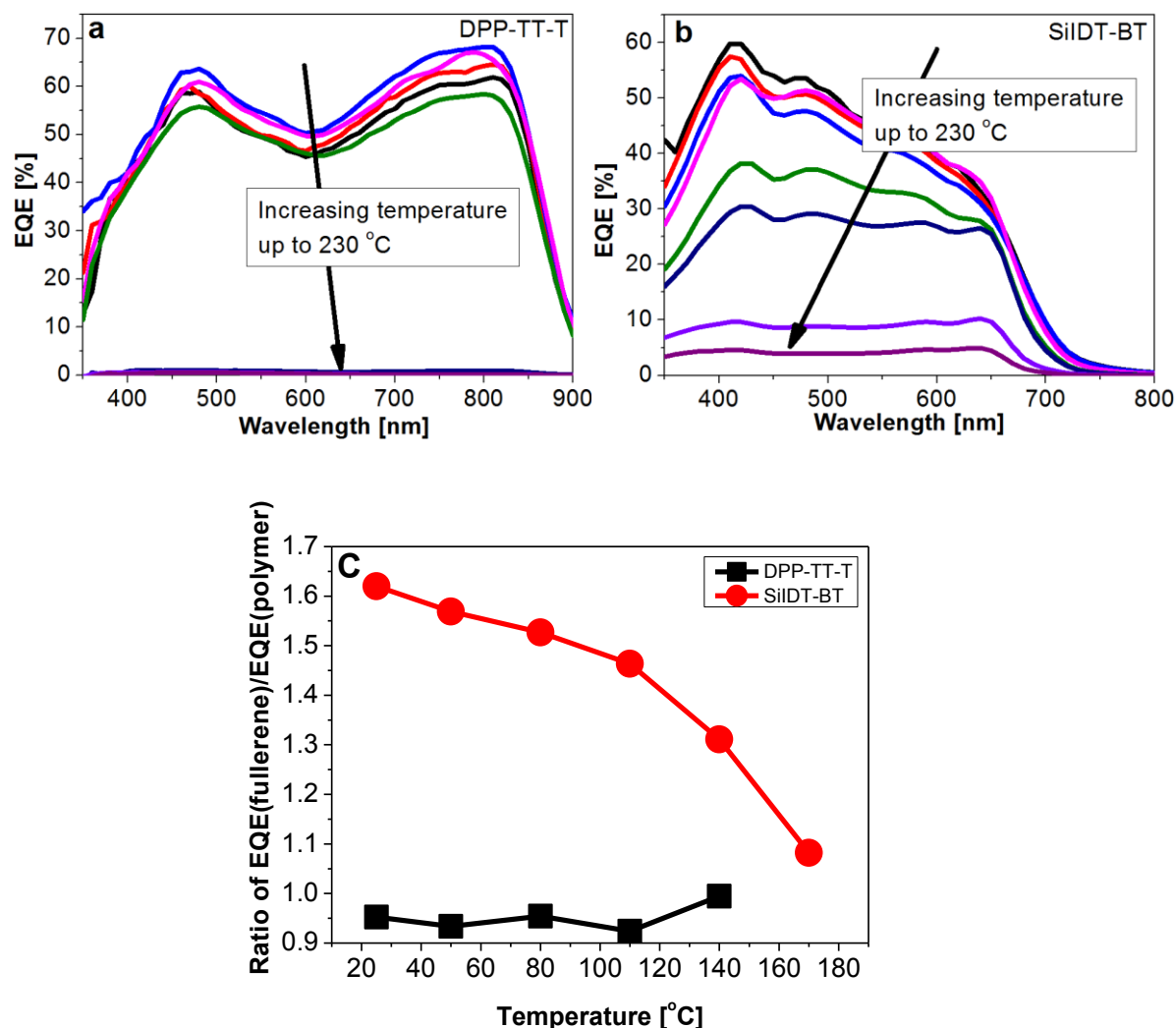


Figure 6.9: The external quantum efficiencies of DPP-TT-T (a) and SiIDT-BT (b) devices as a function of wavelength with various annealing temperature. (c) shows the ratio of EQE(fullerene)/EQE(polymer) to compare the reduction in EQE from fullerene absorption with that from polymer absorption. The data taken to calculate the ratio were the EQE at 800 nm for DPP-TT-T, 640 nm for SiIDT-BT, and 470 nm for PC₇₁BM from each device.

6.3.1d Correlating morphological degradation with device performance

In this section, data from device and morphology analysis are compared in an attempt to establish correlations between device stability and morphological stability. Figure 6.10 shows the normalised short circuit current, fullerene exciton quenching and the amount of the fullerene clusters as a function of annealing temperature for the two polymers. To estimate the amount of the fullerene clusters formed on the films, the % area of the dark spots

observed in figures 6.5 and 6.6 were estimated. For DPP-TT-T, the DS of the polymer lamellar peak is also normalised and compared.

For DPP-TT-T, the evolution of these parameters can be divided into three phases, namely ‘below 80 °C’, ‘from 80 °C to 140 °C’ and ‘above 170 °C (figure 6.10). In the first phase, both the Jsc and polymer crystallinity are improved without having any loss in fullerene quenching. The improvement in device performance most likely is derived from the improved polymer crystallinity, which is known to correlate with improved charge generation as well as charge transportation for P3HT devices.^{17, 22} In the second phase, there is a quantitative match between the decays in short circuit current and fullerene exciton quenching, with steady improvement in polymer crystallinity. This suggests that the device degradation happening within this temperature range is due to, at least in part, the loss in fullerene exciton dissociation, potentially caused by exclusion of fullerenes upon polymer crystallisation.⁴ As temperature further increases from 140 °C to 170 °C, the short circuit current drops faster than the fullerene exciton quenching, suggesting that the loss in device performance cannot be derived only from the loss in fullerene quenching in this phase. A sudden rise in the amount of micron sized fullerene clusters is observed at the same temperature, indicative of formation of micron sized pure domains and fullerene depleted regions.^{12, 15} Previous studies from other polymer system have suggested that the formation of large domain as a result of thermal annealing could be accompanied by other morphology features, such as loss in domain percolation, which are detrimental to device performance.^{4, 7, 19} As such, the rise of micron sized fullerene clusters is believed to give rise to multiple loss pathways, resulting in severe degradation in device performance of DPP-TT-T.

In the case of SiIDT-BT, the short circuit current shows an accelerating decrease as the temperature increases. The steepest decrease is found from 170 °C to 200 °C. Despite the ~30% loss in the short circuit current at temperatures below 140 °C, the PLQ of fullerene exciton remains steady, suggesting the loss in device performance cannot be explained by decreased exciton dissociation efficiency. When the temperature is above 140 °C, the reduction in the short circuit current for SiIDT-BT is less severe than that for DPP-TT-T, consistent with the fewer fullerene clusters formed in this blend observed in the optical microscopy images. As such, the reason for the loss in device performance at this temperature is believed to be similar to that for DPP-TT-T. At this temperature, the rate of device degradation should scale up with the formation of fullerene clusters.

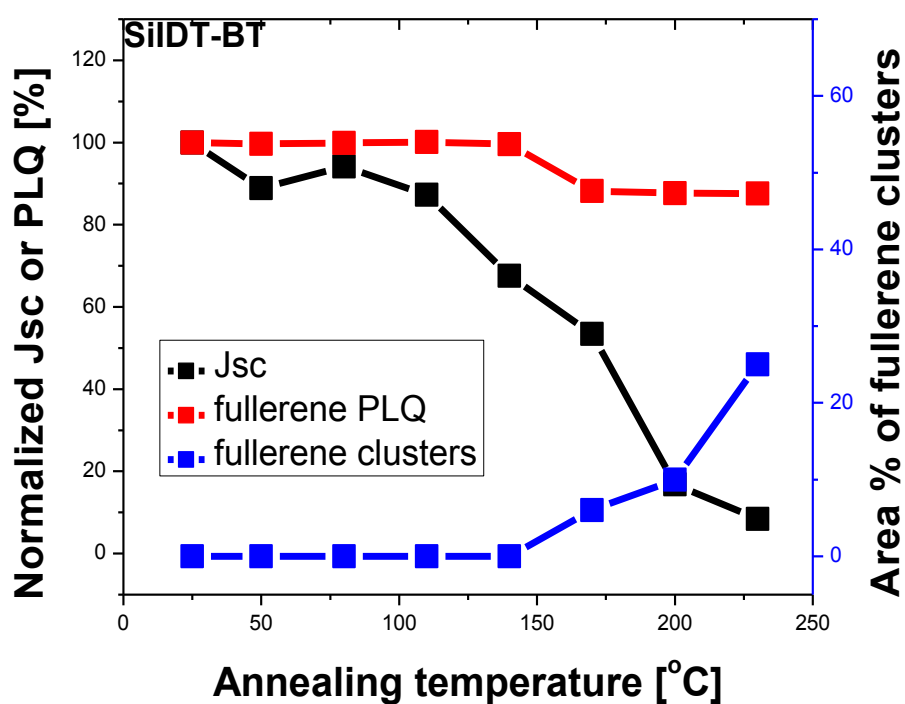
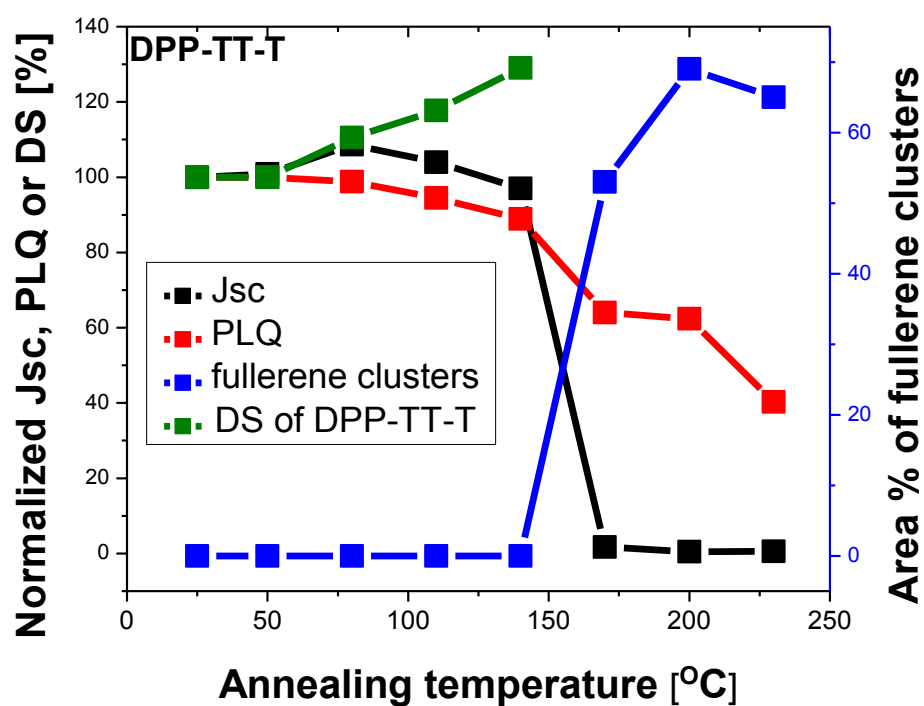


Figure 6.10: Normalised short circuit current, photoluminescence quenching, and fractional area of fullerene clusters as functions of annealing time for DPP-TT-T (top) and SiIDT-BT (bottom) systems. Normalised DS of lamellar packing is also presented for DPP-TT-T.

6.3.2 DPP-TT-T:PC₆₁BM vs DPP-TT-T:PC₇₁BM

In this section, the experiments in section 6.3.1 were repeated on DPP-TT-T:PC₆₁BM in order to compare PC₆₁BM with PC₇₁BM in terms of morphological and device thermal stability.

DPP-TT-T:PC₆₁BM films on glass substrates were annealed at 140°C and 170°C respectively for 100 hours in order to measure the DPP-TT-T:PC₆₁BM miscibility using NEXAFS. As shown in table 6.2, the miscibility of DPP-TT-T:PC₆₁BM is very similar to that of DPP-TT-T:PC₇₁BM. Based on this data, the DPP-TT-T:PC₆₁BM blend should exhibit a similar morphological stability to DPP-TT-T:PC₇₁BM. However, after repeating the WAXS and optical microscopy measurement (figure 6.11), it has been found that an annealing temperature of 140 °C is enough to trigger the formation of micron sized PC₆₁BM clusters compared to 170 °C which is required for PC₇₁BM. This observation is supported by its photoluminescence study which shows that there was a substantial reduction in PC₆₁BM exciton quenching from 110 °C to 140 °C.

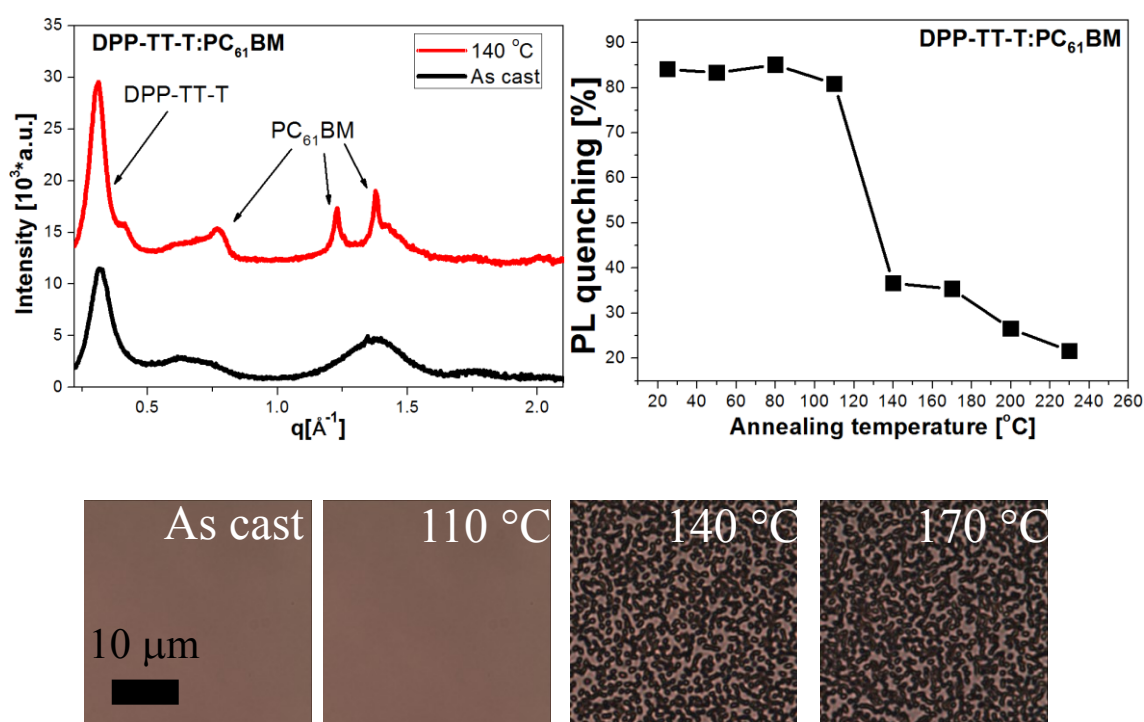


Figure 6.11: WAXS signals (top left), quenching of fullerene emission and optical images (bottom) as functions of annealing temperature obtained from DPP-TT-T:PC₆₁BM blend films on glass substrates under different thermal aging condition. Drop cast films were used for WAXS while spin cast films were used for photoluminescence spectroscopy and optical microscopy. The films were excited at 520 nm for the photoluminescence measurements.

Figure 6.12 shows the performance of DPP-TT-T:PC₆₁BM based devices under different thermal aging conditions. The most substantial degradation in device performance once again matches with the rise of the fullerene clusters, confirming that the fullerene crystallisation is detrimental to device performance. The device degradation for PC₆₁BM happens at a temperature 30 °C lower than PC₇₁BM despite the similar miscibility that they exhibit with DPP-TT-T. This mismatch between the short term annealing experiments (WAXS, PL, optical microscopy and device studies) and the long term annealing experiments (NEXAFS) is discussed in section 6.4.

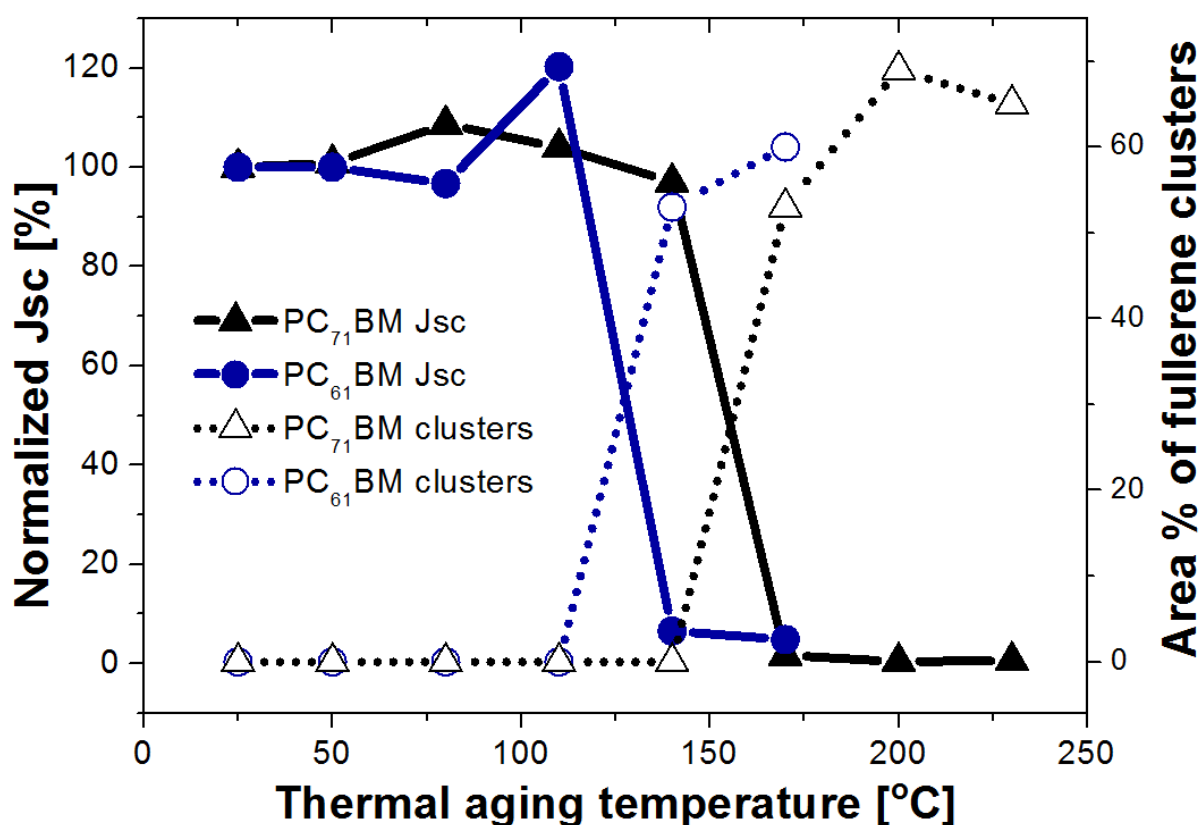


Figure 6.12: Normalised short circuit current and fractional area of fullerene clusters as functions of annealing time for DPP-TT-T:PC₆₁BM (blue) and DPP-TT-T:PC₇₁BM (black) systems. The error (standard deviation of the mean) of the normalised PCE is within $\pm 4\%$.

6.3.3 Growth of fullerene domains

A preliminary experiment was performed to investigate the kinetics of fullerene domains in DPP-TT-T:PC₇₁BM thin films. Figure 6.13 shows the PLQ of fullerene exciton in DPP-TT-T:PC₇₁BM blend film as a function of annealing time for four different annealing temperatures. At 80 °C, the fullerene exciton PLQ stays almost the same for 130 minutes,

suggesting there are minimal changes in terms of fullerene domain size. The decays of fullerene PLQ at temperature above 80 °C is comprised of a fast phase and a slow phase. At 110 °C, the quenching of fullerene emission drops rapidly from 68% to 64% within 10 minutes and then remains unchanged for the following 140 minutes. As the temperature further increases to 170°C, the PLQ decreases to 56% within the first 10 minutes and then reaches 48% gradually in another 145 minutes. The results suggest that the majority fullerene domain evolution is likely to be complete within the first 10 minutes at each temperature. This, to some extent, verifies that the annealing period employed in sections 6.3.1 and 6.3.2 is long enough to assess the fullerene domain evolution.

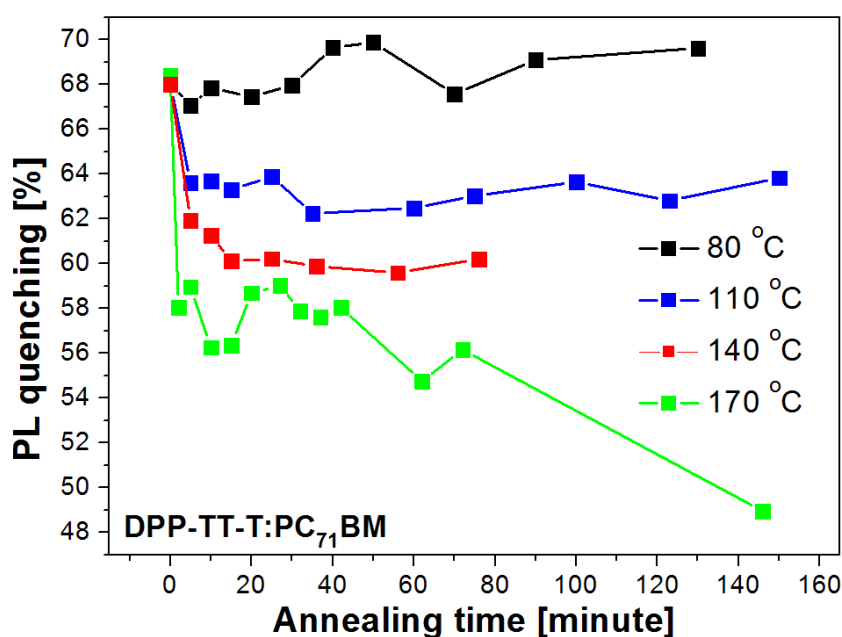


Figure 6.13: Quenching of fullerene photoluminescence from DPP-TT-T:PC₇₁BM thin films as functions of annealing time for four annealing temperatures. The films were excited at 520 nm, and the emission monitored at 707 nm.

6.3.4 Pre-annealing and post-annealing over 250 hours

The device studies in previous sections are based on a pre-annealing treatment in which thermal annealing was introduced prior to cathode deposition. In this section, effects of pre-annealing on device performance are compared to post-annealing in which the thermal annealing is introduced after cathode deposition. The performance of DPP-TT-T:PC₇₁BM devices were measured under pre-annealing or post-annealing at 80 °C, with the results

shown in figure 6.11. The PCE of the devices subjected to pre-annealing increases by approximately 10% in ~ 7 hours and then drops slightly by 5% in the next 230 hours (~ 10 days). The open circuit voltage, short circuit current as well as fill factor roughly exhibit similar variation patterns as a function of time to the PCE. The initial increased PCE potentially is due to the improved polymer crystallinity, as demonstrated in figure 6.4, and the minimal loss in fullerene exciton dissociation, as demonstrated in figure 6.13.

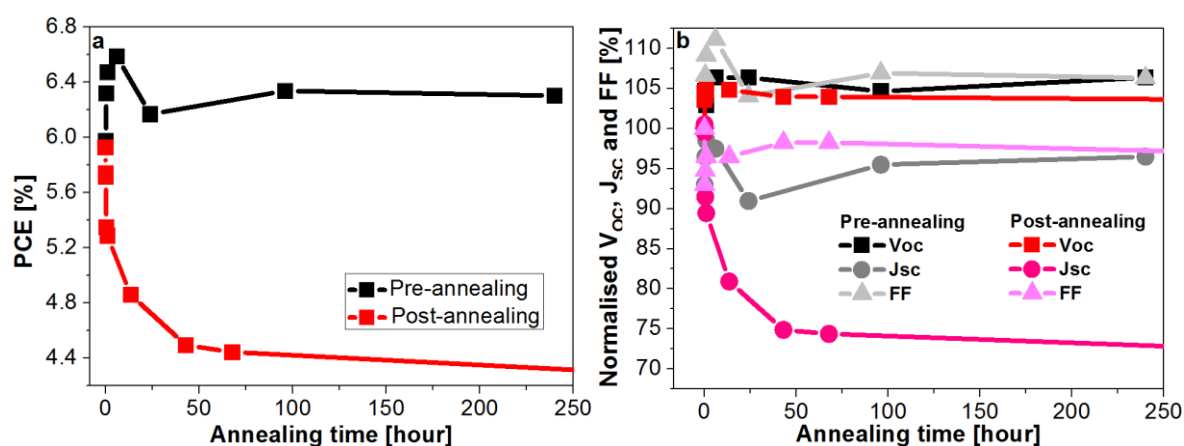


Figure 6.11: Device parameters as functions of annealing time for devices subjected to pre-annealing or post-annealing treatments. PCE is shown in (a) while the other device parameters are normalised and shown in (b). The annealing temperature was 80 °C. The error (standard deviation of the mean) of the PCE is within $\pm 0.2\%$.

In contrast, in the case of post-annealing, the PCE drops rapidly by 25% within the first 43 hours followed by another 1% loss in the next 330 hours (14 days). The drop in PCE for the first 25 hours is approximately 20%, compared to the 10% loss for MDMO-PPV and 10% increase for P3HT in PCE under similar thermal aging conditions as have been reported previously.⁷ This clearly shows the relatively poor thermal stability of DPP-TT-T device under post-annealing treatment. The loss in PCE is due to the fast reduction happens in short circuit current as well as fill factor. Apparently, devices subjected to pre-annealing and post-annealing show different degradation against temperature.

6.3.5 Fullerene light transformation for morphological stability of DPP-TT-T

Colleagues Dr. Zhe Li and Dr. Him Cheng Wong have previously developed an approach which can effectively enhance the device thermal stability of PCDTBT:PC₆₁BM devices utilizing a photo-induced transformation of PC₆₁BM.³² It has been shown above that DPP-TT-T devices suffer from more severe thermal degradation in comparison to P3HT and MDMO-PPV device under post-annealing conditions at 80 °C. In this section, a photo-induced transformation of PC₆₁BM is applied to DPP-TT-T:PC₆₁BM films in order to address this poorer thermal device stability. Throughout this section, samples which were exposed to a standard low-intensity ($\sim 10 \text{ mW cm}^{-2}$) fluorescent lamp for 4 hours in nitrogen are denoted as ‘light’, while samples which were kept in dark are denoted as ‘dark’.

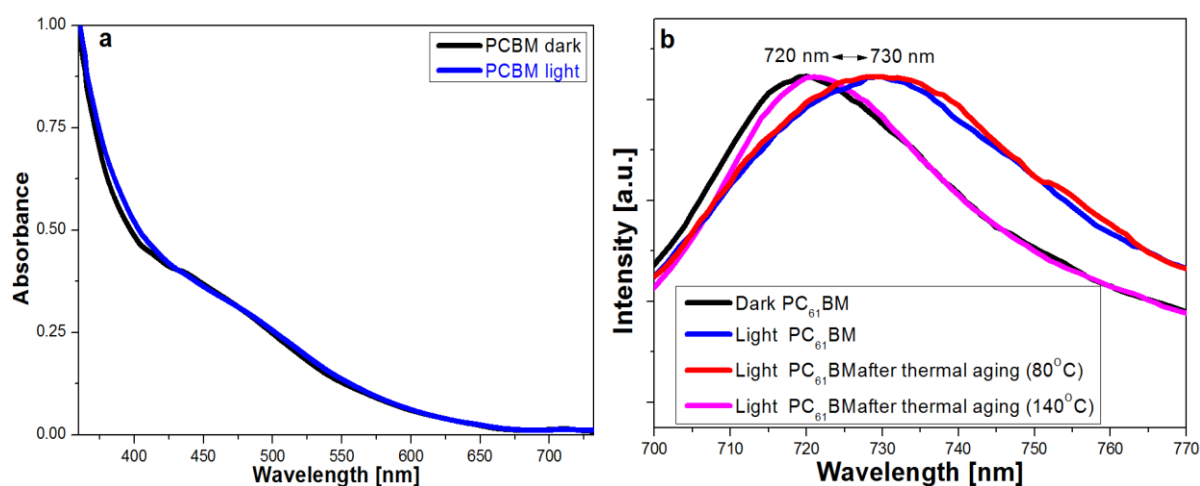


Figure 6.12: (a) UV/visible absorption spectra of pristine (black) and light exposed (blue) PC₆₁BM samples on glass substrates. (b) Steady state photoluminescence of pristine PC₆₁BM (black) and light exposed PC₆₁BM with various conditions (blue: without thermal treatment; red: annealed at 80°C for 60 minutes; pink: annealed at 140°C for 60 minutes)

Previous studies demonstrated that the presence of PC₆₁BM oligomers can be probed using Raman spectroscopy and gel permeation chromatography (GPC).^{32, 34} Other than these approaches, this section demonstrates that light exposure of PC₆₁BM in nitrogen also leads to a red shift in its photoluminescence. The UV/visible absorption spectra of neat PC₆₁BM thin films with and without light treatment are present in figure 6.12 (a). It can be seen that the ‘light’ PC₆₁BM exhibits very similar absorption to the ‘dark’ sample. As shown in figure 6.12 (b), the ‘dark’ sample displays an emission peak at 720 nm, consistent to what have been reported previously.⁴⁶ After the light treatment, the characteristic emission is slightly red-shifted to 730 nm. Annealing the ‘light’ films at 80 °C for 60 minutes results in no changes

in the peak position, whereas annealing at 140 °C for the same duration leads to the return of the peak to 720 nm. This observation is consistent with the photo-induced transformation of fullerene being reversed at high temperature (140 °C), as has been reported previously,^{33, 34} suggesting the red shift in the photoluminescence is due to the formation of PC₆₁BM oligomers. The data also indicates that the fullerene oligomers are relatively stable at 80 °C, thereby implying a more prolonged enhancement in morphological stability compared to 140 °C.

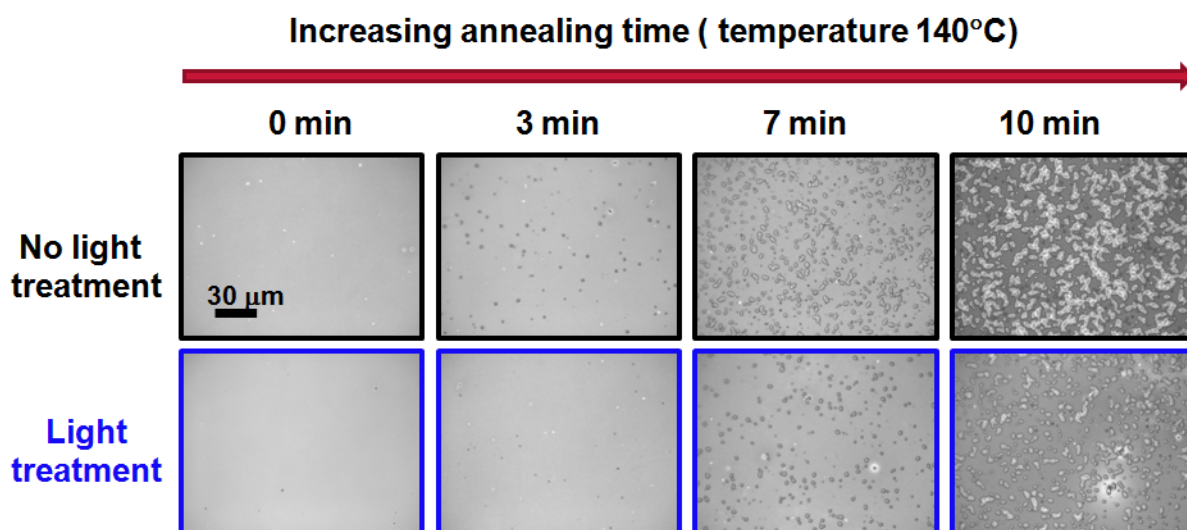


Figure 6.13: Evolution of optical images of DPP-TT-T:PC₆₁BM samples on glass substrates with (bottom row) and without (top row) light treatment under thermal aging condition. The annealing temperature was 140 °C.

In section 6.3.2, it has been demonstrated that annealing DPP-TT-T:PC₆₁BM films at 140 °C for 10 minutes can lead to formation of micron size fullerene clusters, indicative of severe degradation of blend microstructure. In an attempt to address this issue, light treatment was introduced to DPP-TT-T:PC₆₁BM thin films deposited on glass substrates prior to thermal aging. Figure 6.13 shows the comparison of the optical images of DPP-TT-T:PC₆₁BM with and without light treatment as annealing time was increased. It is apparent that the ‘light’ sample exhibits a better morphological stability, as indicated by the fewer fullerene clusters as the morphology evolves. Note that the enhancement in morphological stability for DPP-TT-T is not as big as that for PCDTBT, which was reported to display a completely suppression of fullerene clusters after annealing at 140 °C for an hour.^{32, 33} This is potentially due to the better intrinsic ability of PCDTBT to inhibit fullerene crystallisation, as the fullerene crystal clusters has been reported to only become observable after annealing the

PCDTBT:PC₆₁BM at 155 °C for ~35 minutes,¹¹ compared to DPP-TT-T:PC₆₁BM which requires only 3 minutes at 140 °C in our case.

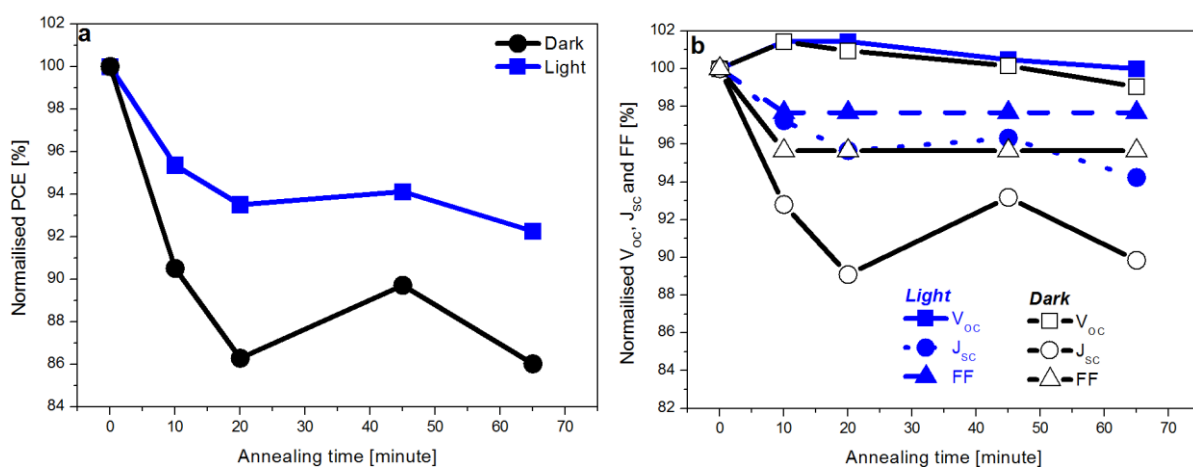


Figure 6.14: Normalised device parameters as functions of annealing time for devices with and without light treatment. PCE is shown in (a) while the other device parameters are shown in (b). The annealing temperature was 80 °C. The error (standard deviation of the mean) of the normalised PCE is within $\pm 4\%$.

<i>Dark</i>					<i>Light</i>				
Annealing time	V _{OC}	J _{SC}	FF	PCE		V _{OC}	J _{SC}	FF	PCE
[minute]	[V]	[mAcm ⁻²]	[%]	[%]		[V]	[mAcm ⁻²]	[%]	[%]
0	0.63	13.2	46	3.8		0.62	12.0	43	3.2
10	0.64	12.3	44	3.4		0.63	11.6	42	3.1
20	0.63	11.8	44	3.3		0.63	11.5	42	3.0
45	0.63	12.3	44	3.4		0.63	11.5	42	3.0
65	0.62	11.9	44	3.3		0.62	11.3	42	3.0

Table 6.3: Device parameters for the solar cells present in figure 6.14.

Having confirmed the enhanced inhibition of micron size fullerene clusters by photo-induced PC₆₁BM transformation, light treatment was introduced to DPP-TT-T solar cells in order to investigate its effect on thermal stability of device performance. All devices had conventional architecture and were made in a manner similar to previous section. For ‘light’ device, light treatment was introduced prior to the cathode deposition. In this experiment, post-annealing was carried out at 80 °C. Figure 6.14 (a) shows the device PCE as a function of annealing time. The PCE decays exhibited biphasic kinetics, with a relatively fast decay for the first 20 minutes followed by a flatter trend in the later 40 minute. Specifically, the PCE of the ‘light’ device is reduced by 7% within the first 20 minutes, compared to the 14% loss in PCE for the

‘dark’ device within the same period. The performance degradations in both cases are primarily driven by the loss in J_{SC} and FF (figure 6.14 (b)). Note that despite of the improved stability, the initial PCE is reduced by light treatment prior to thermal aging, due to a smaller J_{SC} and FF in comparison to the ‘dark’ device (table 6.3). Further discussion is present in section 6.4.

6.4 Discussion

DPP-TT-T vs SiIDT-BT

In the results section, the data have shown the evolution of blend microstructure and device performance under thermal annealing for a short period of 10 minutes for blends of semicrystalline DPP-TT-T and amorphous SiIDT-BT with PC₇₁BM. More specifically, techniques including WAXS, PL spectroscopy and optical microscopy have been used to assess the morphological characteristics such as material crystallinity, domain size (on the scale of exciton diffusion) and formation of micron sized fullerene clusters under thermal aging conditions.

At low temperatures (< 140 °C), DPP-TT-T films show a better morphological stability than SiIDT-BT devices, with thermal annealing at these temperatures resulting a 10% improvement in PCE. This is tentatively assigned to enhanced polymer crystallinity, which has been suggested to benefit the charge generation and mobility for P3HT devices.^{17, 22, 24} In contrast, a 30% loss in the short circuit current of SiIDT-BT devices under these modest annealing conditions is observed, even though there are no changes in domain size indicated by the exciton PLQ. The device performances of OPV cells employing polymers other than P3HT have been shown to undergo deterioration upon thermal annealing.^{25, 48} The reason for this phenomenon is less well understood. The loss in device performance was attributed to the reduction in polymer:fullerene interfacial area⁴⁹ for MDMO-PPV, which is not seen in our study for SiIDI-BT. The blend microstructure should still have good domain percolation at this temperature regime, since the polymer:fullerene miscibility at 140 °C is higher than 20%, which has been suggested to be the threshold concentration of fullerene to ensure good electron transport.^{19, 50} The performance deterioration for SiIDT-BT devices under low temperature annealing probably is associated with changes in morphology in terms of molecular arrangements, such as a loss in ordering of weak polymer π - π stacking or fullerene

intercalation, which has been reported to reduce polymer hole mobility. This hypothesis requires further studies such as grazing incident X-ray scattering or Raman spectroscopy to verify.^{25, 51}

At high temperatures ($> 140\text{ }^{\circ}\text{C}$), the stability of DPP-TT-T:PC₇₁BM blend films becomes worse than those with SiIDT-BT, attributed to the formation of more fullerene clusters. A correlation between fullerene clusters formation and device degradation in this temperature regime has been established, with more fullerene clusters leading to faster device decay, both in our studies comparing the two donor polymers and PC₆₁BM and PC₇₁BM. It has been discussed in section 6.3.1d that formation of these fullerene crystal clusters could be detrimental to device performance. Firstly, the micron size fullerene crystal clusters are likely to be free of polymers, leading to loss in exciton dissociation as demonstrated using photoluminescence spectroscopy.^{7, 12} Secondly, the fullerene-depleted region surrounding the clusters could mean a drastic reduction in fullerene percolation, increasing the possibility of charge recombination.²⁵

Morphological stability has been reported to depend on glass transition temperature of polymers.^{2, 7} In an attempt of measuring the T_g for these two polymers using differential scanning calorimetry (DSC) by our colleague Dr Buchaca and Dr Schroeder, No obvious T_g was observed for these two polymers. Nevertheless, the T_g for neat PCBM films has been reported to be $148\text{ }^{\circ}\text{C}$,⁵² consistent with the temperature regime in which micron sized clusters are observed under optical microscopy in our studies for both polymers. In addition, it has been shown that the miscibility measured using NEXAFS may be a good parameter to predict morphological stability at a specific temperature, with the lower polymer:fullerene miscibility giving a worse morphological stability. The better thermodynamic miscibility of SiIDT-BT with PC₇₁BM probably provides a more viscous environment, and therefore may inhibit the formation of the fullerene crystal clusters. In addition, the crystallisation of DPP-TT-T may also contribute to its poor miscibility with PC₇₁BM. As demonstrated in figure 6.10, upon short term annealing in the temperature regime of $110\text{ }^{\circ}\text{C} < T < 140\text{ }^{\circ}\text{C}$, the loss in fullerene exciton PLQ is likely due to the DPP-TT-T crystallisation which excludes the fullerene to form larger domains. This in turn suggests that the absence of polymer crystallisation in SiIDT-BT should at least partially contribute to its minor changes in domain size. Such conclusion is further supported by our EQE and PLQ data, which show that the photocurrent induced by fullerene absorption decayed faster than that induced by polymer

absorption for SiIDT-BT. This implies the fullerene domain evolution is primarily driven by the fullerene diffusion, with minimal impact from the polymer movement. In comparison, DPP-TT-T devices appear to have similar loss in photocurrent from both polymer absorption and fullerene absorption. The comparison of the two polymers suggests that polymer crystallisation plays an important role in changing the degree of morphological evolution upon thermal aging. The difference in morphological evolution between semicrystalline and amorphous polymers has also been proposed previously.⁷

PC₆₁BM vs PC₇₁BM

Comparing PC₆₁BM with PC₇₁BM, it has been found that both fullerenes display similar miscibility with DPP-TT-T using NEXAFS, suggesting a similar stability between these two fullerenes. From the thin film and device studies, it has been demonstrated that the crystallisation of PC₆₁BM takes place at a lower temperature than that of PC₇₁BM. Note that the samples for NEXAFS had been annealed for 100 hours before the measurement while the annealing time for devices and PL was only 10 minutes. The mismatch between the NEXAFS and other measurements suggest that the device degradation is driven by a kinetic rather than thermodynamic factor. A previous study suggests that C70 has lower diffusion coefficient than C60 in CS₂ solvent.⁵³ As such, PC₇₁BM could be less diffusive than PC₆₁BM in DPP-TT-T matrix, and thereby results in more stable blend morphology in short term.

Pre-annealing vs post-annealing

Pre-annealing treatment and post-annealing treatment were compared in terms of their impact on device performance degradation of DPP-TT-T:PC₇₁BM. Post-annealing treatment leads to much severer device performance decay compared to pre-annealing treatment. There could be three scenarios accounting for the difference in device decay between pre-annealing and post-annealing. Firstly, interdiffusion could happen at blend/cathode interface under post-annealing condition resulting in negative influences on charge injection.⁵⁴ Secondly, previous studies have suggested that presence of electrodes reduces the free volume on top of the active layer, and thereby might alter the movement of polymer and fullerene.^{10, 55} Potentially post-annealing leads to a different morphology evolution which is more detrimental to device performance. Lastly, introducing thermal post-annealing may damage the electrode, as has been reported previously.²³

In contrast, it is striking that the device performance does not drop below its initial performance over a ~240 hours pre-annealing, suggesting the DPP-TT-T:PC₇₁BM blend is remarkably stable at this temperature. This further implies that the device should exhibit a remarkable stability, if a correct electrode is used.

Fullerene light transformation for morphological stability of DPP-TT-T

It has been demonstrated in section 6.3.5 that photoluminescence spectroscopy can be used to assess the presence of photo-induced PC₆₁BM oligomers, which exhibit a slightly red shifted emission in comparison to PC₆₁BM monomer. This observation is consistent with analogous studies of C₆₀ which has been reported to show a lower wavelength emission in its oligomer form,⁵⁶ potentially due to an extended π -conjugation interaction between the fullerene cages.⁵⁷

In terms of stability, it has been shown that light treatment can improve the stability of the blend microstructure as well as device performance for DPP-TT-T against thermal annealing. The degree of the improvement is not as high as that for PCDTBT reported previously.³² This is potentially associated with the poorer miscibility of DPP-TT-T with PC₆₁BM. The stability could be further improved by extending the period for light exposure or increasing the light intensity, as such effects have been found to be light dosage dependent.^{32, 33} In addition, the chapter has also demonstrated that light treatment causes a much larger loss in initial PCE for DPP-TT-T based devices prior to thermal annealing than observed for PCDTBT based devices³². This is potentially due to the loss in electron mobility of fullerene which was reported for both transistor and solar cell devices.^{58, 59} As such, the effect of light treatment on device performance appears to be different from polymer to polymer, with a pronounced trade-off between the initial PCE and device thermal stability that need to be made for DPP-TT-T devices.

6.5 Conclusions

In summary, it has been demonstrated in this chapter that the semicrystalline DPP-TT-T and the amorphous SiIDT-BT polymers display different morphological stabilities depending on thermal annealing temperature. DPP-TT-T shows a greater change in domain size and is less capable of suppressing fullerene cluster formation upon thermal annealing, demonstrated by PLQ and optical microscopy, with the latter has a resolution of micrometers. The movement of both the polymer and fullerene appears to contribute substantially to the evolution. In contrast, the domain evolution in SiIDT-BT blend is less pronounced on these lengthscales, and appears to be primarily driven by fullerene diffusion. Despite greater changes in domain size, DPP-TT-T devices exhibit better stability against thermal stress when temperature is below 140 °C, with an initial device efficiency improvement attributed to polymer crystallisation. In contrast, the degradation of SiIDT-BT device efficiency at the same temperature appears not be derived from domain evolution, but is potentially due to polymer structural changes, such as loss in fullerene intercalation or weak π - π stacking, which is not revealed in our study. In addition, it has also been shown that PC₇₁BM can provide a better morphological stability in blends with DPP-TT-T in comparison to PC₆₁BM, potentially due to its slower diffusion kinetics. The device stability for DPP-TT-T:PC₇₁BM with post-annealing treatment is drastically different from pre-annealing treatment, implying the presence of the electrode has a significant impact on device thermal stability. This should be investigated in future studies. Lastly, photo-induced PC₆₁BM oligomerisation has been shown to improve both blend morphological and device thermal stability in DPP-TT-T system, although a sacrifice in initial device performance is required.

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Chapter 7

Conclusion

The thesis has focussed on investigating the impact of polymer chemical structure on blend microstructure, and thereby on device efficiency as well as stability. The polymers employed are mostly donor-acceptor polymers. It has been shown that polymer fluorination, side chain modification and tuning polymer molecular weight can change blend microstructure, resulting in substantial influences upon device power conversion efficiency. In addition, the role of polymer crystallinity and size of fullerene cage (PC₆₁BM vs PC₇₁BM) upon the stability of blend microstructure and device performance under thermal annealing conditions have also been considered. As such, this thesis provides some guidelines for polymer design to improve device efficiency and stability from a blend microstructure perspective.

Conclusions

In order to improve the performance of polymer:fullerene device, extensive research effort has been made to improve the material energetics by modifying the chemical structure of the polymer. However, such attempt may be accompanied by changes in blend microstructure, which can have substantial impact on device performance. As the blend microstructure is increasingly recognised as a key determinant in device efficiency, the correlation between polymer chemical structure and blend microstructure needs be thoroughly understood.

Chapter 3 demonstrates this idea using fluorination of SiIDT-BT and SiIDT-DTBT as examples. It is shown that polymer fluorination, which was suggested to improve open circuit current,¹ can lead to phase segregation in blend microstructure, limiting the charge generation for devices. This negative impact on device, however, appears to depend on the polymer backbone. With additional thiophene spacers in the polymer backbone, the polymer potentially offers better miscibility with fullerene, compensating any promotion in phase segregation. In addition, the backbone with thiophene spacers also encourages the fluorinated polymer to adopt π - π stacking along the out-of-plane direction, facilitating charge transport. As such, these examples reveal the potential negative impact of polymer fluorination on device performance, which can be avoided by modifying the polymer backbone.

The impact of alkyl side chain modification on PTTV polymers is addressed in Chapter 4. With a linear side chain, a higher degree of PTTV:PC₇₁BM mixing is observed, which in particular improves the poor fullerene exciton dissociation in the system. This subsequently leads to better device performance. The better mixing of C16-PTTV:PC₇₁BM could be due to the potential greater space between side chains in comparison to C2C6-PTTV, which should make the polymer more capable of intercalating fullerene molecules. In addition, it has also been shown that charge generation following fullerene excitation can contribute substantial photocurrent to the device. The relatively poor efficiency of fullerene exciton dissociation for PTTV, as well as for a couple of benchmark materials reported previously,^{2, 3} suggests that the photocurrent following fullerene absorption and that from polymer absorption may require separate consideration in order to optimise the device efficiency.

In Chapter 5, increasing polymer molecular weight is shown to be an effective approach to improve device efficiency, with a more than 2 fold improvement in PCE across the molecular weight range for two DPP-containing polymers. The improvement in device performance is

primarily derived from the better polymer:fullerene mixing in the blend microstructure, resulting in more efficient charge generation. This is different from the improved light absorption and charge transport reported by previous literature employing alternative donor polymers.^{4, 5} The improved polymer:fullerene mixing in the blend microstructure is potentially due to the higher polymer amorphous volume fraction resulting from chain folding at high molecular weights. This chapter once again highlights the important role of blend microstructure to device performance.

Chapter 6 focuses on the stability of blend microstructure upon thermal annealing for device performance. Polymer crystallisation is suggested to be responsible for the reduction in the miscibility between polymer and fullerene, accelerating the device degradation at temperatures above 140 °C. By comparing PC₇₁BM with PC₆₁BM when blending with DPP-TT-T, the improved thermal stability of DPP-TT-T:PC₇₁BM is attributed to possible slower fullerene diffusion kinetics. In addition, it has been found that DPP-TT-T:PC₇₁BM undergoes much faster decay upon post-annealing in comparison to pre-annealing, indicating that the electrode plays a significant role in determining the device stability against thermal annealing in the DPP-TT-T:PC₇₁BM system. Lastly, with respect to the photo-induced fullerene transformation, it has been shown that this can be applied to DPP-TT-T:PC₆₁BM devices to improve the device stability upon post-annealing. This is potentially due to a less diffusive nature of fullerene oligomers compared to its monomer form.

Further work

The thesis has demonstrated that the degree of polymer:fullerene mixing is a key parameter in determining the PCE of polymer based solar cells. This depends strongly on polymer crystallinity and the ability of the polymer to intercalate fullerene. Regarding the correlation between the degree of mixing and polymer crystallisation, wide angle X-ray scattering was used which can only assess the degree of material crystallinity in the out-of-plane direction. Instead, grazing incidence X-ray scattering (GIXS) can be employed, which provides three-dimensional information on molecular packing, to give a more accurate analysis correlating these two parameters. Fullerene intercalation in amorphous polymer region is also likely to have great contribution to polymer:fullerene mixing but requires studies such as Raman spectroscopy to interrogate further.

It has been confirmed that polymer fluorination can have a negative, as well as positive, impacts on device performance, by promoting the phase segregation of blend microstructure. However, this appears to only partially account for the reduced device performance for SiIDT-BT. Another plausible reason for the reduced performance is likely to be associated with the impact of fluorination on dipole moment of the polymer. In the future, this hypothesis can be verified using the Austin model (AM1) in Hyperchem for dipole calculations.

In the case of stability, it has been shown that the amorphous SiIDT-BT exhibits poorer morphological stability at temperature below 140 °C, compared to DPP-TT-T. However, the associated degradation pathway is not clear. This could be due to subtle loss in π - π conjugation or fullerene intercalation, resembling the previous studies on PCDTPT and MDMO-PPV, which can be verified using GIXS or Raman spectroscopy. In addition, it has also been identified that the metal electrode can cause a significant difference in device stability for DPP-TT-T based devices. Research effort in the future should be made to investigate the interaction between the electrodes and blend microstructure and how this contributes to device degradation under thermal stress. Finally, a sacrifice in initial device performance is required to improve the device stability for DPP-TT-T:PC₆₁BM using photo-induced fullerene transformation. Such a sacrifice in PCE is much larger than that reported for PCDTPT:PC₆₁BM. The initial loss shall be minimised in order to make the photo-induced fullerene transformation a more applicable approach for all polymers to improve device stability against thermal annealing.

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