

Charge Generation in Organic Solar Cells

Fiona Jamieson

Imperial College London

Department of Chemistry

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Declaration of originality

Except where specific reference is made to the work of others, this work is original and has not been already submitted either wholly or in part to satisfy any degree requirement at this or any other university.

Fiona Jamieson, June 2012

Abstract

Organic photovoltaic devices are receiving extensive interest, with device efficiencies now exceeding 8%. There is increasing evidence that the efficiency of dissociation of excitons (bound electron-hole pairs) into free charge carriers is a key factor determining device performance. Dissociation of these excitons occurs at the interface between donor and acceptor molecules in the photoactive layer of the device and is driven by a favourable difference in electronic energy levels between the two materials. Several factors can potentially determine the efficiency of this process, including interfacial energetic energies, molecular structure, film microstructure and device electric fields. This thesis employs optical spectroscopic techniques, including photoluminescence quenching and transient absorption spectroscopy to assay the efficiency of charge separation for a range of donor / acceptor blend films and devices, thereby providing new insights into the factors determining the efficiency of this process.

The first results chapter focuses on the experimental technique, transient absorption spectroscopy, and how this can be employed to determine the yield of dissociated charges in donor / acceptor blend films. Three materials systems are studied, firstly looking at the effects of structure of the donor material, followed by a study into the effects of the temperature on charge generation and recombination.

The following two chapters investigate the effects of film morphology on charge generation, specifically focusing upon the fullerene acceptor. Aggregation of phenyl-C61-butyric acid methyl ester (PCBM) is shown to be a key factor in the generation of free charges in the blend film, leading to proposal of a model regarding the role of this aggregation in charge generation. This study has then been extended by using additives to modify the concentration threshold for PCBM aggregation by preventing the intercalation of the PCBM between the polymer side chains, and hence inducing PCBM aggregation at a lower concentration.

In the final chapter, the effects of an externally applied electric field on charge generation in devices have been studied. Such electric fields have been proposed to reduce geminate recombination losses, thereby increasing the dissociation of free charges, and thus leading to an increase in the device photocurrent. Polymer and small molecule blend systems have been studied and shown to exhibit different dependences of charge generation upon applied bias depending on the donor molecule and the morphology of the blend.

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Publication list

Fullerene crystallisation as a key driver of charge separation in polymer/fullerene bulk heterojunction solar cells. *Fiona C. Jamieson, Ester Buchaca Domingo, Thomas McCarthy-Ward, Martin Heeney, Natalie Stingelin and James. R. Durrant*. Chemical Science, **2012**, 2, 485 - 492

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Frequently used acronyms and abbreviations

APFO-3	poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-5,5-(4',7'-di-2-thienyl-2',1,3'-benzothiadiazole)]
BHJ	bulk heterojunction
C60-2	pyrazolinofullerene
CS	charge separation
CT	charge transfer
CV	cyclic voltammetry
ΔOD	change in optical density
DPP(TBFu) ₂	DPP_OT_3,6-bis(5-(benzofuran-2-yl)thiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo [3,4-c]pyrrole-1,4-dione
DSC	differential scanning calorimetry
E _A	electron affinity
FF	fill factor
HOMO	highest occupied molecular orbital
ICBA	indene-C ₆₀ bisadduct
J _{sc}	short circuit current (mA cm ⁻²)
J-V	current / voltage
L _{ex}	exciton diffusion length
LUMO	lowest unoccupied molecular orbital
Me7	methyl octanoate
Me12	methyl dodecanoate
Me14	methyl myristate

ODT	1,8-octanedithiol
OPV	organic photovoltaic
P3HT	poly(3-hexylthiophene)
pATBT	poly(3,6-dialkylthieno[3,2- <i>b</i>]thiophene-co-bithiophene
pBTTT	poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2- <i>b</i>]thiophene)
PCBM	[6,6]-phenyl-C61 butyric acid methyl ester
PC ₇₀ BM	[6,6]-phenyl-C71 butyric acid methyl ester
PCE	power conversion efficiency
PCPDTBT	poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1- <i>b</i> ;3,4- <i>b'</i>]-dithiophene)-alt-4,7-bis(2-thienyl)-2,1,3-benzothiadiazole]]
PL	photoluminescence
PLQ	photoluminescence quenching
PS	polystyrene
PV	photovoltaic
SDT(TDPPTBFu) ₂	3-[bis(2-ethylhexyl)silanol-yl]-5,5'-bis{5-[2,5-bis(2-ethylhexyl)-6-[5-(benzofuran-2-yl)thiophene-2-yl]pyrrolo[3,4- <i>c</i>]pyrrole-1,4-dione-3-yl]-2,2'-bithiophene
Si-PCPDTBT	poly[(4,4'-bis(2-ethylhexyl)dithiene[3,2- <i>b</i> :2',3'- <i>d</i>]silole)-2,6-diyl-alt-(4,7-bis(2-thienyl)-2,1,3-benzothiadiazole)-5,5'-diyl]
SiTPT-BT	poly[2,8-(6,6,12,12-tetradecylsilolindenofluorene)-co-4,7-(2,1,3-benzothiodiazole]
TAS	transient absorption spectroscopy
V _{oc}	open circuit voltage (V)

Chapter 1

Introduction

The recent rise in the cost of all fossil fuel derived energy sources, alongside concerns over their environmental impact, has forged an opportunity in the market for both renewable and cheap energy sources. Considerable research, both academic and industrial, is being conducted into potential alternative routes for energy generation that do not rely on fuel combustion. One of many promising routes for alternative energy generation is solar energy conversion, utilising incident sunlight to create electrical power. Current commercial solar cells are typically fabricated from inorganic materials. However, a new class of plastic electronic devices is emerging in the energy market as alternatives to silicon, and it is these materials that are of interest in this thesis. This chapter introduces some of the fundamental concepts in organic semiconductors, including charge generation and recombination and their role in photovoltaic devices, looking specifically at mixed donor / acceptor blend architectures.

1.1 Motivation for using and developing alternative energy sources to fossil fuels

Energy production, and consumption is vital for sustaining the current world lifestyle and, in particular, facilitating technological growth. An increasing proportion of the world's population are now strongly reliant on recent advances in technology. The increase in affordable and accessible telecommunication, travel and information has been invaluable in facilitating advancements in science, technology, medicine and social mobility, to name just a few areas that have benefited from such advancements. However, these advancements have come at a cost, one of which is an increase in global energy consumption, which is predicted to continue for the foreseeable future.¹⁻³ Whilst this in itself is not a problem, sourcing energy to meet the global demand is not a facile task, as the vast majority of current commercial energy production comes from the combustion of coal, oil or gas.

If concerns over current energy supplies, whether financially, politically or environmentally motivated, are justified, alternative sources of energy generation must be invested in to provide for future needs. Of these potential alternative energy sources to fossil fuels, which include tidal, geothermal and nuclear energy, one area of energy generation receiving wide-spread interest is photovoltaic (PV) solar energy conversion. This method of energy generation relies on sunlight to excite semiconducting materials and thereby creating electrical charge pairs. One potential advantage to this route of energy generation over some of the alternative options mentioned is its social acceptability and its suitability for microgeneration, rather than relying on the centralised sourcing and transport of coal, oil, gas or other geological requirements. This makes

the notion of solar energy conversion an attractive prospect to many people, especially, if as so often quoted, more sunlight reaches the Earth's surface in an hour than the global population currently use in a year.⁴ Therefore, efficient harnessing of sunlight has the potential to alleviate the world's energy problems. This is especially true if the “pay-back time” for solar panels, the length of time it takes for the device to have generated more energy than it cost to make, is kept to a minimum. Currently this pay-back time varies for different materials, but may, in some instances, become less than one year for organic photovoltaics (OPVs).^{5,6}

The concept of utilising solar energy may sound simple in principle, but decades of research have indicated that realising this route, both cost effectively and efficiently, is a significant challenge. A range of technology routes have been explored. This chapter will consider one such technology, based on the use of organic semiconductor materials for application in PV devices for energy conversion, along with the challenges that must be overcome for these materials to break into the commercial market as competitors to current energy sources.

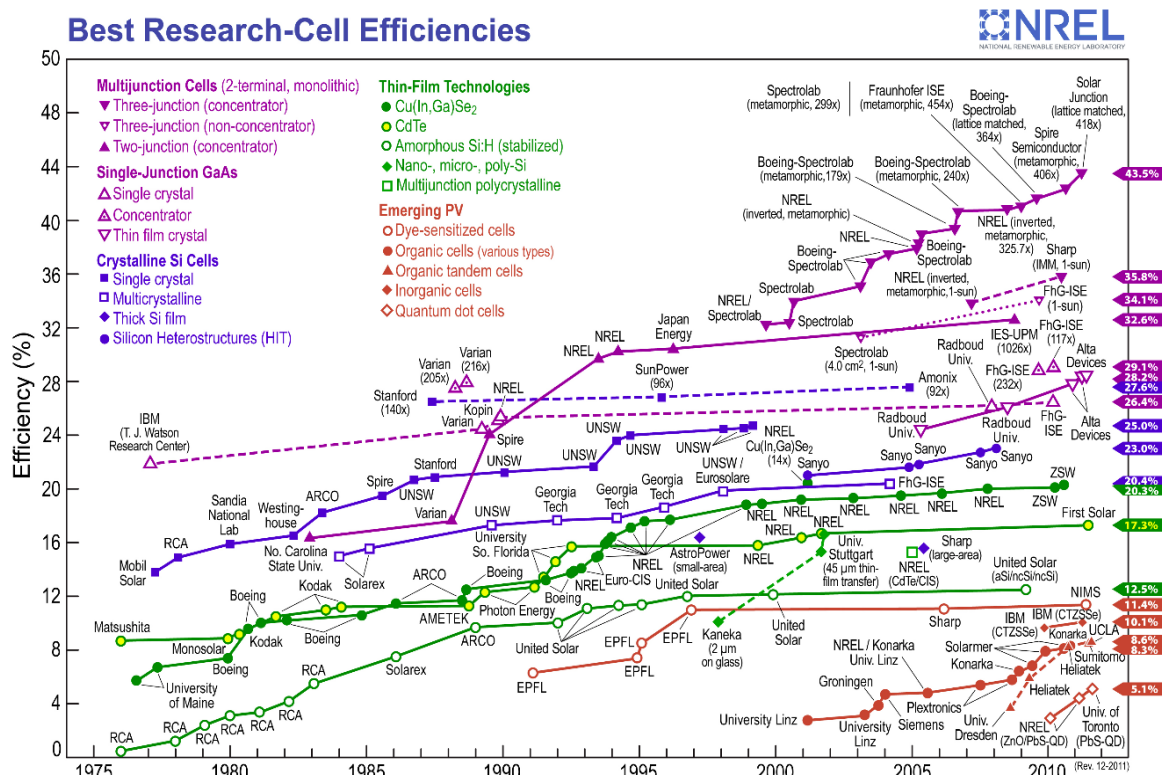


Figure 1.1 – Highest recorded device efficiencies over the past four decades, for multi-junction (light purple) crystalline silicon (dark purple), thin films (green) and emerging PV technologies (red). The organic materials that have emerged over the last decade shown in red in the bottom right hand corner are of particular interest in this thesis.⁷

Figure 1.1 shows some of the highest efficiency PV device data and the institutions accredited for research into these devices over a 35 year period. From this figure it is clear to see that there is an increasing trend in the amount of research conducted, with device efficiencies of all material types reported in this figure steadily increasing.⁸ Whilst inorganic solar cells clearly offer high efficiency devices, organic electronic devices are receiving extensive interest for their applications across a broad range of applications including PVs, transistors and light emitting diodes (LEDs).⁹⁻¹¹ Their potential for low cost, high throughput fabrication makes them an attractive alternative to current inorganic technologies which typically rely on relatively costly fabrication methods. Of particular interest, and presented in this thesis, are thin film PVs fabricated from a mixture of two organic materials, typically comprising semiconducting polymers and small molecules, as the light harvesting materials in devices. Whilst the efficiencies of this type of device occupies only a small corner of Figure 1.1 (closed red circles, bottom right), they offer a significant potential as materials for PV devices as in only a decade there has been a steady increase in certified device efficiencies. Organic electronic devices have the potential to be fabricated conformally on a range of substrates over large areas due to their flexibility and lightweight nature, allowing for integration into the manufacture of existing portable technologies and infrastructure.

1.2 Conjugated polymers as semiconducting materials in photovoltaics

Conjugated polymers utilise their extended π conjugation to create a delocalised network of electrons and this gives rise to their semiconducting properties. The overlapping p_z orbitals, and resulting sp^2 hybridization along the polymer backbone, create a delocalised electron network, essential for dictating the electronic properties of these materials. The formation of interchain interactions is possible if the two segments are spatially confined.¹² The increase in conjugation length along the polymer backbone is desired as it decreases the energy between the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) of the material, lowering the bandgap. The HOMO and LUMO are alternatively described in literature as the valance and conduction bands, respectively, following the language of inorganic semiconductor physics. This increases the potential to absorb more photons across the solar spectrum as the bandgap is reduced, therefore, a reduction in the bandgap of the material may increase the device power conversion efficiency (PCE) through an increase in the short circuit current (J_{sc}) as light absorption increase. However, there is a threshold for the magnitude of the

bandgap as if this is too low, the maximum obtainable open circuit voltage (V_{oc}) becomes too small for efficient device operation and the material is rendered useless for PV operation.

Despite typical polymers containing many ($\sim 10 - 100$) repeat units in one polymer chain, the delocalisation length of any given section may only be a few nanometres long, typically only a few polymer repeat units.¹³ Defects, such as conformational changes, backbone twisting or the presence of end groups, may affect the conjugation length as the delocalisation along the backbone is disrupted, thus hindering charge transport along the chain.

1.3 Photophysics and charge generation in organic blend solar cells

Polymers are employed in the OPV devices used in this thesis as the light harvesting material, Current / voltage (J-V) curves yield information on the overall device performance, as will be discussed further in Section 1.6, but reveal only limited detail into the mechanism and nature of the charge generation or recombination pathways. Investigation specifically into the charge generation mechanisms and the origin of device photocurrent may yield information on the processes governing device efficiencies which in turn made facilitate improvements in the PCE. Organic semiconductor solar cells utilise incident photons to generate electrical charge. The exact mechanism by which this charge generation proceeds in OPVs is not fully agreed on in the literature, and is the subject of extensive research.¹⁴⁻¹⁷ One simplified model describing the processes that may occur, follows a series of sequential steps, in which photon absorption leads to the formation of an excited state, which then yields electrons and holes which may be collected at the electrodes.

1.3.1 Photophysics in organic semiconductors

Light absorption of the incident sunlight leads to the promotion of an electron from the ground state to a higher energy excited state. Typically, photon absorption following photoexcitation of the donor material promotes an electron from the HOMO (π bonding orbital, alternatively described as the S_0 state) into a higher energy state in the material. In π -conjugated systems, such as the polymers of interest in this thesis, the strong vibrational coupling leads to the excited electron relaxing to a lower energy state, the material's LUMO (anti-bonding π^* orbital, S_1) This is the formation of an exciton; a singlet excited state, that typically resides on one material, usually the donor. The Jablonski diagram in Figure 1.2 shows the processes that occur

following photoexcitation in the materials investigated here. These include internal conversion, intersystem crossing to triplet states, fluorescence and phosphorescence.

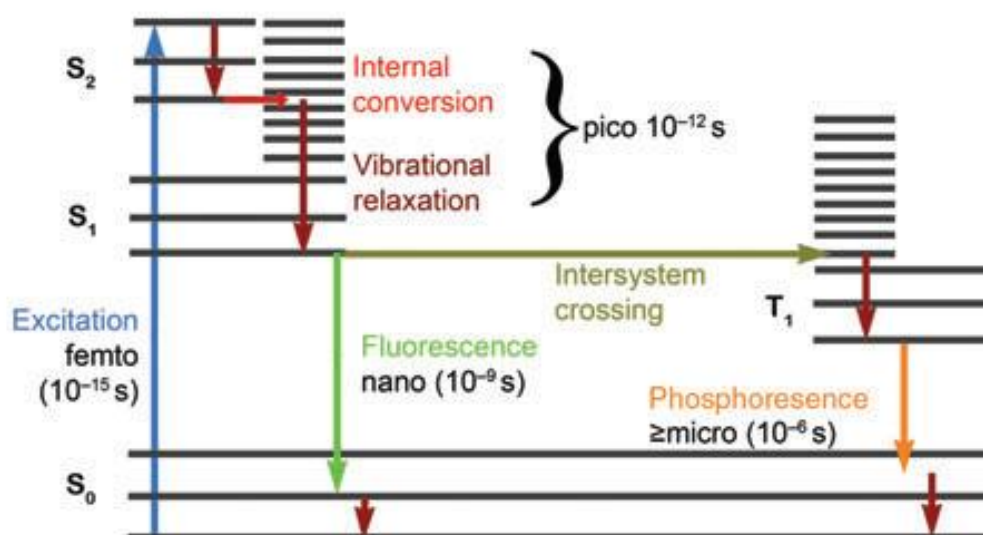


Figure 1.2 – A Jablonski diagram, taken from reference 18, showing some of the processes, and the timescales these processes typically occur on, following promotion of an electron (blue arrow) from the ground state (S_0) to an excited state followed by some of the other processes that may occur.

1.3.2 The role of a donor / acceptor interface in charge generation

For the OPV devices investigated herein, two different materials, with an energy level off-set between them, are required. This energy level offset between the donor and acceptor acts as the driving force for exciton dissociation. The differences in the potential energy between these materials, which may derive from both interface dipoles and chemical orbital energies, is critical for device operation and will be discussed in terms of photophysics in the following section. Some of the specific materials that will be investigated further in this thesis will be discussed in more detail in Section 1.4.

There are two types of excitons which commonly form in semiconductors following excitation; Wannier-Mott and Frenkel excitons. Both of these types of exciton are electron-hole pairs created following excitation of semiconducting materials.¹² It is the latter of these two exciton types that is critical when describing the charge generation process in OPVs, due to the low dielectric constants ($\epsilon \approx 2 - 4$ eV)¹⁹ of the materials compared to that of conventional inorganic semiconductors ($\epsilon \approx 12$ eV for silicon)¹⁴. Frenkel excitons are much more tightly bound as the Coulombic attraction between the electron and hole is much greater than that of the Wannier-Mott exciton. Typical exciton binding energies for organic materials, where this is the potential energy difference between the neutral singlet exciton and the two fully dissociated, relaxed

charges, are in the order of 0.1 – 1 eV,¹⁴ and this high binding energy arises primarily from the low material dielectric constant. The high binding energy of the polymer exciton leads to a low probability of instantaneous free charge carrier generation following photoexcitation. Therefore, to facilitate charge separation in organic blends, an energetic driving force, arising from differences in the materials energy levels must be present. The excitation of the electron from the ground state to an excited state may lead to promotion above the bandgap into a higher excited state. The neutral species with this excess thermal energy are often called hot excitons.²⁰

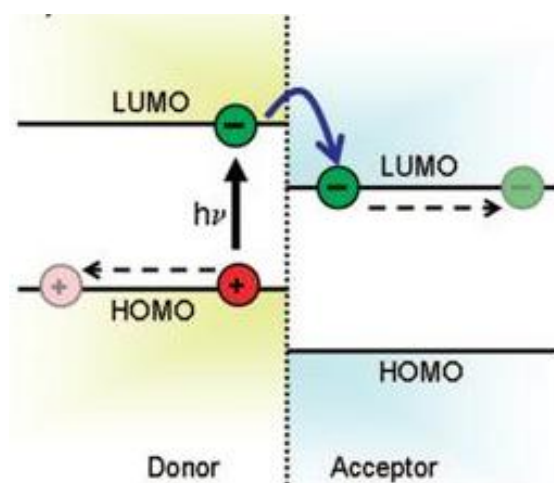


Figure 1.3 – A route to dissociated charge generation following photoexcitation of an electron into the donor LUMO followed by electron transfer to the acceptor HOMO leaving a hole on the donor, before both charges are extracted.¹⁴

Exciton formation may take place anywhere in the active layer and therefore, may not have occurred at a donor / acceptor interface. If this is the case, the exciton would therefore have to migrate to an electron acceptor before dissociation of the charges may occur. Excitons can transport energy without having to transport charge, which may proceed via exciton migration. Exciton diffusion lengths, i.e. the distance an exciton can travel before relaxation back into the ground state, in the organic materials considered in this thesis, is typically reported to be in the order of 5 – 10 nm,²¹ however, there is a significant degree of variation in the diffusion lengths reported.^{22,23} Hence, for charge separation to occur in these materials, an interface must be encountered within the exciton lifetime and before the relaxation of the photogenerated excited state back to the ground state. If an interface between the donor and acceptor with a suitable energetic difference between the two LUMO levels of the materials is encountered before the exciton relaxes back to the ground state, electron transfer from the donor to acceptor may occur. This ultrafast electron transfer from the donor to the acceptor has been shown to occur on the picoseconds timescale,²⁴⁻²⁶ and has also been recorded from as fast as ~45 fs in

poly[2-methoxy, 5-(3',7' dimethyl-octyl-oxy)]-*p*-phenylene vinylene (MDMO-PPV):PCBM blends, as recorded using ultrafast transient absorption spectroscopy²⁷ In this instance exciton formation from the acceptor is not considered, and it has been assumed that the excitons have been formed solely in the donor. It should be noted that exciton generation may occur in the acceptor in some polymer / fullerene blends.²⁸

1.3.3 Charge transfer (CT) states

The potential mechanism for charge generation in OPVs described above, may be an oversimplification of the processes that occur in such devices. One possible route for free charge formation in the organic BHJs discussed here is via the formation of a charge transfer (CT) state. A CT state is an interfacial electron-hole pair which has been partially separated following electron transfer from the donor to the acceptor whilst the hole remains on the donor.^{29,30} Despite the partial separation of the electron / hole pair, these charges are not free from their Coulomb attraction.^{14,30} Herein, any interfacial electron / hole pair describing electrons and holes that are spatially separated across the donor / acceptor but remain electrostatically bound will be called a CT state and is described schematically in Figure 1.4. It should be noted that there is some ambiguity in current literature regarding the nomenclature of these interfacial bound states, with alternative descriptions including exciplex,^{31,32} bound polaron pairs³³ and CT excitons.³⁴ The uncertainty in the literature nomenclature regarding these states may arise from different names being employed to distinguish between small differences in the excited states.³⁵ The formation of CT states is commonly observed using photoluminescence measurements as CT state luminescence is characteristically red shifted compared to the of the singlet excited state.²⁹ However, other techniques, including transient absorption imaging,³⁶ have been used to investigate CT formation.

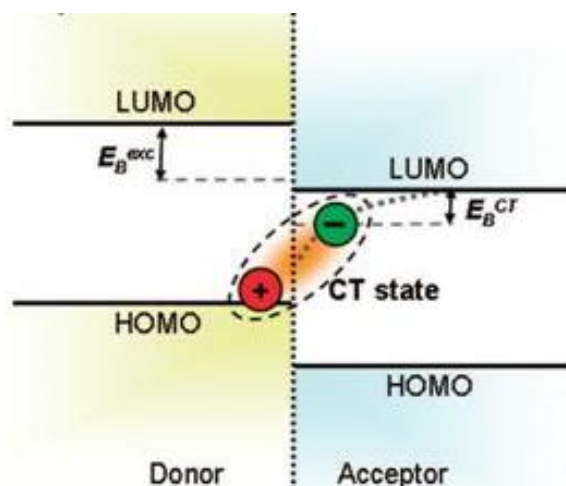


Figure 1.4 – CT state formation following electron transfer from the donor to the acceptor without the charges escaping their Coulombic attraction, as highlighted by the dashed line around the electron and hole. Taken from reference ¹⁴.

Following electron transfer from the donor to the acceptor, the separation of the CT state creates a delocalised charge segment that is accompanied with a structural deformation in the lattice, and this specific coupling of charge formation and structural change is referred to as a polaron. These electron or hole polarons are not typically bound to each other, however, it is possible to form a bound polaron pair between a hole-polaron and an electron-polaron that are Coulombically bound but retain their two distinct wavefunctions. As discussed above, these states will not be distinguished from CT states in this thesis, unless otherwise stated. Polarons have a distinct, typically red shifted absorption spectrum compared to the material ground state and can be thus be monitored optically. The formation of polarons is often experimentally monitored by appearance of this polaron optical absorption as a method of exploring the charge generation in organic blends following photoexcitation, as will be explored in greater detail in Chapter 3.

1.3.4 Kinetics of charge separation

The kinetics and mechanisms of charge separation in OPVs is under significant debate and scrutiny in literature.^{14,37-39} There are some reports proposing that the charge separation process follows a series of steps, and one schematic proposed to explain this route to charge separation suggested by Bredas *et al.* is shown in Figure 1.5. This electronic state diagram describes exciton creation following photoexcitation of an electron from the donor HOMO (S_0) to the donor LUMO (S_1). The CT state formed at the interface (shown in green) may have excess thermal energy. This 'hot' state may relax to a lower energy state (k_{IC}), or, could separate into

dissociated charges (k_{CS}). Or, there may also be some spin mixing of the CT state to a triplet state (T_1). Following the formation of the relaxed CT state, the bound charges may either recombine geminately or dissociate into a charge separated state (CS, shown in red). Dissociation of the 'hot' CT state to the CS state (shown in red), may also occur and depends on the driving force (ΔG^0) which is the difference in energy between the donor LUMO and the charge separation energy.

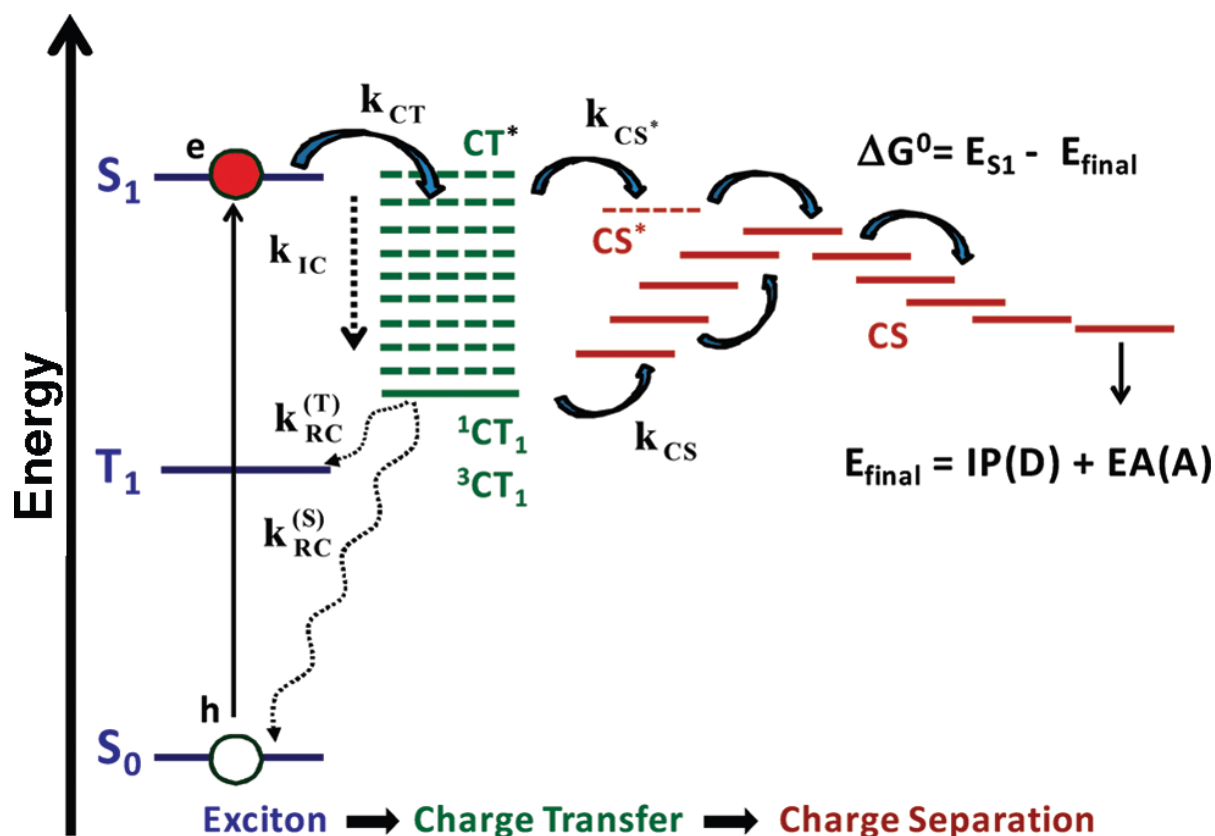


Figure 1.5 – Electronic state diagram describing charge generation, taken from reference 37. This diagram shows the photoexcitation of an electron from the S_0 ground state to S_1 , the first excited state, leaving behind a hole in the S_1 state. This leads to charge transfer at the donor / acceptor interface, creating a CT state, where the electron is now on the acceptor, whilst the hole remains on the donor, where CT* is a 'hot' excited state and $1CT_1$ is the lowest energy CT state. This in turn leads to charge separation where the electron and hole are free from each other and may be collected as charge.

Charge generation following photoexcitation is vital for device operation, however, the photogenerated charges must overcome a number of potential loss pathways before the generation of charges that may be collected at the electrodes. Therefore, identifying and minimising the loss mechanisms which may occur in these devices, is critical for improving device performance. There is significant debate in current literature as to whether CT states and

'hot' CT states, i.e. CT states with excess thermal energy, are important to device performance, with no consensus yet to be reached.^{30,39-42}

1.3.5 Geminate recombination

The first of the loss mechanisms to be considered here is geminate recombination. This is the recombination of a Coulombically or spatially bound electron-hole pair. The recombining charges have originated from the same exciton before the charges have been fully separated from their Coulomb attraction. Geminate recombination has been shown to occur on the 10 ps – 100 ns timescale in polymer / fullerene blends,^{43,44} and is detrimental to device performance as the charges are unable to escape either the strong attractive binding energy between them or are physically confined and are unable to move far enough to suppress the geminate recombination. In addition geminate recombination has been shown to occur in materials systems with a finely intermixed blend of the two components in which no clearly defined domains of either material are formed,⁴⁵ and to be dependent on the fullerene acceptor in blends with certain polymers.⁴⁴ Geminate recombination has also shown to be a significant loss mechanism in polymer / polymer devices,^{46,47} which may be a contributing factor to their poor performances to date compared to polymer / fullerene blend devices. Several studies have suggested that geminate recombination losses may be dependent upon device electric field,^{48,49} as is discussed in section 1.3.7.

1.3.6 Non-geminate recombination

The second of the main loss processes considered here is non-geminate recombination, alternatively called bimolecular recombination in literature. This is the recombination of two dissociated charges that have previously escaped the Coulomb attraction of the original photogenerated exciton and achieved spatial separation from each other. These charges do not in general originate from the same exciton, but may involve the recombination of any dissociated carriers. Non-geminate recombination typically occurs on longer timescales than that of geminate recombination, from the hundreds of nanoseconds and longer,^{50,51} however the decay kinetics may be accelerated at high charge densities.^{52,53}

The significance of non-geminate recombination on cell performance has been extensively studied, particularly in P3HT:PCBM devices,⁵⁴⁻⁶¹ however, there have been conflicting studies regarding its impact. A number of studies have indicated that it has little impact on the overall

cell performance,^{55,56} whilst other reports have claimed that this is the dominate loss pathway in some blend devices.⁵⁷⁻⁶¹ As briefly discussed for geminate recombination, non-geminate recombination may again be a significant loss mechanism in devices with poor nanomorphologies. It has also been suggested that non-geminate recombination may not be significant at short circuit, but becomes more significant towards V_{oc} , as the charge density increases.^{57,62} However, despite not typically being thought to be a significant loss pathway at short circuit, there is some evidence that non-geminate recombination does occur at J_{sc} in some devices, such as non-annealed P3HT:PCBM.⁶³ Regardless of the electronic properties being such that the photogenerated electron and hole have been able to overcome the Coulombic attraction, the active layer morphology may prevent the charge collection if, for example, there is not a suitable percolation pathway to the electrodes.⁶⁴ It has also been shown that the non-geminate recombination rate may be slowed in the presence of defects, which may act as trapping sites.⁶⁵ However, there are also reports that trapping sites may mediate non-geminate recombination,⁶⁶ yet, the effect of trapping sites on device performance is currently under debate in the literature.^{65,67-69}

1.3.7 Onsager-Braun theory of charge dissociation

Exciton formation following electron transfer from the photoexcited donor to the acceptor can result in the formation of a coulombically bound electron / hole pair in organic blends. The mechanisms of charge generation in OPVs are under much debate in literature,^{14,15} however as discussed above, one proposed mechanism for charge generation in OPVs is via dissociation of a CT state by overcoming the Coulomb attraction between the electron and hole. Overcoming this attraction then generates dissociated charge carriers that may be harvested as the device photocurrent. The probability of dissociation of this bound pair in OPVs is often discussed in the context of Onsager's theory of geminate losses in weak electrolytes.⁷⁰ Onsager-Braun theory of charge dissociation is of particular relevance when describing the electric field dependence of charge generation. There are several reports of how an externally applied electric bias may assist charge generation in some OPVs.^{49,71-73} Onsager's model calculates the probability that a Coulombically bound electron-hole pair, following random Brownian motion, will overcome their attractive forces and separate, generating free charge carriers as opposed to recombining back to the ground state. The model proposes the formation of a localised hole and a "hot" electron pair following photoexcitation, where the electron can overcome the Coulombic binding energy by rapid movement away from the hole, to become free from the attractive force

of the hole. The attractive interaction between the electron and hole has been defined by the Coulomb capture radius, r_c , as defined by Equation 1.1.

$$r_c = \frac{e^2}{4\pi\epsilon_r\epsilon_0 k_B T}$$

Equation 1.1

where ϵ_r is the dielectric constant, ϵ_0 is vacuum permittivity k_B is the Boltzmann constant and T is the temperature. The Coulomb capture radius is the distance between the electron and hole when the Coulombic attraction is equal to $k_B T$ and is typically on the order of 10 nm.^{74,75} If the thermalisation length, a , (the distance the excited species may travel before relaxing into its lowest energy state), of the electron is greater than the r_c , the bound charges fully dissociated into free charge carriers.⁷⁶ This is illustrated in the potential energy diagram in Figure 1.6. Due to the low dielectric constants of polymers, the probability that the exciton will escape the Coulombic attraction in organic blends is significantly reduced in comparison with conventional inorganic semiconductors.

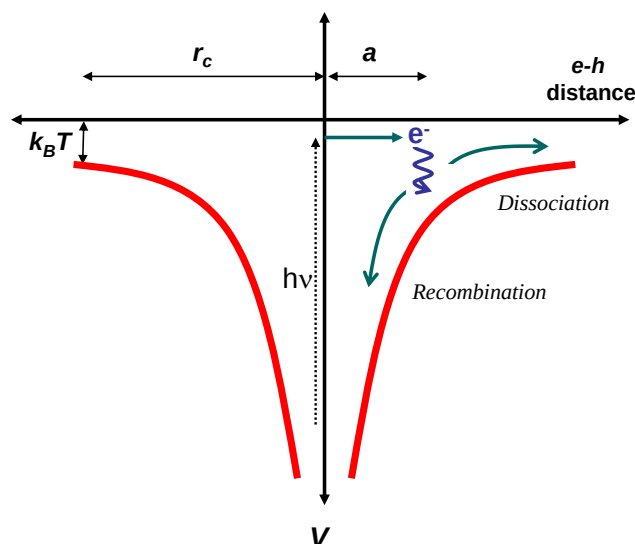


Figure 1.6 – A potential energy diagram detailing Onsager's theory of autoionisation. The red curve is the potential as a function of the electron / hole separation distance. Absorption of a photon creates a mobile electron which may thermalise at a given distance from the resulting hole, denoted by distance a . If the thermalisation length is less than that of the Coulomb capture radius, the original electron-hole pair will recombine geminately, however, if $a > r_c$, the charges may be able to escape the Coulomb attraction. Taken from reference ¹⁴.

Onsager's model assumes if the bound charges do escape the Coulombic attraction, then complete and lasting dissociation ($r = \infty$) of the ions occurs and are removed from the system

completely. One potential method for increasing the fraction of escaping ions may be to apply an electric field, reducing the height of the Coulomb barrier with an increasing field. This model assumes that an externally applied field does not affect the recombination of free ions, only the dissociation of bound pairs.⁷⁷ This model has been widely considered for use in OPV analysis. One notable adaption to Onsager's model was proposed by Braun, who introduced a finite lifetime of the CT state.⁷⁸ Braun's extension differs from Onsager's original theory as he also included in his model that dissociation of the CT state to free carriers is a reversible process and the CT state may be reformed if separation of the charges does not occur.

Despite many references to the Onsager-Braun model of charge dissociation in organic semi-conducting materials, its applicability to OPV materials systems has been questioned.^{79,80} The application of Onsager-Braun theory in OPV devices is often discussed in relation to the electric field dependence of charge separation in device modelling. However Tachiya and co-workers have incorporated the electron mobility into their calculations,⁷⁹ as it has been suggested from these calculations that Onsager's original model is not valid in materials with a high motilities.⁸⁰ The role of electric fields in assisting charge generation and the applicability of Onsager's theory of charge separation will be discussed further in Chapter 6, looking specifically at the effect of external bias on the charge generation in three different materials systems.

1.4 Semiconducting materials in organic solar cells

PV operation is founded upon photoexcitation of a conductive material creating electrical charges which can be harvested. The previous section has discussed some of the charge generation mechanisms proposed in OPVs but we now turn to consider some of the specific materials used in devices relevant to this thesis. Many different materials have been investigated for their potential use in PVs. One of the most commercially successful materials to date in PVs is crystalline silicon.⁸¹ However, many other materials systems have been investigated for their light harvesting abilities, including amorphous silicon,⁸² copper indium gallium diselenide (CIGS),⁸³ dye sensitised solar cells (DSSCs)⁸⁴ and quantum dots;⁸⁵ however, the application of these materials in PVs will not be discussed further in this thesis. We will consider only some of the organic materials employed in bulk heterojunction (BHJ) architectures, firstly looking at donor materials and then at some of the acceptor materials.

1.4.1 Conjugated polymers as donor materials for organic solar cells

One of the most common type of donor materials employed in OPV devices are conjugated polymers. As discussed in Section 1.2, the electrical properties of these materials include, amongst other properties, good conductivity,⁸⁶ charge transport^{87,88} and charge generation.⁸⁹ These materials are also potential candidates for electric devices because their electronic properties may be tuned through modifications in chemical synthesis and, therefore, optimisation of the energy harvesting properties of the polymers may be possible,⁹⁰ which may be beneficial to device performance when exploring the possibilities of nanoscale refinement of the blend morphology.

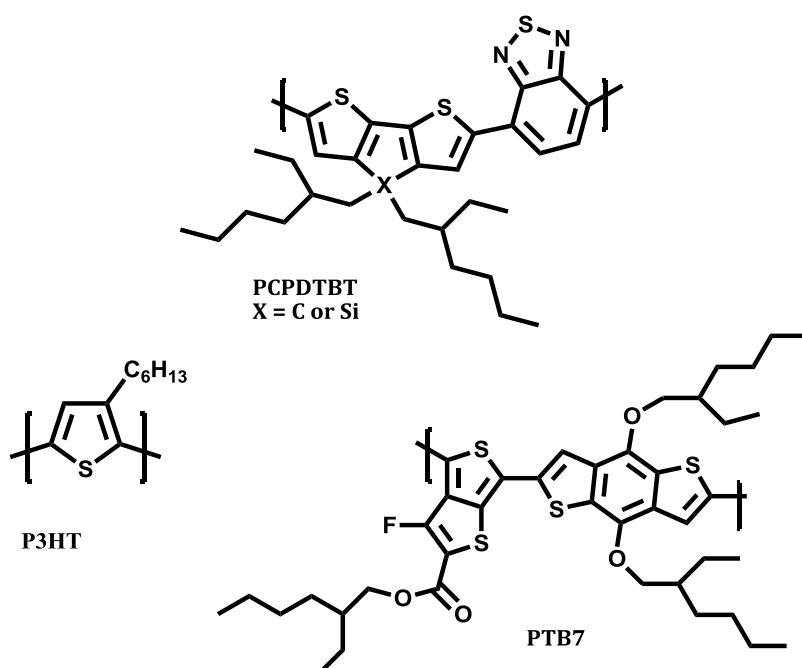


Figure 1.7 – Examples of three common polymers used in OPV devices; PCPDTBT, P3HT and PTB7.

Examples of three of the polymers used as the donor materials in OPVs are shown in Figure 1.7. This includes one of the most extensively characterised polymers, poly(3-hexylthiophene) (P3HT). Devices fabricated using the semi-crystalline polymer P3HT as the donor material and blended with [6,6]-phenyl-C61 butyric acid methyl ester (PCBM) have been extensively reported over the past decade.^{91,92} This blend system is very well characterised in the literature with respect to device efficiency as a function of the blend morphology⁹³⁻⁹⁸ and charge generation yields.⁹⁹⁻¹⁰¹ The effects of thermal annealing,^{99,102} the mechanism of exciton formation,¹⁰³ and the role of charge trapping on the photocurrent,^{67,104} have, amongst other effects, all been investigated in these blends. Thermal annealing of these blends has been shown to

be one method for improving the yield of dissociated charges,⁹⁷ which has been attributed to an increase in the phase segregation due to the PCBM crystallinity in these blends.^{54,93,105} Recombination losses in annealed P3HT:PCBM blends have been shown to be dominated by non-geminate (bimolecular) recombination of dissociated charges, and this particular blend appears not to be severely limited by significant geminate recombination loss.^{57,63,106,107} However, non-annealed blends exhibits a difference in recombination dynamics and the severity of geminate recombination is greater than in annealed blends.⁹⁹ This dependence on film nanostructure demonstrates how critical the fine structure of the active layer is, and the impact that it may have on device performance.

Blends of P3HT and PCBM have consistently been reported achieving device above 4 %.⁹¹ However, despite the extensive research conducted on P3HT:PCBM blends, the highest efficiency devices from polymers blended with PCBM employ co-polymers, with two or more different monomer units in the polymer repeat unit. Such co-polymer structures often contain an electron rich and an electron poor moiety for a “push-pull” effect, to lower the materials bandgap. Examples of such co-polymers include poly(2,6'-4,8-di(5-ethylhexylthienyl)benzo[1,2-b;3-b]dithiophene-alt-5-dibutyloctyl-3,6-bis(5-bromothiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4-dione)⁵⁷ (PBDTT-DPP),¹⁰⁸ poly[N-900-hepta-decanyl-2,7-carbazole-alt-5,5-(40,70-di-2-thienyl-20,10,30-benzothiadiazole)] (PCDTBT)¹⁰⁹, poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']-dithiophene)-alt-4,7-bis(2-thienyl)-2,1,3-benzothiadiazole)] (PCPDTBT),¹¹⁰ 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).¹¹¹ The latter two structures are shown in Figure 1.7, and all of these polymers have shown to have improved device performances when blended with fullerenes compared to P3HT. PBDTT-DPP:PC₇₀BM, the most successful of the blends described above, has a reported device efficiency of 8.6 %, ¹⁰⁸ and is currently one of the most efficient reported materials for use in organic solar cells.

Of particular interest here, specifically with regard to Chapters 3 and 6, blends of PCPDTBT with PC₇₀BM have achieved modest device efficiencies of up to 2.7%.¹¹² Despite the low efficiencies in these blends, the addition of a processing agent, octanedithiol (ODT), during the active layer fabrication has been shown to result in a two-fold increase in the power conversion efficiency compared to those fabricated without ODT.¹¹⁰ Following the success upon the addition of ODT to these blends, there have been numerous reports investigating the origin of this improved device performance. These include the enhanced phase segregation between the polymer and fullerene,^{87,113} improving the electron percolation through the fullerene, or possibly due to an increase in the polymer crystallinity,¹¹⁴ reducing of the ionisation potential of the blend compared to the neat polymer.¹¹⁵

1.4.2 Small molecules as donor materials in organic solar cells

Despite the widespread use of polymers as the donor material in BHJs, there is increasing interest in the use of small molecules to replace polymers as the electron donating material.¹¹⁶⁻¹¹⁹ One of the key reasons encouraging this change in materials system is the reported potential for increased reproducibility in material synthesis compared to that of polymers, in turn hopefully leading to a decrease in the batch to batch variability. This has been suggested to lead to a high degree of reproducibility between small molecule blend devices,¹²⁰ potentially making them favourable for use in large fabrication processes. However, such small molecule donors have been reported to yield poorer device morphologies in small molecule donor blends compared to that with polymers, with the highest PCE for small molecule donor BHJ devices being currently below that of polymer blend systems.^{116,120} Many of these molecular donor materials have similar properties to that of the semiconducting polymers described earlier and retain the electronic properties from the orbital hybridization necessary for use in PV application. One example of one small molecule donor material, DPP_OT_3,6-bis(5-(benzofuran-2-yl)thiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo [3,4-c]pyrrole-1,4-dione (DPP(TBFu)₂) used in PV application, is shown below in Figure 1.8 and will be explored again in Chapter 6.

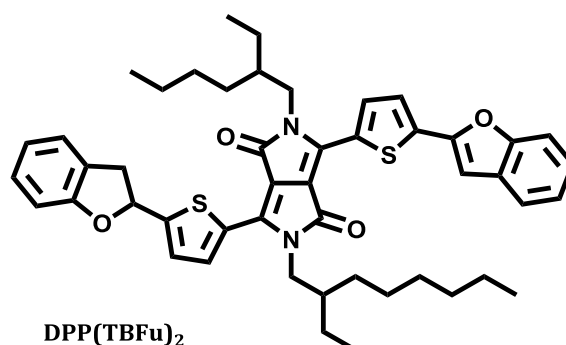


Figure 1.8 – The structure of DPP(TBFu)₂, an example of one small molecule used in for its application as a donor material in OPVs.

1.4.3 Fullerenes as acceptor materials

The semiconducting properties of polymers and small molecules, such as those discussed above, have highlighted their potential for their application as electron donating materials. However, as discussed in Section 1.3, to harvest the energy resulting from photoexcitation of these materials, an electron acceptor with a suitable energy level offset must be present to facilitate exciton splitting. The most common acceptor material in polymer blend BHJ to date is PCBM, a derivative of the symmetric C₆₀ fullerene, with a solubilising methyl ester group attached,¹²¹ and the structure of which is shown in Figure 1.9. This material, and its asymmetric C₇₀ counterpart,

PC₇₀BM, are suitable acceptors in OPVs due to their acceptable energetic levels, good solubility in organic solvents and ability to form crystalline domains.¹²²⁻¹²⁶ These acceptor materials have been shown to have good electron transport, and are able to form percolation pathways, facilitating transport of the electrons towards the cathode.¹²⁷ Whilst fullerenes are typically employed as the electron accepting material, it is possible to generate PCBM excitons that contribute to the device photocurrent.^{28,128}

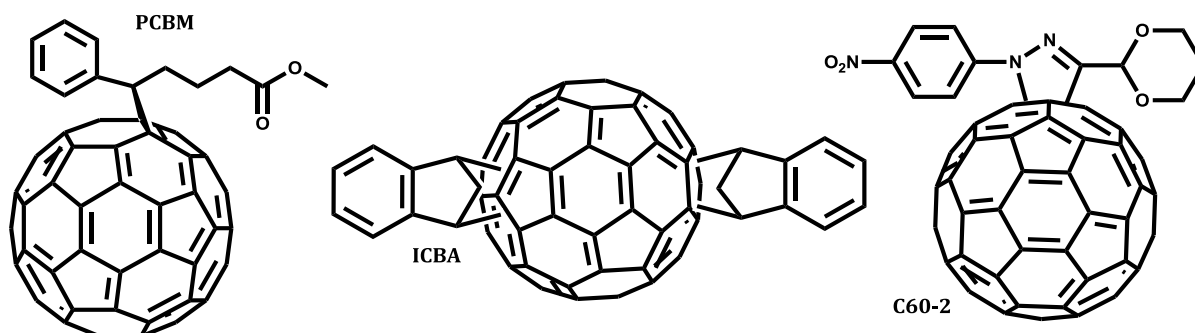


Figure 1.9 – The structures of three of the fullerene derivatives, PCBM, ICBA and C60-2, used as acceptors in organic PVs.

Despite the steady increase in the reported PCE for donor / PCBM blends, this particular acceptor material does not have a good spectral overlap, absorbing primarily in the UV, with only a tail into the visible range of the solar spectrum.¹²⁹ Alternative acceptor materials have been considered for use in OPVs, including bis(1-[3-(methoxycarbonyl)propyl]-1-phenyl)-[6.6]C₆₂ (bis-PCBM),^{130,131} indene-C₆₀ bisadduct (ICBA),^{132,133} pyrazolofullerene (C60-2)¹³⁴ and fullerenes containing metals, including trimetallic nitride endohedral fullerenes,¹³⁵ but these do not exhibit a significant increase in absorption in the visible spectrum. Moreover, these fullerenes have had limited success to date as acceptor materials, with only devices fabricated from these acceptors blended with P3HT as the donor being reported to out-perform the analogous PCBM blend.^{132,133} There is now interest in new electron accepting small molecules that absorb further into the visible spectrum than PCBM.¹³⁶ However, devices fabricated with these molecules as the electron acceptor are yet to reach comparable device efficiencies to fullerene blends.^{136,137} These materials will not be considered further for their application in OPVs in this thesis.

1.5 Device architectures and the active layer morphology

As mentioned previously, a donor / acceptor blend active layer is typically employed in OPVs, and the photoactive layer is placed between two different electrodes. If charge generation occurs in the active layer and there is no electron / hole recombination, these charges are then collected at the electrodes. The two electrodes employed have different work functions, to selectively collect either the electrons or holes, and at least one of these electrodes is transparent to allow light absorption by the active layer. Examples of typical electrodes used include the semi-transparent indium tin oxide (ITO) deposited on glass as the anode, and a metal cathode, such as aluminium. Two common device architectures will be discussed here, bilayers and 'non-inverted' BHJ structures. Other device architectures including 'inverted' heterojunctions, are being developed for use in OPVs,^{138,139} but will not be discussed here.



Figure 1.10 – Morphological pictures of the active layer structure for a) a bilayer b) a random two pure phase BHJ commonly used to describe the blend in many OPV devices, and c) a potential rigid network structure with a controlled and well defined phase segregation.

1.5.1 Bilayers

Bilayer devices have a single interface between the two different material systems in the active layer, as illustrated in Figure 1.10. The photogenerated excitons must diffuse to an interface, where the energy level offset between the donor and acceptor drives charge separation. One of the first reported bilayer device, moving away from the use of single materials, was fabricated from copper phthalocyanine / perylene tetracarboxyl derivative, achieving a modest device efficiencies of $\sim 1\%$.¹⁴⁰ This paper highlighted that efficient charge generation may occur at the interface between the two materials. However, in bilayer devices, the probability of exciton dissociation is small, as only those excitons created in close proximity (within the exciton diffusion length and / or lifetime) of the interface may reach it before recombination of the exciton. Therefore the suitability of the morphology of bilayer devices has been questioned due to the poor ratio between the interface with the bulk material, which leads to poor inefficient

quenching. Potential options for increasing the interfacial area between the two materials have been introduced, and will be discussed in the following section. However, reported efficiencies of 3.5 % have been presented for P3HT:PCBM bilayer devices through the use of orthogonal solvents, calling into question the need for a change in the morphology of the active layer blend.¹⁴¹ Despite the high reported efficiency of this blend, the bilayers described in this publication may not have a single interface between the two materials, due to migration of PCBM, increasing the interfacial area, leading to a higher efficiency than reported elsewhere for bilayers fabricated from these materials

1.5.2 Bulk heterojunctions (BHJ)

As discussed previously, charge generation and recombination typically occurs at an interface between the donor / acceptor, and not in the bulk of the material. Whilst charge generation is possible in neat materials,^{51,101} this process is not as efficient as in blends and this is one of the factors that reduces the charge generation in bilayers, as many of the excitons fail to find an interface for dissociation. To increase the probability of exciton dissociation, a BHJ structure has been introduced in which the surface area between the donor and acceptor materials is increased compared to that of a bilayer structure.^{142,143} This is an intimately mixed blend of the two materials, extending throughout the active layer, as illustrated in Figure 1.10b, allowing for nanoscale phase separation between the donor and acceptor. A random mix of donor and acceptor is formed by the materials tendency to form distinct phases of separate materials rather than one molecularly mixed phase, promoting domain formation in these materials.¹⁴⁴ This nanoscale molecular architecture may indeed lead to an increase in the dissociation of the photogenerated exciton, as the average distance of exciton formation from an interface is reduced compared to that in bilayer devices. The creation of a continuous network of one or both materials across the active layer leads to a potential electron percolation pathway, which is desirable for charge extraction. However, the increase in the surface area between the two materials also leads to an increase in the recombination of the charges as the probability of the charges reaching another interface to recombine is increased with the increased interfacial area, which has been discussed previously in Section 1.3.6.

The morphology and nanostructure of the components in OPVs is critical for device performance. It has previously been suggested that one potential ideal morphology is that of a comb-like structure with ~ 10 nm thick fingers that extend through the film, as illustrated in Figure 1.10c.¹⁴⁵ This rigid structure has been suggested as the exciton diffusion length of polymeric excitons is typically between 5 – 15 nm,¹⁴⁶ and therefore, this structure would allow

for diffusion of the exciton to an interface before geminate recombination occurs. The charges would then split at the interface and be free to diffuse to the electrodes for collection. However, this architecture has yet to be realised in devices and improved methods for increasing the charge generation through this morphological control are still to be developed. Despite desiring structures, such as those described above in devices, typical active layer deposition techniques, such as spin coating from a mixed solution or co-evaporating the two materials, leave little potential for such ordered morphological control of the final blend structure. This lack of structural control makes reproducing the blend morphology and the device characteristics a difficult task..

The BHJ picture shown in Figure 1.10b is typically employed when describing the morphology of donor / acceptor blends. However there is increasing evidence that this may not be a correct description of such blend structures. Erb *et al.* have shown that upon annealing of P3HT:PCBM active layer, there is an amorphous mix of the two materials, in addition to the formation of pure domains of both P3HT and PCBM.¹⁴⁷ Reid *et al.* have also demonstrated how the molecular weight of the P3HT in these blends affects the blend morphology, showing an increase in chain entanglement at high molecular weights, altering the blend morphology.¹⁰¹ If these, and other descriptions of a multi-phase active layer are correct, then there is a need to move away from descriptions such as that in Figure 1.10b towards pictures that include the possibility of mixed domains. This will be investigated further, including considering the effects of intercalation of the acceptor into the donor, in Chapter 4.

1.5.3 The role of the blend morphology and the relationship between device structure and function

There has been a steady increase in the maximum device efficiencies over the past decade¹⁴⁸ and device efficiencies have now been reported in the literature at greater than 8 % for polymer / fullerene blends,¹⁴⁹ and over 6 % for small molecule / fullerene blends.^{150,151} With advances in the field being constantly reported, it is likely that it will not be long before single junction OPV device performances will be reported with efficiencies exceeding 10%. As mentioned in Section 1.4, the majority of the reports of increased device efficiencies comes from the application of novel materials, and not through an improvement in the morphology or design of existing materials. This leaves great scope for improvements in device performance from a deeper understanding of the active layer morphology and the role this plays on charge generation and recombination in devices.

Solution processed device fabrication may be advantageous for its ease of commercialisation, however, this processing technique may lead to problems with reproducibility of the active layer morphology between different samples. One of the reasons for these reproducibility problems arises as the active layer morphology is sensitive to the temperature and solvent. Controlling the morphology and nanostructure of bulk heterojunction devices is often difficult to achieve but may be manipulated through annealing,¹⁵² both thermally^{99,105} and with a solvent atmosphere.^{102,126} The addition of a third component, such as an additive or surfactant^{110,114,153} or changing the blend ratio between the donor and acceptor,^{97,154,155} may also change the morphology. Whilst these techniques are invaluable in their effect on device performance for some materials systems, there is often little correlation and overlap between processing techniques in different materials systems, with one system responding positively to one technique which is detrimental to device performance in another system. Moreover, many of these advances in device performance do not arise from improvement of the morphology or fine tuning of the electronic properties in well characterised blends, but from the introduction of entirely new donor materials into the blend. This raises interest in not only how the electronic properties are changing between each material system, but how the morphology and structure is changing with each new blend.

Understanding the structural and functional relationship between the donor and acceptor materials is a key consideration in facilitating improvements in device performance. The morphology of the blend is critical for efficient charge generation and has been directly linked to device performance.^{101,156,157} However, controlling the morphology in BHJs is not a simple task. The molecular miscibility between the donor and acceptor materials and the degree to which this occurs plays a critical role on the active layer morphology.^{95,158} Understanding and being able to predict the morphology of the components will be key to fabricating the ideal morphology for maximising the charge generation and minimising recombination.

1.6 Device operation

Photovoltaic device efficiency is measured as a function of the current / voltage (J-V) characteristics of device, under standard 1 sun, AM1.5 conditions. These measurements are used to gain information on the photocurrent generation measured as a function of bias, typically between -1 V to +1 V. The power conversion efficiency (PCE) is often the primary method for determining the device performance and can be calculated from the short circuit current (J_{sc}), the open circuit voltage (V_{oc}) and the fill factor (FF). J_{sc} is the photocurrent measured when there is no potential difference between the electrodes, and V_{oc} is the potential

difference with no current generation. A typical J-V, under both light (red) and dark (black) conditions is shown in Figure 1.11, showing J_{SC} , V_{OC} and the maximum power point.

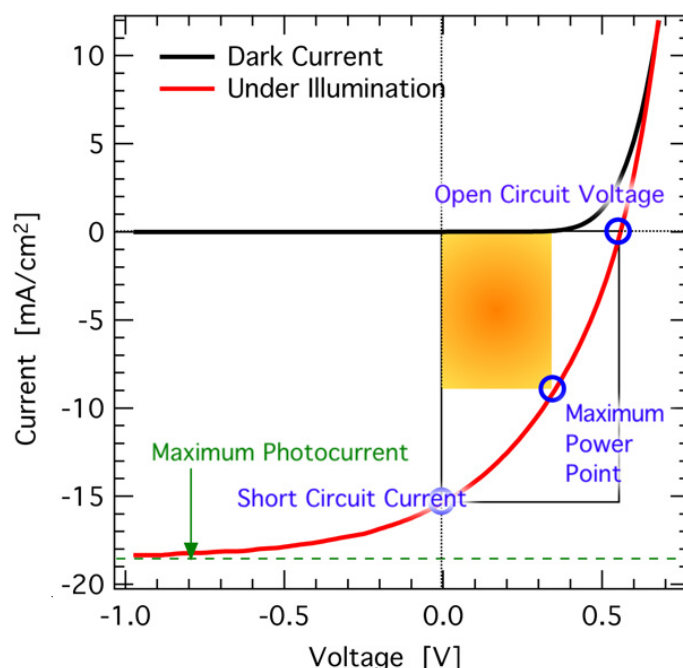


Figure 1.11 - A typical J-V curve showing J_{SC} ($\sim 15 \text{ mAcm}^{-2}$), V_{OC} ($\sim 0.55 \text{ V}$), maximum power point and the maximum photocurrent generation ($\sim 18.5 \text{ mAcm}^{-2}$) attainable using a flat generation profile.¹⁷

The FF is a ratio between the potential power output, as determined from J_{SC} and V_{OC} (white box) and the measured current / voltage at the maximum power point (orange box). The FF is often used as an indication of the degree of losses in devices and a low FF indicates significant losses. Typically reported FFs in OPVs are between 0.35 – 0.65,^{108,110,111} and it are these low values for the FF which are one of the limitations to OPV device efficiencies.

It may be possible to estimate values for device parameters before they are experimentally recorded. V_{OC} may be estimated from the difference between the donor HOMO and acceptor LUMO,¹⁵⁹ however, this potential difference be suppressed if may significant electron / hole recombination occurs. J_{SC} is a measure of the photocurrent generation, and the following section investigates some of the methods for charge generation in some of the organic materials used in OPVs.

1.7 Areas of research to be addressed in this thesis

Understanding the fundamental processes that occur in organic BHJ devices is paramount to facilitate advances in module efficiency. One process that is imperative for device performance is the process of the generation of dissociated charge carriers. Understanding the efficiency of charge generation by the fraction of charges that are able to escape the Coulomb attraction may provide information on the fundamental processes limiting device performance. Furthermore, investigation into whether changes in the internal morphology or the external electric field affect the dissociation yield will be discussed. This thesis will focus on the optical properties of semiconducting materials for their use in organic BHJ PVs, based primarily on conjugated polymers blended with fullerenes, with some research into small molecule / PC₇₀BM blends. In order to investigate the charge generation in these systems, a range of experimental techniques have been employed. These include optical and electronic methods, the details of which are presented in Chapter 2.

Chapter 3 presents a general introduction to the experimental technique of transient absorption spectroscopy (TAS), and its application to studies of charge generation in three specific donor / acceptor thin film blends. The effects of the composition of the donor are investigated, considering the formation of triplet states in poly[2,8-(6,6,12,12-tetradecylsiloindenofluorene)-co-4,7-(2,1,3-benzothiodiazole)] (SiTPT-BT) and differences in the active layer composition through changes in the chemical structure and the use of additives in PCPDTBT:PC₇₀BM blends. The process of charge generation as a function of temperature is also investigated in P3HT:PCBM.

The role of nanomorphology, specifically the formation of domains as a function of donor / acceptor blend ratio, is presented in Chapter 4. This chapter considers the information gathered from photoluminescence data regarding exciton diffusion lengths before investigating the role of blend composition in one specific system; poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-*b*]thiophene) (pBTTT) blended with PCBM. Following this, the remainder of the chapter looks specifically at the role of fullerene crystallisation, employing three different fullerene acceptors, and the effect of this on the formation of dissociated charge carriers in blend systems with these acceptor materials. We also propose a new functional model describing the active layer structure, which is founded upon the notion that each material may exhibit different degrees of crystallinity and that a two pure phase structure is not an appropriate description. A potential method for controlling the morphology and the formation of pure domains is investigated in Chapter 5, which introduces the use of short chain methyl ester additives into pBTTT:PCBM blends. The introduction of these additives to the blend films

before fabrication is investigated as a potential route for changing the crystallisation threshold in these blends. The differences in optical and electrochemical properties of these different blends systems are considered as a method for the use a lower fraction of PCBM in these blend devices.

Finally, Chapter 6 addresses the role of external bias in facilitating charge generation in BHJs with both, polymer and small molecule donor materials blended with PC₇₀BM. This chapter will consider if Onsager theory of geminate pair recombination can be extended for use in OPV materials. From this theory it may be expected that an externally applied electric field would induce charge pair separation, increasing the generation of dissociated charges and the device photocurrent if Onsager theory is applicable. This hypothesis is investigated using TAS with an external bias across the device, to measure the charge generation yield and whether this correlates with an increase in the yield of dissociated charges with external bias.

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Chapter 2

Experimental Techniques

This chapter examines the fabrication techniques and experimental methods used throughout this thesis to study charge generation in thin films and devices. These include:

- 2.1 Materials
- 2.2 Film and device preparation
- 2.3 Ground state absorption spectroscopy
- 2.4 Steady state photoluminescence spectroscopy (PL)
- 2.5 Transient absorption spectroscopy (TAS)
- 2.6 Cyclic voltammetry (CV)
- 2.7 Current / voltage characteristics (J-V)
- 2.8 Transient optical microscopy
- 2.9 Differential scanning calorimetry (DSC)

2.1 Materials

All the materials were used as received. P3HT used in Chapter 3 was purchased from Reike Metals. PCPDTBT used in Chapters 3 (neat material) and 6 (complete devices) was kindly supplied by Konarka Technology, Austria. pBTTT (Mn ~ 39k, Mw ~ 66k) and pATBT (Mn ~ 41k, Mw ~ 99k) used in Chapters 4 and 5 were synthesised by Thomas McCarthy-Ward at Imperial College London. Polystyrene (PS, Mw ~ 250k) used in Chapter 4 was purchased from Scientific Polymer Products Inc and the short chain esters used in Chapter 5 were supplied by Sigma Aldrich. Regarding the fullerenes, PCBM used throughout in Chapters 3, 4, 5 and 6 was purchased from Solenne, ICBA was gratefully received from Plextronic, USA and C60-2 was kindly supplied by Nazario Martin, Universidad de Compultense, Spain.

2.2 Film and device preparation

Fabrication of the active layer was achieved by depositing solutions of the neat material or blend, onto the desired substrate; either pristine glass (VWR) or ITO glass (Psiotech) coated glass to create a homogeneous thin film.

Solutions were prepared by dissolving the desired material composition in a solvent, typically ortho-dichlorobenzene (oDCB, Aldrich) in a glass vial and left to stir on a hot plate between 50 – 80 °C, for an excess of 4 hours, until all the material was fully dissolved. Typical solution concentrations were 10 – 20 mg/mL. These solutions were then used to coat the substrate. All substrates were cleaned prior to film deposition by sonication with first, acetone and secondly isopropanol (Sigma Aldrich), each for 15 minutes, before being dried with nitrogen.

Thin films were fabricated by either spin coating, wirebar coating,¹ or drop casting. Spin coated (Laurell Technologies Corporation, WS400A-6NPP Lite) films were cast onto 1 cm² substrates at room temperature. Substrates were spun for 1 minute, and the normal spin speeds conditions used were between 1000 – 1500 rpm. Wirebar films were deposited onto larger substrates (25 mm x 70 mm) for optical measurements, and 1 cm² substrates for electrical measurements, using an 18M bar with 2 coats, onto a temperature controlled stage at either room temperature or 35°C. Drop cast films were fabricated by completely coating a glass slide in the material solution and allowing for the solvent to evaporate overnight. For all film deposition techniques, the films were fabricated in the fumehood and if required, annealed in air, on a hot plate in a fumehood for 20 minutes at the desired temperature (~ 150 °C).

Devices fabricated at Imperial College London were made with Dr. Pabitra Shakya Tuladhur and Dr. Ester Domingo Buchaca in a cleanroom facility using a conventional glass / ITO (Psiotech Ltd) / PEDOT:PSS (H. C. Starck) / Active layer / Al (Sigma Aldrich) device architecture.² Devices fabricated at the University of California, Santa Barbara were made and encapsulated by Dr. Bright Walker, and devices made by Konarka Technologies were fabricated by Dr. Hamed Azimi, both as described previously.^{3,4}

2.3 Ground state absorption

Solid-state absorption spectroscopy may be used to gain information on the structure, packing and crystallinity of both solutions and thin films. Information that may be acquired from this technique includes finding the optical bandgap (energy between the HOMO and LUMO levels) which may yield information about the polymer conjugation length. As well as this, it is possible to gain an indication on the order which may be alluded to from the lower energy, fine structure and hence this technique is useful for an initial indication of the film microstructure.⁵⁻⁷

Steady state absorption measurements were conducted on thin films in air. These were measured between 300 – 1000 nm on samples cast onto glass slides and using a blank glass reference, on a Perkin Elmer Lambda 25 UV/Vis spectrometer.

2.4 Steady state photoluminescence quenching (PL)

Photoluminescence quenching (PLQ) of materials investigates the emission from the photogenerated excited states. This techniques can be used a measure of how efficiently the photogenerated excitons are quenched at donor / acceptor interface between materials. PLQ can be used to measure the non-radiative decay of the photoexcited state to the ground state. The degree of exciton quenching in mixed BHJ structures compared to that of the pristine material, may yield an indication about the blend microstructure and the level of mixing between the two components.⁸ The PLQ is a measure of how efficiently the emission from the blend is quenched compared to that of the neat material and can be expressed as the following equation:

$$PLQ = \frac{PL}{PL_0}$$

Equation 2.1

Where PL is the photoluminescence of the blend and PL_0 , is the photoluminescence of the pristine material. However, this does not yield information on the mechanism of the exciton quenching, i.e. whether it has been dissociated at an interface between the two materials or if there has been energy transfer and cannot be readily used to investigate the behaviour of non-emissive states.

For polymer PLQ studies, films were excited at the peak ground state absorbance which varied for each system, but was typically between 520 – 550 nm, and for PCBM quenching studies, the films were excited at 430 nm, at the tail of the ground state absorption. Following this excitation, the emission was monitored at longer wavelengths, up to 800 nm. The polymer and PCBM excitation measurements were taken with an integration time of 0.2 s and 1 s, respectively, using a steady state spectrofluorimeter (Horiba Jobin Yvon, Spex Fluoromax 1).

2.5 Transient absorption spectroscopy (TAS)

Transient absorption spectroscopy (TAS) is a pump / probe optical technique designed to explore the photophysical properties of materials. Photogenerated species are created following laser excitation, and are measured by changes in the optical density at either a specific wavelength as a function of time or at a specific timescale as a function of probe wavelength.⁹⁻¹¹

TAS measurements may be employed on both active layer thin films or on complete devices, to study the charge generation and recombination of photogenerated species.¹² For thin films the measurement is conducted in transmission, through the film. For devices, the experiment is carried out in reflection, where the probe beam is reflected off the opaque contact (typically the aluminium electrode) and back through the active layer before being collected at a detector. TAS is a useful assay for predicted photocurrent generation in devices, as there has shown to be a correlation between the charge generation at 1 μ s, as measured using TAS and J_{sc} measured in devices.¹³ This technique provides a quick and easy way to investigate materials and their potential for use in PVs without the need for costly fabrication. It is also possible to use this technique to investigate how the charge generation of dissociated carriers changes with the application of an applied bias. These measurements can also be correlated to the device function as they may be able to predict how the current changes with bias.

To take these measurements, the sample (either the thin film active layer or complete device) is excited by a short (~ 5 ns) laser pulse and the resulting excitation is monitored by a change in absorbance of the continuous probe beam. Changes in the optical density of the absorption

signal, due to the formation of transient species, are then recorded. These measurements use the Beer Lambert Law:

$$A = \epsilon cl$$

Equation 2.2

Where A is the absorbance, ϵ , the extinction coefficient, c , is the concentration of charges (in this instance the charge carrier) and l , the path length, which is equal to the film thickness. The molar extinction coefficient is calculated for each donor and is usually in the order of 20 000 mol⁻¹,¹⁴ and the active layer thickness is typically around 100 nm.^{3,15} The concentration of charge carriers depends on the excitation density of the pump source, but is typically around 10¹⁷ cm⁻³,^{12,16,17} and often much larger than those of standard device operating conditions ($\sim 10^{14}$ cm⁻³). From this, it is possible to relate A to the change in the incident light (I_0) and transmitted light (I) following excitation:

$$A = -\log\left(\frac{I}{I_0}\right)$$

Equation 2.3

The measured change in absorbance in TAS measurements is the change in optical density (ΔOD) measured here. From these equations, it is then possible to correlate the change in the optical density with the charge density, n (assuming $n = p$), and as a function of time.

$$\Delta OD \propto t^{-\alpha} \propto n$$

Equation 2.4

Transient spectra may be recorded as a function of wavelength at desired specific time, to investigate the absorption of the transient species, that can in turn be used to identify the presence of the polarons. Following the assignment of the transient species, data are then recorded as a function of time. Exciton formation and dissociation occurs on the femtosecond timescale^{18,19} and therefore this process is unable to be recorded on the experimental set-up described here due to the limits in the time resolution of the equipment. The dissociation of geminate charge pairs is has been reported on the nanosecond timescale²⁰⁻²² and the formation and recombination of fully dissociated charge pairs occurs on the microsecond to millisecond timescales.^{9,23,24} Data collected herein is on the nanosecond to millisecond timescale and is therefore primarily concerned with the dissociation of bound charges (whether geminate or more loosely coupled pairs) to fully dissociated charges and resultant non-geminate

recombination. Geminate and non-geminate recombination processes follow different kinetic behaviour and TAS therefore may be used to distinguish between the two processes. Geminate recombination is a monomolecular process and will show exponential decay characteristics. A non-geminate recombination process will display power law decay kinetics, where α is the gradient of this decay on a log/log plot. This is demonstrated in Figure 2.1, showing a geminate (monomolecular) and non-geminate (bimolecular) decays. Experimental data for two different materials are shown in green and black. monoexponential (red) and power law (grey) decays have been fit to this data to show the differences between these two dynamics.

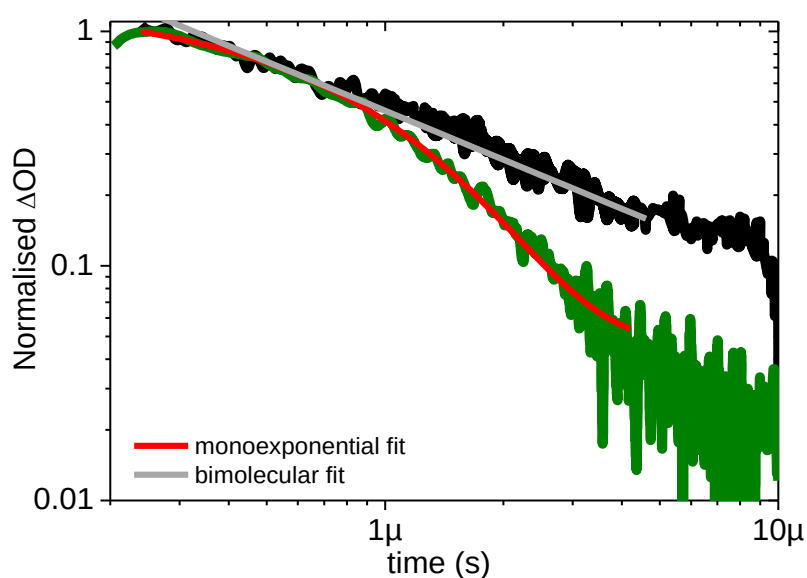


Figure 2.1 – Typical TAS decays recorded as a function of time at a fixed wavelength. Two different decay dynamics are shown, a monomolecular decay in green (with the corresponding theoretic fit in grey) and a bimolecular decay in black (theoretical fit in red).

Many of the experiments conducted herein are concerned with the formation and study of polymer polarons, which may contribute to the device photocurrent. However, triplet formation and decay may also be investigated using oxygen quenching studies, as reported elsewhere.²⁵ This will be expanded on in Chapter 3.1, which look at specifically at one polymer / PCBM blend that shows the presence of triplets in the TAS decays. The charge generation yield, the magnitude of the recorded ΔOD signal, is dependent on the excitation density of the pump source.

The application of an external bias to complete devices has been used to investigate the role of electric fields in charge generation and dissociation. The device is held at the desired voltage throughout the course of the experiment. The application of an external bias to these devices

was confirmed by measuring a change in the recorded current upon illumination with external bias. The light and voltage dependent measurements monitoring the current confirmed that a bias was applied across the pixel tested.

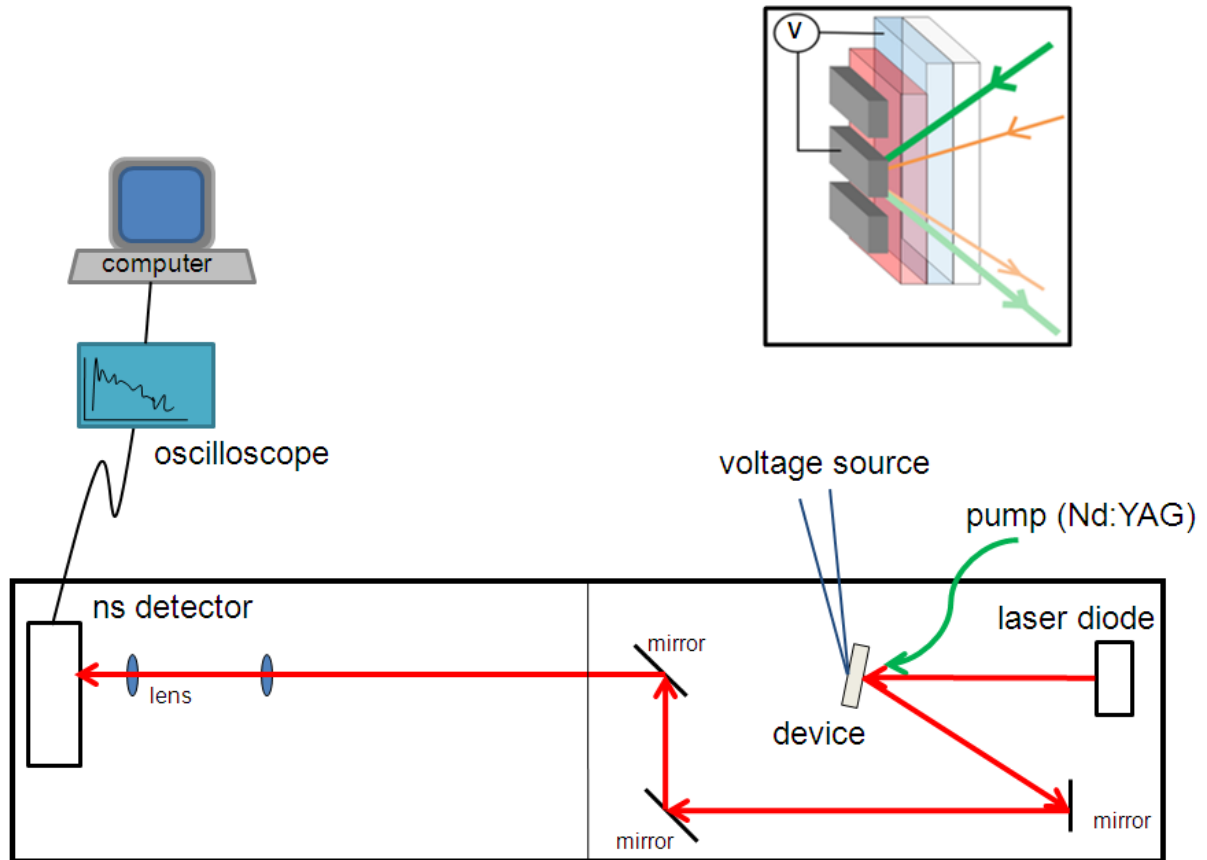


Figure 2.2 - A schematic detailing the TAS experiment on devices in reflection mode, with an applied bias. The probe beam is reflected off the back contact (Al electrode) before being directed onto the detector by a series of mirrors. Inset a diagram of device orientation in reflection. For transmission measurements the mirrors are not required and the probe beam is directly monitored by the detector.

Two probe sources have been used for the transient measurements, due to different time resolution requirements. First, a quartz halogen lamp probe (Bentham, IL6) with a stabilised power supply (Bentham, 605) and a monochromator (PTI) for wavelength selection has been employed and data was collected between approximately 500 ns to 10 ms. To probe faster timescales (from ~ 50 ns), a fixed probe laser diode system (Thorlabs TCLDM9, 50mW, single mode) with an external current and temperature controller (Thorlabs ITC502) was employed. The laser diode probe source facilitates the use of a faster detector as a lower gain can be used compared to the white light probe source. The system resolution was limited by the laser pulse, as measured by both the full width half maximum (FWHM) and the 10 – 90 rise time of the laser

spike recorded by the oscilloscope and determined to be ~ 50 ns from both of these analyses. Long pass filters between 690 – 1000 nm were used after the sample, throughout the experiments to remove absorption of the laser pulse by the detectors.

A schematic drawing of the experimental set up used for reflection TAS measurements is seen in Figure 2.2. The probe beam (red) is reflected off the back of the device's opaque electrode onto a series of mirrors that direct the beam to the InGaAs photodiode detector (Hamamatsu G8370-82). In both instances, the signal was amplified (Costronics Electronics) and collected on a digital oscilloscope (Tektronics, TDS220). Data acquisition software was written by Dr. S. King at Imperial College London. The variable wavelength laser pump was the same in both instances (OPO LD 355, Quantel, Big Sky Laser) and the excitation wavelengths were chosen from the ground state absorption of the blends. Typical energy densities used were 5 – 10 μJcm^{-2} , to minimise saturation effects.

An external bias was applied with a power supply (TTi PL303-P) and the biases for the electric field measurements were applied in a random order to ensure that no cumulative effects of systematic voltage application were observed. All the field dependent measurements were conducted in the dark.

Temperature dependent measurements were conducted in a liquid nitrogen cooled cryostat (Oxford Instruments) and the temperature regulated using a liquid nitrogen reservoir and an externally controlled thermostat. The temperature of the device was recorded inside the cryostat with a thermocouple and the temperatures were recorded in a random order to minimise any possible cumulative effects of decreasing temperature.

2.6 Cyclic voltammetry (CV)

Cyclic voltammetry (CV) is an electrochemical technique used to investigate the ionisation and reduction potentials of materials by linearly sweeping a voltage across a sample and recording the current. The current change is then used to determine how the electrochemical properties change with blend composition. A three electrode system is used in these experiments, employing a redox inactive electrolyte: a working electrode comprising a film of the material studied deposited on ITO, as well as Pt reference and Ag/AgCl counter electrode. The change in voltage applied to the working electrode relative to the reference electrode results in a change in current is measured between the working and counter electrodes.

The oxidation and reduction currents measured can be used to quantify the materials HOMO and LUMO levels respectively. This in turn yields valuable information on the electrochemical properties of the materials systems. However, this is not an easy measurement to conduct due to the rather irreversible electrochemistry often observed for many organic semiconductors, as well as uncertainty over how best to determine HOMO and LUMO energies from the voltamogram (e.g.: from peak positions, current onsets etc). Therefore, in this thesis these measurements have been used to determine only the relative changes in these levels as a function of film composition and not absolute values. Many reports of CV measurements on polymeric systems are conducted in solution, rather than on thin films.^{26,27} However, to investigate the active layer compositions and structures that are closest to that in devices, CVs were performed on films deposited onto ITO glass. This method is not without its disadvantages compared to that of solution CVs. These include degradation of the film in the electrolyte and non-reproducible scans which may arise due to an inhomogeneous film structure. However they have the advantage of allowing an in situ measurement of energy levels in films as a function of film processing and composition, which is the primary consideration of the CV measurements reported herein.

A home built set-up with a Pt gauze counter electrode (Sigma Aldrich), Ag/AgCl reference electrode (Bioanalytical systems) and the active layer on ITO glass (Delta Technologies, Ltd) as the working electrode, was used employing a 0.1M tetrabutylammonium perchlorate (Alfa Aesar) in dry acetonitrile (AcN, Sigma Aldrich) electrolyte. The bias was applied with a potentiostat (Autolab) and data were typically recorded between +1.5 V and -1.5 V for each film and recorded using Nova 2.0 data acquisition software. Typical scan rates of 100 mVs⁻¹ however scans were also performed at 10 mVs⁻¹, to investigate any potential kinetic effects that may arise from the slow kinetics of film oxidation/reduction.

2.7 Current / voltage (J-V) device measurements

A universal approach of testing device efficiencies is by the measurement of a current / voltage (J-V) curve. This is a measurement of the electrical characteristics of the device, measuring the current density as a function of bias. From this, information on J_{SC} , V_{OC} , FF and the power conversion efficiency can be deduced.

J-V curves were measured using a Keithley 238 Source Measure Unit, typically between -1 V to +1 V. Devices were illuminated through the ITO electrode by a 300W xenon arc lamp solar simulator (Sciencetech SCI200) and calibrated using a silicon photodiode (Newport UV-818)

with appropriate longpass filters. Calibration of the light source was performed before the device J-Vs were collected, under the industry standard AM 1.5 conditions.

2.8 Transition optical microscopy

Transition optical microscopy, recorded as a function of temperature, on thin films offers an insight into the phase behaviour of the materials through observation of melting and phase transitions. These measurements were carried out with an Olympus BX51 microscope in the Stingelin Laboratory in the Material Department under the supervision of Dr. E. Buchaca Domingo. This was equipped with a Mettler Toledo FP82HT hot stage, heated at 10 °C / min, that was continuously flushed with nitrogen. Images were recorded either at room temperature or as a function of temperature. For temperature dependent measurements, the film images were captured at 25 °C intervals up to 275 °C.

2.9 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) is a thermal technique, probing the materials properties of pristine materials and blends through their heat capacities, by comparison to a reference sample. The materials are linearly heated from 25 – 300 °C and the heat flux is recorded as a function of temperature. For these measurements, the first heating was taken and the enthalpy of fusion recorded. Complete melting of primary crystals, as well as melting of the neat materials, correspond to end melting temperatures in the DSC thermograms.

DSCs were undertaken and analysed in the Materials Department at Imperial College London by Dr. E Buchaca Domingo. Neat material and blend powders were produced by preparing homogeneous solutions of 1 wt% total material content in oDCB, followed by drop casting onto glass slides at 35 °C, and the solvent was evaporated at ambient pressure in air. Following fabrication, the film was scratched off from the substrate and placed into an aluminium crucible for heating. Each sample was weighed before heated, and typically 2 – 4 mg of materials was used for each measurement. DSC measurements were conducted under nitrogen at scan rate of 20 °C min⁻¹ with a Mettler Toledo DSC822 instrument.

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Chapter 3

Transient absorption spectroscopy as a tool to monitor charge generation and recombination in polymer / fullerene blends

Abstract

Transient absorption spectroscopy (TAS) is a useful tool in for investigating charge generation and recombination in organic BHJ active layer films. This chapter uses TAS to probe the effects of the excitation density, the onset of the both geminate and non-geminate recombination and the effects of oxygen quenching as an indication for the presence of triplets, in donor / acceptor thin films. The donor materials investigated in this chapter are the extensively characterised polymers P3HT, PCPDTBT and a novel low bandgap polymer, poly[2,8-(6,6,12,12-tetradecylsiloindenofluorene)-co-4,7-(2,1,3-benzothiodiazole)] (SiTPT-BT). The formation of triplet states in organic films has been monitored by oxygen quenching TAS studies in neat films of SiTPT-BT and blended with PCBM, and shows the formation of triplets in theses blends. Following this insight into triplet formation, this chapter also explores the fast phase in P3HT:PCBM blends, arising from non-geminate recombination of free charges. Finally, the effects of morphology on the formation of dissociated charges are explored in the low bandgap material PCPDTBT, blended with PC₇₀BM, showing the charge generation and recombination to be dependent on the film processing conditions

3.1 Introduction

OPV device operation is dependent on the splitting of photogenerated excitons into free charges (electrons / holes), that may be extracted at the electrodes. The probability of splitting these Coulombically bound charges into free carriers, and the resultant competition between the recombination and extraction of free charges, determines the device operating efficiency. However, the mechanism of free charge generation in OPVs continues to be under considerable debate in literature,¹⁻⁴ with several different routes suggested as possible mechanisms for the formation of dissociated charges in BHJs. Potential routes discussed in literature for this includes via the formation of a Coulombically bound interfacial CT states,⁵⁻⁹ or via “hot” excitons.¹⁰ Understanding the charge generation mechanism in OPVs is crucial for facilitating improvements in device design and fabrication. Possible methods for exploring the charge / photocurrent generation, include electrical measurements, such as external quantum efficiency (EQE) or transient photocurrent (TPC) measurements on devices. Optical techniques, including TAS and PL, study the active layer and can therefore be conducted on thin films, without the requirement for electrodes.

As discussed in Chapter 2, TAS may be used to monitor charge formation and recombination as a function of either wavelength, yielding transient spectra, or, as a function of time, probing the decay dynamics of the blend. Ultrafast TAS, on the femto to picoseconds timescale, has been widely employed in literature as a method to probe exciton generation and charge separation.¹¹⁻¹⁵ This chapter focuses on the information that can be extracted from transient decay dynamics on the nano to millisecond timescales, and will outline how this technique can distinguish between different transient species on this timescale. There are fewer groups who use transient absorption spectroscopy on these timescales to investigate the charge dynamics, however valuable information may still be gained regarding the nature of the transient species. The assignment of the origin of the transient species in the slower timescale experiments may be simpler than in ultrafast measurements as the presence of singlet excitons may be avoided as they are not observed on this timescale.¹⁶ In addition, the yield of free charges, from the magnitude of the ΔOD signal, recorded at 1 μs has been shown to positively correlate with device function (from the short circuit current).¹⁷ TAS on thin films is, therefore, a useful assay of device performance without the need for complete device fabrication and can allow for comparative studies on a wide range of materials relatively quickly compared to ultrafast measurements. This chapter will consider some of the kinetic information that may be gain from TAS. We employ three different materials systems to highlight the differences in decay dynamics that may be observed on the nano to millisecond timescales and moreover go on to assess the physical origin of these states. We note that this chapter is concerned only with the

transient spectroscopy of films and no devices have been explored here, however, Chapter 6 will explore some of the possible outcomes of studying complete devices using TAS.

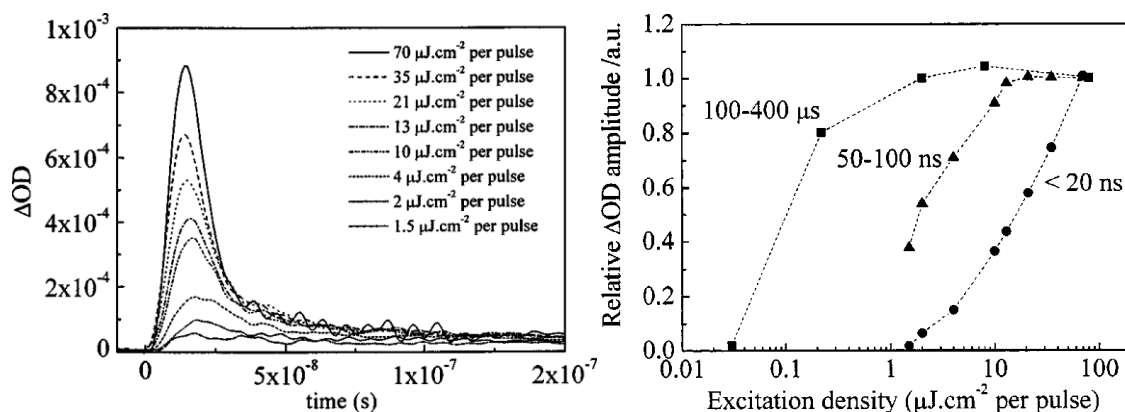


Figure 3.1 – The excitation density dependence of the charge generation yield, as monitored using TAS, for MDMO-PPV:PCBM blends as a function of excitation density. Taken from reference ¹⁸.

The first detailed study of the transient decay dynamics on the microsecond timescale of a BHJ film was shown in poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV):PCBM blends.¹⁸ This study resolved the appearance of biphasic decay, as presented in Figure 3.1 as a function of excitation density, in MDMO-PPV:PCBM blends at different times. At high laser energies the transient decays show an excitation density dependent fast phase, from 20 ns, that is limited by the instrument response. Whereas on longer timescales (100 – 400 μs) the signal amplitude is less affected by the excitation density than on fast timescales. The biphasic decay dynamics in these MDMO-PPV:PCBM blends has been attributed to non-geminate recombination, where the fast decay (< 20 ns) is recombination of the mobile species and the slow phase is recombination of the trapped states.¹⁹ This analysis has shown that the origin of the biphasic decay in MDMO-PPV arises from non-geminate recombination of dissociated charges and not from triplet states or geminate recombination.

The onset of non-geminate recombination may be monitored using TAS, through the observation of a plateau in the recorded ΔOD signal, before the signal decays, and by a power law decay fit to the data. Non-geminate recombination of charges can be monitored using TAS, via the fitting of the experimental data to a power law decay, described by Equation 3.1. This is displayed as a straight line on a log-log plot of charge generation (ΔOD) as a function of time (t):

$$\Delta OD \propto t^{-\alpha}$$

Equation 3.1

where α is the gradient of the power law decay, and yields information on the energetic distribution of the charged species including an indication on the degree of trapping. This equation may be used to describe the nature of the non-geminate recombination, as α varies as a function of the energetic energy, which changes with morphology and crystallinity, and is typically between 0.3 – 0.7 for annealed P3HT:PCBM blends.^{16,17,20}

In general, biphasic decays, with a exponential ‘fast’ phase on the nano to microsecond timescale followed by a power law is observed for most of the BHJ films studied in this thesis. The relative magnitude of the TAS amplitudes of these phases varies between different films and is dependent on the material composition and film processing conditions. In addition, as reported by Soon *et al.*, the assignment of the fast phase is not always clear, with for some neat and blend films showing triplets.²¹ In this chapter we look at the transient absorption spectra of three representative polymer / fullerene blend systems, one showing the presence of triplets, one showing non-geminate recombination and a final system showing that triplet formation is sensitive to the film processing conditions. The structures of these three donor materials, PCPDTBT, P3HT and (poly[2,8-(6,6,12,12-tetradecylsiloindenofluorene)-co-4,7-(2,1,3-benzothiodiazole)] (SiTPT-BT), are shown below in Figure 3.2.

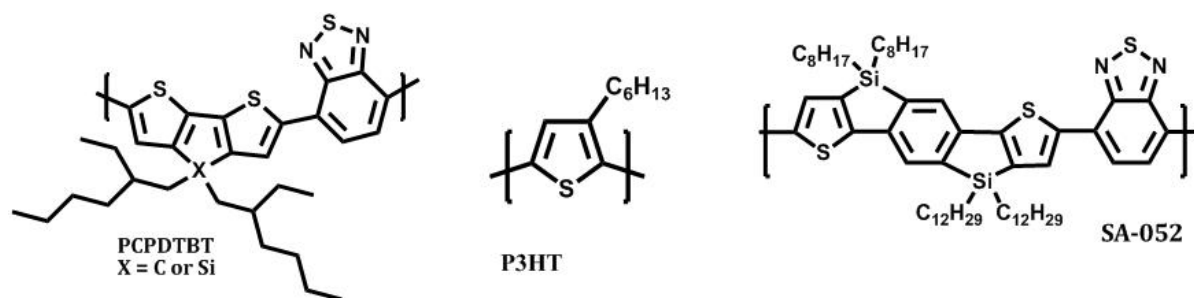


Figure 3.2 – The chemical structures of the polymers studied in this chapter; PCPDTBT (carbon and silicon bridged), P3HT and SiTPT-BT.

Whilst P3HT:PCBM blends have been extensively characterised for their use in OPVs, many other polymers have been tested as the donor material in BHJ devices, many of which now outperform P3HT as the donor material. An example of one donor material is the charge transfer polymer PCPDTBT, that has received extensive interest as a donor due to the lower bandgap of the material compared to that of P3HT.²²⁻²⁴ Charge generation in these blends has been proposed in the literature to proceed via the formation of mobile charge carriers on the ultrafast timescale, and not via an intermediate bound charge transfer prior to the generation of free charges.²⁵ However, in contrast to this, it has been suggested by Di Nuzzo *et al.* that the poor

charge generation in these devices originates from the formation of a long lived triplet state that cannot be harvested to contribute to the photocurrent.²⁶ Our own previous studies investigating the redox potentials of these materials show, from cyclic voltammetry, that the first oxidation peak that the addition of the blends with the addition of 1,8-octanedithiol (ODT) to C-PCPDTBT:PC₇₀BM films reduces the oxidation potential of blends compared to those blends without the processing agent, by approximately 200 meV. This corresponds to ΔG , as discussed in Section 1.3, which acts as a driving force for charge separation. This significant reduction in the ionisation potential of the blend, is attributed to the increase in crystallinity of the polymer upon addition of ODT to the blend, compared to those without. The increase in crystallinity observed either, by the addition of ODT as a processing agent, or by substitution of one carbon atom for a silicon atom appears to be beneficial to device performance, as observed by the increase in efficiency through improvements in both J_{sc} and FF. This chapter investigates the outcome of these modifications on the charge generation yield and whether this corresponds with the observed increase in device efficiency.

As previously discussed, TAS can be used as a method of screening materials before device fabrication to optimise the blend composition where the kinetics observed when investigating devices has been previously reported as been similar to those in thin films, with only a loss in signal amplitude being of note.¹⁷ However, there are some devices that do not perform as predicted from TAS measurements, such as poly[2,8-(6,6,12,12-tetraoctylindenofluorene)-co-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiodiazole)] (IF8TBTT), blended with PCBM.²⁷ Devices blended from this polymer perform better than expected, due to a higher J_{sc} than is predicted from TAS data. This difference may arise from the presence of electrodes on the device that influences the internal electric field, which may in turn increase the probability of dissociation. Studying the transient kinetics in devices yields valuable information on how the charge generation is effected by the presence of electrodes and both the internal and external electric fields, which will be investigated in more detail in Chapter 6.

3.2 Experimental

P3HT and PCBM / PC₇₀BM were purchased from Reike and Solenne, respectively, and used as received. PCPDTBT was kindly supplied by Konarka, Linz, and used as received. SiTPT-BT was synthesised by Dr. Shahid Ashraf, in the McCulloch group, at Imperial College London and used as received.

Solutions were prepared as described in Chapter 2. P3HT:PCBM films were annealed at 140 °C for 20 minutes. PCPDTBT films were fabricated by Dr. Tiziano Agostinelli from the Department of Physics, Imperial College London and were deposited by spin coating from a hot solution (80°C) onto a quartz substrate. SiTPT-BT and SiTPT-BT:PCBM films were spin cast at room temperature onto glass substrates

Absorption spectra were taken on glass (P3HT / P3HT:PCBM / SiTPT-BT / SiTPT-BT:PCBM) or quartz (PCPDTBT / PCPDTBT:PC₇₀BM) slides between 300 – 900 nm.

PLQ was measured following excitation at 540 nm for P3HT and P3HT:PCBM and at 720nm for all PCPDTBT and PCPDTBT:PC₇₀BM films.

TAS decays were measured as described previously in Chapter 2, on films under a nitrogen atmosphere, unless otherwise stated. Samples were excited at 520 nm (P3HT), 532 nm (PCPDTBT) or, 600 nm (SiTPT-BT), with an excitation density of 2 – 85 μJcm^{-2} and the resulting change in optical density were recorded using a fixed wavelength laser diode. Temperature dependent measurements were performed in a liquid nitrogen cooled cryostat (Oxford Instruments) and temperatures were recorded in a random order to insure no cumulative temperature effects were induced or recorded.

3.3 Results and Discussion

The structures of the donor materials used for analysis as the photoactive layers in this chapter have been shown above in Figure 3.2. This section will provide evidence for the applicability of TAS in investigating triplet states, non-geminate recombination and the role of active layer morphology.

3.3.1 The formation and observation of triplet states in SiTPT-BT:PCBM blends

The ground state and transient absorption spectra of non-annealed SiTPT-BT and SiTPT-BT:PCBM blends are shown in Figure 3.3. The maximum ground state absorbance in the neat polymer film is observed at ~ 620 nm, and there is negligible change in the peak position of the ground state absorption maximum when blending this polymer with PCBM. There is however an increase in the higher energy absorption upon the addition of PCBM, accompanied by a broadening of the absorption in this region.

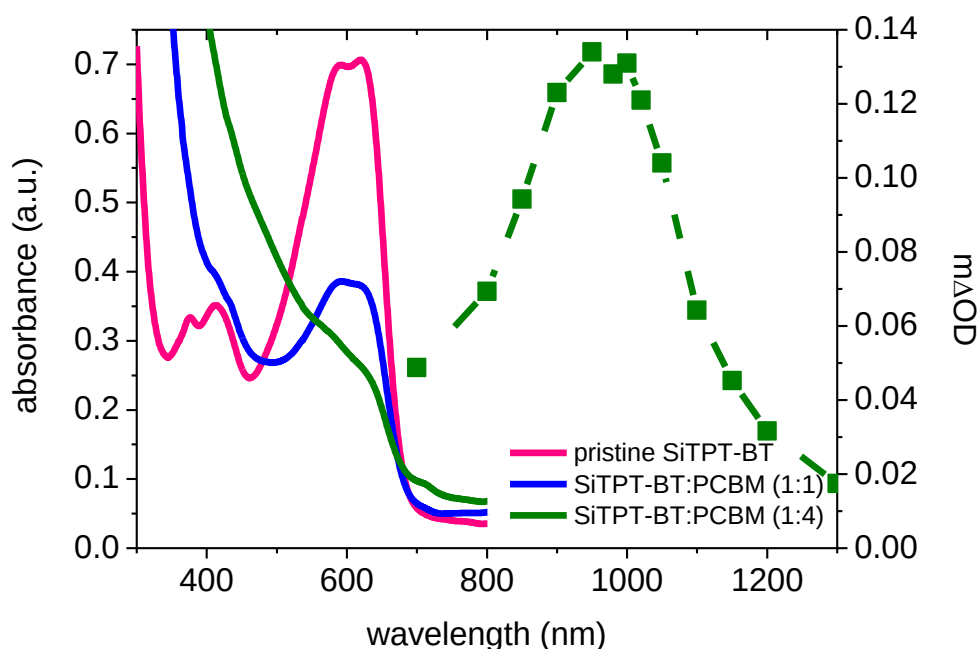


Figure 3.3 – Ground state spectra (solid lines) of neat SiTPT-BT (pink) and SiTPT-BT:PCBM (1:1, blue and 1:4, green) blends and the transient spectrum of 1:4 blend (squares and dashed line).

The transient spectra for the 1:4 (SiTPT-BT:PCBM) blend was recorded at 1 μ s in an inert atmosphere. This data shows a broad absorption peak between 900 – 1100 nm, however, this data was not repeated in the presence of oxygen.

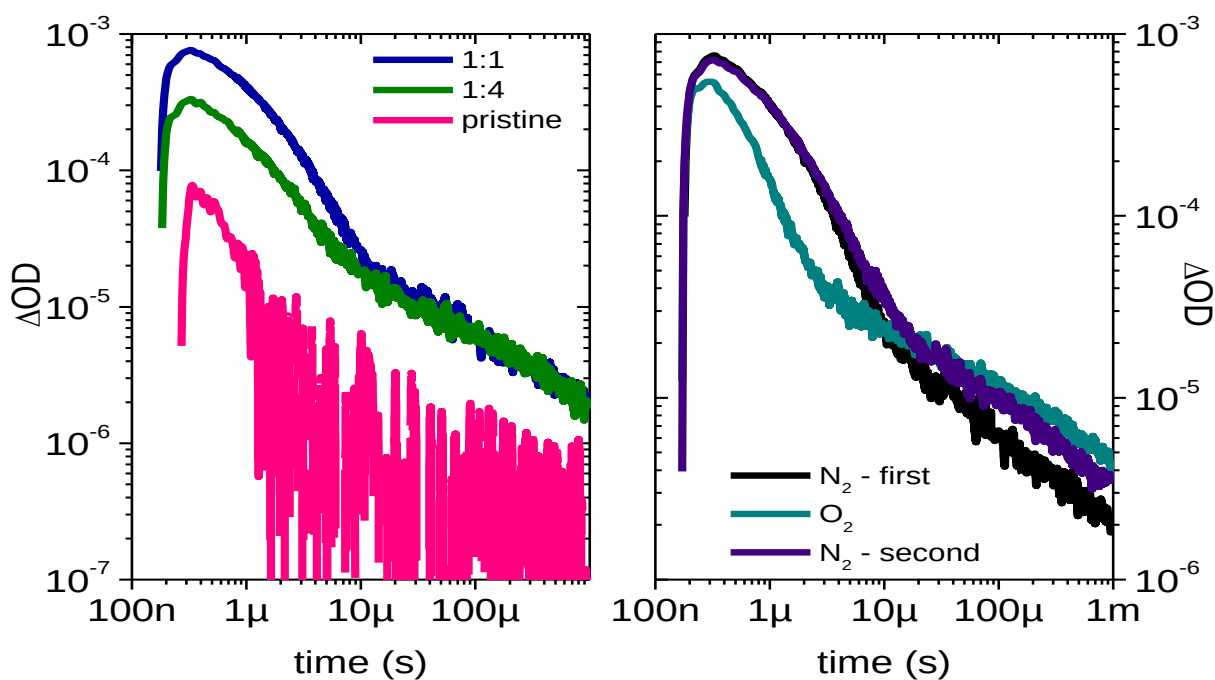


Figure 3.4 – a) Transient decays of neat SiTPT-BT (pink) and blends as a function of PCBM concentration (1:1, blue, and 1:4, green). **b)** Transient decays of a 1:4 blend as a function of the film environment. Decays taken in an inert atmosphere (nitrogen) are shown in purple, with the decay kinetics recorded in an oxygen rich environment are shown in green.

To confirm the nature of the transient species observed at these wavelengths, transient decay kinetics were recorded. The transient absorption decays presented above show the composition (a) and oxygen dependence (b) of the decay dynamics in SiTPT-BT. Both the neat material and blend films exhibit biphasic decay behaviour, as seen in Figure 3.4a. In each instance, the fast phase can be fit to a mono-exponential decay and the slow phase from 1 μ s in the neat film and 10 μ s in the blend films, can be fit to a power law decay. The slow power law decay is indicative of non-geminate recombination of dissociated charges. The fast phase is present in the two blend films between ~ 300 ns – 10 μ s, before the onset of the power law decay kinetics is observed, may arise from the presence of triplets. The formation and presence of triplets in both the neat and blend films is confirmed by oxygen quenching studies shown in Figure 3.4b. The decay dynamics of the film is first recorded under an inert atmosphere before the sample was exposed to air and the decay recorded again to record the triplet quenching from oxygen.

Finally, the film was returned to an inert atmosphere and the decay kinetics were recorded once again on the same sample to verify the presence of the triplets,²⁸ in the neat material, as well as blends with PCBM. The longer time decays (from 10 μ s) may be fit to a power law decay where $\alpha = 0.44$ for the 1:4 blend and $\alpha = 0.49$ for the 1:1 blend and arises from the non-geminate recombination of charges.

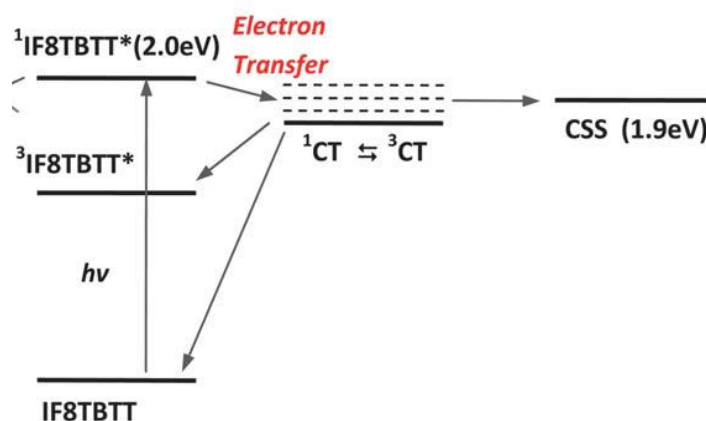


Figure 3.5 – The schematic, taken from reference ²¹ is a summary of the photophysics of on particular polymer/ fullerene blend film (IF8TBTT/PCBM) that has been shown to generate triplets. Photogeneration of IF8TBTT singlet excitons results in the formation of interfacial CT states. These CT states either dissociate to yield free charges or undergo geminate recombination to the triplet CT state.

The data presented in here for pristine SiTPT-BT and blends with PCBM, show the clear formation of triplets in this blend. This is observed from by the 1.3 μ s monoexponential fast phase that is quenched in the presence of oxygen, as observed in TAS studies. The observation of triplets in these blends may arise if these states are lower in energy than the charge separated states. The kinetic scheme in Figure 3.5 describes some of the processes occurring in an IF8TBTT:PCBM blend that has a significant triplet yield, as observed using oxygen sensitive TAS measurements.²¹ Following photoexcitation to the polymer LUMO, the formation of triplet states by energy transfer is in kinetic competition with the formation of the charge separated states. The triplet formation in the SiTPT-BT films investigated here most probably follows the same mechanism as that presented for IF8TBTT.

The presence of triplets may be detrimental to device performance as these charges are unable to be harvested to contribute to the photocurrent.^{12,21,26,29} It has been suggested that the energy level offset between the donor and acceptor needs to be sufficiently large to hinder triplet formation.²⁹

3.3.2 Charge generation in P3HT:PCBM

The following BHJ blend system to be studied in this chapter is P3HT:PCBM, investigating the effects of temperature on charge generation. The absorption (solid lines) and PL (dashed lines) of annealed neat P3HT (green) and a 1:1 (by weight) blend of P3HT:PCBM (blue) are shown in Figure 3.6.

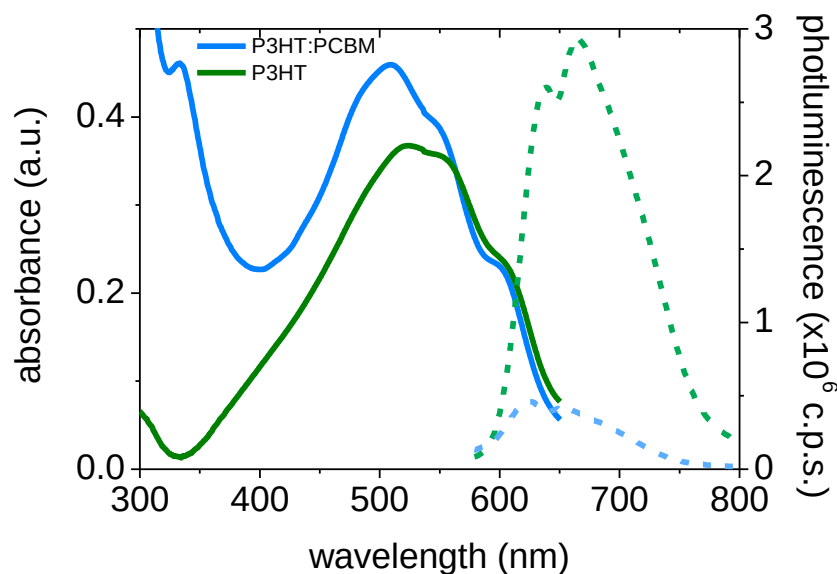


Figure 3.6 – Absorption (solid lines) and emission (dashed lines) spectra for neat P3HT (green) and a 1:1 blend of P3HT:PCBM.

These data show a broad ground state absorbance, with a peak maximum at ~ 520 nm for the neat film and ~ 510 nm for the blend. For both films, a low energy shoulder is present at ~ 610 nm and ~ 595 nm, for the neat and blend films, respectively. The observation of this shoulder is consistent with an increase in crystallinity of the polymer upon annealing.²⁰ The PL of these films, following excitation of the polymer, is also shown in Figure 3.6 (dashed lines), showing that the blend film is $\sim 85\%$ quenched compared to the emission from the neat P3HT film, highlighting the incomplete quenching of the photogenerated excitons in the 1:1 blend. This indicates that the formation of some domains that are larger than the exciton diffusion length may be present in this blend and that not all the excitons are able to reach an interface for dissociation before they recombine, as will be discussed in more detail in Chapter 4. This is an indication of some charge loss in these blends, however, previous compositional studies have shown that 1:1 blend studied here, is the optimal blend ratio for annealed P3HT:PCBM blends.²⁰ To investigate the charge generation yield in 1:1 P3HT:PCBM blend, TAS has been employed to

further understand the charge generation mechanism, as a function of wavelength, excitation density and temperature.

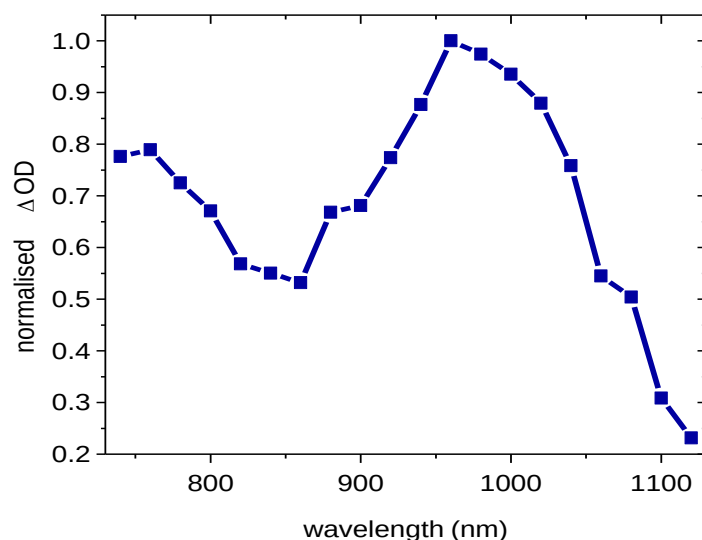


Figure 3.7 – The transient spectra of P3HT:PCBM (1:1) blend. These data both show two photoinduced absorptions peak at ~ 1000 nm and ~ 775 nm, which have both been assigned to P3HT polarons.

The transient spectra of P3HT:PCBM films have been reported previously³⁰ and is shown again in Figure 3.7 for the sample studied here, taken at 1 μ s. These data show two, is a narrow absorption between 950 – 1050 nm, and the onset of another higher energy peak, with a maximum at ~ 775 nm. The first, low energy, peak has been assigned to the localised P3HT polarons in disordered P3HT domains.^{31,32} The higher energy peak at 775 nm has been assigned to two dimensional delocalised P3HT polarons in regions of higher crystallinity.^{33,34} Following this assignment, the P3HT polaron has been monitored herein at 980 nm. We note that the spectra for P3HT:PCBM blends has been reported to be time dependent, and the contribution from the higher energy peak decreasing at longer timescales.

The formation of triplets in regio-regular P3HT:PCBM blends has shown elsewhere not to be a significant loss mechanism in this blend,^{12,35} therefore, the origin of the fast phase observed in Figure 3.8, may be attributed either to geminate recombination of bound charges or non-geminate recombination of dissociated charges. The excitation density-dependent fast phase on the early microsecond time scale was therefore investigated further by extending the time resolution into the nanosecond regime. The TAS kinetics as a function of excitation density are shown in Figure 3.8 of an annealed P3HT:PCBM blend. Excitation density dependence measurements of the charge generation yield (ΔOD amplitude) provide information the nature

of the recombination kinetics occurring at the timescales investigated. Excitation independent TAS yield is indicative of geminate recombination of bound charges, as the rate of recombination does not increase with a higher density of geminate pairs. In contrast, an excitation density dependent generation is indicative of non-geminate recombination of free charges. The charge generation yield changes as the number of free charges increases, and will therefore, change the charge generation yield and recombination dynamics of the blend.¹⁸ These data show an excitation density dependence on the charge generation yield, which is most prominent at early timescales. A plateau is also observed at the earlier timescales for all but the highest of the excitation densities investigated, but is most pronounced for the two lowest excitation densities (5 and 10 $\mu\text{J cm}^{-2}$), as shown previously in Figure 3.2 for the 10 $\mu\text{J cm}^{-2}$ excitation density.

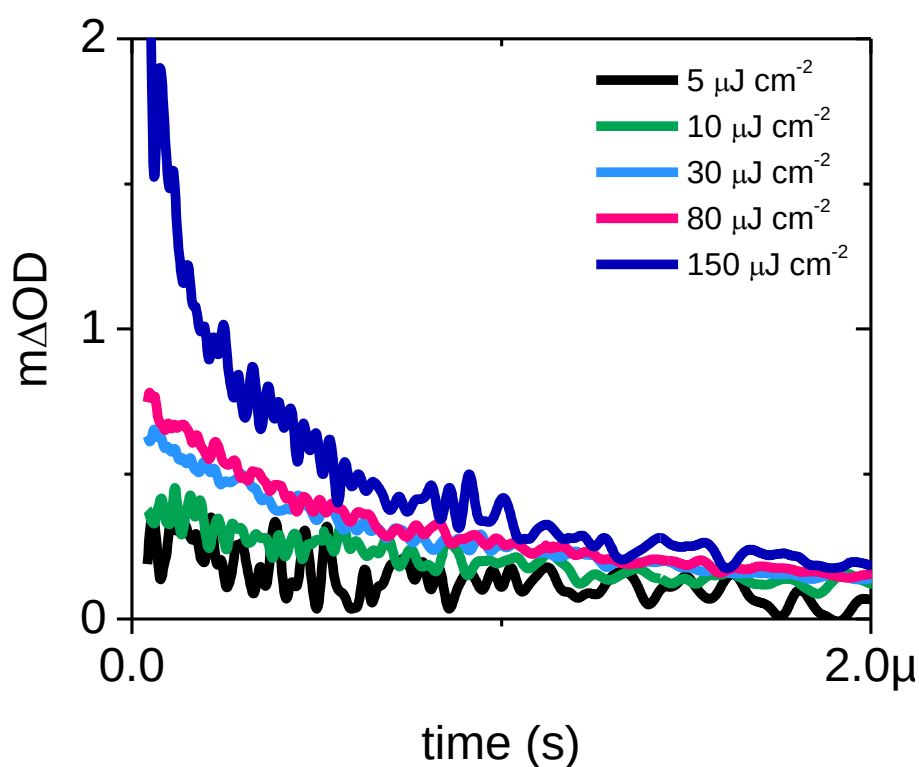


Figure 3.8 -The excitation density dependence of an unannealed P3HT:PCBM (1:1) film, excited at 532 nm, and probed at 980nm.

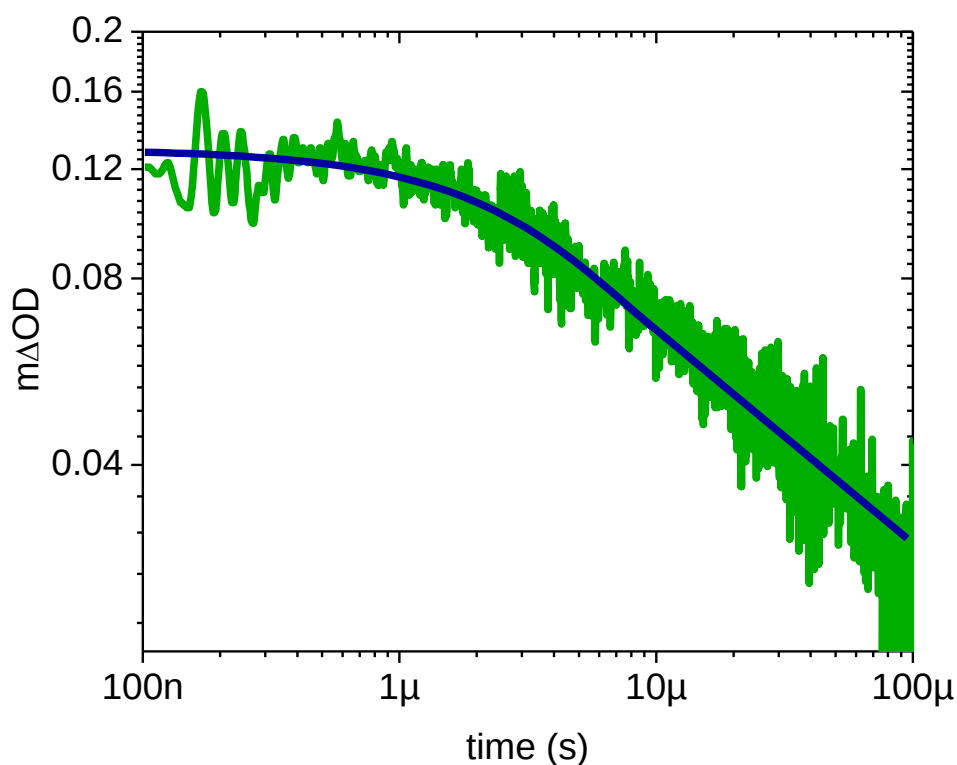


Figure 3.9 – TAS decay for a P3HT:PCBM film, fit to a bimolecular decay showing the initial plateau in the signal.

Further identification of the measurement of non-geminate recombination in organic blends may arise from the observation of an initial plateau in the recorded change in optical density before the signal decays.¹⁷ The experimental observation of this plateau may also be fit theoretically using Equation 3.1, to describe the recombination, as shown in Figure 3.9, fitting the decay dynamics of an annealed P3HT:PCBM film with an excitation density of $10 \mu\text{J cm}^{-2}$. The onset of decay from the initial plateau, arising from the onset of non-geminate recombination, appears at earlier times as the excitation density is increased, due to the increase in the excitation density increasing the photogenerated charge density.¹⁶

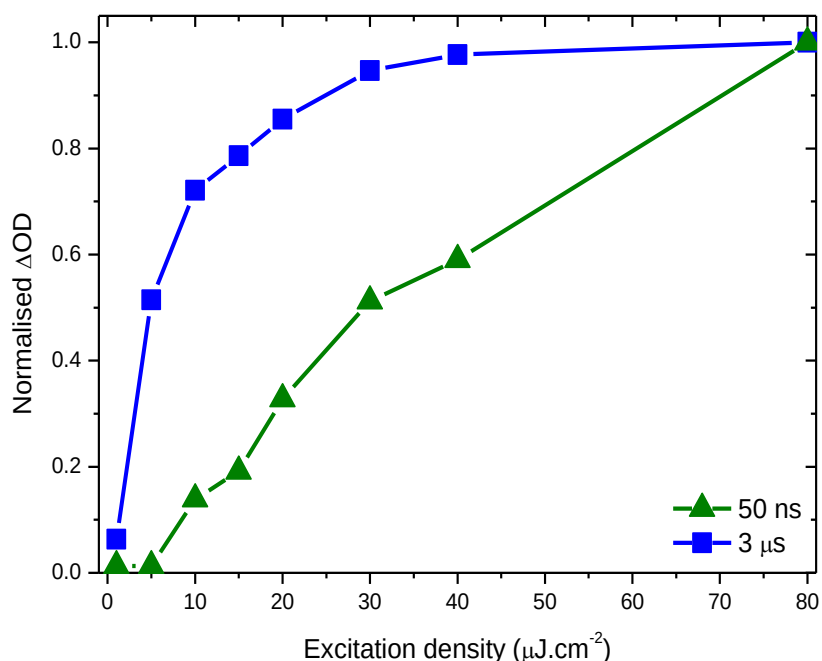


Figure 3.10 – The excitation density dependence of an unannealed P3HT:PCBM (1:1) film, at 50 ns and 3 μs .

Figure 3.10 compares the excitation density dependences of the fast and slow decay phases. It is apparent that there is a threshold excitation density of $\sim 5 \mu\text{J cm}^{-2}$; above this threshold the amplitude of the slow phase (3 μs) starts to saturate, correlated with the appearance of the fast phase (50 ns). This significant excitation density dependence of the fast phase is consistent with non-geminate rather than geminate recombination. We note that some contribution of geminate recombination dynamics to the fast phase cannot be ruled out, however, the pronounced excitation density dependence data shown in Figure 3.10 clearly indicates that this contribution, if present, is relatively minor. As such, the observation of polaron decay dynamics correlated with excitation density, and hence the number of charges in the film, is consistent with second order (or higher) kinetics. The presence of two non-geminate recombination phases is in good qualitative agreement with previously reported analysis for MDMO-PPV:PCBM blends^{19,36} and is thus consistent with the trap model proposed to account for the recombination behavior observed in this system.³⁷ This comparison therefore strongly supports the assignment of these fast and slow phases of P3HT:PCBM blends to trap-free and trap-limited non-geminate recombination respectively and not arising from geminate recombination.³⁸

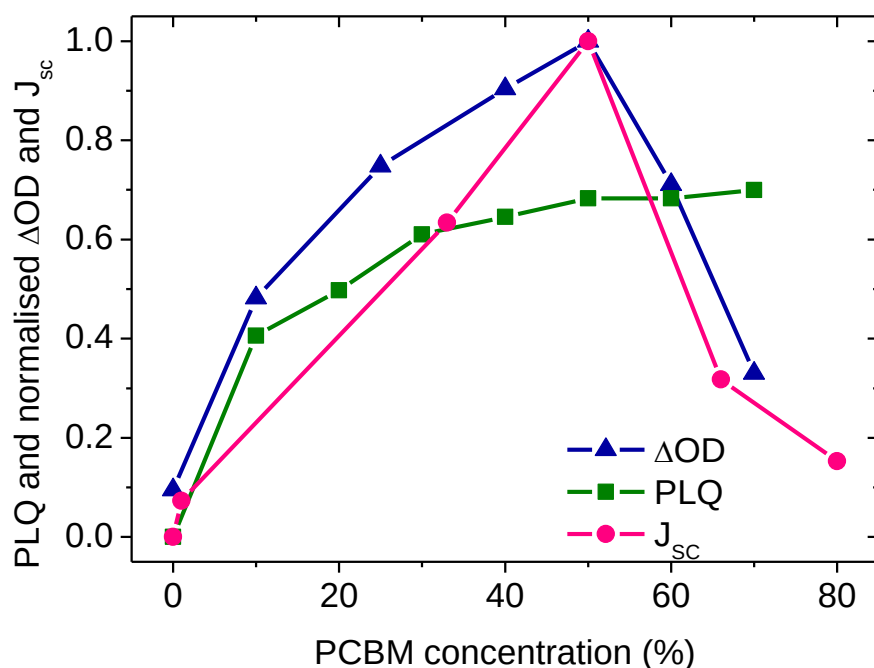


Figure 3.11 - The concentration dependence of exciton quenching (PLQ), the charge generation yield from TAS (ΔOD) and device photocurrent (J_{sc}), as a function of PCBM.

There has been extensive publication of the composition dependence of P3HT:PCBM blends.²⁰ The combined data for P3HT:PCBM blends as a function of PCBM concentration are shown in Figure 3.11, data has been normalised for the maximum J_{sc} and ΔOD recorded. These data show a peak maximum at 50 wt% for both the charge generation yield (ΔOD) and photocurrent data (J_{sc}). This comparison confirms the correlation between TAS recorded on thin films at $1\mu s$ and J_{sc} in devices, these data are also in agreement with extensive research on this materials system, indicating the most efficient device compositions for P3HT:PCBM blends is 1:1.^{20,39} The decrease in charge generation yield above 50 wt % PCBM may probably arise from a decrease in the optical absorbance compared with the polymer rich films.

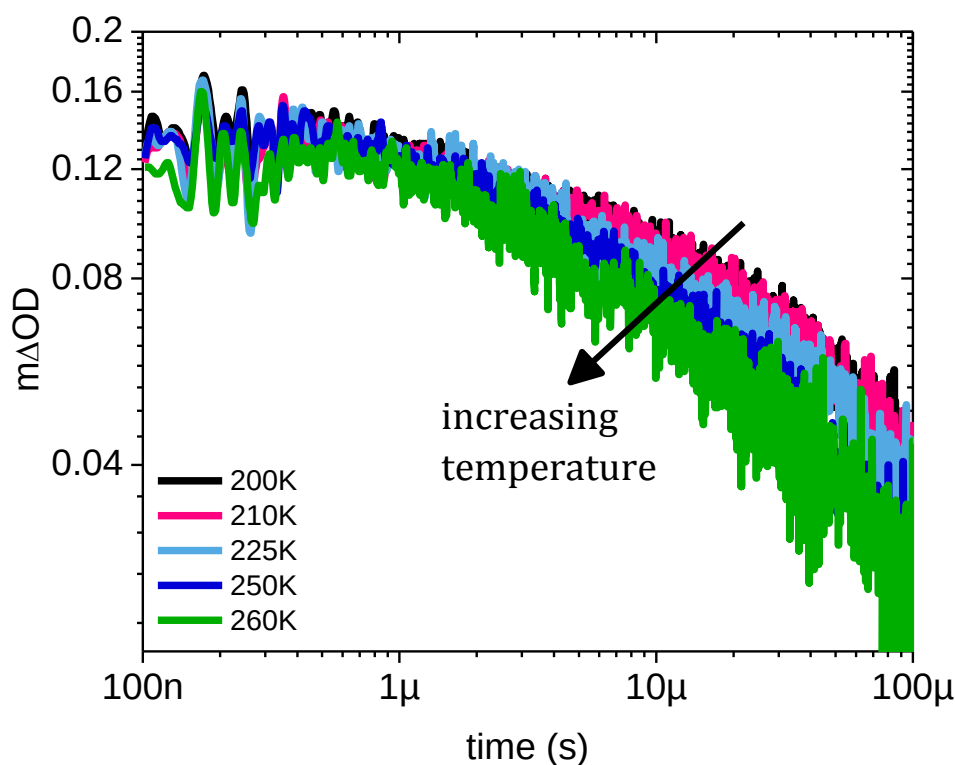


Figure 3.12 – TAS of an annealed P3HT:PCBM (1:1) film as a function of temperature, probing the polymer polaron at 980 nm, following an excitation of $6 \mu\text{Jcm}^{-2}$ at 520 nm.

Finally, an investigation into the temperature dependent nature and mechanism of charge recombination in P3HT:PCBM solar cells is presented in Figure 3.12. These measurements have been studied on an annealed 1:1 blend films between 200K – 260K, from 100 ns to 100 μs . The initial plateau in the optical signal, between ~ 100 ns to ~ 800 ns, is indicative of the onset of the generation of charge carriers and the resultant non-geminate recombination of the dissociated charges. As indicated by the arrow, the increase in temperature of the film environment leads to an acceleration of non-geminate recombination losses. The initial amplitude of the signal is relatively temperature invariant, consistent with studies reported elsewhere.⁴⁰ This may arise from an increased thermal energy of the charges at room temperature, compared to the lower temperatures, consistent with previous experimental and modelling studies of MDMO-PPV:PCBM films.¹⁹ This increase in thermal energy increases the probability of charges escaping trapped states and is consistent with a thermally activated de-trapping model.⁴¹ These temperature dependent TAS results on annealed P3HT:PCBM films are consistent with the presence of trap state in the P3HT:PCBM blends.³⁸

3.3.3 The influence of the polymer bridging atom and the addition of a processing agent on charge generation in PCPDTBT:PC₇₀BM blends

The final section of this chapter is concerned with understanding the charge generation in PCPDTBT:PC₇₀BM blend films. Three different active layers compositions have been investigated herein; PCPDTBT:PC₇₀BM, PCPDTBT:PC₇₀BM + ODT and Si-PCPDTBT:PC₇₀BM. Devices fabricated with these active layer blend compositions have shown considerable differences in the J_{SC} , despite only a small variation in the active layer composition.^{23,42} This section has chosen to investigate whether these changes can be correlated to the differences in the donor molecular structure and film microstructure or from the addition of a processing agent.

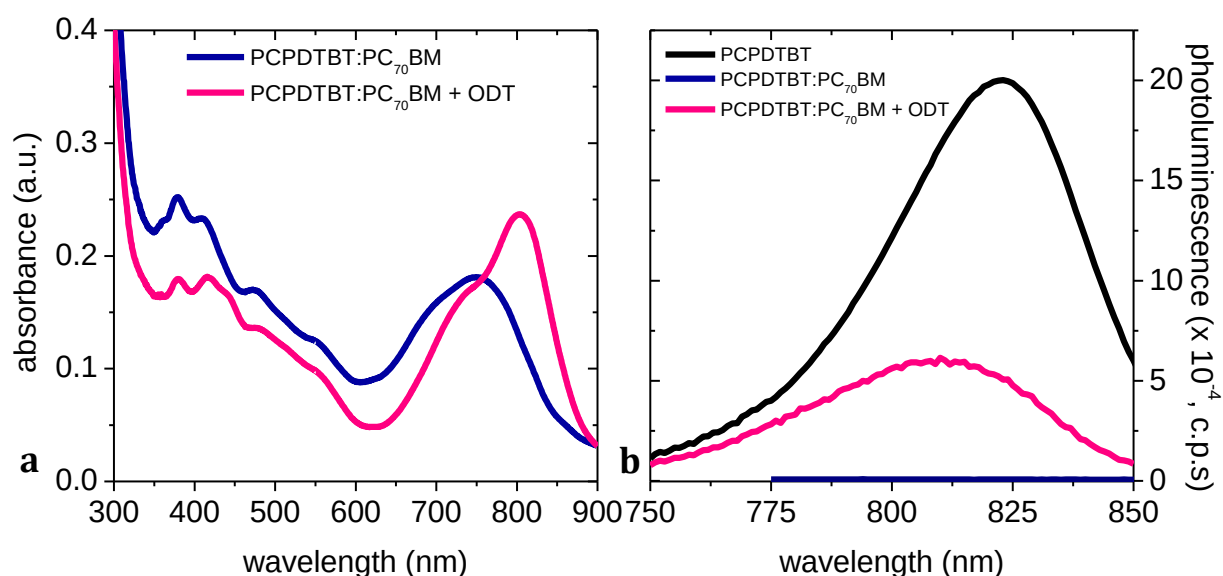


Figure 3.13 – a) Ground state absorption spectra of C-PCPDTBT:PC₇₀BM (light blue) and C-PCPDTBT:PC₇₀BM + ODT (pink) films. b) PL of the films following polymer excitation at 730 nm.

The absorption (a) and corresponding PLQ (b) of pristine and blend PCPDTBT films are shown in Figure 3.13a,b. The absorption spectrum of a pristine PCPDTBT film (black) shows a broad absorption towards the near infra-red, with a peak absorption at ~ 780 nm. The maximum absorption in these blends is ~ 250 nm longer than that for P3HT blends, arising from the lower bandgap of this material, compared to P3HT. The addition of PC₇₀BM to the blends leads to an increase in the absorbance across the visible spectra, with peaks at ~ 360 nm, corresponding to the absorption of PC₇₀BM. There is some loss in the fine structure of the C-PCPDTBT blend with the addition of PC₇₀BM (light blue), possibly arising from a disruption in the polymer packing

upon the addition of PC₇₀BM.⁴³ However, the addition of ODT to the blend increases the peak wavelength absorbance by ~ 25 nm. The polymer PL data in Figure 3.13b,, show the emissive nature of the neat materials, where the neat carbon bridged analogue is approximately four times more emissive that that of the silicon derivative. In blends of both materials, near unity (~ 98 %) quenching of the photogenerated excitons following excitation at 730 nm for both the carbon derivatives. This high degree of quenching is indicative of extensive molecular scale mixing of the two materials.

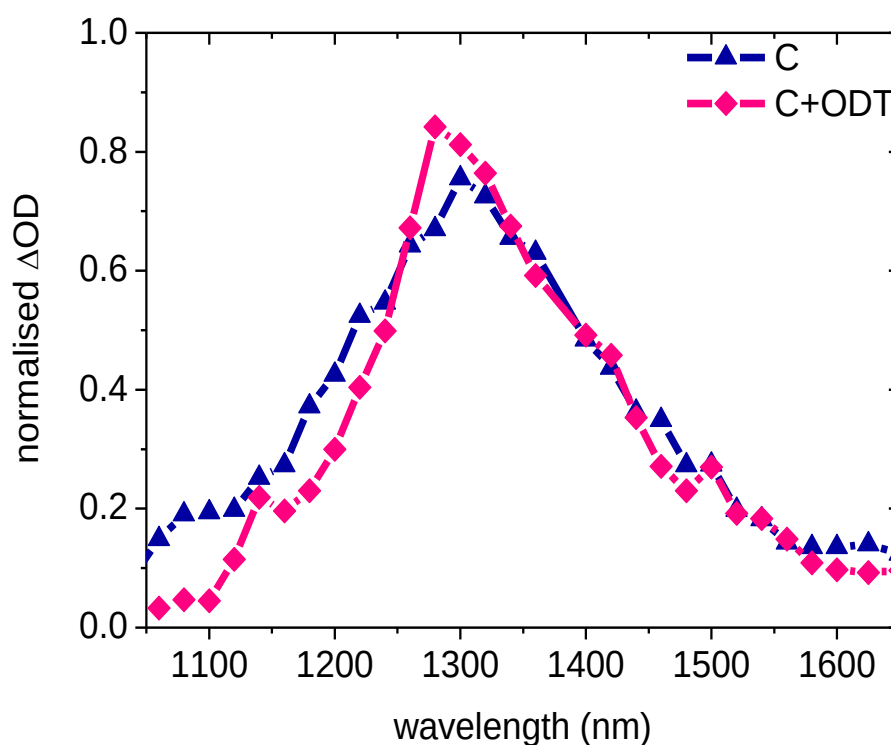


Figure 3.14 – Transient absorption spectra recorded at 1 μ s, for the PCPDTBT blends; C-PCPDTBT:PC₇₀BM (dark blue triangles and C-PCPDTBT:PC₇₀BM + ODT (pink diamonds). The broad peak observed at ~ 1300 nm in each blend, has been assigned to the polymer polaron.

Following the steady state analyses presented above, the following time resolved measurements were conducted in order to investigate the charge generation in these blends. The transient spectra for the three different blend systems (1:2), measured at 1 μ s, are shown in Figure 3.14. Each spectrum shows a broad transient absorbance, with a peak at ~ 1300 nm for all three materials. In each instance the peak wavelength position, and Δ OD signal magnitude, are insensitive to an oxygen atmosphere, as seen in Figure 3.15 for a C-PCPDTBT:PC₇₀BM blend. This shows the decay dynamics of the film in an inert atmosphere (nitrogen, green) and then in an oxygen atmosphere. There is no significant change in the decay dynamics between the two

environments therefore this signal is unlikely to arise from the contribution of triplets, and hence the origin of this peak has been assigned to that of the polymer polaron. The decay dynamics for these blends follow a power law decay in both sample environments, again consistent with the assignment of polaron kinetics and not from the formation of triplets. We note that this polaron band is slightly lower in energy than reported elsewhere, with observations of a long lived photo-induced absorption band recorded at 1200 nm.²⁵ We also note that this assignment is inconsistent with data from Janssen and co-workers who assign the origin of the photoinduced absorption peak at ~ 1240 nm to arise from the combination of both triplet and singlet states, that have very similar energies.²⁶ However, due to the insensitivity of the spectral peak position and decay kinetics for the materials tested here to an oxygen rich atmosphere, the assignment of the polymer polaron at 1300 nm is considered valid for these blends. Therefore, following our assignment of long lived charges observed at these wavelengths, herein TAS decays were recorded at 1310 nm, as a function of time, probing the generation, and decay of the polymer polarons.

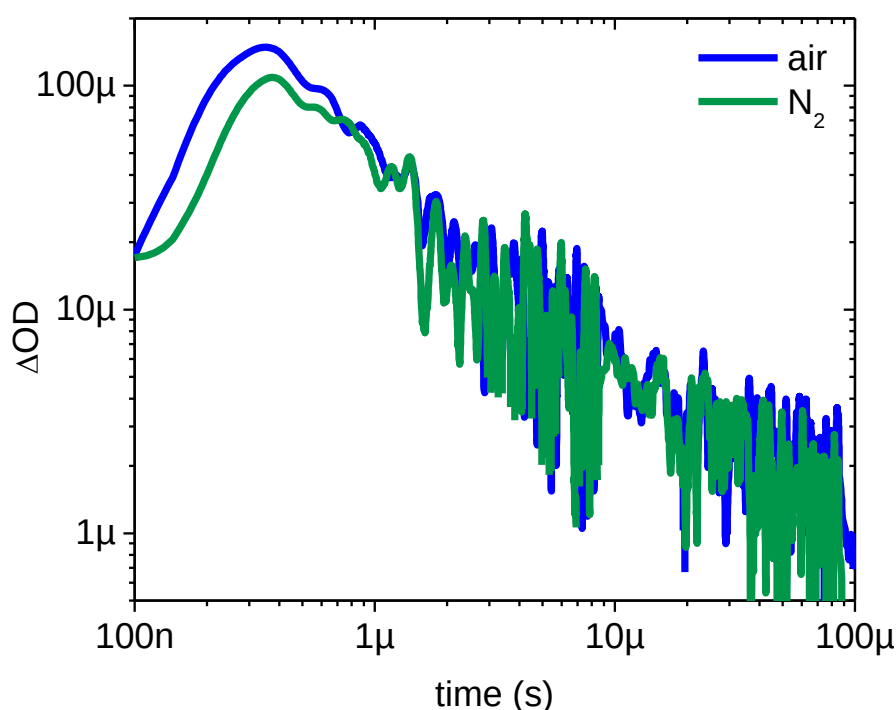


Figure 3.15 – TAS decays of a C-PCPDTBT:PC₇₀BM (1:3) film recorded initially in a nitrogen atmosphere, followed by an oxygen rich atmosphere to confirm that triplet states do not significantly contribute to the charge generation recorded here.

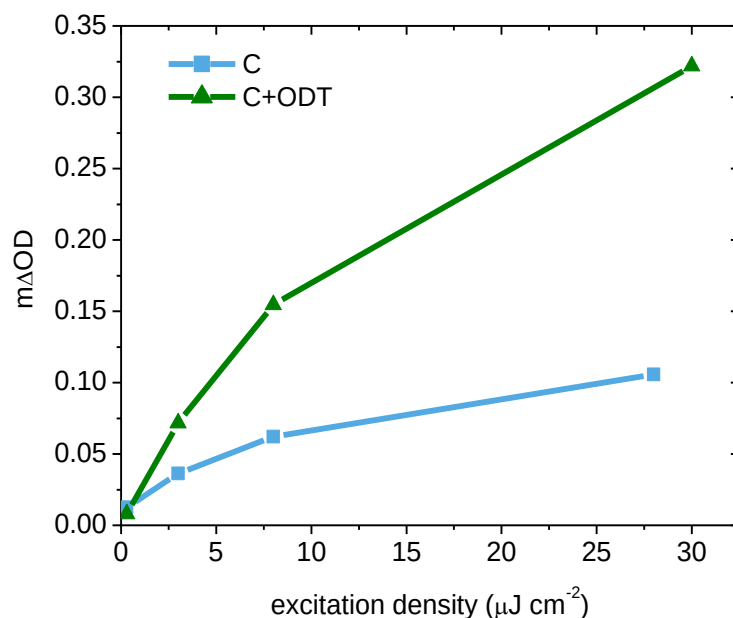


Figure 3.16 –Comparison of the excitation density dependence between the two carbon bridged blends (with ODT, green and without ODT, blue) at 1 μ s following polymer excitation at 532 nm.

Figure 3.16 shows the transient signal amplitude at 1 μ s as a function of excitation density for both the carbon bridged (blue) and carbon blend with ODT (green). These data show an increase in Δ OD with excitation density for all three blends studied, and are indicative of probing the non-geminate recombination of dissociated charges, and not geminate recombination of bound charge pairs. This is consistent with the data presented above in Section 3.3.2 for P3HT:PCBM blends that also exhibit this excitation density dependent data.

The transient decay kinetics shown in Figure 3.15 are typical of the decay dynamics recorded, exhibiting power law decay dynamics that are indicative of non-geminate recombination of dissociated charges. However, the data presented in Figure 3.17 shows the decay dynamics of three films that all apparently have the same blend composition and have undergone the nominally similar fabrication methods. These samples were all excited at 650 nm, with excitation densities between 26 – 30 $\mu\text{J cm}^{-2}$, probing the polaron decay at 1300 nm. The three films all exhibit power law decay dynamics on the longer timescales, from ~ 10 μ s, indicative of non-geminate recombination. However, there are clear differences in the initial signal amplitude and decay dynamics over the first two time decades recorded here. For two of the blends shown here, there is a clear fast phase, which may be indicative of triplets in these films. Whereas for the film shown in black, the presence of a fast phase is not as clear, despite the same apparent processing conditions and transient set up being employed throughout.

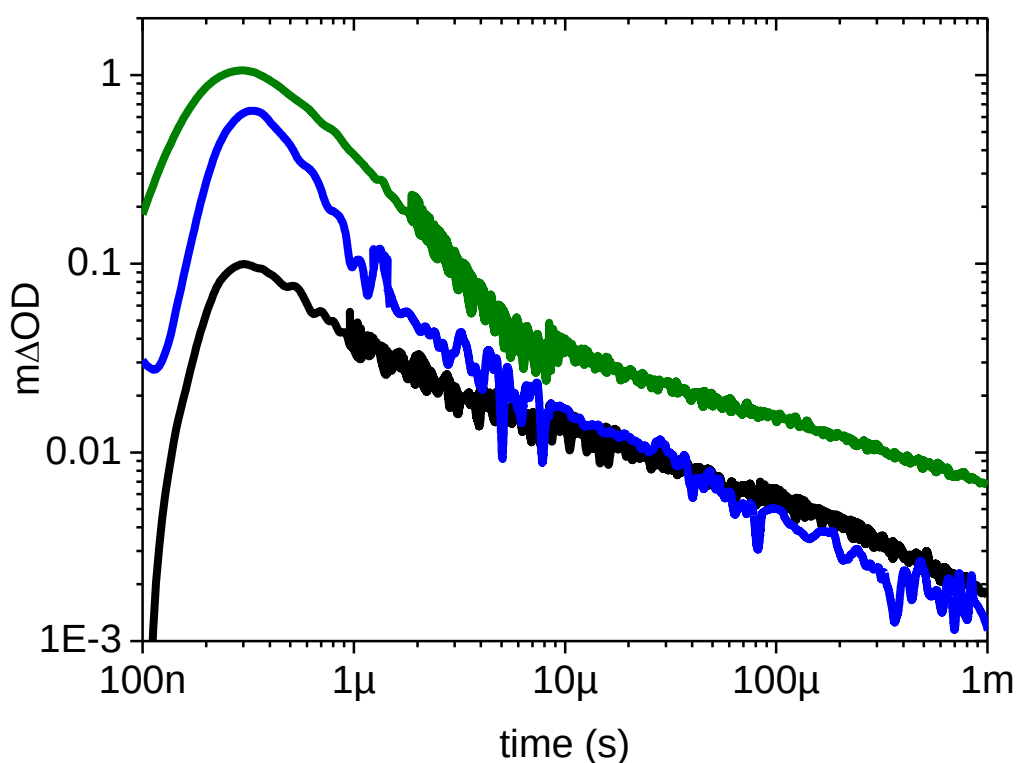


Figure 3.17 – Transient absorption decays of C-PCPDTBT:PC₇₀BM (1:2) films, all of which were excited at 650 nm, with excitation densities between 26 – 30 $\mu\text{J cm}^{-2}$ and probed at 1300 nm, highlighting potential problems that may arise due to the irreproducible nature of some materials.

The differences in these data highlight some of the difficulties that have arisen when analysing data due to the irreproducibility of studying different films despite the same materials employed in each instance. The origin of these differences is not clear from these data, but may originate from differences in the blend morphology of each films due to different polymer and fullerene batches used and differences in the film fabrication. This highlights how sensitive the charge generation and recombination is to the film microstructure and the effect this has on the decay dynamics probed using TAS. It has been considered that triplet formation has may be most significant in amorphous materials, and therefore the film processing conditions are critical for reproducibility. The decay dynamics of most significance to this thesis are those resembling the decay dynamics of shown in devices and therefore investigating the role of the triplet becomes only significant if it is observed in devices. The power law decay dynamics without a significant fast phase, as shown in Figure 3.15 are similar to those exhibited in the devices analysed in Chapter 6.

3.4 Application of TAS for investigating the charge generation in donor / acceptor blend films

The examples presented above show some of the information that may be gained by employing TAS on thin films and its applicability in OPV materials testing and screening. This includes information on the charge generation and the origin of the transient species observed in addition to an indication of the nature of the recombination mechanisms, both geminate and non-geminate recombination, including trap free and trap limited non-geminate recombination.

3.4.1 Advantages

One of the primary advantages of TAS regarding the testing of materials is that only the active layer needs to be tested, simply on a glass substrate, with no need to fabricate devices. This therefore makes TAS a relatively quick method for material screening, including the ability to quickly complete composition and fabrication studies to ascertain the optimal active layer composition for devices. This has been demonstrated by Clarke *et al.* comparing the charge generation yield recorded as the ΔOD signal at 1 μs in the TAS decays with the device J_{sc} and internal quantum efficiency (IQE), as shown in Figure 3.18. Data reported in this thesis support this conclusion.

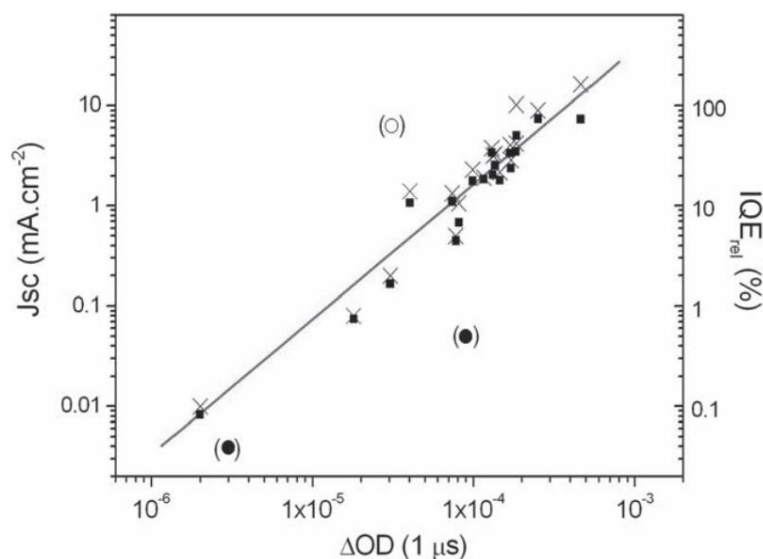


Figure 3.18 – The correlation between the charge generation yield (ΔOD) recorded at 1 μs using TAS and the device short circuit current under 1 sun illumination.

TAS may also be employed when identifying between different photogenerated species and the different recombination pathways. As shown in Figure 3.4 for SiTPT-BT and SiTPT-BT:PCBM blends, triplet states may be identified by oxygen quenching studies. This is a quick and simple method for characterising the transient species recorded. The recombination mechanisms may also be investigated using TAS, employing excitation density measurements and numerical analysis of the kinetics, as outlined above.

3.4.2 Limitations

Whilst TAS is a useful technique for investigating charge generation, there are some limitations to this method. One of the biggest concerns is the magnitude of the charge densities generated using this technique. The typical charge densities generated in TAS measurements are in the order of $\sim 10^{17} \text{ cm}^{-2}$, as determined from a manipulation of the Beer Lambert law, and are considerably larger than those typically present in devices ($\sim 10^{15} \text{ cm}^{-2}$).¹⁷ Therefore, the charge generation yields measured in TAS experiments may not reflect the photogeneration under standard device illumination and may in turn alter the recombination dynamics with the charge density.

As illustrated in Figure 3.16 for C-PCPDTBT:PC₇₀BM, the sensitivity of the charge generation and recombination to processing conditions and batch variability may be observed through the a change in signal amplitude and decay dynamics observed. The origin of these differences has not been investigated here, but may arise from different batches used for sample fabrication, along with different processing conditions.

Different experimental routes have been undertaken to overcome these potential problems that can occur in TAS measurement and analysis mentioned here, the analyses presented in the remainder of this thesis. Film and device fabrication has been optimised for each material through extensive TAS, UV-Vis, PLQ and device analysis and the transient analysis has been conducted on more than one sample for each of the experiments to verify the reproducibility of the outcomes recorded. Wherever possible the same material batch has been used throughout a series of experiments to minimise changes that may arise from slight differences in the materials. The film microstructure is particularly sensitive to processing conditions, and spin coating deposition technique allows for little control of the morphology. Wirebar coating has been employed on some of the systems investigated as this may allow for a small improvement in the sample reproducibility.

The timescale resolution of the set-up employed in this analysis is limited to 50 ns and is limited to longer timescales than 50 ns, therefore TAS has been primarily employed to probe the non-geminate recombination of dissociated charge generation. Exciton formation and dissociation is unable to be monitored on the timescales available here, and only the tail of geminate recombination may be studied, depending on the lifetime in the blends studied.

3.5 Conclusions

Charge generation in organic blends may be investigated using transient absorption spectroscopy to monitor the photoinduced change in optical density, which corresponds to the charge carrier density. This use of this technique has been demonstrated in the analysis of three different polymer / fullerene blend systems.

The observation of triplets in BHJs has been shown in SiTPT-BT:PCBM blend, by the presence of an 1.3 μ s monoexponential fast phase that is quenched in the presence of oxygen. This is followed by a long lived power law decay, that is unaffected by oxygen quenching, indicating that charge carriers are formed after the triplets. This analysis demonstrates that TAS may be employed in the analysis and ascertain the origin of the observed charge species.

The biphasic decay observed in the P3HT:PCBM devices studied here have not been attributed to triplet formation, rather to non-geminate recombination. The increase in recombination decay dynamics with increasing temperature support the assignment of the two phases to trap free and trap limited non-geminate recombination.

Finally the changes in the active layer morphology through the use of additives has shown a considerable difference in the charge generation yield in PCPDTBT:PC₇₀BM films. This trend in charge generation yield ($C + ODT > C$), as observed using TAS at 1 μ s, is in agreement with published device data yielding the same correlation between the different blends, for device performance.⁴³ This positive correlation between thin film and device measurements demonstrates the usefulness and validity of these TAS measurements for initial indications of the active layer performance and efficiency. This study has also highlighted the dependence and sensitivity of the charge generation yield on the morphology of the active layer.

3.6 References

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Chapter 4

Fullerene crystallisation as a key driver of charge separation in polymer / fullerene bulk heterojunction solar cells

Abstract

This chapter investigates the molecular mixing of polymer / PCBM blends from PL spectra and focuses primarily upon the behaviour of blends of the donor polymer poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene) (pBTTT) with PCBM. Evidence is presented on the impact of formation of a relatively pure, molecularly ordered phase of PCBM upon the generation of long lived charge carriers. PCBM crystallisation is shown to result in an increase in its electron affinity, providing an energetic driving force for spatial separation of electrons and holes. This crystallisation is indicated to be specific to PCBM, as it is not observed in two other fullerenes investigated. Based upon these observations, a functional model is proposed, potentially applicable to many organic bulk heterojunction devices, based upon charge generation in a finely intermixed polymer / fullerene phase followed by spatial separation of electrons and holes by a crystallisation induced LUMO level offset at the interface of this mixed phase with crystalline PCBM domains. This is suggested to be the key factor driving the spatial separation of photogenerated electrons and holes in many polymer / PCBM devices.

4.1 Introduction

Extensive successes in the development of new polymers as donor materials in OPVs have been widely reported.¹⁻⁵ However, progress in developing alternative electron acceptors to PCBM / PC₇₀BM has been much more limited to date.^{6,7} PCBM has been the most widely employed electron acceptor in OPVs for almost two decades,^{8,9} and the contrast in the reported development and publication of new acceptor materials compared to that of donors, is striking. There are many possible explanations for this apparent void in the development of successful acceptor materials. However, the reasons behind PCBM's success are only recently starting to be revealed, with attention particularly focusing upon the degree of mixing and interaction between donor and acceptor materials in blend films.^{10,11}

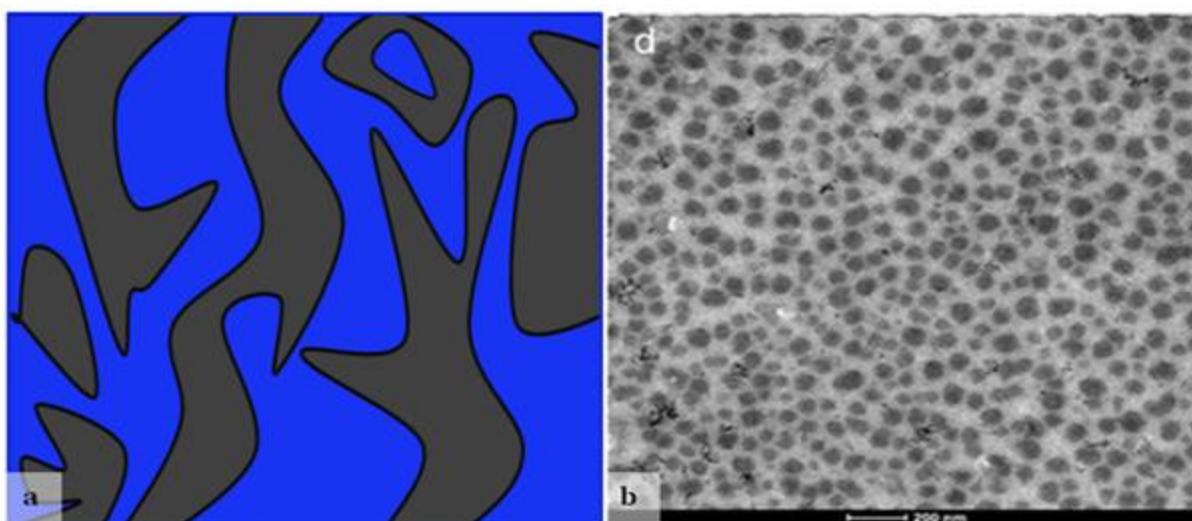


Figure 4.1 – a) A typical schematic picture used to describe the active layer structure as a blend of two pure phases of a donor and acceptor, arising from TEM images, such as that in b) A TEM image of a 1:1 P2:PCBM blend showing the apparent formation of domains of ~ 50 - 100 nm in size. The darker parts have been attributed to the imaging of PCBM domains, as the electron scattering density of PCBM is greater than the polymer and no staining was reportedly employed in this analysis. TEM image was taken from reference ¹².

The polymer / PCBM bulk heterojunction film forming the photoactive layer of OPV devices is typically described most simply as a two component, bicontinuous blend comprising of one polymer and one fullerene phase, as illustrated in Figure 4.1a. The function of such films is then described as light absorption in one or both phases, exciton diffusion to the polymer / fullerene interface, exciton dissociation at this donor / acceptor interface to yield electrons and holes, and transport of these charges through the two phases to the device contacts, as discussed previously in Chapter 1.3 and TEM images, such as that in Figure 4.1b of a 1:1 blend of

poly((9,9-dioctylfluorene)-2,7-diyl-(4,7-bis(thien-2-yl)2-dodecyl-benzo[1,2,3]triazole))

(P2):PCBM, are often used as a experimental evidence for this model.¹² Such micrographs appear to show a two phase blend, as observed by the contrast of one material in grey and one in black. This image shows domains of the two different materials on the 50 – 100 nm length scale, with the dark domains observed being assigned to domains of pure PCBM. However, this two pure phase morphology may not be an accurate description of this blend as the atomic force microscopy (AFM) images accompanying this TEM analysis have reportedly shown a smooth film topography, and the thermal analysis shows no clear melting point of the material, indicative of a relatively amorphous mixture. Therefore, the formation of pure domains in this blends, as inferred from the TEM analysis of the image above, may not be a suitable description for this blend.

Despite the widespread acceptance of this two phase model, more detailed analyses are increasingly questioning whether this pure polymer phase / pure fullerene phase structural model is an appropriate description of OPV blends.¹³⁻¹⁶ Concerns are being raised regarding, for example, phase purity,¹³ variations in the polymer and fullerene crystallinity / aggregation within the film^{14,15} and vertical composition profiles.¹⁶ As such, there is increasing interest in developing structural and functional models of such devices which take into account more realistic considerations of blend nanomorphology. There have been several studies addressing the issue of phase composition or 'purity' in polymer / fullerene blend films, employing a range of microstructural analysis techniques.¹⁷⁻²³ These techniques include X-ray analysis,¹⁷⁻²⁰ optical and confocal microscopy,²¹ raman spectroscopy²¹ and thermal characterisation.^{22,23} Such studies have indicated that even where a clear phase segregation is apparent, the two phases may comprise chemically mixed domains, differing only in the percentage composition of donor and acceptors. It should however be noted that many of these studies have been conducted on P3HT:PCBM blends, and have not been extended further to different materials systems used as the photoactive layer in OPVs.

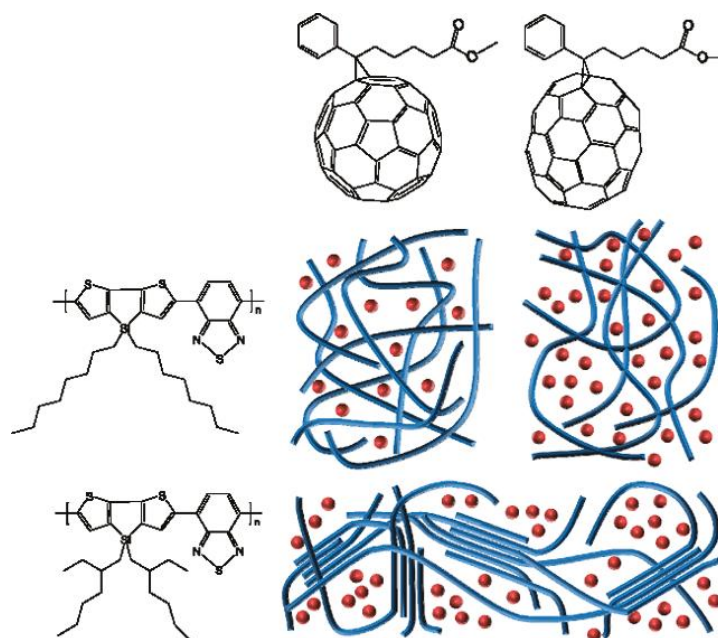


Figure 4.2 – A schematic of the blend morphology as a function of composition for a Si-PCPDTBT donor (blue strands) with straight and branched side chains blended with PCBM and PC₇₀BM acceptors (red balls), taken from reference ¹¹. The blends with the straight side chain polymer are highly miscible with either PCBM studied, whereas the branched side chain unit forms polymer aggregates. This difference highlights the dependence of the nanoscale morphology on the different materials.

X-ray absorption measurements, including near edge X-ray absorption fine structure (NEXAFS) and scanning transmission X-ray microscope (STXM) measurements have increasingly been employed to assay the miscibility of donor polymers with PCBM, most notably by Ade *et al.*^{11,13,24} Such studies have indicated that this miscibility depends upon donor polymer employed, as indicated by the schematic in Figure 4.2. This illustrates the differences in molecular mixing in Si-PCPDTBT with straight (top) and branched (bottom) side chains blended with PCBM / PC₇₀BM.¹¹ These data have indicated that miscibility may play an important role in device efficiency. The straight side chain polymer is amorphous and devices blended with PC₇₀BM are considerably less efficient than those of the branched chain version, which has been shown to be semi-crystalline.²⁵ The differences in the degree of crystallinity of the polymers may be responsible for differences in the miscibility and mixing of these materials. Other studies which emphasise the presence and significance of intimately mixed, amorphous polymer / fullerene domains include investigations employing visible light microscopy (VLM) and grazing incidence wide X-ray scattering (GI-WAXS).

There is extensive evidence that intimately mixed, single phase polymer / fullerene films exhibit rapid recombination losses, as the electrons and holes are not spatially separated, thereby preventing efficient charge collection.²⁶ One example of the effects of molecular mixing includes previous studies of charge recombination in blend films of P3HT with the pyrazolinofullerene,

C60-2 and blends of these two materials have been reported showing significant levels of geminate recombination.²⁷ This fullerene was found to be highly miscible with P3HT, resulting in no observable phase segregation in the blend film, which may account for this fast recombination. This indicates that the degree of mixing and miscibility between the two materials is of critical importance for charge generation and recombination. A finely intermixed blend with no clear definition of either a donor or acceptor phase, such as P3HT:C60-2 blends, does not allow for efficient charge separation as potential recombination sites are in close proximity to many of the free charges. Other studies also indicate that intimately mixed donor / acceptor films exhibit rapid recombination losses include charge-carrier extraction by linearly increasing voltage (photo-CELIV),²⁸ and TRMC measurements,²⁹ therefore, morphologies such as these have little potential as the active layer in OPVs, as the charge separation is poor.

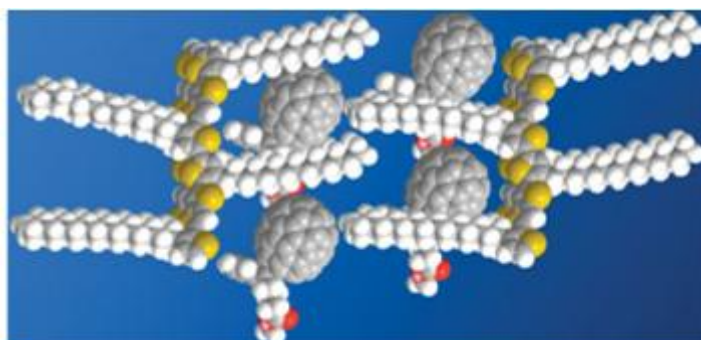


Figure 4.3 – A model showing the intercalation of PCBM (grey balls) into the pBTTT side chains (white).³⁰

Whilst there is some consensus that photoactive layers comprising a single, intimately mixed donor / acceptor phase do not result in efficient OPV devices, McGehee and co-workers have shown that a pure polymer phase is not required for efficient device performance in some OPV devices.³¹ The intercalation of PCBM with polymers, including with pBTTT as shown in Figure 4.3, prevents the formation of pure polymer domains. Despite this intercalation of the materials, promising device efficiencies have been achieved for these blends.³² This conclusion of molecularly mixed systems, however, leaves unresolved the extent and importance of phase segregation in such films, particularly with regard to the PCBM component of the blend film.

The highly molecularly mixed system between the polymer / fullerene is also consistent with recent GI-WAXS and dynamic secondary ion mass spectrometry (SIMS),^{13,33} as well as with time resolved studies of ultrafast exciton quenching and charge separation in a range of other

polymer / fullerene blend films,³⁴⁻³⁶ which all show nanoscale mixing of the polymer and fullerene.

In addition to the potential limitations associated with excessively intimate mixing of donor and acceptor, the formation of pure domains on significantly larger lengthscales than the exciton diffusion length does not permit efficient exciton quenching as the excitons are unable to find an interface within their lifetime, which is again detrimental to the formation of free charges. Therefore, considering both of these observations, finding an optimal blend composition is a product of the physical properties such as miscibility and phase segregation, as well as the electronic properties of the materials. Phase segregation in blend films is often discussed as a function of crystallinity and / or aggregation of one or both of the materials in the blend. However the distinction between the two terms is often a little ambiguous and the two descriptions are commonly used interchangeably without being fully defined. We acknowledge that there may be differences when defining these terms, especially crystallinity. Herein, the term “crystallinity” refers to materials that exhibit some short range interactions between neighbouring molecules. This does not necessarily refer to structures with a regular, repeating and well defined lattice structure that forms macroscopic crystals, but may refer to nanoscale changes in morphology. The degree of crystallinity discussed here may be measured using thermal analysis techniques, such as differential scanning calorimetry (DSC), to investigate the changes in melting temperatures, or, electrochemically using cyclic voltammetry (CV), to monitor the changes in electron affinity. As well as considering the role of molecular mixing in donor / acceptor blends, this chapter is also focused particularly upon the functional and structural properties of the PCBM electron acceptor in BHJ organic solar cells. There have also been several reports in the literature on the tendency for PCBM to form aggregated domains or crystallites in such polymer / fullerene blend films.^{17,21,26,37,38} Such aggregate or crystallite formation has been related to the formation both of electron percolation pathways and of enhanced charge separation.^{29,39,40} It has also been related to the loss of device efficiency observed following thermal treatments of some bulk heterojunction devices.^{32,41} Other studies have demonstrated that PCBM can diffuse rapidly through polymer domains, particularly under thermal annealing conditions.^{16,42-44} Most recently, and of particular relevance to this chapter Piersimoni *et al.* has correlated a shift in the charge transfer state emission of a PPV:PCBM blend film with the formation of PCBM nanocrystals.⁴⁵ These studies demonstrate the significance of the PCBM domain formation for efficient device performance.

In this chapter, evidence is presented for the importance of PCBM phase-separating from a finely intermixed phase with the donor polymer to form crystalline fullerene domains is, with this phase segregation modulating the electron affinity of PCBM and thereby providing an

energetic driving force to enable spatial separation of electrons and holes. We moreover go on to demonstrate that this aggregation induced modulation of electron affinity is rather specific to PCBM. This shift is not observed for alternative fullerene acceptors, including the promising indene-C₆₀ bisadduct, ICBA,^{4,46} and the pyrazolinofullerene discussed above, C60-2. Blends of P3HT with ICBA have been reported to achieved device efficiencies up to 6.5 %, ⁴⁶ considerably higher than analogous devices with PCBM. The success of this fullerene has been attributed to the higher LUMO of ICBA compared to PCBM, increasing the V_{oc} by ~ 250 mV.⁴⁶ However, despite the success in blends with P3HT, ICBA significantly under-performs in blends with other many other polymers, regardless of the increase in V_{oc} , due to lower J_{sc} and FF. As discussed above, the highly miscible blends of P3HT:C60-2 shows high levels of geminate recombination and hence do not offer an ideal morphology for use in OPVs. Therefore, further investigation into the fullerene interactions in this blend may yield more information regarding the poor charge generation.

The apparently unique combination of P3HT with ICBA is not well understood and as such these studies on both ICBA and C60-2, may provide further insight into addressing the question of why it has proved so challenging to develop alternative electron acceptors to PCBM for bulk heterojunction solar cells. This chapter starts with an introduction to molecular mixing in polymer / PCBM films, using PL as a method to quantify this, then moves onto focusing specifically on pBTTT:PCBM blends, before finally considering the role of the fullerene in the film morphology.

4.2 Experimental

Films were fabricated as outlined in Chapter 2, and were deposited on glass, by wirebar coating from a hot solution (100 °C) onto a 35°C to ensure intercalation of the PCBM into the pBTTT side chains. Devices were fabricated with Dr. E. Buchaca Domingo by depositing PEDOT:PSS onto ITO glass by spin coating and annealing for 30 minutes at 150 °C before depositing the active layer by spin coating from a hot solution (100 °C) and evaporating Al electrodes. J-Vs of each device were measured in a nitrogen atmosphere sample chamber at 1 sun light intensity.

Absorption spectra were taken on film deposited on glass between 300 – 800 nm using a glass reference. PLQ was measured using a steady state spectrofluorimeter all films were deposited on glass. For polymer excitation measurements, the films were excited at the following wavelengths; pBTTT at 520 nm, pATBT at 520 nm, P3HT at 520 nm, PCPDTBT at 650 nm, IF8TBT at 540 nm, and PCDTBT at 560 nm and the emission was recorded from 20 nm after each excitation. For all the fullerenes measured, excitation wavelength used was 430 nm and the emission recorded from 450 nm.

The diffusion length (L_{ex}) of a polymer exciton in the absence of quencher, such as PCBM, is related to its lifetime τ_0 by; $L_{ex} = (D * \tau_0)^{1/2}$. In the presence of PCBM, both the exciton lifetime τ and the diffusion length L are reduced such that $L = (D * \tau)^{1/2}$. Assuming that the addition of PCBM only introduces an a new exciton quenching pathway, and does not otherwise change the properties of the polymer excitons, the fractional residual photoluminescence emission intensity, $\frac{PL}{PL_0} = 1 - PLQ$, where PL and PL_0 are the emission intensities in the presence and absence of PCBM, is related to the exciton lifetime by $1 - PLQ = \frac{\tau}{\tau_0}$. Combining these equations gives: $L = L_{ex}(1 - PLQ)^{1/2}$ (Equation 4.1). We note that L_{ex} is typically measured for diffusion to flat (2-dimensional) quenching interfaces, whilst the quenching site distribution we are describing is most probably 3-dimensional. This difference is likely to result in a small underestimation in our determination of exciton diffusion lengths in the presence of PCBM. We also note that our analysis assumes that diffusion of a polymer exciton to adjacent to a PCBM results in ultrafast, irreversible quenching (and so in this regard is an upper limit for the diffusion length).

DSC measurements were conducted and analysed in the Materials Department at Imperial College London by Dr. E. Buchaca Domingo, as described in Chapter 2.9. Complete melting of primary crystals as well as melting of the neat materials corresponds to end melting temperatures in the DSC thermograms. Complete analysis regarding the determination of the

enthalpies of fusion, ΔH_f , requires integration of the DSC melting peak and was undertaken by Dr E. Buchaca Domingo.

Transmission optical microscopy was carried out on hot stage that was continuously flushed with nitrogen, in the Materials Department at Imperial College London with the help of Dr. E. Buchaca Domingo.

TAS decays were measured on films under a nitrogen atmosphere. Samples were excited at 520nm with an excitation density of between 3 – 8 μJcm^{-2} .

Film cyclic voltammograms were recorded between +1.5V and -1.5V for each film, employing a 0.1M TBAP in AcN electrolyte. Data was recorded for scan rates of 100 mVs^{-1} , and 10 mVs^{-1} . The counter and reference electrodes were Pt and Ag/AgCl respectively.

4.3 Results

4.3.1 Exciton quenching in polymer / PCBM blends

Probably the simplest evidence for the presence of intimately mixed polymer / fullerene domains in many BHJ films, rather than pure polymer domains, comes from optical data based upon quantitative consideration of polymer PLQ. We start this results chapter by considering the evidence that, for most BHJ devices, structural models based upon the formation of pure polymer and pure fullerene domains appear inappropriate, as determined from PLQ data.

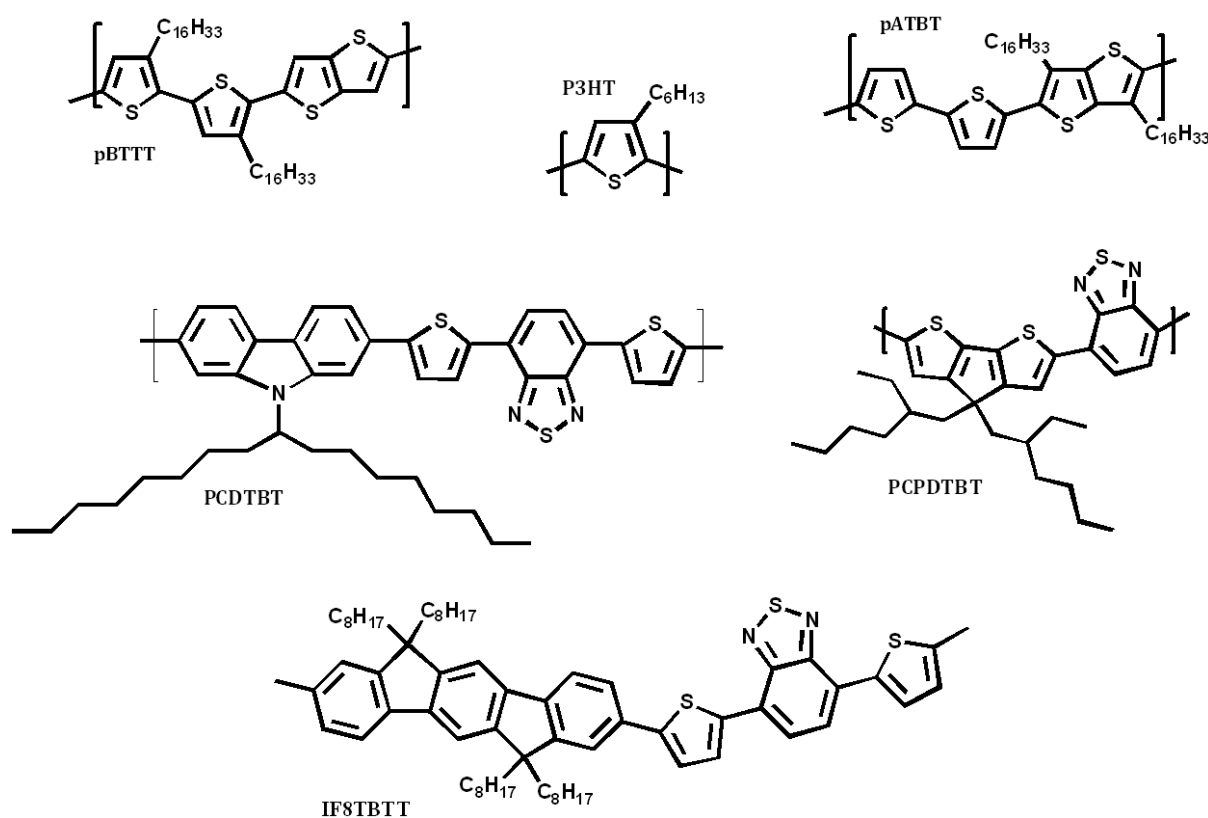


Figure 4.4 – Chemical structures of the polymers investigated in the PLQ study in Figure.4.5.

Exciton quenching was measured for a series of different polymers blended with PCBM, the structures of which are shown in Figure 4.4. These donor polymers include the semi-crystalline or liquid-crystalline donor polymers pBTTT,³⁰ poly(3,6-dialkylthieno[3,2-b]thiophene-co-bithiophene (pATBT)⁴⁷ and P3HT,⁴⁸ as well as the molecularly less ordered polymers poly[2,8-(6,6,12,12-tetraoctylindenofluorene)-co-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiodiazole] (IF8TBT),⁴⁹ PCPDTBT⁵⁰ and PCDTBT.² The latter two polymers are examples of low band gap

polymers currently yielding promising OPV device efficiencies.^{51,52} In each case, the films were excited near the peak polymer absorption, between 520 – 650 nm, as detailed in the experimental section. Typical PL quenching data (i.e.: PL emission data for these blend films with PCBM normalised against the PL of the corresponding neat polymer film) are shown in Figure 4.5 for this range of donor polymers in 1:1 blends by weight with PCBM or PC₇₀BM.

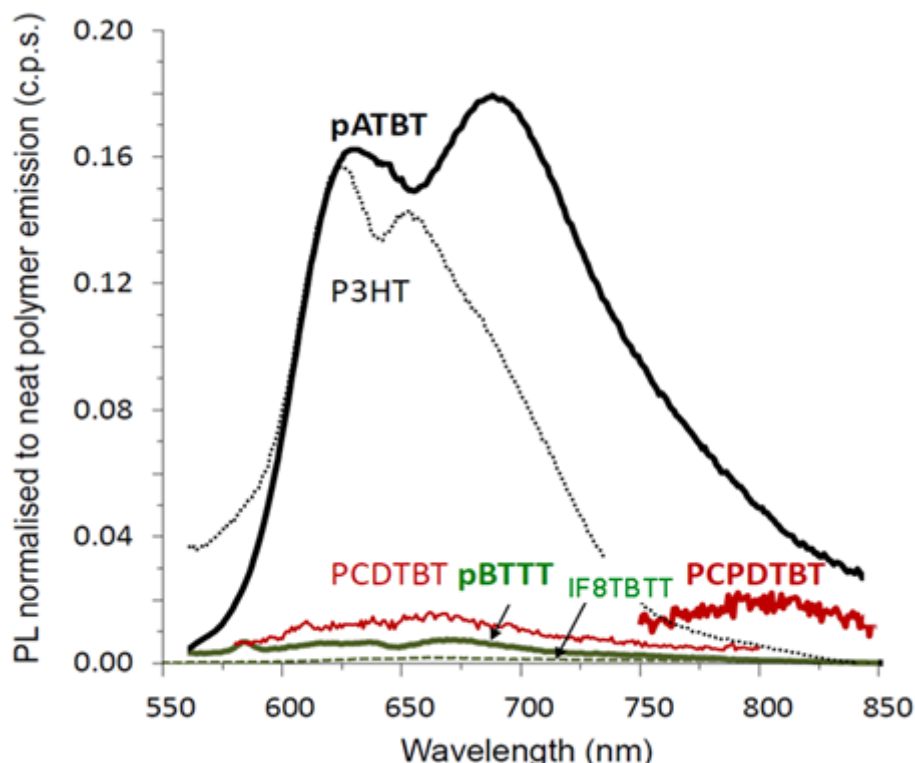


Figure 4.5 – PLQ data for 1:1 polymer:PCBM blend films. Data normalised against PL data for the corresponding neat polymer films. Data is shown for pATBT, pBTTT, P3HT, PCPDTBT, PCDTBT and IF8TBT. It is apparent that all donors very strong PL quenching (>98%) except for the two semi-crystalline polymers P3HT and pATBT.

These PL quenching data can be employed to estimate the typical distance L a polymer exciton diffuses before reaching a quenching site (i.e.: a fullerene) from:

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

Equation 4.1

where PLQ is the fractional PL quenching relative to neat polymer films and L_{ex} the neat polymer exciton diffusion length (defined as the distance an exciton can diffuse within its lifetime in a neat polymer film). See Experimental Section 4.2 for a derivation of L_{ex} , but typical

values for L_{ex} of neat polymer films are 5 – 10 nm.^{53,54} For efficient exciton quenching and charge separation, the mixing between the donor and acceptor should be on a lengthscale shorter than the exciton diffusion length. Ultrafast fluorescence measurements and numerical modelling analysis of polymer / PCBM blends from Haque, Nelson and co-workers have elegantly modelled the exciton diffusion length in PCBM multiadducts (mono, bis and tris – PCBM). The exciton diffusion length in blends of these acceptors with the polymer poly9,9-dioctyl-fluorene-co-N-4-butylphenyl-diphenylamine (TFB) has been shown to be ~ 7.5 nm.⁵⁵ This, however, is greater than the distance between the polymer and fullerene in molecularly mixed blends presented here. Therefore, the exciton diffusion length may not be critical in defining the exciton quenching in some polymer/ fullerene blends.

With the exception of P3HT and pATBT, the polymers studied herein exhibited PL quenching of > 98 %, as is indeed typical for most blend films yielding high OPV device efficiencies.^{25,32} This high PL quenching yields a value for $L \sim 0.9$ nm in these blends with PL quenching of > 98 %, as determined using Equation 4.1. We note that this length scale is similar to the size of a monomer unit of most of these polymers, and of the diameter of a single fullerene. As such, we conclude that for these blend films, polymer excitons must be generated effectively directly adjacent to a PCBM molecule, indicative of close molecular mixing of virtually all of the polymer in the film with PCBM on the < 1 nm length scale. This PL analysis of molecularly mixed phases in systems with near unity quenching may extend further than just the polymers measured in Figure 4.5. This has been demonstrated from other analyses in literature showing fine mixing of the polymer / PCBM and efficient PLQ.^{56,57}

The notable exceptions to this behaviour are the two semi-crystalline polymers P3HT and pATBT, which exhibit PLQ of only ~ 0.85 , indicative of an average length scale for exciton diffusion within the blend film of several nanometers, consistent with observations that blend films with these polymers feature relatively well ordered, phase pure crystalline polymer domains.⁵⁸ This incomplete PL quenching has also been demonstrated in other semi-crystalline polymers, including poly(thiazolothiazole)(PSOTT) from alternative analyses within the group. XRD analysis of this material indicates that PSOTT is a relatively crystalline polymer, which when blended with PCBM, retains its crystalline structure, as determined from the full width half maximum (FWHM) of the lamella packing peak. Analyses of this peak indicate that the degree of crystallinity, as determined from the FWHM, may correlate with the extent of the PLQ in polymer / fullerene blends. These data, for semi-crystalline polymers blended with PCBM, indicate that complete PLQ may not be essential for device operation.

The key conclusion of these PL quenching data is that for many polymer / PCBM blend films, and particularly for more amorphous polymers, essentially all the polymer in the film is intimately mixed on a molecular length scale with at least a certain fraction of the PCBM. This conclusion is in conflict with many current models describing the polymer / fullerene morphology describing the morphology as a function of two pure domains. If this is indeed the case, the photogenerated excitons will be generated and delocalised across the intimately mixed polymer / fullerene interface.

4.3.2 Investigation into fullerene concentration in pBTTT:PCBM blends

The following section is primarily focused on the pBTTT:PCBM blend system, investigating the effects of varying the donor / acceptor compositions and the changes in morphology along with the resulting effect on charge generation and device performance.

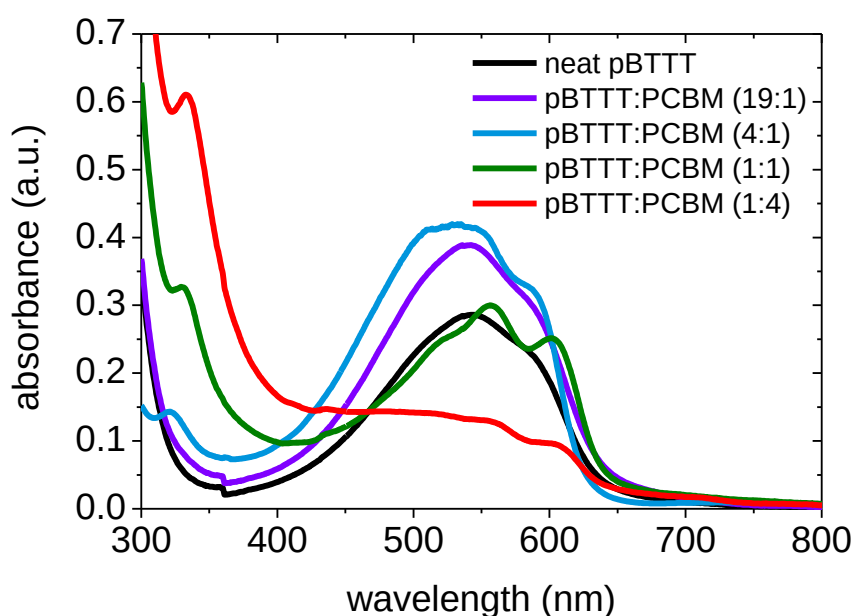


Figure 4.6 - Ground state absorption for neat pBTTT and pBTTT:PCBM films as a function of blend compositions (19:1, 4:1, 1:1 and 1:4 pBTTT:PCBM).

The ground state absorption of neat pBTTT and pBTTT:PCBM blends are shown in Figure 4.6. The neat pBTTT film (black) shows a broad absorption with a peak at ~540 nm, with no observable fine structure. The addition of 50 wt % PCBM induces a small shift in the peak absorption to 560 nm. A low energy peak is clearly visible in the 1:1 blend (green), however in the 19:1 blend (purple) there is the onset of the peak formation. The lower energy shoulder at ~

600 nm becomes more pronounced with increasing PCBM concentration, possibly indicative of increased molecular order. The increased molecular interactions between the polymer and PCBM arise as the PCBM molecules intercalate between the polymer side chains, forming a co-crystal, as has been reported elsewhere by McGehee and co-workers, and shown in Figure 4.3.³⁰

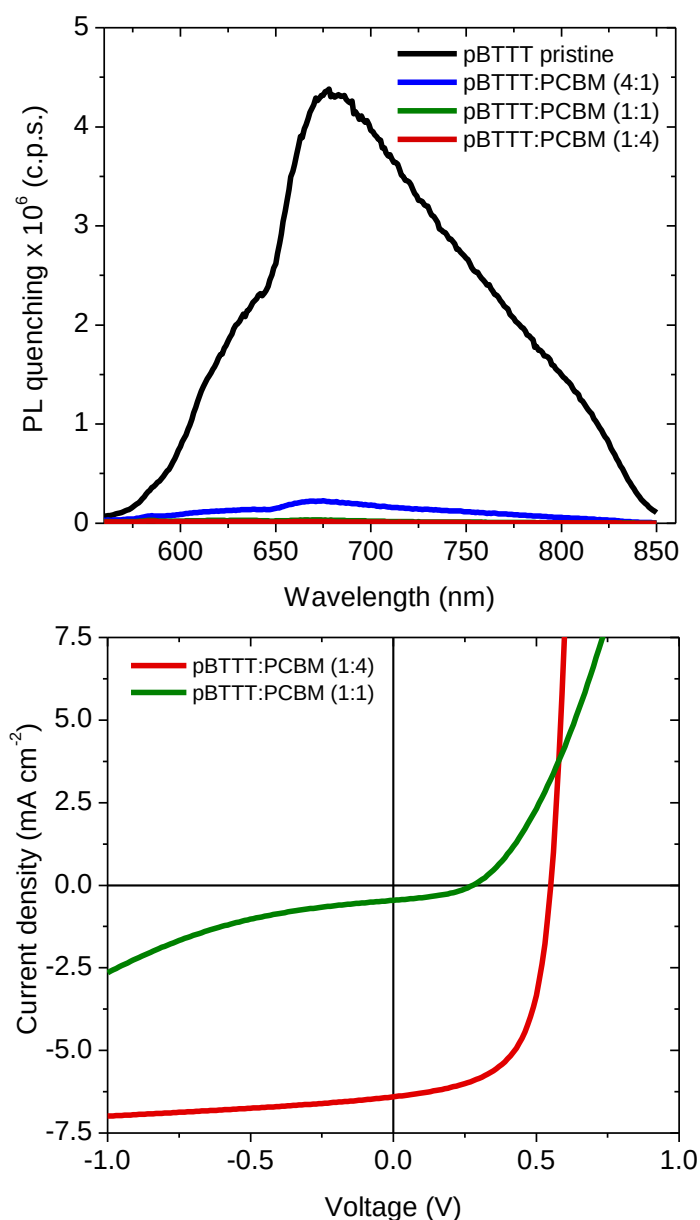


Figure 4.7 - a) PLQ of neat pBTTT (black) and blends of pBTTT:PCBM. The 4:1 pBTTT:PCBM blend (blue) is 95% quenched compared to that of the neat pBTTT film. 1:1 (green) and 1:4 (red) blends are >99 % quenched compared to the pristine pBTTT. b) J-V characteristics for a 1:1 (green) and 1:4 (red) pBTTT:PCBM blend devices under 1 sun illumination. Devices fabricated and tested by Dr. E. Buchaca Domingo.

The PL quenching of the polymer exciton, in Figure 4.7a, shows efficient quenching of the photogenerated excitons in all of the polymer / fullerene blends tested here. The PL quenching of the exciton with the addition of 20 wt% PCBM is 95% and for both 50 wt% and 80 wt % PCBM, the PL quenching is > 99 %. This behaviour is indicative of a highly intermixed blend system, on the order of the molecular scale, in agreement with the proposed formation of a molecularly ordered co-crystal in this blend. The J-V curves for blends of pBTTT:PCBM are shown in Figure 4.7b for two compositions, 1:1 (green) and 1:4 (red) devices. The power conversion efficiencies for these devices for the 1:1 and 1:4 are 0.05 % and 2.12 % respectively. The J_{sc} is increased by over an order of magnitude from 0.43 mAcm^{-2} to 6.44 mAcm^{-2} and the V_{oc} is doubled from 0.28 V to 0.55 V with the increase in PCBM concentration from 50 wt% to 80 wt%. These improvements in voltage and current lead to a 30 % increase in the FF, to 0.60 with increased the PCBM content, consistent with previous reports by McGehee and co-workers who see a pronounced increase in the photocurrent and FF in 1:4 blends compared to 1:1 blends.³²

One possible explanation of these device characteristics is inefficient quenching of the photogenerated excitons in the 1:1 blends, only as the PCBM loading is increased does the exciton quenching become sufficient for device operation. However, this origin of the requirement for high PCBM loading for efficient devices is inconsistent with the PL quenching reported in Figure 4.7a. This PL data suggests that it is not poor quenching of the excitons that is limiting device performance, but some other loss mechanism that is hindering the charge formation or the collection of dissociated charges. The increase in device efficiency from increasing the PCBM loading in these devices is unlikely to arise from an increase in charge generation as a result of increased photon absorption, as seen in the ground state absorption spectra in Figure 4.6. The increase in the PCBM content within the blend leads to an increase in absorption at $\sim 350 \text{ nm}$, characteristic of the PCBM ground state absorption, however there is a decrease in the peak absorption at $\sim 520 \text{ nm}$ with increasing PCBM loading from 50 wt% to 80 wt%.

We now turn to address other reasons why the high PCBM concentration is required in this blend composition. Further studies were conducted in conjunction with the Materials Department at Imperial College London, to investigate the material properties of these blends. Thermal analyses of the neat materials and the blends are shown in Figure 4.8. These data were taken with the help of Dr Ester Buchaca Domingo who completed the full analysis of these data.

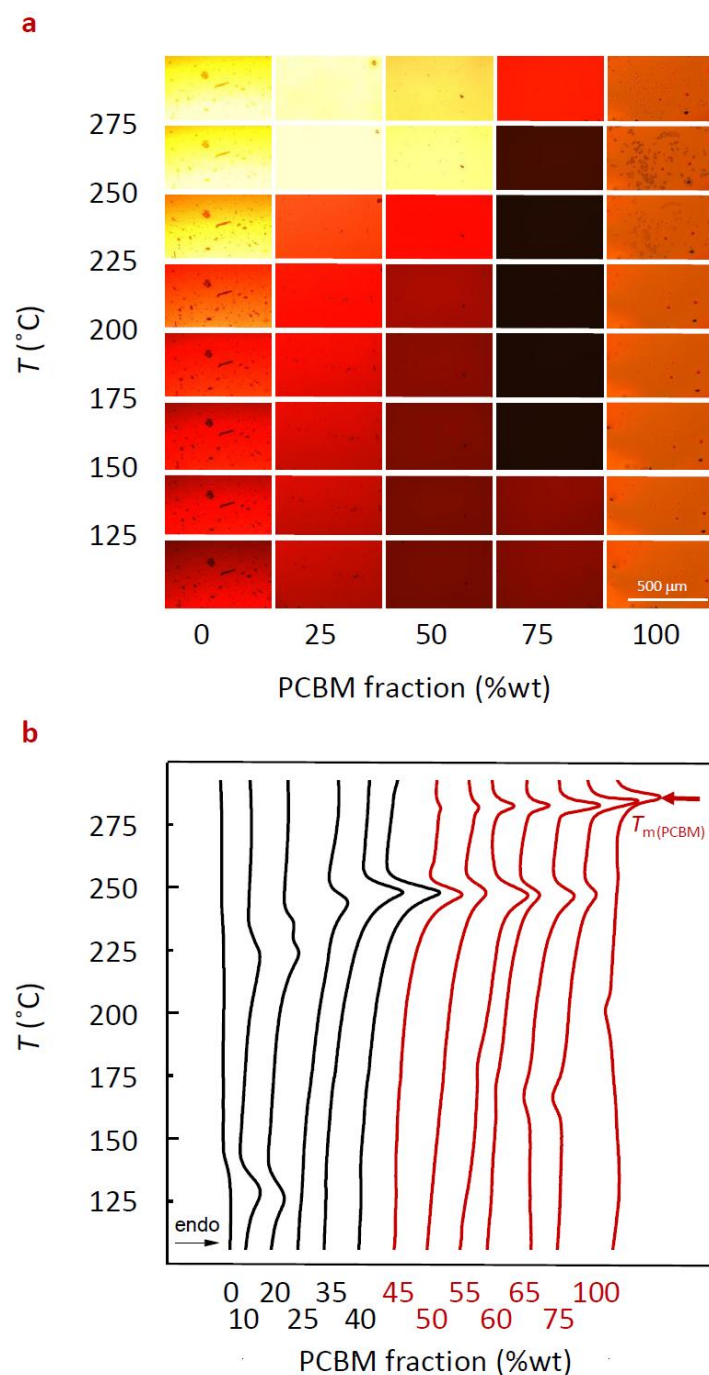


Figure 4.8 – a) Optical microscopy images of different blend compositions of pBTTT:PCBM, including the neat materials as a function of temperature. The melt of the polymer is observed at $\sim 225^{\circ}\text{C}$. b) DSC melting endotherms for the first heating of pBTTT:PCBM blends with varying blend compositions. The melt of the crystalline PCBM peak is observed at $\sim 280^{\circ}\text{C}$, and the melt at $\sim 230^{\circ}\text{C}$ is attributed to that of the bimolecular co-crystal.

Optical microscopy, shown in Figure 4.8a, of the neat and blend films, indicates an on-set of melting of neat pBTTT and the pBTTT/PCBM co-crystal at, respectively, $\sim 230^{\circ}\text{C}$ and $\sim 250^{\circ}\text{C}$. These data provide clear evidence that at high PCBM content, the excess fullerene that cannot intercalate within the pBTTT/PCBM co-crystal phase separates into PCBM domains, in

agreement with previous observations.³⁰ In addition, the intermixed phase comprises a well-defined pBTTT/PCBM co-crystal, thereby facilitating our structural analyses of such blend films.³⁰

Figure 4.8b shows the temperature / composition behaviour for pBTTT:PCBM films determined from the DSC data (first heating thermograms). These data show the melt of the pBTTT/PCBM co-crystal at ~ 240 °C and the melt of crystalline PCBM domains at ~ 280 °C in agreement with the optical thermal analysis in Figure 4.8a. Of particular note, the DSC data on blends with a content of PCBM ≥ 44 wt% (red lines) show a clear melting endotherm for PCBM, assigned to the presence of crystalline PCBM domains in blend films for PCBM compositions. This indicates that in low concentration PCBM blends there are no large domains of pure PCBM but that the PCBM is incorporated into the co-crystal. This observation is indicative of polymer exciton quenching occurring within the finely intermixed pBTTT/PCBM phase, independent of the formation of separate PCBM domains above this threshold, correlating to the PL quenching data in Figure 4.7a. The thermal analysis presented above, along with the PL quenching show the high level of intermixing on the molecular scale, which appears to be detrimental to device performance, as seen in Figure 4.7b.

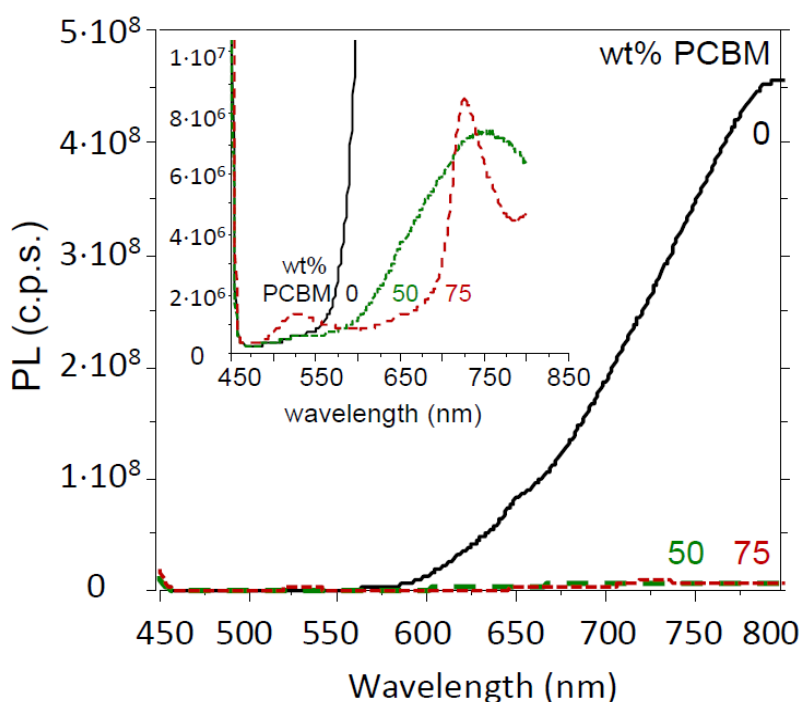


Figure 4.9 – Photoluminescence quenching of pBTTT:PCBM blends following excitation at 430 nm. Inset is a magnification of the data, highlighting the differences in PCBM emission with crystallisation.

The formation of crystalline PCBM domains can also be observed using PL, selectively exciting the PCBM. Figure 4.9 shows the PLQ following excitation of the PCBM at 430 nm. The main figure shows efficient quenching of the PCBM excitons with PL > 98 % relative to that of the neat pBTTT film. However, it has been previously shown that PCBM aggregation can be monitored by the appearance of a new photoluminescence band at ~ 520 nm.⁵⁹ This band is clearly observed in this pBTTT:PCBM blend film with 75 wt% PCBM, but not at lower PCBM concentrations, as shown in Figure 4.9, again indicative of a composition threshold for PCBM aggregation. The strong PL quenching and the materials analysis presented above show efficient quenching of excitons in these blends however, it is only those blends that contain some a significant crystalline PCBM content (in blends with > 66 wt% PCBM) that show correlates with a higher photocurrent. We now turn to investigate the charge generation in pBTTT:PCBM blends, employing TAS to monitor the formation of long lived, dissociated charges.

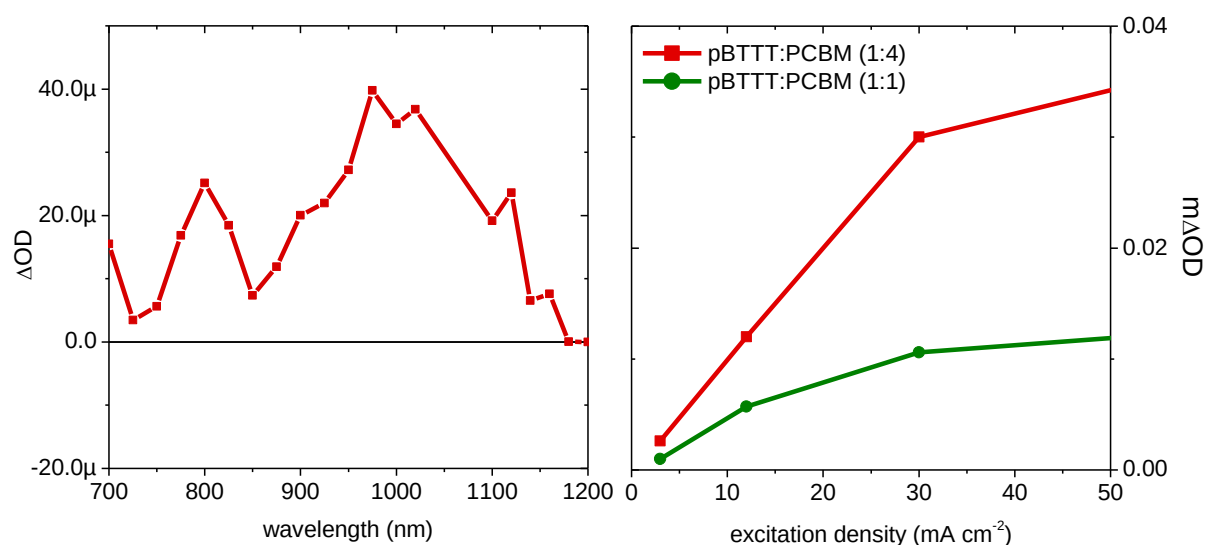


Figure 4.10 – a) TAS spectrum of pBTTT:PCBM (1:4) at 1μs in an inert atmosphere. A broad peak transient peak is observed between 900 – 1050 nm. b) Excitation density dependence of charge generation for 1:1 (green) and 1:4 (red) pBTTT:PCBM blends.

The transient spectra, taken as a function of wavelength for pBTTT:PCBM (1:4) is shown in Figure 4.10a. Initial investigations at 1μs show the appearance of two peaks; a broad peak between 900 – 1100 nm and a narrower one at ~ 800nm. This peak was confirmed not to arise from triplets by oxygen quenching studies, which showed no change in the decay dynamics when the samples were exposed to an oxygen rich environment. Excitation density dependent data are shown in Figure 4.10b for two pBTTT:PCBM blends (1:1 and 1:4) at 1 μs. Both of the

blends studied show a linear increase with excitation density up to $30 \mu\text{J cm}^{-2}$, before deviating at higher light intensities. Therefore, following these TAS analyses, all samples herein were excited out with typical excitation densities of $5 \mu\text{J cm}^{-2}$, and the transient species was probed at 980 nm.

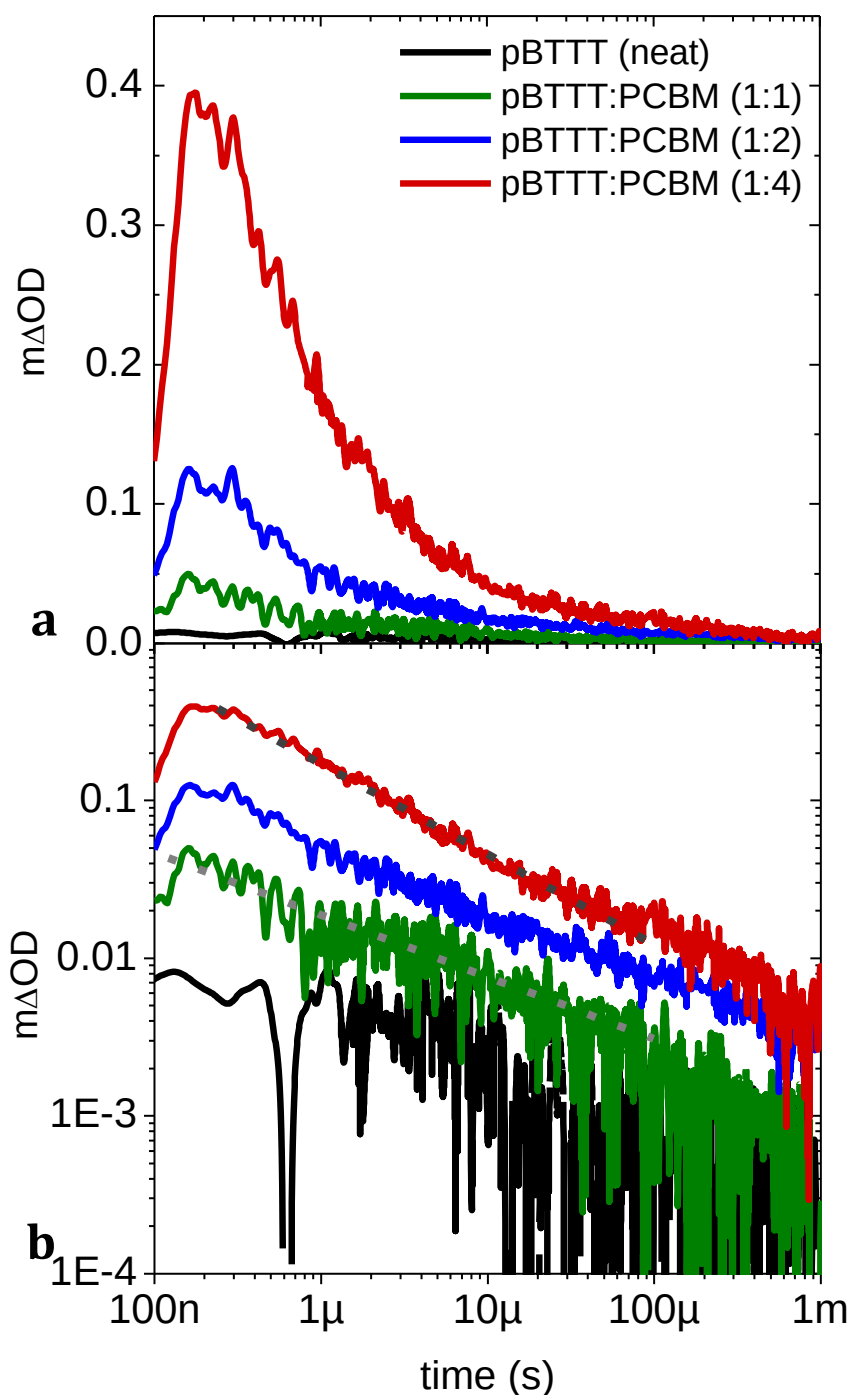


Figure 4.11 - TAS decays of neat pBTTT (black) and blends with increasing PCBM content (detailed in the figure). a) Shows the clear composition threshold with $> 50 \text{ wt\%}$ PCBM required for charge generation. b) The same data displayed on a log-log plot to show the power law decay kinetics of these blends.

The TAS kinetics, probed at 980 nm, for pBTTT films blended with PCBM are shown in Figure 4.11 as a function of blend composition from 100 ns – 1 ms, normalised for photon absorption. These data show a 10 fold increase in the generation of dissociated charges by increasing the PCBM concentration from 50 wt% (green) to 80 wt% (red). The order of magnitude increase in charge generation of dissociated charges from 50 wt% PCBM to 80 wt% PCBM is consistent with the increase in device J_{sc} observed in Figure 4.7b. The observed transients in Figure 4.11b on a log-log scale, all exhibit power law decays, as shown for 1:1 and 1:4 blend, on the 100 ns – 100 μ s timescale. For the 1:1 blend, $\alpha = 0.40$ and for the 1:4 blend $\alpha = 0.55$. These decays are characteristic of non-geminate recombination of dissociated polarons and not the geminate recombination of bound charges. The slightly faster decay exhibited by the 1:4 blend may be attributed to the higher charge densities in this composition compared to that in the 1:1 blend, which lead to an increased probability of recombination as the number of free charges increases.

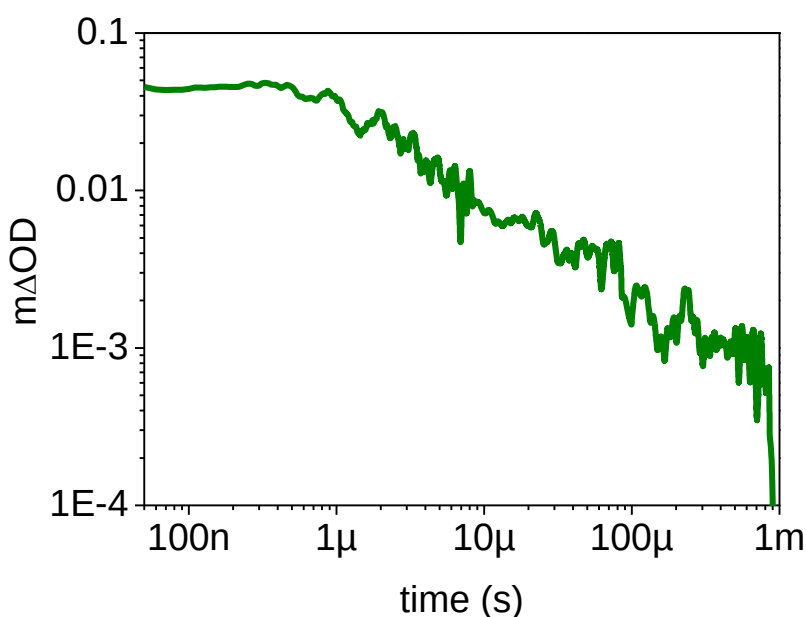


Figure 4.12 – The TAS decay kinetics for a 1:1, pBTTT:PCBM blend film showing a plateau in the generation of the dissociate charges on the nanosecond timescale before a power law decay.

The charge generation in these blends at earlier timescales was investigated from 50 ns onwards, as seen in Figure 4.12, which shows the TAS decay for a 1:1 pBTTT:PCBM blend. The power law decay from 1 μ s, as observed previously in Figure 4.11b, is still of the same amplitude, $\alpha = 0.6$. However on the early time scales, a plateau in the data is observed from the start of the experiment at $\sim 50 - 800$ ns. The plateau is indicative of dissociated charge generation, and not that of the bound geminate pairs. This indicates that the geminate

recombination happens faster than our time resolution and can therefore not be fully investigated.

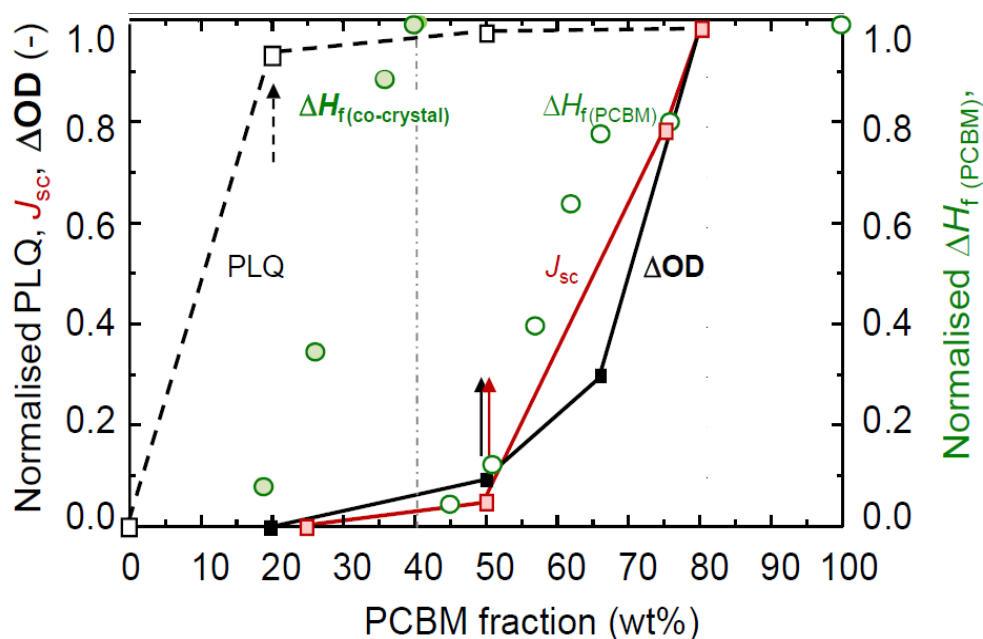


Figure 4.13 – The compositional dependence of the structural and functional data collected for pBTTT:PCBM blends as a function of PCBM concentration, including data from J_{sc} , ΔOD , PLQ, and ΔH_f .

Figure 4.13 overlays the composition dependence of the structural and functional data for pBTTT:PCBM blend films. It is apparent that both short circuit photocurrent (J_{sc}) and dissociated polaron yield (ΔOD) rapidly increase once the PCBM content exceeds the eutectic composition of the co-crystal/PCBM binary (~ 44 wt% PCBM); i.e. at compositions phase-pure primary PCBM crystals start to develop, as seen previously in the DSC data in Figure 4.8b. This figure shows that there is a clear correlation between the enthalpy of fusion ΔH_f (PCBM) deduced from the corresponding PCBM melting endotherms (indicating the amount of crystalline PCBM present in the blend films) and our functional assays J_{sc} and ΔOD , from devices and films. In contrast to the development of J_{sc} and ΔOD , polymer PL quenching saturates at a relatively low PCBM composition, and correlates rather with co-crystal formation. These data confirm that whilst PLQ is a good assay of the exciton dissociation, it does not necessarily correlate with device performance as it does not distinguish between the resulting geminate and non-geminate recombination.

4.3.3 Formation of fullerene domains in donor / acceptor blends

The formation of PCBM domains in pBTTT:PCBM blends has been shown to be vital for device performance. The importance of the formation of relatively pure PCBM in such bulk heterojunction blend films is now considered. One proposed reason for the improved charge generation in blends with a high PCBM loading, was a change in the PCBM electron affinity that occurs as aggregated or crystalline domains are formed. To investigate the role of the fullerene crystallinity in blends and whether this is specific to PCBM, further data were obtained with alternative fullerenes; the pyrazolinofullerene used in previous studies of charge recombination²⁷ and ICBA, both blended with polystyrene (PS). In order to investigate such a shift in PCBM electron affinity (E_A), film CV was performed as a function of film composition with the corresponding fullerene structure, as shown in Figure 4.14.

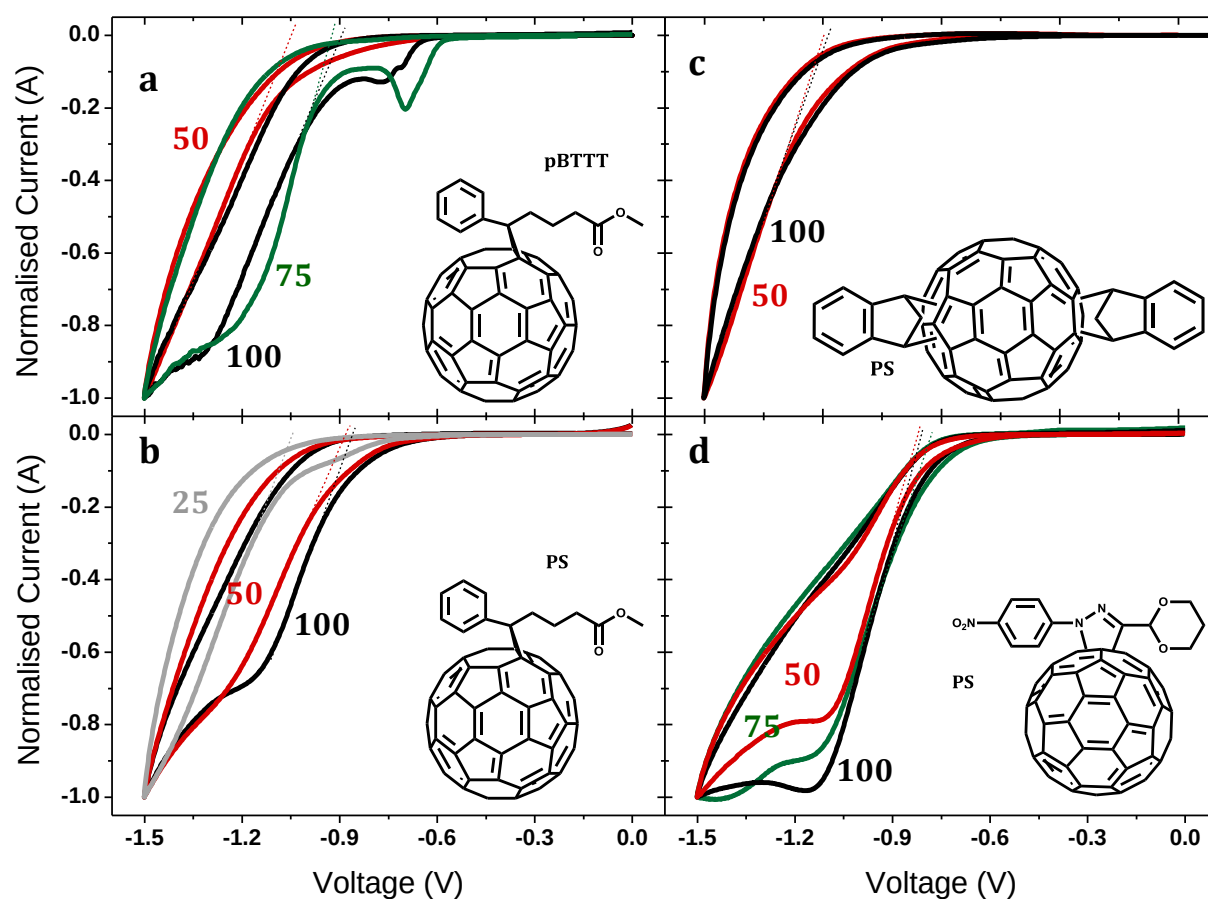


Figure 4.14 – CVs of a) pBTTT:PCBM, b) PS:PCBM, c) PS:ICBA and d) PS:C60-2 as a function of fullerene concentration. The films were used as the working electrode with Ag/AgCl and Pt used as the reference and counter electrodes, respectively. The structure of the fullerene is shown for each experiment with the weight percentage detailed on each figure, along with the name of the polymer used.

The CVs in Figure 4.14, show the reduction potentials, between -1.5 V to 0 V, for four polymer/fullerene blends systems as a function of blend composition. Data has been normalised against the maximum current at -1.5 V. The left hand panels, a) and b) are CVs of two blends containing the most widely used fullerene PCBM; pBTTT:PCBM and PS:PCBM, respectively. On the right hand side the alternative fullerenes have been investigated with PS; c) is PS:ICBA and d) is PS:C60-2. PS was chosen as the alternative polymer in b), c) and d), as it known that PS disrupts the PCBM aggregation when blended in films,⁵⁹ although for polystyrene this results in a finely intermixed amorphous film rather than the co-crystals observed for pBTTT:PCBM. For polymer both systems blended with PCBM, in a) and b), there is a change in the reduction potential with varying blend composition. It is apparent from these CV data that PCBM's crystallisation observed at high PCBM content is correlated with a conspicuous $\sim 100 - 200$ meV increase in its electron affinity, observed in a) from blends with 50 wt% PS to neat PCBM. This shift is observed for blends with both polymers (pBTTT and PS) blended with PCBM and is therefore clearly not specific to pBTTT/PCBM binaries but is rather a general property of PCBM. Consistent with this observation, no (< 20 meV) shift of electron affinity with blend composition was observed with either ICBA or C60-2 fullerenes, in Figure 4.14c+d. For both of these fullerenes, the onset of the CV reduction potential waves at 0 A does not change as a function of blend composition, unlike the data presented for both PCBM blends in Figure 4.14a+b. The difference in E_A between the neat material and the 1:1 blend is 0.01 A and 0.03 A for ICBA and C60-2, respectively. This apparent lack of change in E_A for blends with either of these fullerenes is indicative of no significant change in the crystallinity of these fullerenes when blended with PS. This indicates that the crystallisation of PCBM in organic blends may be unique to this fullerene and is not observable in other fullerene blends. To investigate this effect further, PLQ following fullerene excitation has been studied.

Following the PL analysis presented in Figure 4.9 investigating the PCBM emission in pBTTT:PCBM blends, the same analysis was carried out as a function of PS concentration in all three fullerenes, shown in Figure 4.15. This is to verify whether the observed change in E_A can be correlated with a change in the PCBM crystallinity. The alternative fullerenes (ICBA and C60-2) both showed only a relatively weak 520 nm PL band independent of polystyrene addition, as observed in Figure 4.15b+c. These data have been normalised to the low energy peak at ~ 720 nm to clearly show the strength of the emission band at ~ 520 nm relative to that of the low energy band. This band at ~ 520 nm has been shown previously in PCBM⁵⁹ and has been attributed to weak intermolecular coupling, even for the neat fullerene film, indicative of PCBM crystallisation. These observations are consistent with a recent report of a shift in an interfacial

charge transfer state emission with PCBM composition in a PPV:PCBM blend film, with this shift not been observed if PCBM was replaced with the alternative methanofullerene DPM-12.⁴⁵

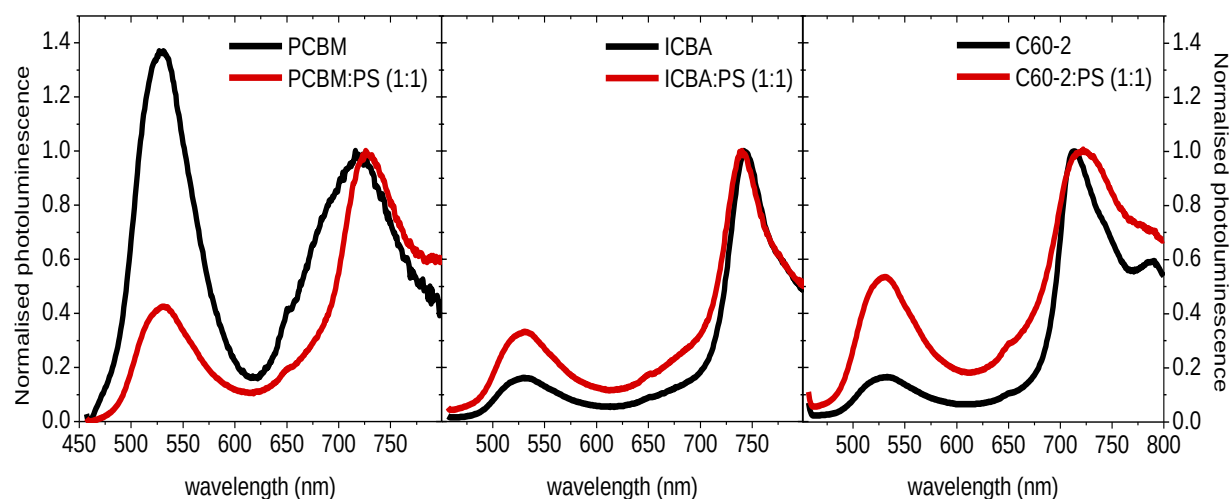


Figure 4.15- PL emission spectra of a) neat PCBM and PS:PCBM (1:1), b) neat ICBA and PS:ICBA (1:1) and c) neat C60-2 and PS:C60-2 (1:1) following excitation of the fullerene at 430 nm.

4.4 Discussion

The results shown above have shown the PLQ for a variety of polymer / PCBM blends, before further investigation into the charge generation and nanoscale morphology of pBTTT:PCBM blends and finally showing the change in the reduction potential of different fullerenes and the effects of blending with polymers.

The PLQ results presented for a variety of 1:1 polymer / PCBM blends, including pBTTT:PCBM have highlighted the different dependencies of the blend composition on the degree of PLQ. The correlation between a high (> 95 %) PLQ and fast charge separation showing a significant degree of intermixing between the two materials has been reported elsewhere.⁶⁰ For many of the polymer / PCBM blends investigated here, exciton diffusion is not a key requirement in these blends, as many of the excitons are generated at the donor / acceptor interface, as indicated by the efficient PLQ shown in Figure 4.5. These studies highlight the requirement for an adjustment in device models, away from the two phase models such as that suggested in Figure 4.1b, towards ones that consider molecular mixing of the two materials as well as the formation of pure domains.

The clear composition threshold for the formation of crystalline PCBM domains shown previously in the thermal analysis in Figure 4.8, coincides with thresholds for both charge photogeneration and photovoltaic performance, as observed in Figure 4.11 and Figure 4.8b. It is apparent from the TAS data in Figure 4.11 that there is a clear composition threshold for the formation of these dissociated charges, with significant long lived charge generation only being observed for PCBM compositions ≥ 50 wt%. The low yields of dissociated polarons observed for films with low PCBM content is assigned to rapid (< 10 ns) electron / hole recombination within the pBTTT/PCBM co-crystal, consistent with previous observation of rapid charge recombination within intimately mixed polymer / fullerene blends.²⁷ Optical excitation of this single phase, intimately mixed film resulted in efficient photoluminescence quenching but also rapid recombination of the photogenerated charge carriers (on 100 ns and faster timescales), thereby preventing photocurrent generation. Similar conclusions have been reached from studies where the donor and acceptor are covalently attached, thus ensuring molecular scale mixing of donor and acceptor, and again typically fast recombination.⁶¹⁻⁶³

The increase in yield of dissociated polarons at PCBM compositions ≥ 50 wt% is qualitatively consistent with electron transfer to the crystalline PCBM domains, as has been suggested previously.^{29,31} However the magnitude of the increase in charge carrier lifetime resulting from the formation of these domains (from < 10 ns at low PCBM content to > 1 μ s in the presence of the crystalline PCBM domains) is striking. If we assume a simple model of random electron diffusion between the pBTTT/PCBM co-crystal and the co-existent crystalline PCBM domains, then we would expect an increase in recombination lifetime for a 1:4 blend film of at most fourfold relative to the 1:1 blend film (as the proportion of PCBM in the mixed co-crystal phase changes from ~ 100 wt% to ~ 25 wt%). In other words, if electrons were free to diffuse between fullerenes in the co-crystal and pure PCBM domains, then such electrons would not be clearly spatially separated from photogenerated polymer polarons, and as such rather fast electron / hole recombination would be expected.

One possible explanation for the observed dramatic (at least 100 fold) retardation of recombination kinetics would be that the crystalline PCBM domains are energetic sinks for electrons. This could correspond to the crystalline PCBM domains exhibiting a higher electron affinity than the pBTTT/PCBM co-crystal, with this difference in electron affinity providing the energetic driving force for spatial separation of photogenerated electrons and holes (an alternative explanation could be formation of an interface dipole). Quantitatively a 100 meV shift in electron affinity with PCBM crystallisation would shift the electron equilibrium between co-crystal and crystalline PCBM domains 50 fold, enough to explain the transient data shown in Figure 4.11.

We conclude from this CV data, that the crystalline PCBM domains observed in pBTTT:PCBM blend films at high PCBM compositions indeed exhibit a 100 – 200 meV shift in their electron affinity relative to non-aggregated PCBM. Most importantly, the magnitude of the shift in PCBM electron affinity reported herein is sufficient to achieve a spatial separation of photogenerated electrons and holes, consistent with the observation of long lived, dissociated charge carriers at high PCBM blend compositions, as seen in Figure 4.14, and resulting in the observed composition dependent onset of photocurrent generation. This change in E_A upon aggregation of PCBM is also clearly shown in blends with PS, shown in green. However, both ICBA (black) and C60-2 (blue) show no such change with the addition of PS. The E_A of both of these materials remains relatively unaffected by the addition of PS, indicative of no significant change in the crystallinity of these materials with PS. Therefore, when considering a fullerene for use as an acceptor material in a blend, it is not the neat material's E_A that must be considered, rather, that of the electron affinity of the fullerene when blended with the donor.

Piersimoni *et al.* have shown a clear difference in the V_{OC} dependence of MDMO-PPV blends with two different fullerenes.⁴⁵ Blends with PCBM as the acceptor show a decrease in V_{OC} as the fullerene content is increased, whilst the alternative fullerene, DPM-12, shows no change in V_{OC} as a function of blend composition. The decrease in V_{OC} observed for high PCBM content has been attributed to an increase in the fraction of PCBM nanocrystals and increased phase separation, which in turn appears to lower the CT state energy. However, DPM-12 blends show no change in V_{OC} as there is no observable change in fullerene crystallisation at different DPM-12 concentrations and in turn there is no change in the CT energy. These data corroborate the hypothesis presented here for PCBM crystallisation acting as the driving force for charge separation in polymer / PCBM blends, which is not observed for the other fullerene investigated here.

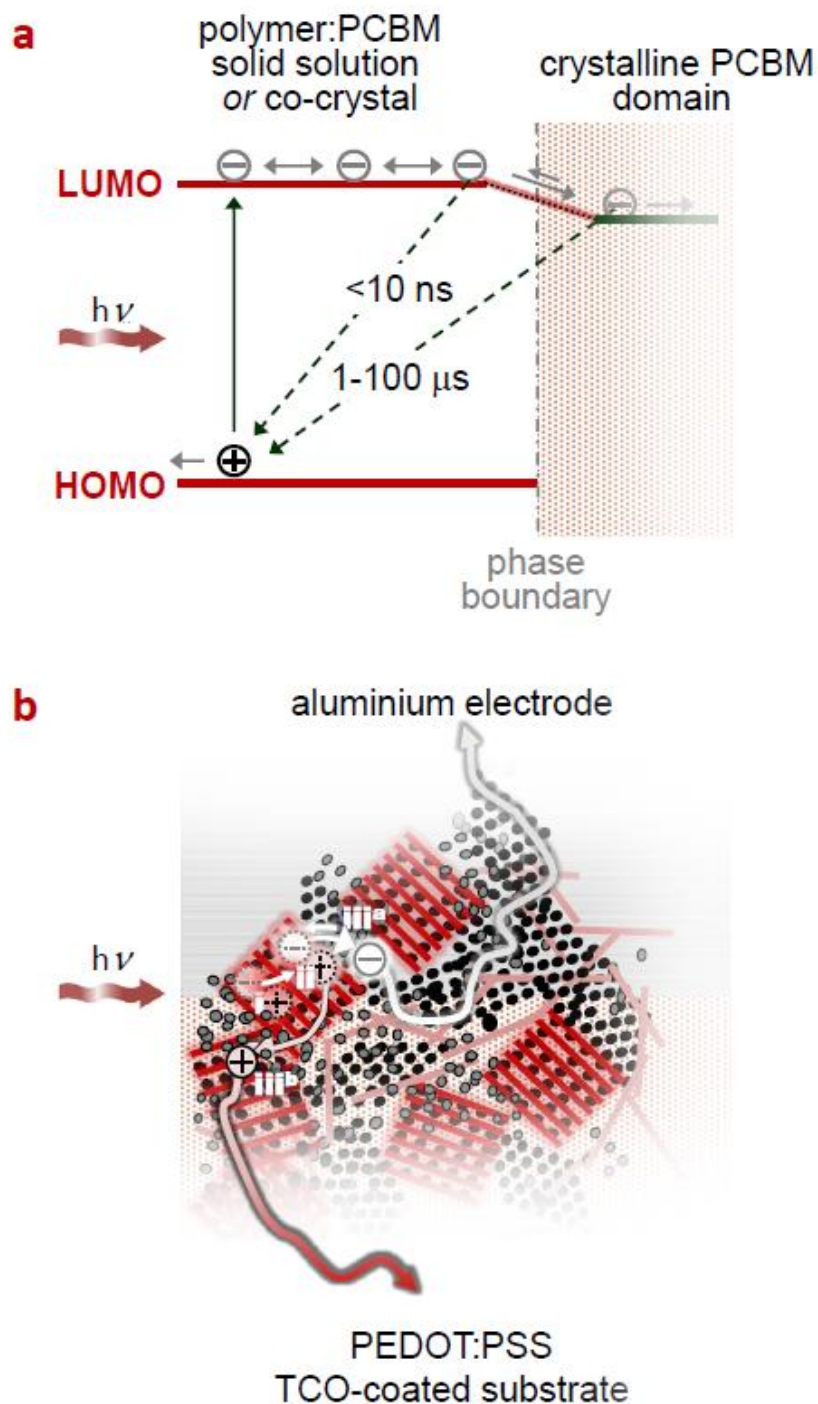


Figure 4.16 – a) Proposed functional model of charge formation within blend systems. The photogenerated charges are created in the mixed polymer:PCBM phase, which may undergo rapid ($< 10 \text{ ns}$) geminate recombination. If the charges find a crystalline PCBM domain with a lower lying LUMO, they may undergo non-geminate recombination of the free charges or, preferentially, are collected by the electrodes as electrical charge. b) Schematic detailing the structure of a pBTTT:PCBM blend. The red tubes are the pBTTT and the black circles are PCBM. The intercalated bimolecular crystal is shown, along with the crystalline PCBM regions. Excitons are generated in the bi-molecular crystal, split and then if near a PCBM cluster, will be sufficiently spatially separated and may be collected at the electrodes.

Figure 4.16 summarises our conclusions concerning the structure and function of the BHJ films studied herein. Our model is based upon the formation of a finely intermixed polymer / fullerene phase, with excess fullerene segregating from this intermixed two-component phase to form relatively pure, crystalline fullerene domains. Functionally the model is based upon light absorption and exciton quenching within the intermixed polymer / fullerene phase, with the fine mixing of polymer and fullerene in this phase resulting in no requirement for exciton diffusion. We note that Coulomb attraction of photogenerated electrons and holes is likely to significantly impact upon the behaviour of these charge carriers within this mixed phase, including the formation of CT states, as has been widely discussed elsewhere.⁶⁴ Photogenerated electrons then diffuse to the interface between the two-component phase and crystalline PCBM domains (either as dissociated electrons, or as mobile charge transfer states), where the difference in fullerene electron affinity between the two phases stabilises the spatial separation of electron and holes, enabling charge separation with a lifetime sufficient for charge collection. Subsequently the charges are transported to the device electrodes, with electrons most probably travelling through the PCBM domains and holes through the mixed polymer / fullerene phase.

The key component of our model is our observation that relatively pure, crystalline fullerene domains are formed which are of higher electron affinity than the finely intermixed polymer / fullerene phase. We note that the mechanistic origin of this high electron affinity is unclear; as it appears to be rather specific to PCBM, it is more likely to result from particular intermolecular interactions rather than simply from the larger dielectric constant typically reported for fullerenes compared to donor polymers.⁶⁵ We note in this context that alternative fullerenes investigated for OPV applications, such as the pyrazolinofullerene studied herein, typically show less tendency than PCBM to crystallise, and therefore most probably display relatively invariant electron affinities within such blend films (as evidenced by Figure 4.14, right hand panels). This may explain why attempts to use such fullerenes with alternative, molecularly relatively unordered donor polymers, have been relatively unsuccessful to date.⁷

The formation of crystalline PCBM domains has been shown to increase the fullerene E_A , however, consideration of the donor crystallinity has not been investigated in this chapter. Whilst ICBA, does not show a tendency to form crystalline domains itself, its success with P3HT may arise from the polymers ability to crystallise instead. In this instance, P3HT's semi-crystalline nature may be the driving force required to facilitate charge separation that is otherwise hindered by the high levels of molecular mixing in polymer / ICBA blends. As such, the tendency of PCBM to form crystalline domains with a higher electron affinity may be a key reason behind its widespread success in OPV devices, especially with amorphous polymers.

Much of the data supporting this model were obtained herein for pBTTT:PCBM blend films. However, it appears likely that this model may be applicable to a broad range of OPV materials systems. The formation of an intimately mixed polymer / PCBM phase appears to be general to many donor polymers we have studied, as evidenced by our polymer PLQ data, with the notable exception of polymers which show strong tendency to form pure, crystalline polymer domains, such as P3HT and pATBT. Furthermore the formation, at high PCBM compositions, of relatively pure and crystalline PCBM domains with an enhanced electron affinity is clearly not specific to pBTTT/PCBM blend films, as we observe a similar shift in electron affinity with an amorphous, non-conjugated polymer (polystyrene). We note that previous studies have also reported a composition threshold for the formation of crystalline or aggregated PCBM domains in blend films with other donor polymers.²⁶ We furthermore note that we have also previously observed a similar PCBM composition dependence of ΔOD , J_{sc} and PLQ for an alternative, molecularly relatively unordered polymer, IF8TBTT, with both ΔOD and J_{sc} increasing markedly above a specific threshold PCBM composition.⁴⁹ As such, whilst pBTTT may be unusual in forming a polymer / PCBM co-crystal, the concept of a phase segregated blend structure comprising an intimately mixed polymer / PCBM phase (either as a co-crystal or an amorphous solid solution⁶⁶), and a relatively pure single-component, crystalline PCBM phase, may be applicable to many of the polymer / PCBM films currently of interest for high efficiency OPV devices. This includes the polymers P3HT, MDMO-PPV¹³ and Si-PCPDTBT,¹¹ which have all shown a significant degree of mixing between the polymer and PCBM in addition to some larger phase segregation between the two materials.

We note that the success of P3HT as a donor polymer in BHJ solar cells has been widely suggested to result, at least in part, from its strong tendency to form relatively pure crystalline polymer domains that are interconnected through molecularly less ordered, amorphous domains. We have previously shown that such crystallisation reduces P3HT's ionisation potential,^{48,67} such that these crystalline P3HT domains provide energetic sinks for photogenerated holes. This functions as an additional strategy for achieving the spatial separation of electrons and holes (in addition to the PCBM crystallisation induced shift in electron affinity reported herein), consistent with the observed remarkably slow non-geminate recombination rate constant observed in annealed blend films of these materials.⁶⁸ As such, P3HT / fullerene blend films may be less functionally dependent upon fullerene crystallisation than other donor polymers. This is consistent with recent observations of efficient OPV device performance for P3HT blends with alternative, less crystalline, fullerenes such as ICBA,⁴⁶ but only relatively poor performance when such lower crystallinity fullerenes are blended with less crystalline polymers.

4.5 Conclusion

The formation of a molecularly ordered pBTTT/PCBM co-crystal in blends of these materials has been confirmed by thermal and spectroscopic analysis. The formation of such material leads to very efficient quenching of the excitons, however, the formation of free charges is hindered until an excess of PCBM is present in the blends.

We conclude that a key design requirement of materials for BHJ organic solar cells is their tendency to form phase-pure, crystalline domains which function as energetic sinks for photogenerated charge carriers relative to amorphous or mixed domains. Our results therefore suggest that a key attribute of PCBM, which may be one of the key reasons behind its dominance to date as the electron acceptor in efficient organic BHJ devices, is its ability to both mix with donor polymers, so as to enable efficient exciton quenching, as well as its tendency to form co-existing relatively pure crystalline domains with a higher electron affinity, thereby enabling the spatial separation of photogenerated charges. Two alternative fullerene acceptor materials, ICBA and C60-2, do not demonstrate the same tendency of PCBM to crystallise, as determined from CV and PL data. This may result in an unfavourable morphology in blends with these acceptors and may be a contributing factor in these materials poor performance with many donor materials.

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Chapter 5

Investigating the role of additives and polymer side chain position on the photophysics of pBTTT:PCBM blends

Abstract

This chapter investigates possible methods for changing the onset of PCBM crystallisation in two donor / acceptor blend BHJ systems. In particular these studies are focused on photophysical evaluation of methodologies for reducing the concentration threshold for fullerene crystallite formation in blends with pBTTT. A change in PCBM crystallisation onset is through both the use of short chain methyl ester additives in the film processing and through modification of the polymer side chain position. The lower concentration onset for PCBM aggregation with the addition of a series of methyl esters, results in an increase in the charge generation yield of 1:1 blends compared to blends fabricated without the additive, as monitored using transient absorption studies. In addition to this, shifting the polymer side chains from the free thiophenes along the pBTTT backbone onto the fused thiophene ring, is also shown to reduce the PCBM content required for charge generation, consistent with a lowering of the PCBM aggregation onset compared to that in pBTTT:PCBM blends as intercalation of the PCBM into the polymer side chains is hindered.

5.1 Introduction

The previous chapter has reported a photophysical and electrochemical analysis of PCBM concentration in blends with pBTTT alongside the importance of the formation of PCBM domains in these blends.¹⁻³ These results have highlighted the requirement for an adjustment in structural models employed when depicting the morphology of the BHJ structure, moving away from two pure phase pictures such as that in Figure 1.10, as discussed in Section 1.5, towards a multiphase description. McGehee and co-workers have shown that upon the addition of excess PCBM to pBTTT, the PCBM is fully intercalated with the pBTTT.⁴⁻⁷ This necessity for excess PCBM has not only been observed in pBTTT but has been observed in other polymers / fullerene blends that have shown to need a high PCBM concentration in the blend for efficient charge generation.^{3,8,9} As discussed in Chapter 4, once the intercalation of PCBM is complete, the excess PCBM has been shown to form crystalline domains, which have a higher E_A than the intercalated PCBM, from the CV measurements in Figure 4.14, and it is the formation of these domains that is key for device performance. This chapter considers whether it is possible to control the PCBM intercalation and lower the PCBM concentration in these blends.

If the majority of the excitons are generated in the pBTTT and not in the PCBM, finding a method of increasing the PCBM crystallisation at a lower concentration in the blend is desirable. However, an increase in the charge generation will only occur if a suitable method of controlling the phase segregation between the two components can be found, hindering the formation of the pBTTT/PCBM co-crystal. If this is possible, the decrease in mixing between the materials would be expected to reduce the severity of geminate recombination of spatially bound electrons and holes and in turn increase the yield of dissociated charge carriers as the lowered electron affinity of the crystalline PCBM acts as an electron sink. This effect has previously been observed in pBTTT blends with the PC₇₀BM fullerene bisadduct derivative, (bis-PC₇₁BM), which has been shown not to intercalate with pBTTT, due to the bulkier nature of this molecule from the attachment of a second methyl ester side group.^{4,6} In these blends the optimal blend ratio for device performance for these two materials has been demonstrated to be 1:1, confirmed by an increase in J_{sc} and V_{oc} in devices fabricated in a 1:1 blends compared to blends with higher PCBM concentrations.

The morphological dependence of charge generation yield within the active layer upon acceptor material described above illustrates how critical precise control of the blend structure is to device performance. Casting techniques, such as spin coating, offer little control over the composition and structure of the resultant film and therefore, the variability between different films can be vast. It has been shown to be possible to improve device efficiencies by the

formation of favourable morphologies with post-production thermal¹⁰ and solvent¹¹ annealing. Annealing films has been reported to typically result in a more defined phase segregation between the two components, increasing the crystallinity of at least one of the materials, most notably in P3HT:PCBM blends.^{12,13} Thermal annealing has shown to suppress the degree of intermixing between pBTTT and PC₇₀BM in blends, where heating of the blend expels the PC₇₀BM from within the co-crystal,⁵ which is followed by rapid cooling of the film forming PC₇₀BM domains, as verified by XRD data.⁶

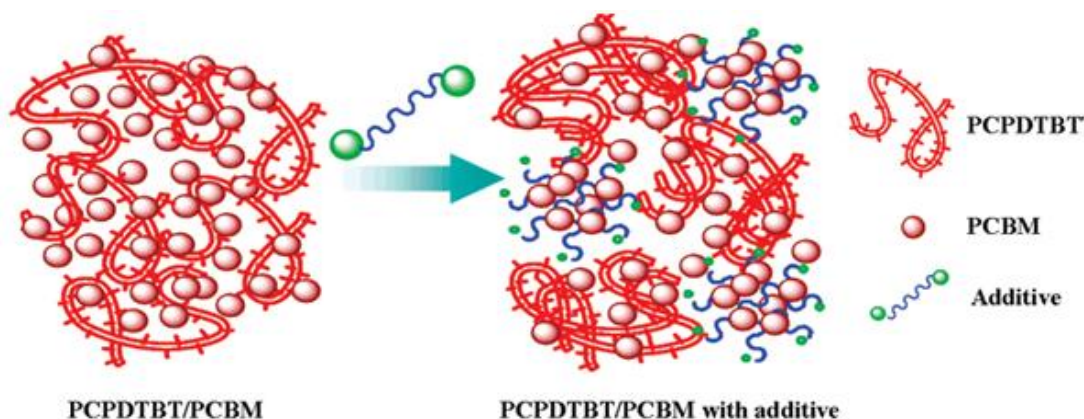


Figure 5.1 – A schematic taken from reference 14, depicting a potential change in morphology in PCPDTBT:PCBM blends upon the addition of the ODT additive, selectively dissolving the fullerene thereby promoting fullerene crystallisation and the formation of PCBM domains.

The inclusion of additives,¹⁵⁻¹⁸ or surfactants¹⁹⁻²² in organic BHJ active layer blends have been widely reported leading to modifications to the morphology of the active layer. These materials are reportedly responsible for changing the crystallinity,¹⁶ domain size,¹⁹ or, degree of mixing between the donor and acceptor,^{15,22} compared to analogous films without these processing agents. It has also been suggested that enhancements in the charge pair dissociation,^{20,23} mobility of one of the charge carriers,^{17,18} or tuning of the energy levels,²¹ may also arise from the addition of another component in the active layer blend. These techniques may be used in place of thermal or solvent annealing to control the morphology of the donor and acceptor. Some of the processing agents used in polymer / fullerene blend solar cells reported to date are short chain alkanedithiols,¹⁵ or ethers.²² It has been suggested by Yang Yang and co-workers in P3HT:PCBM blends, the addition of 1,8-octanedithiol, encourages the formation of PCBM clusters during spin coating of the blend. This has been understood to arise from the poor solubility of the PCBM is the additive, which enhances the P3HT ordering compared to films prepared without the additive.²² They have extended this model for use with other additives, including di(ethylene glycol)-diethyl ether. The addition of these materials to the active layer may lead to an increase in charge generation through the improvement in the blend

morphology. Lee *et al.* have demonstrated how the ODT acts as a processing agent, in this instance selectively solvating the fullerene, and not the polymer, as illustrated in Figure 5.1. This then ensures slow drying of the fullerene and enhances the PCBM crystallisation, due to the higher boiling point of the additive, compared to that of the main solvent, which appears to be beneficial for device performance.¹⁴

A potential in-situ method for facilitating and promoting PCBM crystallisation in pBTTT:PCBM blends is the use of short chain methyl esters as additives in the blend. These materials were initially investigated as surfactants in blends as they would act as a chemical barrier at the interface between the donor and acceptor which may slow geminate recombination. However, it was found that these esters do not act as surfactants but compete with PCBM for intercalation into the pBTTT side chains when added in a 1:1 molar ratio. This chapter considers the photophysical effects arising from changing the degree of mixing between pBTTT and poly(3,6-dialkylthieno[3,2-b]thiophene-co-bithiophene (pATBT), the structure of which is shown in Figure 5.2, with PCBM in blend films through the use of either short chain methyl esters, as additives in pBTTT:PCBM blends or by changing the position of the polymer side chains. The structures of the methyl esters additives (chain length C = 7, 12 or 14) used in this chapter are also shown in Figure 5.2.

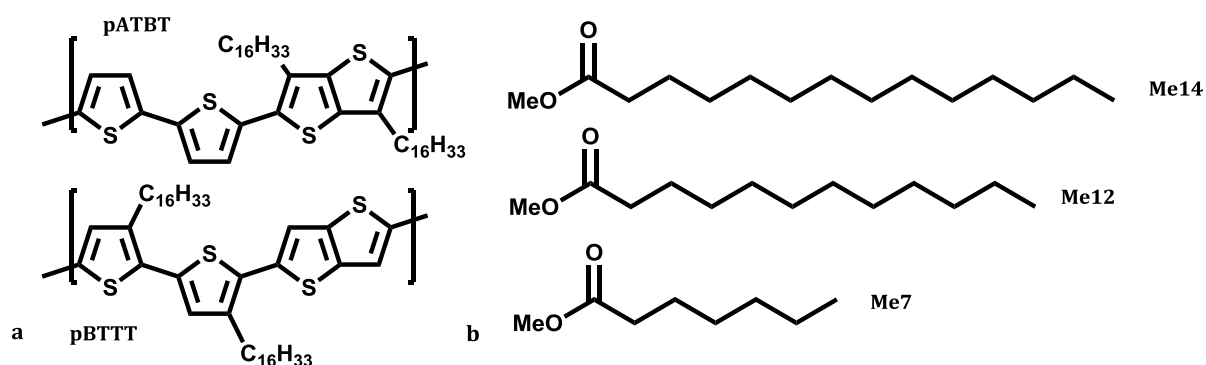


Figure 5.2 - a) Top, the structure of the new polymer, studied in this chapter pATBT, and below, the structure of pBTTT for comparison. b) The methyl esters (Me7, Me12 or Me14), used as additives with pBTTT:PCBM.

It is hoped that hindering of the co-crystal formation would prevent the rapid recombination of the geminately bound charge pairs formed in pBTTT as the distance to a PCBM interface is increased. This in turn is hoped to lead to an optimal blend ratio of the active layer with larger proportion of the light absorbing pBTTT in the blend than has previously been observed. This may be particularly significant as pBTTT is known to have a high hole mobility²⁴ which may be

exploited through an increase in the pBTTT content in these blends. These surfactants or additive may be used to increase the crystallinity at the interface between the two materials. The chemical structures of the esters chosen and studied herein are shown in Figure 5.2b. These particular esters have been chosen for their ease of addition into blends, as they are all liquids at room temperature and can be easily incorporated into the blends.

An increase in the molecular packing of the neat materials and the degree of mixing between two materials may also arise from chemical modifications in the polymer. As described previously in Chapter 3, changing just one atom in a polymer in the PCPDTBT backbone can lead to significant changes in the charge generation and device performance.²⁵ Another possible approach to changing the mixing may be via altering the degree of intercalation of PCBM into the side chains of pBTTT is modifying the positions of the side chains from the free thiophene rings to the fused bithiophene. This new polymer, pATBT, differs structurally from pBTTT only in the position of the side chains that are now positioned on the fused thiophene ring instead of the two free thiophenes.²⁶ The movement of the two $C_{16}H_{33}$ side chains from the individual thiophene rings on the backbone prevents the intercalation of PCBM between the side chains,²⁷ however, there is interdigitation of the alkyl side chains in pATBT, as observed in pBTTT.²⁶ The modification in the side chain position does have a small effect on the structural and physiochemical properties of the polymer. The HOMO of pATBT lies a little lower than that of pBTTT (~ 0.1 eV)²⁶ which may arise from a decrease in the π -orbital delocalisation as a consequence of torsion along the backbone.²⁸ The melt of the neat pATBT material is also slightly elevated compared to that of pBTTT and there is a small different lamellar packing in pATBT compared to that of pBTTT, as observed from X-ray scattering patterns.²⁶ Despite this, both polymers are relatively crystalline, compared to many of the low bandgap polymers reported.

Controlling the morphology through the use of processing agents, additives and surfactants is a useful tool in OPV manufacturing. Understanding the interactions that occur between the donor, acceptor and additive are crucial for the design and development of these processing conditions. This chapter aims to investigate whether the changes in morphology by the addition of a processing agent, or, changing the polymer side chain leads to an increase in the generation of free charge carriers or a retardation of the recombination of the charges compared to a 1:1 pBTTT:PCBM blend. The first part of this chapter looks specifically at the role of the short chain esters and the second part of this chapter considers whether despite the vast similarities between pBTTT and pATBT, the prevention of intercalation of PCBM between the polymer side chains has an effect on the free charge carrier generation or recombination.

5.2 Experimental

pBTTT (Mw ~66 KDa, Mn 34 KDa) and pATBT (Mw ~99 KDa, Mn 49 KDa) were used as received from the Heeney group at Imperial College London, synthesis describe elsewhere.²⁴ Solutions were prepared by dissolving the solids, and additive if used, in ortho-dichlorobenzene and left stirring for more than 4 hours at 100 °C to fully dissolve the polymer. The methyl esters were added in a weight ratio to the pBTTT / PCBM, where 10 times more additive corresponds approximately to a molar ratio of 1:1 with a pBTTT monomer or PCBM molecule. All pBTTT blend films were fabricated by Dr. E. Buchaca Domingo in the Materials Department and deposited on glass, by wirebar coating from a hot solution (~100 °C) onto a 35 °C substrate. All pATBT blend films were fabricated in the Chemistry Department and were spin coated onto glass substrates (~100 °C) onto a room temperature substrate at 1500 rpm for 1 minute.

XRD experiments were undertaken by Dr. E. Buchaca Domingo to monitor the change in intercalation upon the addition of the esters, as shown in Figure 5.3 and Figure 5.4 to investigate whether the additives do prevent intercalation of the PCBM into the pBTTT side chains. WAXS were carried out with a Panalytical X' PERT-PRO MRD diffractometer equipped with a nickel-filtered Cu-K α 1 beam and X'CELERATOR detector, using current $I = 40$ mA and accelerating voltage $U = 40$ kv. The WAXS is shown for the each of the additives used (Me7, Me12 and Me14), comparing the change in the interchain distance for the neat materials (pBTTT, PCBM and the three additives), binary blends (pBTTT:PCBM, additive:pBTTT and additive:PCBM) and the tertiary blend (pBTTT:additive:PCBM), shown in Figure 5.4. For each of the additives investigated here, the XRD is shown for pBTTT (red), PCBM (brown) and pBTTT:PCBM (black) to show the intercalation of the PCBM by the decrease the q value, indicating an increasing in the spacing between the pBTTT chains, in the binary blend compared to the q value observed for the neat pBTTT. The peak at $\sim 0.3 \text{ \AA}^{-1}$ corresponds to the π - π stacking between pBTTT chains and is observed in all the neat pBTTT diffraction data shown in Figure 5.4. This peak is not observed for the pBTTT:PCBM blends due to the intercalation of the PCBM into the pBTTT, but is present again in the pBTTT:additive:PCBM blends, indicating that the PCBM is now no longer intercalating with the pBTTT in these blend compositions. Different amounts of the additives were investigated for their use in these films. For the 1:5:1 molar ratio the XRD pattern is more similar to the pBTTT, indicating that there was incomplete displacement of the intercalated PCBM. However from 1:10:1 new features have been observed in the XRD at lower distances (higher angles), as seen in Figure 5.3. These have been attributed either from higher order PCBM or PCBM/additive complex. These data, in conjunction with more taken by Dr E. Buchaca Domingo, indicate that the additives are preventing the fullerenes

intercalation into the pBTTT as there is no shift in the pBTTT peak position in the tertiary blend compared to the neat pBTTT.

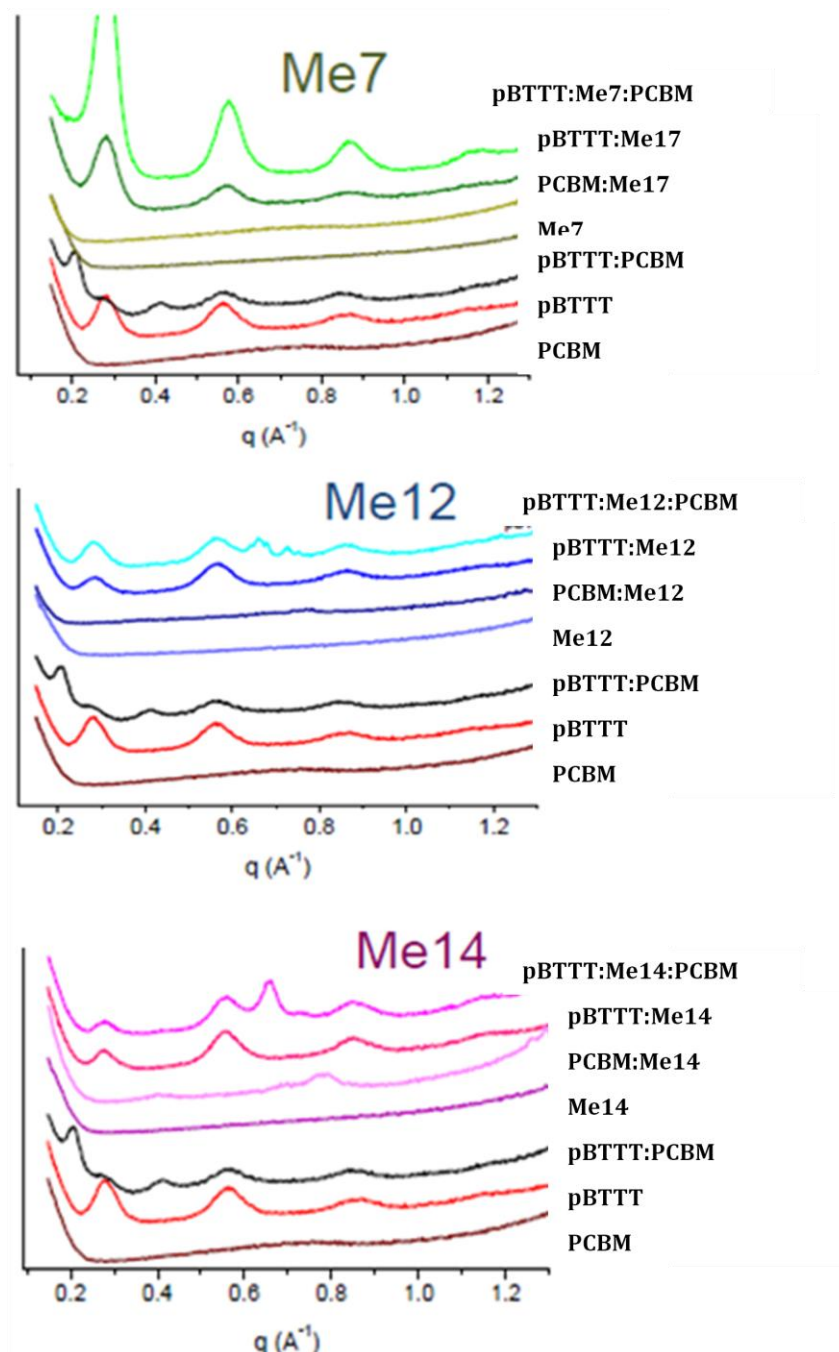


Figure 5.3 – XRD data taken by Dr E. Buchaca Domingo as a function of composition for three different additives (Me7, Me12 and Me14) with pBTTT / PCBM in the corresponding binary and tertiary blends for drop cast films.

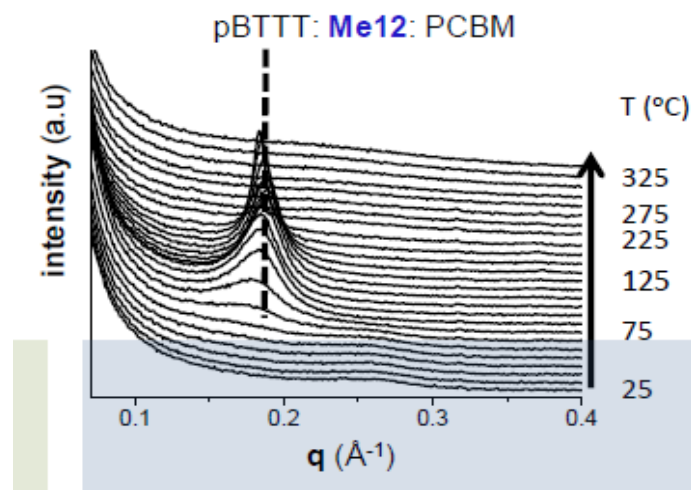


Figure 5.4 – XRD taken by Dr E. Buchaca Domingo as a function of temperature for pBTTT:Me12:PCBM (1:10:1) drop cast tertiary blend.

Figure 5.4 shows XRD data for a tertiary blend, pBTTT:Me12:PCBM, as a function of temperature taken by Dr E. Buchaca Domingo. The figure plots the diffracted peaks with increasing temperature, in order to ascertain the stability of the additive in the ternary system. Samples were cast at RT and from these data the Me12 additive appears to prevent intercalation until around 50 – 60 °C above which a new peak is observed. At higher temperatures, but below the melting temperature of the polymer, a more intense peak is observed arising from the pBTTT which increases the quality of the lamellar packing and / or increase in the size of domains. Upon melting of the whole system at ~ 275 – 280 °C, the peak XRD peak is lost as liquids do not refract. These data indicate that the addition of the Me12 surfactant to a 1:1 pBTTT:PCBM blend does prevent the intercalation of PCBM when films are cast at room temperature.

Absorption spectra were taken on glass slides between 300 – 900 nm, using a glass reference. Photoluminescence quenching was measured following polymer excitation at 520 nm.

Transient absorption decays were measured on films under a nitrogen atmosphere. Samples were excited at 520nm with an excitation density between 5 – 8 μJcm^{-2} and the resulting charges probed at 980 nm with a 100 W quartz halogen lamp.

Film CVs were recorded between +1.5V and -1.5V for each film, at scan rates of 100 mVs^{-1} , and 10 mVs^{-1} . The counter and reference electrodes were Pt and Ag/AgCl respectively.

5.3 Results

5.3.1 Photophysics of pBTTT:PCBM blends with methyl ester additives

The absorption spectra are shown in Figure 5.4 for neat pBTTT (light blue) and pBTTT:PCBM (1:1 by weight), without the additive (pink), herein called the binary blend, and in the tertiary blend films with the Me7 (blue) and Me12 (light green) additives films. The pristine pBTTT film exhibits a peak maximum at 550 nm with the onset of a low energy shoulder at ~ 595 nm, consistent with the data presented previously in Figure 4.6. The increase in the fine structure, specifically the low energy absorption band, upon the addition of PCBM, is again consistent with data presented previously. The increase in oscillator strength is seen from the addition of just 20 wt% PCBM and is pronounced here in the 1:1 blends. However, the absorption spectra of the both the tertiary blends show negligible difference in the ground state peak position compared to the binary blend absorption. The two absorption maxima at 560 and 605 nm, in pBTTT:PCBM (1:1) does not change wavelength maxima on addition of either the Me7 or Me12 additive to the blend, which may arise from partial intercalation of the PCBM with pBTTT, because, as seen in Figure 4.6, the fine structure is observed with just 5 wt% PCBM added to the blend. The PCBM peak absorption at 330 nm in the binary blend does not change upon addition of either the Me7 or Me12. This is an indication that the additives are not contributing to the number of photons absorbed by the film, therefore any enhancements in the charge generation yield upon the addition of the methyl ester will not arise from an increase in photon absorption.

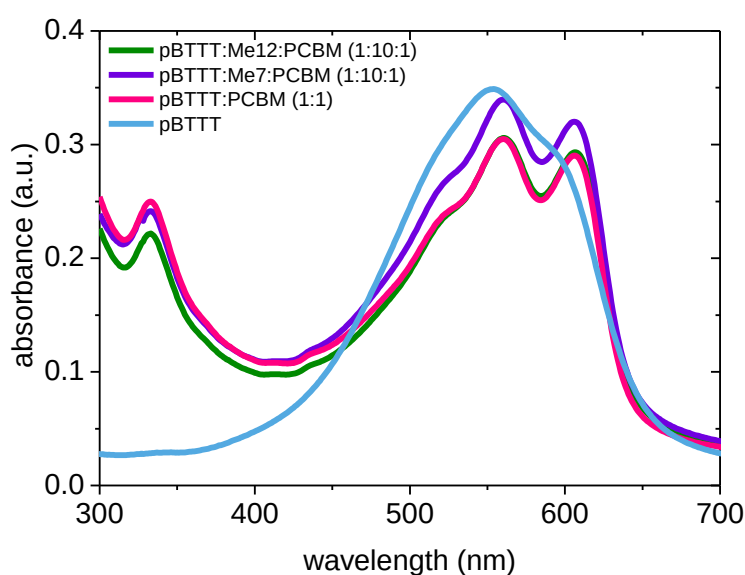


Figure 5.5 – Absorption spectra of neat pBTTT (light blue), pBTTT:PCBM (1:1, pink), pBTTT:Me7:PCBM (1:10:1 blue) and pBTTT:Me12:PCBM (1:10:1, green) blend films.

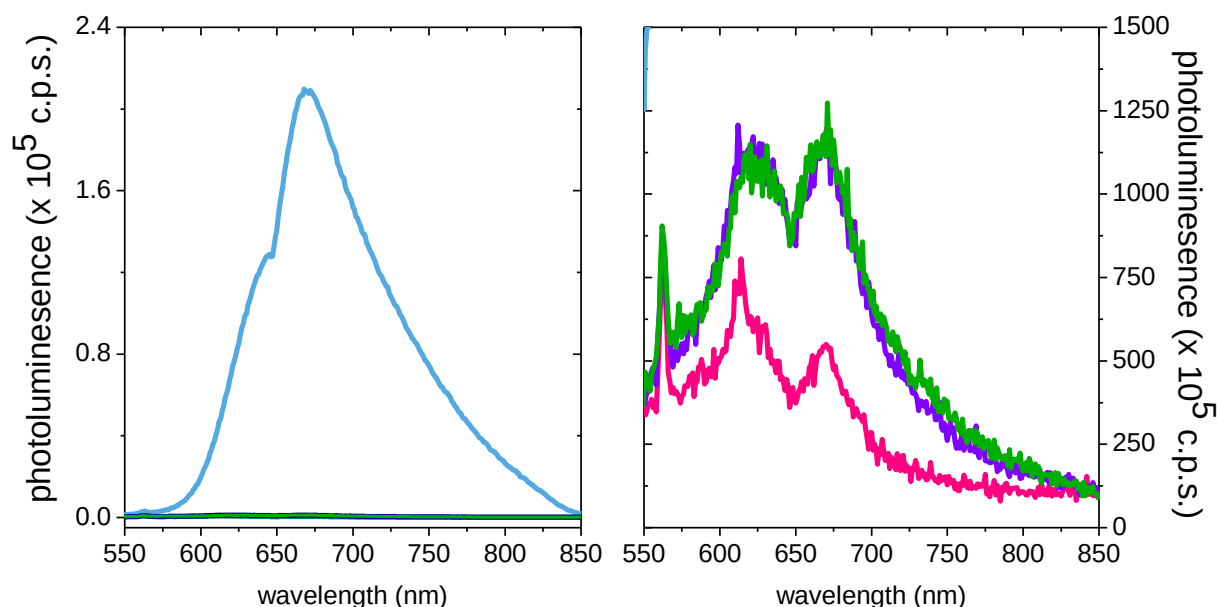


Figure 5.6 - Photoluminescence spectra of neat pBTTT (light blue), pBTTT:PCBM (1:1, pink), pBTTT:Me7:PCBM (1:10:1 purple) and pBTTT:Me12:PCBM (1:10:1, green) blend films. A close up of the PL spectra of the binary and tertiary blends are shown in the spectra on the right.

The PL spectra in Figure 5.6 show a near unity quenching ($\sim 99\%$) of the excitons generated in the binary blend pBTTT:PCBM (1:1), consistent with the data reported in Chapter 4. The addition of either Me7 or Me12 additives show a modest change in the PL quenching compared to that of the binary pBTTT:PCBM blend, as observed in Figure 5.6b. For both of the tertiary blends studied here, the PLQ, relative to that of the neat at the pBTTT peak emission at 680 nm is 97% compared to that of the neat polymer. We turn now to investigate the effects of the additives on dissociated charge generation, in both 1:1 and 1:4 blends, to further investigate the role of these methyl ester additives in charge generation in pBTTT:PCBM blends. As shown previously in Figure 4.10, the pBTTT polaron is experimentally observed at 980 nm and is hence this wavelength used herein to monitor charge generation in these blends. Both the binary and tertiary films were excited at 520 nm, and corrected for the optical density at this wavelength.

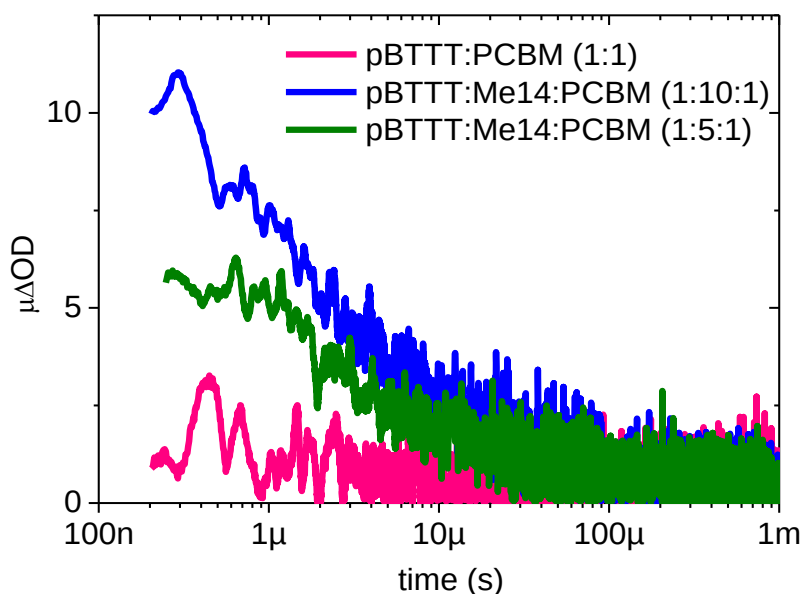


Figure 5.7 – TAS decays of pBTTT:PCBM (1:1) as a function of the Me14 additive concentration.

Initial observations regarding the concentration dependence of the Me14 additive on the charge generation yield compared to the binary blends, are shown in Figure 5.7. These data show a clear increase in the charge generation yield in two tertiary blends shown here, 1:5:1 and 1:10:1, compared to the binary blend. This result is consistent with the XRD data shown in Figure 5.3, showing a decrease in the q value in the tertiary Me14 blends compared to the binary blend. This indicates that the change in the packing between the pBTTT and PCBM in the tertiary blends compared to the binary blends does have an impact on the charge generation yield. Following these results, the remainder of the chapter investigates the effects of 10 times more additive in the tertiary blend than polymer.

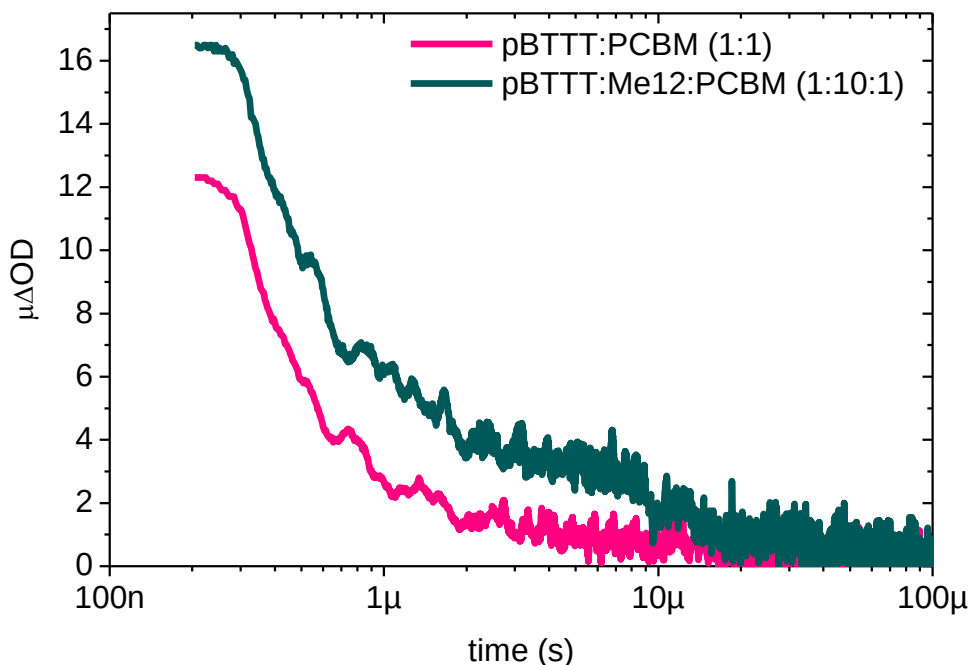


Figure 5.8 – TAS decays of pBTTT:PCBM (pink) and pBTTT:PCBM with the Me12 additive (dark green).

The TAS decays in Figure 5.8 show the kinetic behaviour of the pBTTT polaron in 1:1 blend of pBTTT:PCBM with (pink) and without (dark green) the Me12 additive. As seen from the increase in the ΔOD signal, the charge generation yield of dissociated charge carriers is increased upon addition of the methyl ester to the blend. The initial charge generation recorded at 200 ns, $\Delta OD = 12 \mu OD$ in the binary blend, but in the tertiary blend with the Me12 additive, $\Delta OD = 17 \mu OD$. This change in ΔOD amplitude is smaller than shown for different blends presented in Figure 5.7, but does follow the same trend as previously presented. Some difficulties were presented regarding the reproducibility of this data, especially with respect to the magnitude of ΔOD following the addition of the esters. This highlights the sensitivity of the TAS technique to the changes in the morphology following the addition of the esters and the difficulties in controlling the morphology with the additives. Despite the difficulties with reproducibility, there was typically a significant change in the signal between the binary and ternary blends.

Following the initial charge generation, the kinetic decays of both films, with and without the additive, can be fit to a power law decay on a log-log plot. These data exhibit biphasic behaviour typical of non-geminate recombination of dissociated charges that dominates over the timescales investigated in this study. From these data, $\alpha = 0.88$ for the additive free binary blend, and for the tertiary blend with the Me12 additive, $\alpha = 0.35$. Following the investigation into the charge generation yield with the addition of the methyl ester, the reduction potentials

were also investigated, conducting the same analysis as employed in Chapter 4 regarding the PCBM crystallinity and change in E_A .

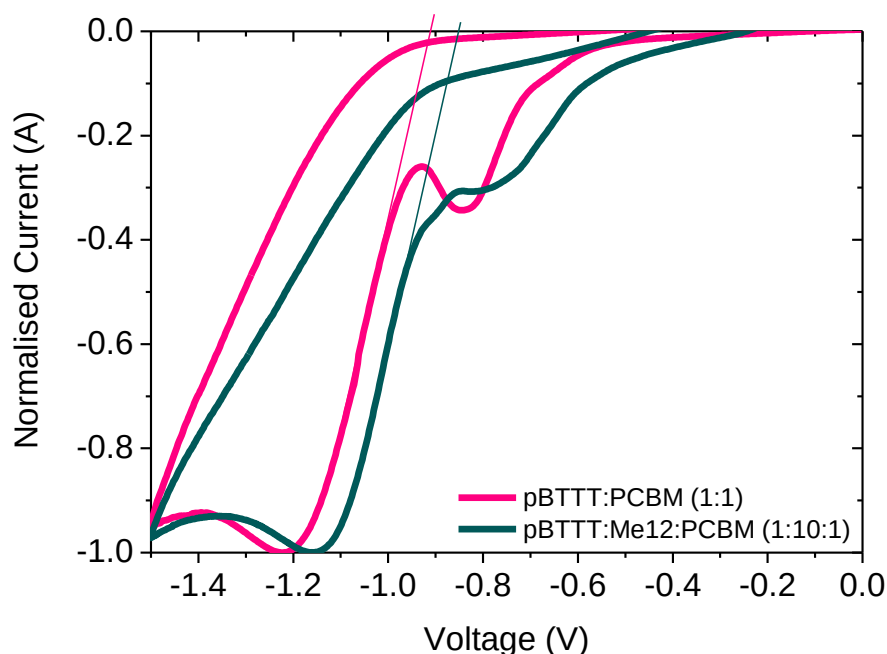


Figure 5.9 – The CVs for pBTTT:PCBM (pink) and pBTTT:Me12:PCBM (green) in a TBAP in AcN electrolyte with Pt and Ag/AgCl reference and counter electrodes, respectively, taken at a scan speed of 100 mV/s. A line of fit has been added for each scan as a guide to show the reduction potential onset employed in this analysis.

The cyclic voltammograms of pBTTT:PCBM with (pink), and without (dark green), the addition of the Me12 additive are shown in Figure 5.9 for the first reduction potential. The neat binary blend (1:1) is shown in dark green and pBTTT:Me12:PCBM ternary blend (1:10:1) is shown in light green. For pBTTT:PCBM without the additive, the onset of the reduction potential is recorded at -0.91 V, as indicated by the dark green line, similar to that recorded previously in Chapter 4. The first, smaller, peak observed in both the binary and tertiary CV has been attributed to the presence of water in the electrolyte and not arising from either the pBTTT or PCBM and is therefore not considered in the analysis of these blends. The onset of the reduction potential has been defined here from where the line of fit for the reduction current intersects the y-axis. From these data the onset of the reduction potential in the pBTTT:Me12:PCBM is lowered compared to that of the binary blend without the ester, and is recorded at -0.85 V, as indicated by the light green line. There is ~ 60 mV shift in E_A upon the addition of the Me12 additive to these blends, consistent with the proposal of an increase change in PCBM crystallisation between these blends.

The data shown above regarding the effects of the methyl esters on the charge generation and E_A has been presented for 1:1 pBTTT:PCBM blends, which as demonstrated from the TAS data in Chapter 4, this binary blend does not efficiently dissociate charges due to the fast recombination of the spatially confined charges. The following analysis of the effects of methyl esters is conducted on 1:4 pBTTT:PCBM blends which have been shown to be significantly more efficient at generating dissociated charges than 1:1 blends due to the decrease in the PCBM E_A upon crystallisation.

Figure 5.10 shows the both TAS and CV analysis for the 1:4 pBTTT:PCBM blends. The TAS data shows a positive result upon the addition of the Me12 additive in the blends with a high PCBM fraction, whereas there is a less pronounced effect in the CV data between the two blends. The TAS data in Figure 5.10a, shows a twofold increase in the initial charge generation with the addition of the Me12 ester to the blend from 13.0 $\mu\Delta OD$ to 26.3 $\mu\Delta OD$, at 300 ns. At 1 μs the difference in TAS signal amplitude is more pronounced between the two materials as OD = 16.0 $\mu\Delta OD$ the tertiary blend and 5.0 $\mu\Delta OD$ for the binary. The initial increase in the charge generation with the addition of Me12 to the blend is also accompanied with a retardation in the recombination kinetics for the tertiary blend, $\alpha = 0.96$, whereas for the tertiary blend, $\alpha = 0.82$. These data suggest some change in the active layer morphology with the addition of Me12, despite the presence of some crystalline PCBM already in the binary blend.

The CV data shown in Figure 5.10b, are normalised against the maximum current recorded at -1.5 V. These data show only a small change in the reduction potential with the addition of the Me12 additive to the 1:4 blend again indicated by the fit lines. There is a ~ 20 mV increase in E_A with the addition of Me12, compared to the binary blend, however this increase is not as pronounced as the change observed in the 1:1 blends upon the addition of Me12, as shown previously in Figure 5.9. This is consistent with a modest change in the degree of crystallinity of the PCBM upon the addition of the ester to the blend. However this modest change in E_A is unlikely to account for the twofold increase in the initial charge generation yield, which may arise from a reduction in the geminate recombination.

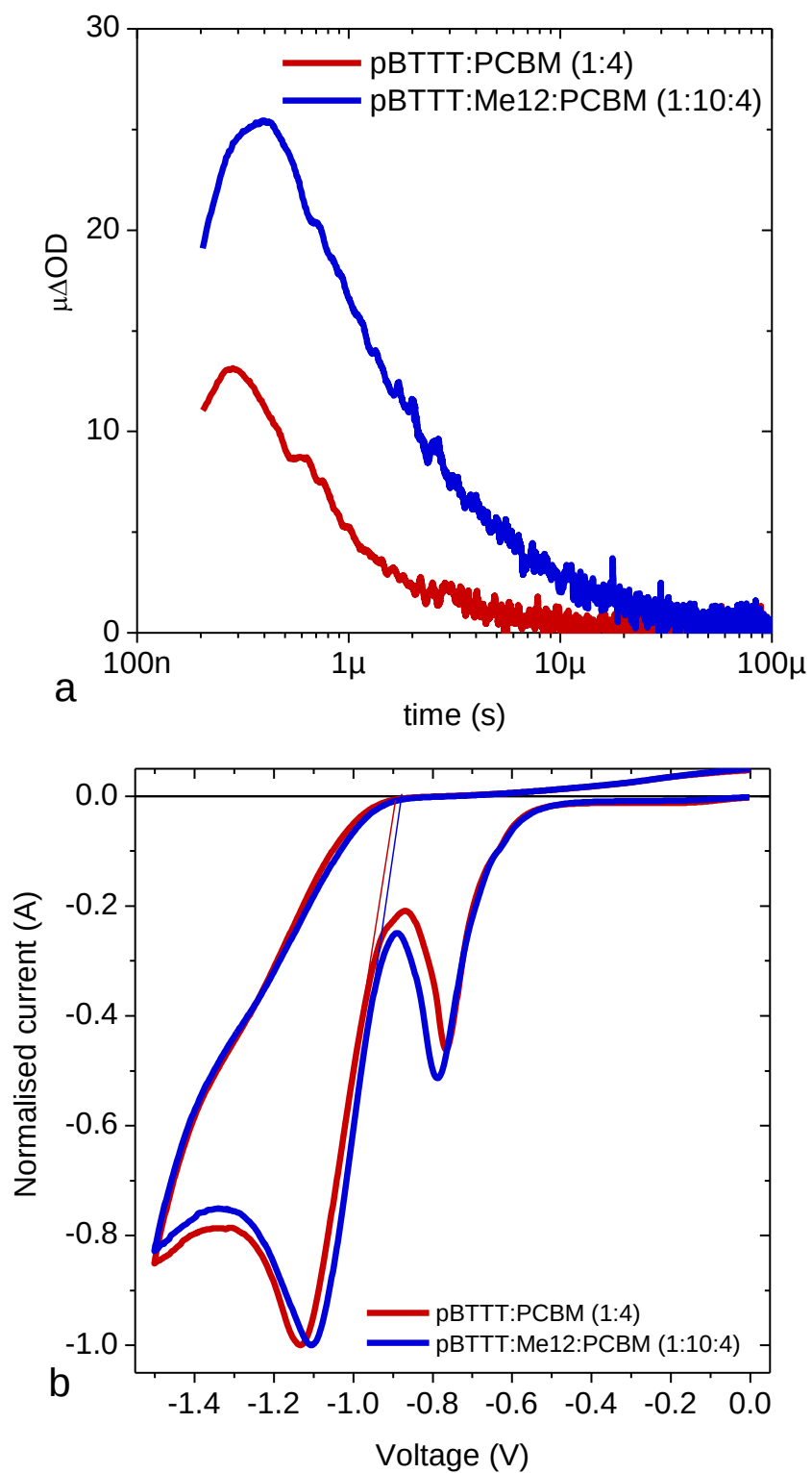


Figure 5.10- a) The TAS decay kinetics for pBTTT:PCBM (1:4, green) and pBTTT:Me12:PCBM (1:10:4, blue). b) CV data showing the reduction potential for the binary (green) and tertiary (blue) blends.

5.3.2 pATBT:PCBM – the role of polymer side chain position in blends for changing the PCBM crystallisation onset

This chapter will now turn to focus upon the modification of the position of the $C_{16}H_{33}$ side chains on the polymer backbone creating the new polymer, pATBT, and the role of this modification on changing the PCBM crystallisation and the effects of this on the photophysics of these blends will be investigated herein.

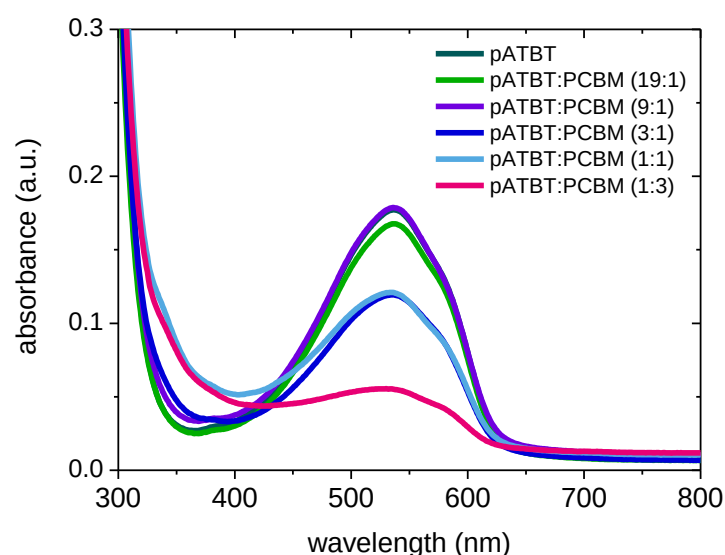


Figure 5.11 – The absorption spectra of thin films of pATBT as a function of PCBM concentration, including neat pATBT.

The absorption spectra of neat pATBT and pATBT:PCBM blend films as a function of PCBM concentration are shown in Figure 5.11. The neat pATBT film has an absorption maximum at ~ 535 nm and the onset of a lower energy shoulder is observed at ~ 580 nm. The addition of PCBM to pATBT does not change the absorption maxima, nor the position or relative magnitude of the low energy shoulder compared to neat pATBT. The increased absorption at 350 nm with the addition of PCBM arises from the absorption of the PCBM.

The PL quenching of pATBT, following excitation of the polymer at 520 nm (a) and PCBM at 430 nm (b), is shown as a function of PCBM concentration in Figure 5.12. These data show that the polymer PL is not highly quenched upon the addition of 50 wt% PCBM, as is observed for pBTTT:PCBM blends, but is only $\sim 80\%$ quenched in a 1:1 pATBT:PCBM blend, relative to the neat pATBT emission. The PLQ upon the addition of excess PCBM, in a 1:3 pATBT:PCBM ratio, is increased to 86%, however even at this high PCBM concentration the photoluminescence is not

fully quenched. To investigate these effects of the change induced by the side chain position further, TAS has been employed, looking at the generation of charges as a function of PCBM concentration. As investigated previously for pBTTT in Figure 4.9, the PCBM PLQ is shown in Figure 5.12b for pATBT as a function of PCBM concentration following excitation at 430 nm, where PCBM aggregation can be monitored by the appearance of a PL band at ~ 520 nm.² This band is clearly observed in 1:3 pATBT:PCBM blend film, as is the case for 1:3 pBTTT:PCBM, but is also seen for the 1:1 pATBT:PCBM and there is a small band observed at lower concentrations. This is in contrast to pBTTT:PCBM which shows no PL band at 520 nm in blends with less than 75 wt% PCBM.

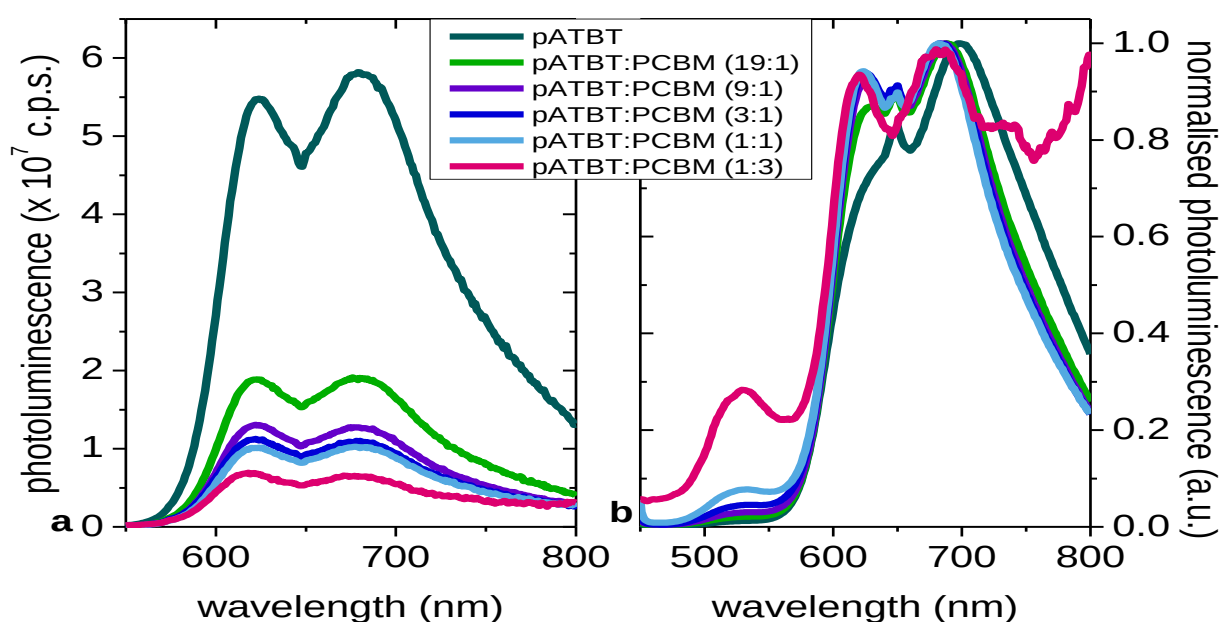


Figure 5.12 – PL quenching of pATBT as a function of PCBM concentration. a) PL following excitation of the pATBT, at 520 nm, showing decreasing PL with increasing PCBM content. b) Normalised PL following excitation of the PCBM, at 433 nm, with the small high energy shoulder at ~ 520 nm increasing in intensity with PCBM concentration.

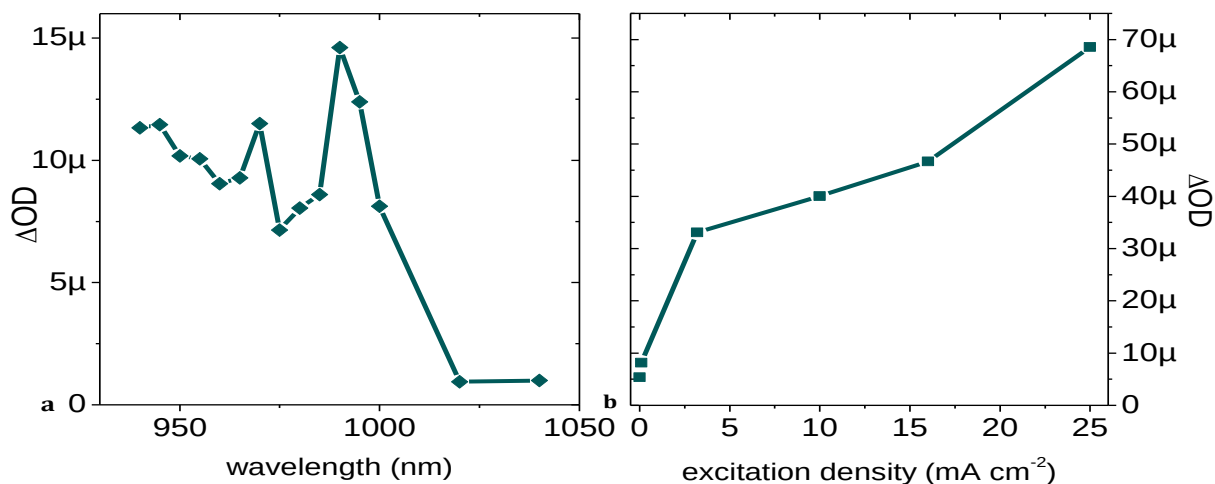


Figure 5.13 - a) Transient spectra for pATBT:PCBM (1:1) at 1 μ s, following excitation at 520 nm and b) Excitation density dependence of charge generation in pATBT:PCBM (1:1) at 980 nm, following excitation at 520 nm.

The transient spectra recorded at 1 μ s for pATBT:PCBM (1:1), in Figure 5.13a, show a narrow peak at 990 nm. The peak position and magnitude is not altered in an air environment and is therefore not due to the appearance of triplets in these blends. Therefore, this peak has been attributed to arise from the presence of the pATBT polaron. The charge generation yield as a function of excitation density for a 1:1 blend is shown in Figure 5.13b.

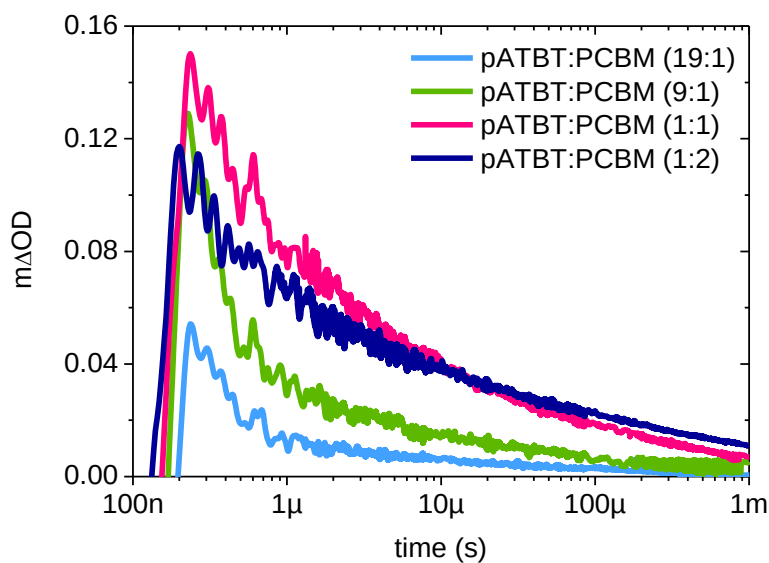


Figure 5.14 - TAS decay kinetics of pATBT blends as a function of PCBM concentration probed at 980 nm and normalised for optical absorbance at the 520 nm, pump wavelength.

The TAS decay kinetics for pATBT as a function of PCBM concentration between 200 ns – 100 μ s, are shown in Figure 5.14. These data were recorded following excitation at 520 nm, with an excitation density of 5 μ Jcm⁻². The initial charge generation yield at 200 ns is greatest in the 1:1 blend at $\sim$ 0.15 m Δ OD, 25 % greater than the initial charge generation in the 1:2 blend (Δ OD = 0.12 m Δ OD at 200 ns). All of the blends shown here exhibit biphasic behaviour except for the 1:2 blend, with a fast phase observed between 200 to 700 ns before the decay then extends into a slow phase beyond this. The observed reduction in Δ OD amplitude in the 1:2 pATBT:PCBM is in contrast to the data recorded for pBTTT:PCBM which shows an increase in the Δ OD amplitude with increasing PCBM. For pATBT:PCBM blends the highest charge generation yield at 200 ns is recorded for the 1:1 blend, however for pBTTT:PCBM the highest Δ OD amplitude is recorded for the 1:4 after the formation of PCBM domains.

5.4 Discussion

5.4.1 Modification of pBTTT:PCBM blends with methyl ester additives

Initial morphological analysis, presented in Figure 5.3 and Figure 5.4 by Dr E. Buchaca Domingo show the addition of the three esters, Me7, Me12 or Me 14, to pBTTT:PCBM blends does hinder the intercalation of PCBM into the pBTTT side chains. This is shown in the XRD by the increase in the pBTTT q value upon the addition of the methyl esters, showing a decrease in the interchain distance, indicating the displacement of PCBM from the pBTTT side chains. The nature of the effect of the additives on the blend morphology has not been investigated in this chapter. However following these observation, this chapter has focused upon the photophysical effects of the change in intercalation upon inclusion of the additive in the blend.

The addition of the short chain, liquid methyl esters investigated here to pBTTT:PCBM blends has been shown to have a positive effect on the degree of PLQ and charge generation yield monitored by Δ OD compared to additive free blends for both 1:1 and 1:4 blends and a significant change in E_A for the 1:1 blend with the additive. The fractional decrease in the PLQ of the tertiary blends compared to the binary (1:1) blends indicates a small change in the degree of mixing between the polymer and fullerene. As discussed in Chapter 4, intercalation of the PCBM into the pBTTT facilitates almost complete quenching of the photogenerated excitons because no exciton diffusion is required in these blends to split the charges, as discussed in Chapter 4 due to the finely intermixed nature of the blend. The decrease in the exciton quenching efficiency with the both Me12 and Me7 additives are indicative of a disruption in the PCBM intercalation. The near unity quenching of the binary pBTTT:PCBM blends arises from the fine

intermixing of the two materials following the formation of the co-crystal. The small decrease in the quenching with the addition of the esters indicates a slight change in the degree of molecular mixing between the pBTTT and the PCBM in the tertiary blends compared to the binary blends. From these data it is possible to infer that not all of the photogenerated excitons reach an interface between the donor and acceptor before recombination indicating that there may be a change in the nanoscale morphology with these esters. The nature of the interaction between the additives and the materials is unclear from the photophysical data presented here. However, these data do indicate that some of the PCBM is not intercalating with the pBTTT, which may in turn lead to the formation of PCBM domains, which is consistent with the XRD data presented in Figure 5.3. One possible explanation for the changes observed with the addition of Me12, is preferential intercalation of the additive into the pBTTT side chains, displacing the PCBM and facilitating the formation of PCBM at lower concentrations than previously observed in pBTTT:PCBM (1:1) blends.

A decrease in mixing between the donor and acceptor materials would be expected to yield a change in the charge generation yield between the different blends with and without the esters. A large energetic barrier at the interface is expected to slow the recombination kinetics. However, this large interfacial barrier may also lead to a retardation in the separation efficiency of the free charges, however as shown in the PLQ data in Chapter 4, this process is already very efficient in these blends. This has been shown by an increase the charge generation yield of the tertiary blends, compared to the binary blends without the esters, in both 1:1 and 1:4 pBTTT:PCBM blends. This increase in charge generation in the tertiary blends is accompanied by a retardation in the recombination kinetics upon the addition of Me12 to both the 1:1 and 1:4 blends. It should be noted here that the reproducibility of these results, both the magnitude of the change in the ΔOD signal and the change in the kinetics, upon the addition of the methyl esters was low for these blends. In the majority of the films investigated, there was some change in the both the charge generation and recombination kinetics upon the introduction of the additive, however the magnitude was dependent on the film tested. This suggests that the charge generation and recombination are heavily dependent on the film processing conditions which change the morphology of the films. These data are again, along with the reduction in PLQ upon addition of the methyl esters, indicative of a change in the molecular mixing between the polymer and fullerene. In the 1:1 blends, the esters appear to facilitate the formation of PCBM crystals, which has been shown by the increase in the E_A in the tertiary blends. The 60 mV increase in the electron affinity upon the addition of the esters is of the same magnitude reported in the previous chapter as the PCBM crystallinity is increased by increasing the PCBM loading in the blends. This change in E_A reported here is an indication that the addition of Me12

to the pBTTT:PCBM (1:1) is altering the crystallinity of the PCBM within these blends. This has been shown to increase the charge generation yield. However, the addition of the Me12 ester to the 1:4 blend, that is known to already contain a crystalline PCBM fraction, still exhibits an increase in the charge generation compared to the binary blend. This increase in charge generation in the 1:4 blend, is not accompanied by a significant (~ 20 mV) change in PCBM crystallinity. The increase in charge generation may arise from a suppression in the geminate recombination if the degree of mixing between the polymer and the PCBM, is hindered, despite the formation of crystalline PCBM already present. This may in turn explain yield information on the small change in the E_A upon addition of the Me12 to the blends, as the change in PCBM crystallinity is negligible. Continuing on from discussion in Chapter 4, the increased PCBM content in this blend is necessary for the formation of crystalline PCBM domains with a lower E_A compared to the intercalated PCBM. This may arise from the already significant proportion of crystalline PCBM in these blends, as indicated from the DSC data in shown in Figure 4.8b, therefore the degree of crystallinity is not increased further upon the addition of the additive to the 1:4 blends.

The addition of these methyl esters may prevent the intercalation of PCBM into the polymer side chains, arising because the esters tested here may preferentially intercalate between the pBTTT side chains over the PCBM molecules. This in turn may facilitates PCBM aggregation, at lower PCBM concentrations than has been previously observed in pBTTT:PCBM blends with the additives. The preferential intercalation of the methyl esters over the PCBM could arise from a combination of factors including; size of the molecule, surface interactions between the ester group and the pBTTT, thermodynamics, or, possibly electron driving force.

5.4.2 pATBT:PCBM – the role of polymer side chain position in blends for facilitating PCBM crystalisation

The change in the side chain position along the polymer backbone has also shown to have a impact on the nature of the PLQ and charge generation in these blends compared to neat pBTTT and pBTTT:PCBM blends. The PLQ of the pATBT:PCBM blends is significantly different to that of pBTTT:PCBM blends, as shown in Figure 5.12. The incomplete PLQ in pATBT:PCBM blends, even with 75 wt% PCBM in the blend, is indicative of a system that forms well defined domains of neat pATBT and / or PCBM, even without the addition of an additive. This suppressed PLQ is also indicative of no significant intercalation of the PCBM into the pATBT side chains, as this would be expected to lead to very efficient PL quenching, as observed in pBTTT:PCBM in the molecularly mixed co-crystal. The incomplete PLQ in 1:1 blend indicates that there is not a

significant degree of nanoscale mixing, but rather the formation of neat pATBT / PCBM domains and these domains may be greater in size than the exciton diffusion length, which is hindering the PL quenching even at high PCBM concentrations.

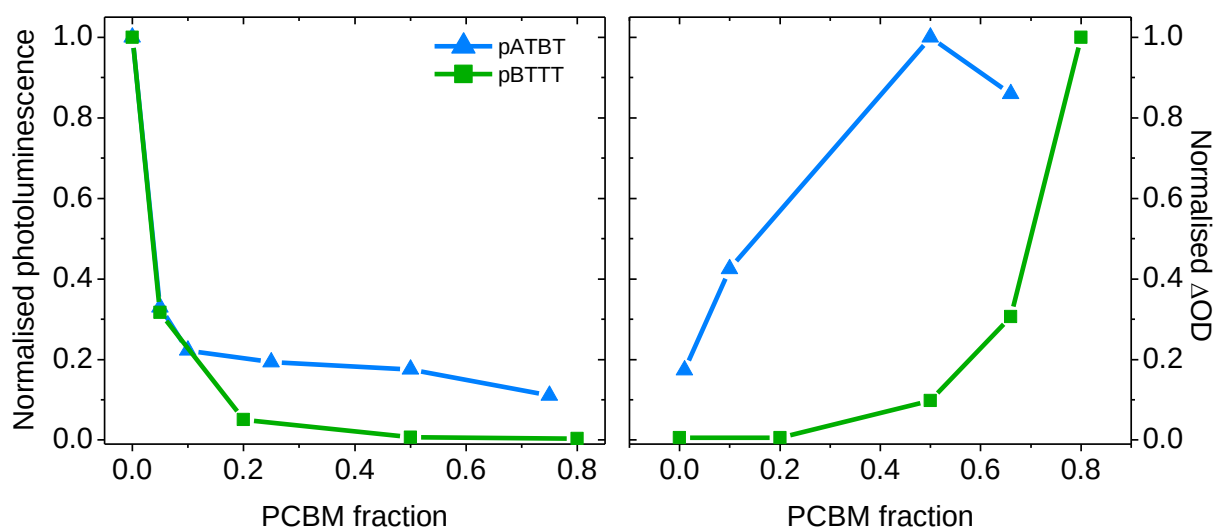


Figure 5.15 – a) Normalised PL quenching of pATBT (blue) and pBTTT (green) relative to the neat polymer and b) TAS yield at 1 μs, both as a function of PCBM concentration.

To correlate the differences in exciton quenching between pATBT and pBTTT, the normalised PLQ relative to the emission of the neat polymer and TAS yield at 1 μs are shown for both polymers as a function of PCBM concentration in Figure 5.15. As discussed in Chapter 4, pBTTT is known to exhibit a high PL quenching at low PCBM concentrations due to the intercalation of the PCBM molecules in between the polymer side chains and the intercalation of PCBM into the pBTTT side chains leads to the majority of excitons being created close to, or at, an interface between the polymer and fullerene. This leads to very efficient exciton dissociation and high PL quenching even at low PCBM concentrations. Surprisingly the pATBT polymer exciton quenching follows the same initial trend as that of pBTTT, as both the polymer blends containing 5 wt% PCBM exhibit ~ 30 % PLQ relative to the neat polymer. However, beyond the addition of 10 wt% PCBM to the polymer, the PLQ changes between the two polymers and the pATBT excitons are not as efficiently quenched as in pBTTT. In a 1:1 blend, pATBT is only 80% quenched relative to the neat polymer, and in a 1:3 pATBT:PCBM blend, there remains incomplete quenching of the photogenerated excitons, which is not the case for pBTTT:PCBM blends which show near unity PLQ at these concentrations. This indicates that that the degree of molecular mixing between the two materials is much lower than observed for pBTTT:PCBM

blends. This difference in exciton quenching between these two blends may indicate some differences in the crystallinity and blending between the donor and acceptor in these two blends. The TAS yields in Figure 5.15b show the difference in the charge generation yield as a function of PCBM concentration. This shows for pATBT:PCBM blends the highest charge generation yield at 1 μ s is recorded for the 1:1 blend, unlike pBTTT:PCBM blends which have the highest charge generation in 1:4 blends. The charge generation yields in pATBT:PCBM blends do not follow the same trend as pBTTT:PCBM blends. The initial fast phase is excitation density dependent, and therefore not attributed to geminate recombination of charges. Instead this may be the result of an initially high charge generation of dissociated charges, before entering a trap limited regime, which slows recombination as the charges are unable to escape the traps and recombine. The incremental increase in the charge generation yield between the 19:1 and 9:1 blends indicates that the charge generation yield in these blends is not hindered by the morphology of the blend, rather due to a lack of quenching sites due to the low PCBM concentration, which is in contrast to the behaviour of pBTTT:PCBM blends. The 1:3 pATBT:PCBM blend does not exhibit the lowest highest charge generation yield of the blends studied here as is the case in pBTTT:PCBM blends, however, this blend composition exhibits the slowest recombination of the pATBT:PCBM blends studied. The magnitude of the initial Δ OD signal recorded here is greatest in the 1:1 blend up to 10 μ s, and this may indicate that the optimal blend ratio for charge generation in these blends is 1:1, unlike pBTTT:PCBM blends which require a significantly larger PCBM content for efficient charge separation.

As discussed in Chapter 4, the formation of crystalline PCBM domains is critical for the separation of free charges in pBTTT:PCBM blends. This difference may be responsible for the relative increase in the yield of dissociated charges in a 1:1 pATBT:PCBM blend relative to the pBTTT:PCBM 1:1 blends. This morphological change may also lead to a change in the energetic driving force from the crystalline PCBM for the formation of dissociated charges, however no CV data were recorded for these blends to confirm whether the PCBM crystallisation is affected.

5.5 Conclusions

Two methods for decreasing the concentration threshold for PCBM crystallinity have been shown in pBTTT:PCBM blends along with the effects on the photophysics, specifically the photoluminescence quenching and the charge generation yield. The addition of short chain esters to pBTTT:PCBM blend solutions before film fabrication prevents the intercalation of PCBM into the pBTTT side chains, as shown by the XRD data. This has had an effect on the exciton quenching as demonstrated by a small decrease in the PLQ, alongside a twofold increase

in the charge generation yield as measured using TAS and a 80 mV increase in the E_A from the CV data, in 1:1 pBTTT:PCBM blends. The nature of this change of the active layer morphology upon addition of the esters has not been extensively discussed in detail here but may arise from a displacement of PCBM from the pBTTT side chains, preventing intercalation and the formation of a thermodynamically stable co-crystal of the two materials with molecular scale mixing. This displacement may in turn facilitate PCBM aggregation at a lower concentration compared to that of the binary blend in which PCBM intercalation is known to occur.

It has also been possible to prevent intercalation of PCBM into the polymer side chains through modification of the side chains position the polymer backbone. The movement of the $C_{16}H_{33}$ side chains on pBTTT from the fused thiophene rings to the free thiophene rings has also had an impact on the PLQ and charge generation yield compared to pBTTT:PCBM blends. The PLQ in these blends is incomplete, even in blends with 75 wt% PCBM and the TAS data suggests that the optimal blend ratio for this material is 1:1 pATBT:PCBM as the charge generation yield of dissociated carriers, as determined from the magnitude of the ΔOD signal is greatest at this concentration. These data suggest that the side chain position prevents PCBM intercalation with the polymer, creating the formation of neat polymer and PCBM domains and not the formation of a co-crystal with nanoscale mixing of the two materials.

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Chapter 6

The influence of an externally applied electric bias on charge generation in donor / acceptor blend solar cells

Abstract

Transient absorption spectroscopy on the nano to microsecond timescale has been employed to investigate the effect of an externally applied electrical bias on the charge generation yield in organic solar cells employing different polymer and small molecule donor materials. When blended with PC₇₀BM, both the carbon and silicon bridged analogues of PCPDTBT, including the carbon bridged polymer with a processing additive, showed no significant dependence of charge generation on applied bias. In contrast, cells employing poly((9,9-dioctylfluorenyl-2,7-diyl)-co-5,5-(4',7'-di-2-thienyl-2',1,3'-benzothioadiazole) (APFO-3) and the small molecule donor materials [3,6-bis[5-(benzofuran-2-yl)thiophen-2-yl]-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4-dione] (DPP(TBFu)₂) and [3-[bis(2-ethylhexyl)silanol-yl]-5,5'-bis{5-[2,5-bis(2-ethylhexyl)-6-[5-(benzofuran-2-yl)thiophene-2-yl]pyrrolo[3,4-c]pyrrole-1,4-dione-3-yl]-2,2'-bithiophene}] (SDT(TDPPTBFu)₂) show a 30 – 35% increase in the generation yield with increasing reverse bias between open circuit and short circuit conditions, implying that charge photogeneration is modulated by the device's internal electric field. We find that the electric field dependence of charge generation in these devices may be linked to significant geminate pair recombination on the timescales investigated. We go on to show that, for the two small molecule blends, the experimentally observed field dependence of charge generation is necessary to explain the shape of their J-V curves.

6.1 Introduction

Solar energy conversion in organic BHJ cell is based upon the separation of photogenerated excited states (excitons) at the donor / acceptor interface, yielding dissociated electrons and holes. A key consideration for the charge photogeneration process in BHJs is that the initially generated electron and hole pairs may form charge transfer (CT) states at the donor / acceptor interface before directly dissociating to free charges. Previous chapters have used TAS to investigate the charge generation yield in thin films. This chapter will consider the charge generation yield in complete devices, and in particular the impact of the electrodes, and the associated device electric field on that yield. To this end, we employ TAS to probe the electric field dependence of charge photogeneration in three series of different donor materials systems for organic solar cells blended with PCBM / PC₇₀BM. These measurements are combined with separate measurements quantifying non-geminate recombination losses in these devices to allow recreation of the device current / voltage curves. We show that rather than there being a universal mechanism of charge generation in OPVs, the loss processes can vary significantly between devices.

Electric field dependencies of charge generation in OPV devices have typically been discussed in the context of Onsager-Braun theory of geminate losses in weak electrolytes.^{1,2} As outlined in Chapter 1.3.7, this model considers the probability of charge pair dissociation and recombination in a dielectric medium. The low dielectric constants of semiconducting polymers typically lead to a low probability of charge separation in these materials, especially compared to that of inorganic semiconductors. The Onsager-Braun model suggests that an externally applied field can aid the dissociation of these bound pairs and increases the dissociation yield. However, there has been some debate in literature as to whether this model is a suitable approximation in organic semiconductor systems,^{3,4} and the extent to which macroscopic electric fields affect the dissociation of geminate pairs within the active layer is currently the subject of significant controversy.⁵⁻¹⁴

Electric field dependent geminate recombination of bound electron / hole pairs has been used to describe the shape of the J-V curve of a range of organic solar cells.¹⁴⁻¹⁸ Recombination of geminate pairs before separation has been suggested to be a key loss pathway limiting the efficiency of organic solar cells,^{2,15,17,19-23} specifically limiting device short circuit current and FF, where a non-zero gradient in the J-V curve through J_{sc} often leads to a poor FF and this has, in some publications, previously been assigned to field dependent geminate recombination.^{13,16} In this regard, it has been widely suggested that macroscopic electric fields, present in such organic solar cells due to charge accumulation on the device electrodes, may be a key factor in

enabling dissociation of the CT states, thereby reducing geminate recombination losses. As the magnitude of these electric fields is dependent upon device voltage, electric field dependent charge generation has been suggested to be a key factor determining the shape of J-V curve, and particularly the FF, of such devices.^{6,9,13}

Indirect investigations of field-dependent geminate recombination within the power-generating quadrant of OPV devices have yielded conflicting conclusions regarding the dependence of geminate recombination upon device electric fields. Many of these indirect analyses rely on the application of device models to fit the theoretical data and despite some analyses concluding that the field is too weak to impact significantly upon device FF and V_{OC} ,^{5,10,24-29} others have shown that there is a significant impact of the device electric fields.^{14,30} More direct experimental studies of charge photogeneration as a function of applied field have been relatively limited to date, but include PLQ studies,^{12,17} electroluminescence (EL),^{11,31} photocurrent measurements^{7,30,32} and TAS.^{8,9} BHJ systems that have been reported in literature to show electric field assisted charge generation include P3HT:PCBM,⁹ poly[2,7-(9,9-dioctylfluorene)-alt-5,5-(4',7'-di-2-thienyl-2',1',3-benzo-thiadiazole)] (APFO-3):PCBM,¹⁰ C-PCPDTBT:PC₇₀BM,³⁰ and the small molecule donor system poly[[N-(20-decyltetradecyl)carbazole]-2,7-diyl:bis(2-(1-ethylhexyl-4,5-dicyanoimidazol-2-yl)vinyl)benzo[c]1,2,5-thiadiazole] (PCz:EV-BT).¹⁶ However, these direct measurements of such field-dependent losses have often observed these to be important only under strong reverse bias (> -5 V), which is of less significance for the operation of photovoltaic cells.⁸⁻¹⁰

Of particular interest here, several previous studies, have interpreted changes in the photoluminescence of interfacial CT states (sometimes called 'exciplex' emission) observed under strong reverse bias conditions in terms of electric field dependent dissociation of these charge transfer states,^{10,11,17} a conclusion recently supported by a transient absorption study by Marsh *et al.* on P3HT:PCBM devices.⁹ This conclusion however contrasts with some transient photoinduced absorption studies, investigating the yield of long lived, dissociated polarons in P3HT:PCBM based solar cells. For example, Shuttle *et al.* observed that, for applied voltages between 0 and +1 V, the yield of dissociated polarons was not strongly dependent upon applied bias.⁸ To support this conclusion, Shuttle *et al.* employed a range of transient optoelectronic measurements to provide evidence that the shape of the current / voltage curve of P3HT:PCBM solar cells, and in particular the device FF, originates not from electric field dependence of charge photogeneration (and the associated geminate recombination losses). Rather, this analysis suggests the origin of the FF may arise from the charge density dependence of non-geminate recombination of dissociated charges.²⁸ From these data, specifically using the non-geminate rate constant, the J-V curve was reconstructed without the use of any fitting

parameters, and utilising a bias independent generation profile across the J-V curve.²⁸ One of the key considerations in this analysis compared to that of other models is the discussion of the degree to which field assisted geminate pair splitting contributes to the photocurrent. These literature results reported above, in addition to the results that will be presented here, of bias dependencies have implications on our understanding of the mechanistic nature of charge generation in organic photovoltaic devices.

Despite many reports of bias-dependent charge separation in BHJ solar cells, there is increasing evidence suggesting field independent generation of dissociated charges occurs in some OPVs. Devices that have shown to exhibit this behaviour include poly[2-methoxy-5-(30,70-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV):PCBM,¹⁶ P3HT:PCBM^{5,8} and the polymer / small molecule system poly[2,5-dimethoxy-1,4-phenylene-1,2-ethylene-2-methoxy-5-(2-ethylhexyloxy)-(1,4-phenylenevinylene-1,2-ethenylene):4,7-bis[2-(hexyl-4,5-dicyanoimidazol-2-yl)vinyl]benzo[c]-[1,2,5]-thiadiazole (ME3H-PPV:HV-BT).¹² In the latter system it has been concluded from their photocurrent and PL emission data, that the generation of dissociated charges does not occur via a CT precursor,^{12,19} rather via a state that is unaffected by an external field and therefore, the splitting of the CT state by an electric field does not significantly change the photocurrent generation.

The first part of this chapter is concerned with the effect of an external field on the yield of dissociated charges for a series of three different PCPDTBT:PC₇₀BM blend analogues, the structures of which are shown in Figure 3.2 . Charge photogeneration in PCPDTBT blend films has been discussed in depth in Chapter 3, and we now turn to evaluate the overall cell performance of these blends. The three blends considered are C-PCPDTBT:PC₇₀BM , C-PCPDTBT:PC₇₀BM + ODT and Si-PCPDTBT:PC₇₀BM. The poor device performance in C-PCPDTBT:PC₇₀BM, as seen by both a low J_{SC} and FF, has previously been suggested to arise from a large electric field dependence on the hole mobility,³³ that may be the result of a poor nanomorphology in these blends with a high degree of intermixing between the two materials, potentially hindering the charge separation. The use of the processing agent ODT in device fabrication leads to a dramatic improvement in both J_{SC} and FF, with efficiencies of ~ 5 % reported for C-PCPDTBT:PC₇₀BM + ODT blends.^{34,35} This enhanced efficiency may arise from an increase in the crystallinity of the blends with ODT.^{36,37} The most efficient devices for this polymer series, Si-PCPDTBT:PC₇₀BM, with reported efficiencies > 5 %.^{38,39} have also shown an improvement in the crystallinity⁴⁰ and molecular packing⁴¹ of the material compared to the carbon based blend.

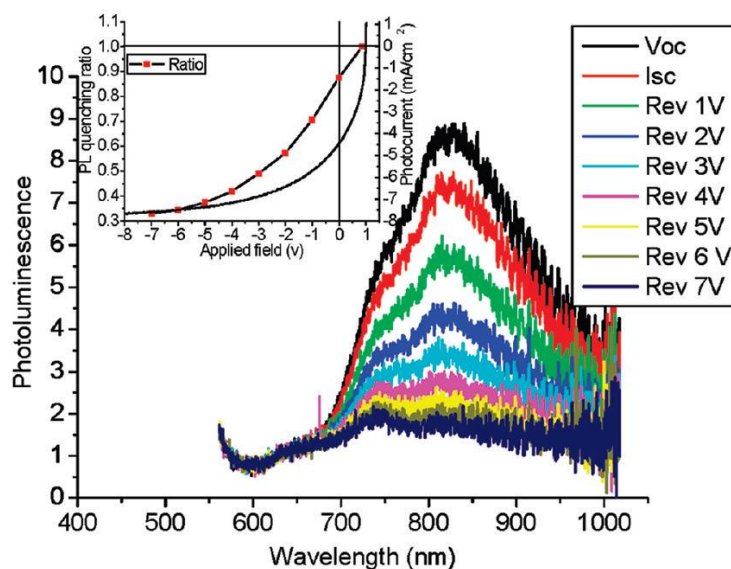


Figure 6.1 – Electric field dependent PLQ of an APFO-3:PCBM (1:4) blend, reproduced from reference 10. Inset, the PL maximum as a function of applied bias, (red squares) compared to the device photocurrent.

Another donor material that has been investigated elsewhere in the literature with respect to field-dependent photogeneration is APFO-3 (alternatively called F8DTBT in some publications). APFO-3:PCBM blend PVs have been reported to produced device efficiencies above 4 %.⁴² However, despite the moderate device efficiencies in these blends, Sundström and co-workers have reported that the device performance is severely limited by a significant, electric field dependent, geminate recombination losses.⁴³ They have employed TAS to confirm this loss mechanism and observe a 30 ns fast phase in these blends, attributed to geminate recombination of bound charges.⁴⁴⁻⁴⁶ The role of electric field dependent charge generation in these blends has been investigated elsewhere^{11,17} as a function of steady state and time resolved PL and EL measurements. Electric field dependent PLQ of APFO-3:PCBM has been reported by Tvingstedt *et al.*, as shown in Figure 6.1. These data show an increase in the PLQ with the application of an applied bias.¹⁰ These measurements indicate that the emissive state investigated in this study is indeed affected by an applied bias, however, there is no indication from these results as to whether dissociation of this state contributes to the photocurrent. EL measurements from the same group have characterises the observed emission in APFO-3:PCBM blends to arise from recombination via interfacial CT states in these blends.¹¹ This is confirmed by the inset in Figure 6.1 showing the maximum PL as a function of applied bias (red squares). However, the photocurrent generation (solid black line) does not match the PLQ, indicating that the extractable charge is greater than suggested from the PLQ. These data suggest that photocurrent generation in these blends does not solely occur via formation of an emissive CT state.

The final part of this chapter focuses on two small molecule / PC₇₀BM blends and the charge generation and the contribution to the geminate recombination losses for these systems. Until recently, solution processed small molecule / PC₇₀BM cell efficiencies have not been as high as their polymer counterparts, often limited by a low FF.^{47,48} However, recent developments small molecule blend device fabrication have led to substantial improvements in devices performance, with efficiencies of greater than 6 % now reported in both solution-processed blends,^{49,50} and vacuum deposited devices.⁵¹ The small molecule donors investigated herein are 3,6-bis[5-(benzofuran-2-yl)thiophen-2-yl]-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4-dione (DPP(TBFu)₂)⁵² and 3-[bis(2-ethylhexyl)silanol-yl]-5,5'-bis{5-[2,5-bis(2-ethylhexyl)-6-[5-(benzofuran-2-yl)thiophene-2-yl]pyrrolo[3,4-c]pyrrole-1,4-dione-3-yl]-2,2'-bithiophene (SDT(TDPPTBFu)₂), both of which are blended with PC₇₀BM. The efficiency of these devices is limited by a poor FF, the origin of which was unclear but will be investigated herein. It had been suggested this low FF was dependent on the degree of non-geminate recombination,⁵³ a suggestion which will be considered in this analysis.

The observed variation in photocurrent with bias is often attributed to, amongst other effects, light dependent shunt resistances,⁵⁴ non-geminate recombination losses, or electric field dependent charge generation.¹⁴ Identifying, understanding and quantifying the degree to which these mechanisms contribute to the shape of the J-V is a complex task, and cannot simply be determined from a simple observation of the J-V curve. This chapter aims to investigate further the effects of device electrodes on the charge generation and the impact this may have on the device J-V.

6.2 Experimental

Encapsulated C-PCPDTBT:PC₇₀BM (1:2), C-PCPDTBT:PC₇₀BM + ODT (1:2) and Si-PCPDTBT:PC₇₀BM (1:2) devices were fabricated by Dr Hamed Azimi at Konarka Technologies, Linz, as described previously.⁵⁵ APFO-3:PCBM (1:4) devices were fabricated at Imperial College London by George Dibb and kept in a nitrogen atmosphere under constant gas flow. DPP(TBFu)₂:PC₇₀BM (3:2) and SDT(TDPPTBFu)₂:PC₇₀BM (3:2) devices were fabricated and encapsulated by Dr Bright Walker at the University of California, Santa Barbara, as described previously.⁴⁹ The active layer thicknesses for all materials tested were comparable throughout; 90 nm ± 20 nm for PCPDTBT:PC₇₀BM and its analogous blends, 95 nm ± 20 nm for APFO-3:PCBM and for both DPP(TBFu)₂:PC₇₀BM and SDT(TDPPTBFu)₂:PC₇₀BM devices thicknesses were 95 nm ± 10 nm. The device pixel areas were 0.14 cm² for all PCPDTBT:PC₇₀BM devices, 0.045 cm² for APFO-3:PCBM devices and 0.16 cm² for DPP(TBFu)₂:PC₇₀BM and SDT(TDPPTBFu)₂:PC₇₀BM devices.

TAS decays were measured in reflection mode, reflecting off the aluminium electrode, following optical excitation at 532 nm for all PCPDTBT:PC₇₀BM devices, 520 nm for APFO-3:PCBM and 600 nm for both DPP(TBFu)₂:PC₇₀BM and SDT(TDPPTBFu)₂:PC₇₀BM devices, with an OPO Nd:YAG laser. Excitation densities employed were 8 μJcm⁻² and 80 μJcm⁻² for PCPDTBT:PC₇₀BM blends, with a pulse repetition frequency of 20 Hz. For APFO-3:PCBM and the small molecule blends, pump intensities of 3 – 6 μJcm⁻² were employed at 4 Hz. A laser diode probe source was used at 1310nm (for all PCPDTBT:PC₇₀BM devices) and 980 nm (APFO-3:PCBM, DPP(TBFu)₂:PC₇₀BM and SDT(TDPPTBFu)₂:PC₇₀BM devices), with 10 mW and 30 mW power, respectively. The external bias was applied with power supply, in a random order to ensure no cumulative voltage effects were recorded.

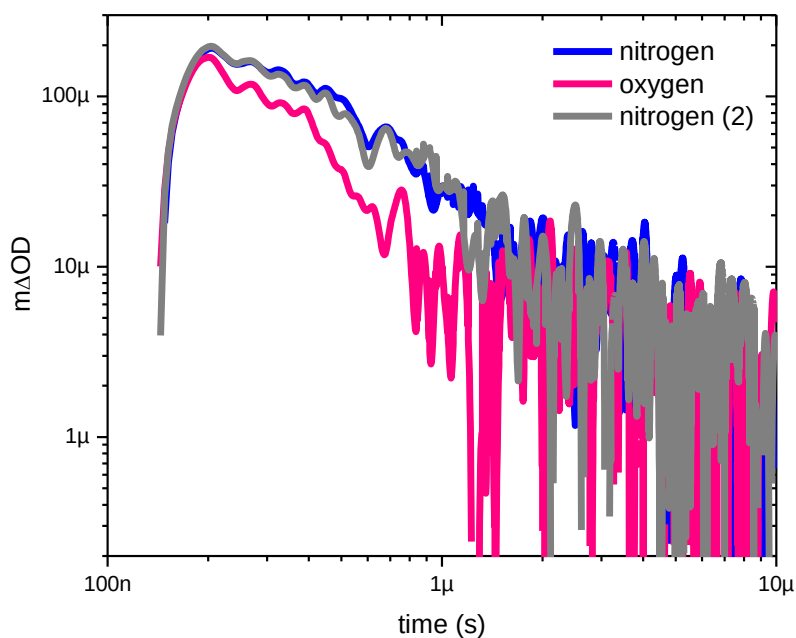


Figure 6.2 - TAS decays of APFO-3:PCBM (1:1) taken by Yvonne Soon on thin films in an inert atmosphere (nitrogen, blue) and then in an oxygen rich atmosphere (pink) to confirm the presence of triplets.

TAS decays of APFO-3:PCBM (1:1) taken by Yvonne Soon at Imperial College London are shown in Figure 6.2 as a function of sample atmosphere to investigate the formation of triplets in these blends. The oxygen dependence of the decay dynamics confirm the presence of triplets, and this assignment from the thin film analysis is assumed in the transient analysis presented in Section 6.3.2. From $\sim 1 \mu\text{s}$ the decay kinetics may be fit to a power law decay, indicating the presence of charges after the triplet observation.

6.3 Results

6.3.1 PCPDTBT:PC₇₀BM blend devices - electric field independent charge generation

The first of the donor materials systems to be studied under an applied electric field is PCPDTBT, the structure of which has been shown in Chapter 3, Figure 3.2. The steady state absorption, PLQ, transient absorption spectra and transient decay kinetics of the three PCPDTBT:PC₇₀BM blend studied in this section has been described previously in Chapter 3, on thin films and the following analyses on complete devices will continue from this thin film analysis. From these TAS investigations of the charge generation yield, the silicon bridged blend device is expected to have the highest J_{sc} (from the magnitude of ΔOD), followed by the carbon blend with ODT. Finally the C-PCPDTBT:PC₇₀BM devices are expected to be the least efficient materials composition in this series because of the lowest ΔOD amplitude observed at 1 μs .

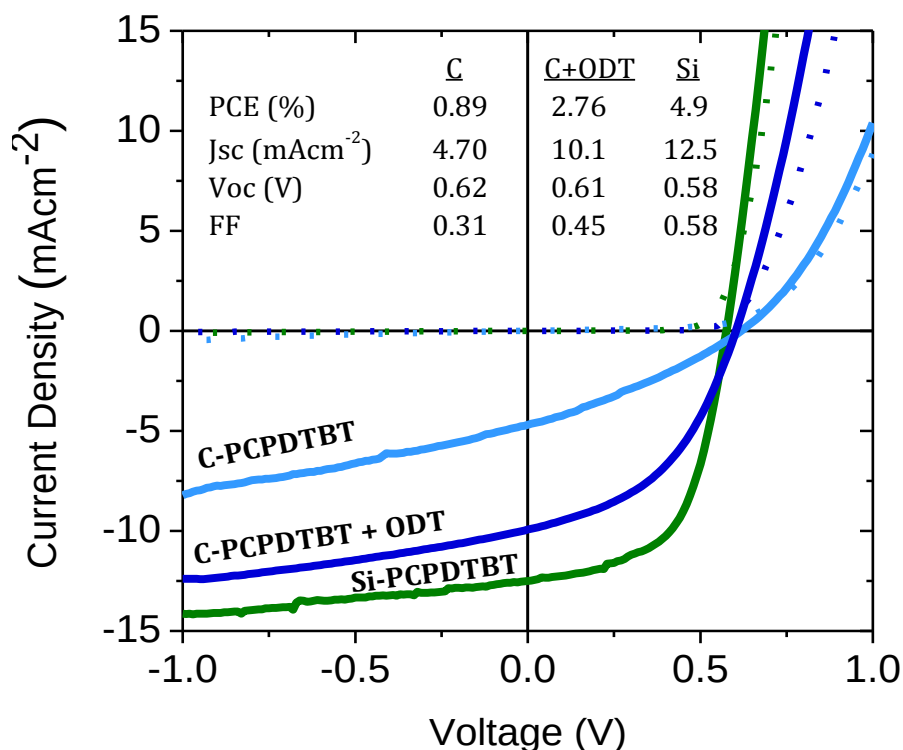


Figure 6.3 - J-V curves for C-PCPDTBT:PC₇₀BM (dark green), C-PCPDTBT:PC₇₀BM + ODT (blue) and Si-PCPDTBT:PC₇₀BM (light green) blends between -1 to +1 V at 1 sun light intensity. Inset, device parameters for the devices tested here.

The J-V curves in Figure 6.3 shows the device characteristics of C-PCPDTBT:PC₇₀BM (light blue), C-PCPDTBT:PC₇₀BM + ODT (blue) and Si-PCPDTBT:PC₇₀BM (light green) devices between -1 V to +1 V, at 1 sun light intensity. These efficiencies are typical of those reported previously for these blend compositions,^{34,38} and from these initial data (J_{SC} and FF), it is possible to see that the device performances vary greatly between these three different blends, as expected from the differences in the TAS yields described in Chapter 3. We also highlight the large variation in the shapes of the J-V curves, demonstrating that only a small chemical modification in the active layer is required to cause considerable differences in both J_{SC} and FF of these devices. As discussed in the introduction, the bias dependence of the photocurrent, as inferred from its gradient through 0 V, has previously been assigned to electric field dependent charge photogeneration.^{13,14} This gradient is observed to be largest in this series for C-PCPDTBT:PC₇₀BM blends, yielding a device FF of only 33%, which is considerably smaller than both that observed for the C-PCPDTBT:PC₇₀BM + ODT blend (FF = 45%) and Si-PCPDTBT:PC₇₀BM blend (FF = 58%) studied here. The observed increase in both J_{SC} and FF correlates with an approximate fivefold increase in power conversion efficiency from 0.9% for the carbon analogue, to 4.9 % for the silicon bridged polymer blend.

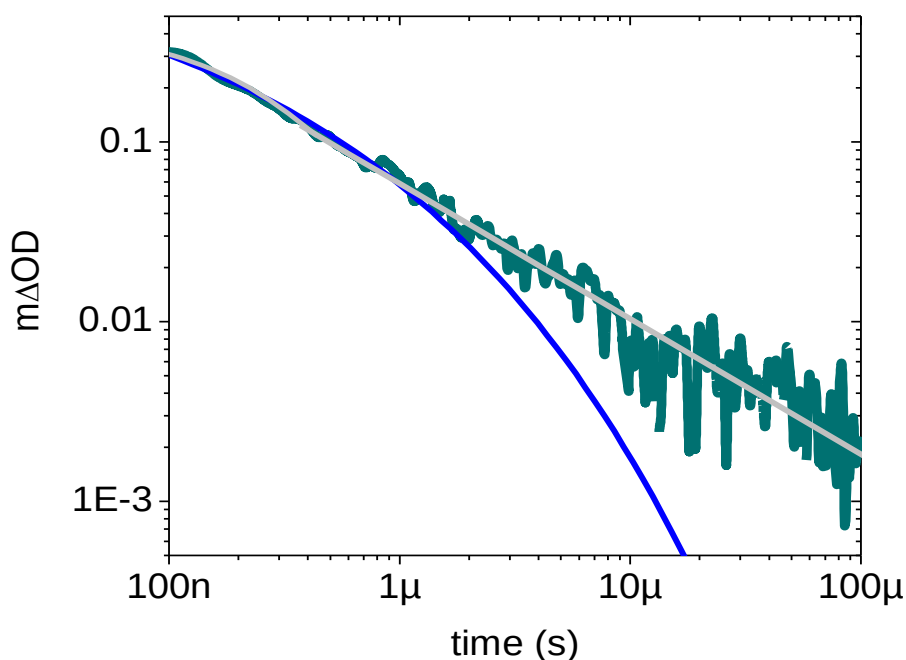


Figure 6.4 – A typical TAS decay of a C-PCPDTBT:PC₇₀BM + ODT device following polymer excitation. Overlaid is non-geminate (power law, grey) and monomolecular (stretched exponential, blue) fits to this decay. It is apparent that only the non-geminate (power law) analysis fits the experimental data, and not the monomolecular decay.

TAS has been employed herein to investigate the charge generation yield in the devices presented above. Transient spectra recorded as a function of wavelength at a time delay of 1 μ s for the corresponding films of the three different blends all exhibited a well-defined absorption band between 1200 and 1400 nm, as shown previously in Figure 3.14, which has been assigned to the polymer polaron. Following this assignment, the transient absorption all three compositions were monitored at 1310 nm. Figure 6.4 shows a comparison of a power law (grey) stretched exponential (blue) fits to a C-PCPDTBT:PC₇₀BM + ODT decay, confirming these decay dynamics exhibit power law rather than exponential behaviour, and are therefore, indicative of non-geminate recombination dominating the loss mechanisms on the timescales investigated here. The exponent, α , of the power law decays for this C-PCPDTBT:PC₇₀BM device was found to be ~ 0.75 , consistent with our previous studies of analogous films as described in Figure 3.15. Such non-geminate recombination kinetics can be readily distinguished from geminate recombination in such blend films, with the latter exhibiting monomolecular (exponential) decay dynamics on the picoseconds to nanosecond timescales, which therefore occur before the timescale of these experiments, as has been shown previously.⁵⁶⁻⁵⁹ The non-geminate decay characteristics of the carbon blends have been shown previously in Figure 3.15. Following this assignment of non-geminate recombination to the long-time power-law decays in this device, we have explored the hypothesis of electric field assisted charge generation using TAS to investigate the change in charge generation yield as a function of applied bias.

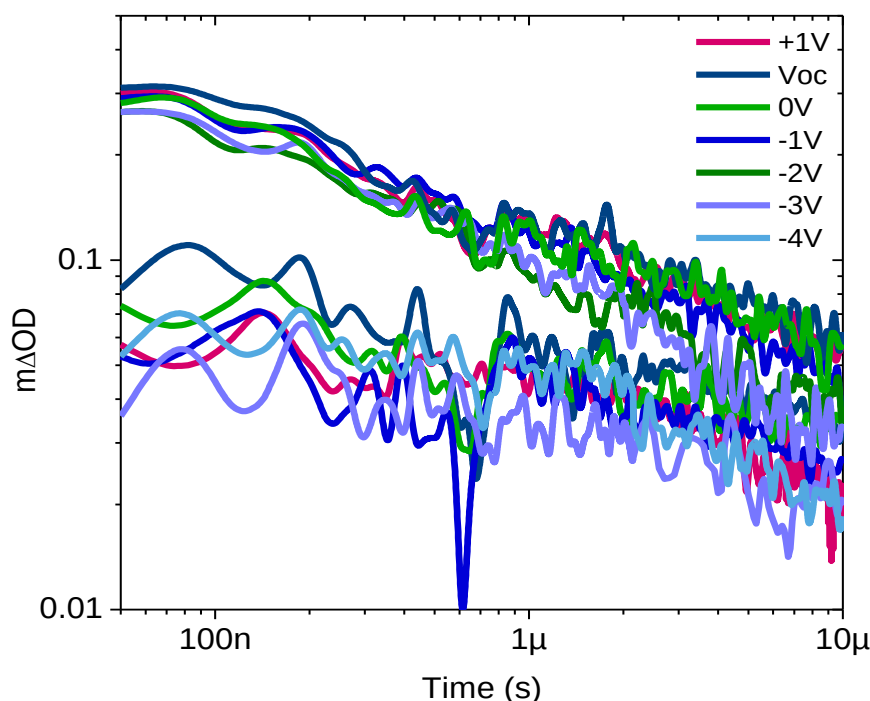


Figure 6.5 - Photoinduced absorption transients measured at 1310 nm for C-PCPDTBT:PC₇₀BM with ODT devices, with excitation densities at 8 μJcm^{-2} for the lower transients and 85 μJcm^{-2} for the upper transients, between 20 ns – 10 μs with applied biases ranging between +1 V and -4 V.

Figure 6.5 shows typical absorption transients measured at 1310 nm for a C-PCPDTBT:PC₇₀BM + ODT device measured as a function of applied electric bias, between +1 V and -4 V, for two different excitation densities $\sim 8 \mu\text{Jcm}^{-2}$ (lower transients) and $\sim 85 \mu\text{Jcm}^{-2}$ (upper transients). We note that at the pump excitation at 532 nm, the film has an optical density of ~ 0.1 , such that $\sim 10\%$ of the incident excitation intensity is absorbed by the film. It is apparent that all of these transients exhibit power-law decays, with plateaux at early times. As discussed above, and shown in Figure 6.5, such power law kinetics are characteristic of diffusion limited non-geminate recombination of dissociated charge carriers and not of geminate recombination of bound charge pairs.⁶⁰ The plateaux of the transient decays at early times is again typical of non-geminate recombination processes,⁸ with the plateaux time corresponding to the onset of non-geminate recombination. As expected, this plateaux onset is later at lower excitation densities, consistent with the slower non-geminate recombination losses expected at a lower charge carrier density. We note that our initial transient absorption signal size at 8 $\mu\text{J cm}^{-2}$ ($\Delta\text{OD} = 4 \times 10^{-5}$) is almost two orders of magnitude smaller than reported recently in an analogous study of P3HT:PCBM devices,⁹ reflecting the low excitation conditions used in our study. We further note that carrier sweep-out by the device electrodes may also contribute to the later time decay data, as has been discussed elsewhere.⁸

We turn now to considering the effect of applied bias upon this charge photogeneration yield. It is already apparent from the data in Figure 6.5, that the amplitude of polaron absorption signal observed for C-PCPDTBT:PC₇₀BM + ODT devices is not significantly dependent upon applied bias, for bias ranging from +1 V forward bias to -4 V reverse bias, corresponding to electric fields ranging from ~ 0 to $\sim 5 \times 10^5$ Vcm⁻¹. This dependence upon bias voltage (or lack thereof) is addressed in more detail in Figure 6.6, where we plot data on linear axes, and include data for devices employing all three different photoactive layers. It is apparent that for all three devices, the magnitude of the initial transient absorption signal, assigned to the yield of dissociated polarons, is, within the limits of our signal-to-noise ratio ($\sim \pm 10$ %) independent of applied bias. Similar bias independent data were obtained for several different cells of each type and all showed negligible reverse bias dependence on charge photogeneration.

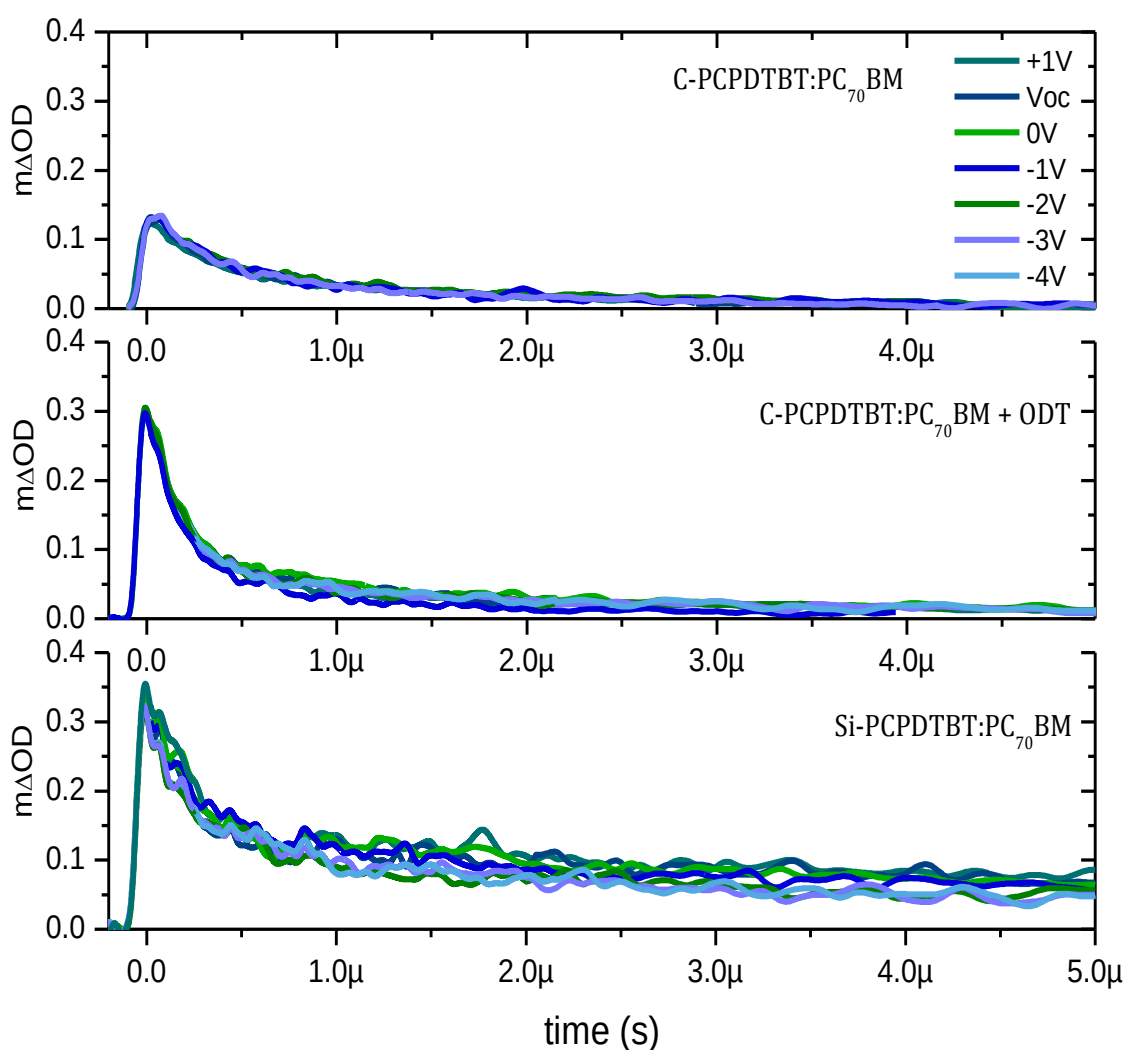


Figure 6.6 - Photoinduced absorption transients measured for all three PCPDTBT blend devices at an excitation density of $85 \mu\text{Jcm}^{-2}$, with varying applied biases between +1V and -4V. Top, C-PCPDTBT:PC₇₀BM, middle, C-PCPDTBT:PC₇₀BM + ODT, bottom, Si-PCPDTBT:PC₇₀BM.

It is also apparent from Figure 6.6 that the initial magnitude of the transient absorption signals, corresponding to the yield of dissociated polarons, correlates with J_{sc} . We emphasise however, that whilst we observe the yield of charge photogeneration, and therefore geminate recombination, to vary between devices, for all three devices we observe no influence of device electric field, indicating that geminate recombination losses in these devices are not strongly dependent upon electric field.

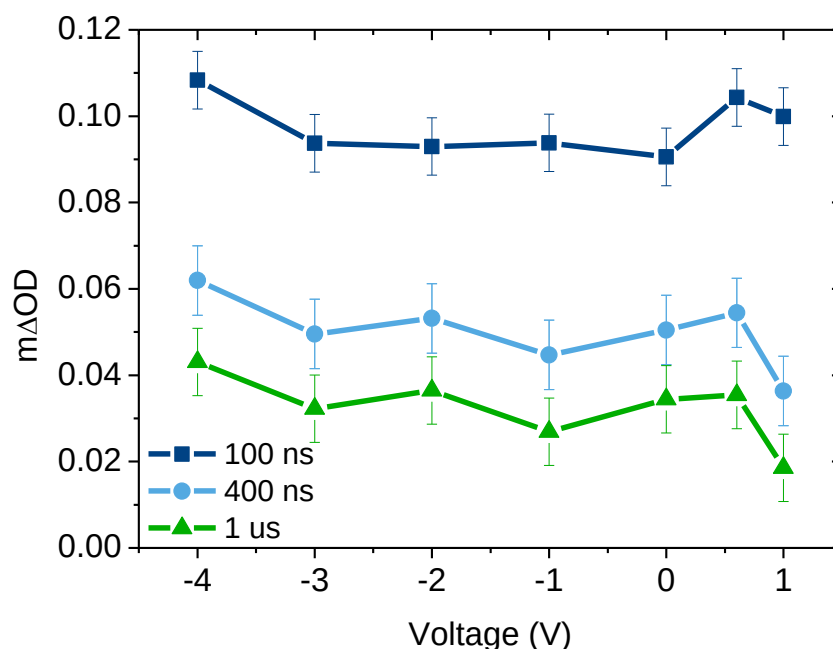


Figure 6.7 – The ΔOD signal recorded for C+ODT devices as a function of applied bias at different times after polymer excitation at 532 nm. From these data there is no discernable change (within the noise of the system) in the charge generation as a function of applied bias with time.

The data in Figure 6.7 shows the voltage dependence of the charge generation yield recorded from the TAS decays in Figure 6.5, as a function of time, at 100 ns (squares), 400 ns (circles) and 1 μs (triangles) for C-PCPDTBT:PC₇₀BM + ODT. The amplitudes of these data for these data decrease with time, as expected, as non-geminate recombination of free charges occurs, removing these free charges from the system. From these data there is no observable change in the generation yield of dissociated charges (from the magnitude of the ΔOD signal) with either an external bias or time. This indicates that electric field assisted splitting of geminate charges does not significantly contribute to overall yield of dissociated charges that contribute to the device photocurrent. However, above voltages that correspond to one sun V_{oc} (0.65 V) the charge densities start to decrease, most significantly at longer timescales (> 400 ns), which may arise from an increase in non-geminate recombination above V_{oc} , as the charge density in such

devices has been observed to increase exponentially with applied voltage under forward bias, with an associated significant acceleration of non-geminate recombination losses.

6.3.2 APFO-3:PCBM devices - electric field assisted charge generation in a polymer / fullerene blend

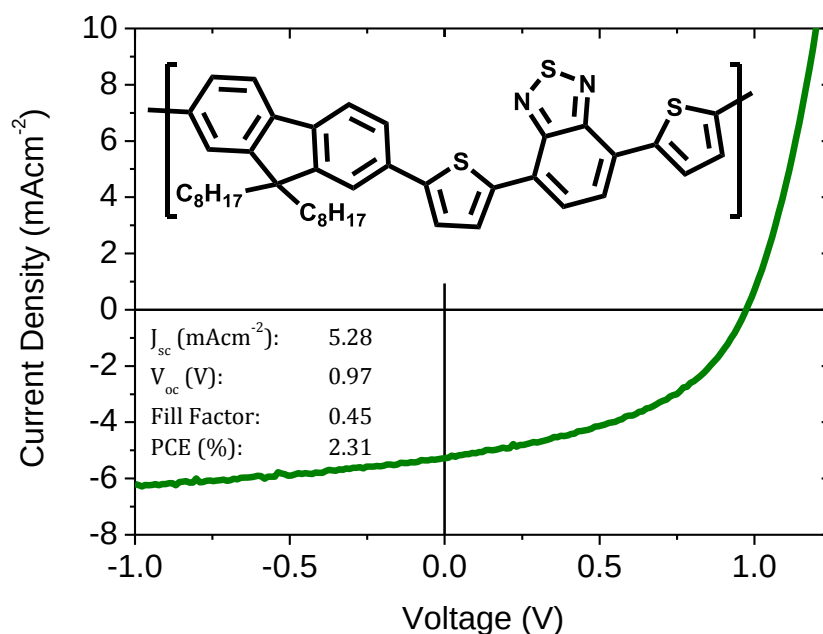


Figure 6.8 - J-V curve for an APFO-3:PCBM (1:4) device under 1 sun illumination. Inset, the chemical structure of APFO-3.

The J-V curve for a 1:4 blend, the most efficient blend ratio for this blend,¹⁷ and chemical structure of one monomer unit of APFO-3 are shown in Figure 6.8. Previous analysis on blends of this material have shown that the most efficient blend composition for these devices is 1:4 APFO-3:PCBM,⁶¹ which is used herein. In this blend $V_{oc} = 0.97$ V, typical for this device composition, as reported elsewhere,⁶² and considerably higher than that typically shown in P3HT:PCBM blends. Despite the high V_{oc} , the device exhibits only a modest power conversion efficiency of 2.3 %. This efficiency may be limited to both the low J_{sc} (5.4 mA cm⁻²), low FF = 0.45, which is influenced by the modest gradient through 0 V.

Transient analyses from Inganas and co-workers has shown the observation of a transient peak at 1000 nm,^{44,45} and this wavelength has been used to probe the transient species herein. However, this peak may not arise solely from the formation of polarons, but also may also

contain a significant triplet contribution, as these two states have very similar energies and are too similar to be distinguished between using these TAS analyses. Despite some ambiguity of the origin of the transient peak, the electric field dependence of this species has been investigated at this wavelength.

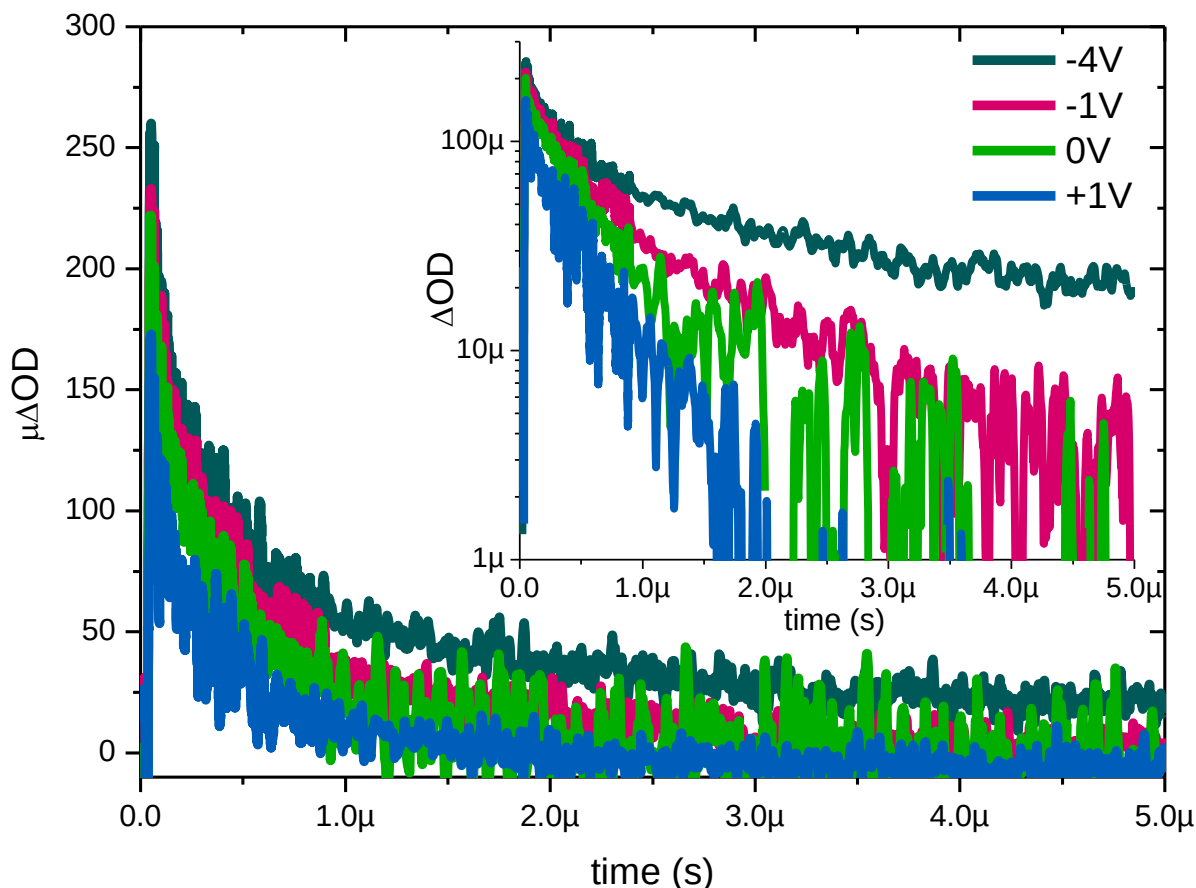


Figure 6.9 – TAS decay kinetics of an APFO-3:PCBM device as a function of four different applied biases (+1 V, 0 V, -1 V and -4 V). Inset, identical data on a log/lin axes to highlight the change in decay dynamics with the application of increasing reverse bias.

The TAS kinetics between 50 ns to 5 μ s are shown in Figure 6.9 as a function of four different applied biases; +1 V (dark blue), 0 V (green), -1 V (pink) and -4 V (dark green). From these data, a small increase in the initial ΔOD at 50 ns is observed with increasing reverse bias, from 0.17 m ΔOD at +1 V to 0.26 m ΔOD at -4 V. Despite only a modest change in the initial signal amplitude, there is a more significant change in ΔOD with the application of an increased reverse bias at later times, as shown in Figure 6.10. In addition to a change in the optical density upon the application of a bias, a change in the decay dynamics is also observed as a function of bias. The application of a reverse bias yields a retardation in the recombination kinetics, that

cannot be assigned to sweep-out of carriers to the device electrodes, as we would expect this process to become slower towards open circuit. The two transient decays recorded with a negative applied bias exhibit biphasic behaviour, as seen in the inset on a log-lin plot of Figure 6.9, whereas the dynamics recorded at short circuit and forward bias conditions do not show significant biphasic behaviour and show exponential decay phase followed by a slower power-law decay. The decay dynamics recorded at +1 V may be fit to a mono-exponential decay, with a lifetime of ~ 300 ns. This mono-exponential decay is indicative of a significant contribution to the ΔOD from triplets, as seen in electrode free thin film analyses of this material, consistent with the thin film analysis presented in Figure 6.2. Upon the application of a reverse bias, the decay becomes biphasic in nature, and this is most pronounced in the decay at -4 V, which may be fit to a stretched exponential, which suggests that the formation of triplet states is being hindered by the applied field. It is apparent from Figure 6.10 that this field dependent geminate recombination results in an approximate halving of the yield of dissociated charges between -4 V and +1 V bias by 100 ns, and $\sim 90\%$ reduction in the initial yield of charges recorded here by 1 μ s. The deviation from this single profile at longer times (> 1 μ s) for APFO-3:PCBM may be as a result of a change in the triplet contribution to the overall signal.

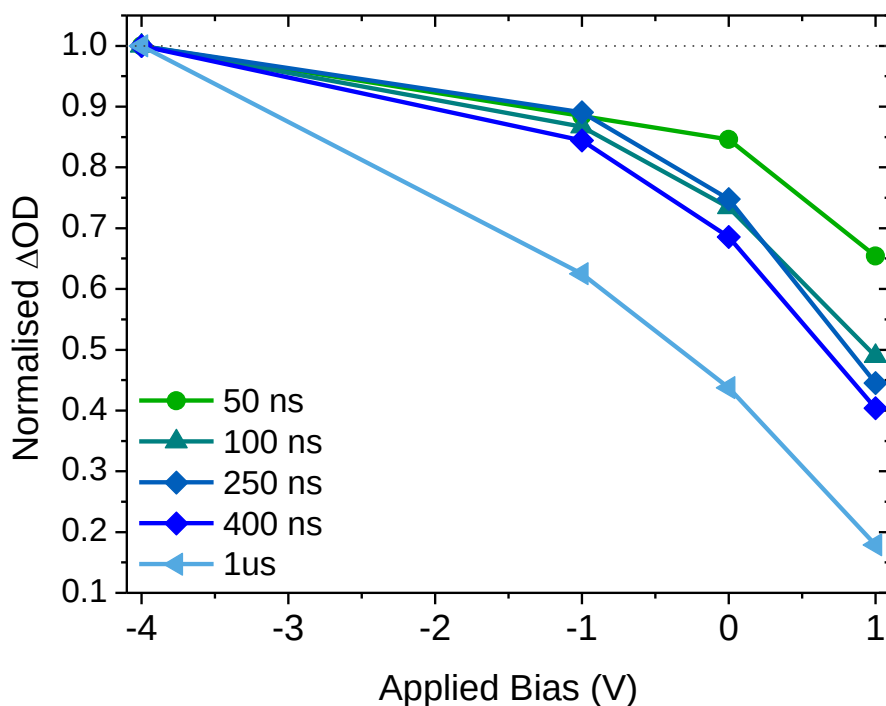


Figure 6.10 – Normalised ΔOD signal as a function of applied bias (between +1 V to -4 V) for APFO-3:PCBM between 50 ns and 1 μ s.

6.3.3 Small Molecule:PC₇₀BM devices – electric field assisted charge generation

The final results section of this chapter focuses on the electric field dependence of two small molecule / PC₇₀BM blends. This data is then in turn used in device modelling to recreate the J-V curve from the experimentally derived generation yield. The structures of the two small molecule donor materials investigated in this section are shown in Figure 6.11.

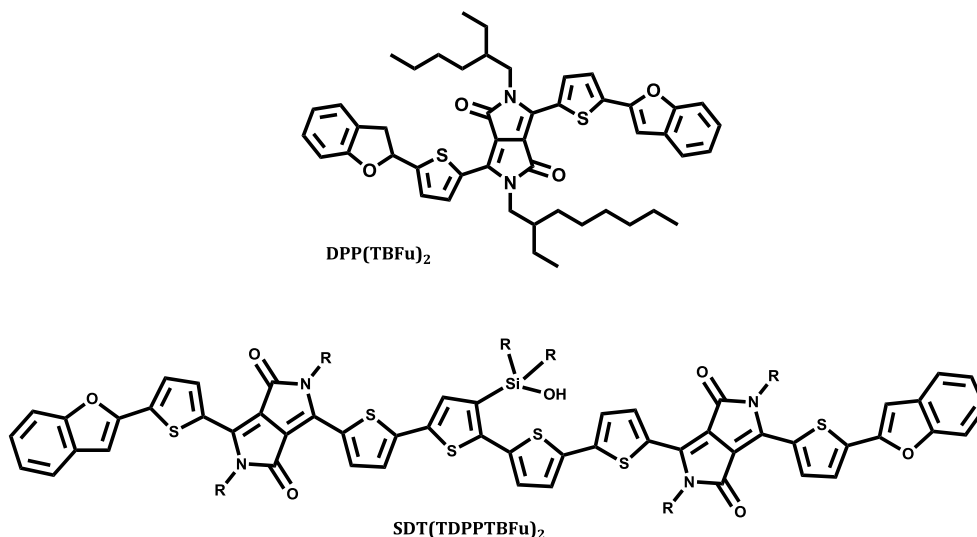


Figure 6.11 – The chemical structures of the two small molecule donors materials DPP(TBFu)₂ (top) and SDT(TFPPTBFu)₂ (bottom), where R = 2-ethylhexyl.

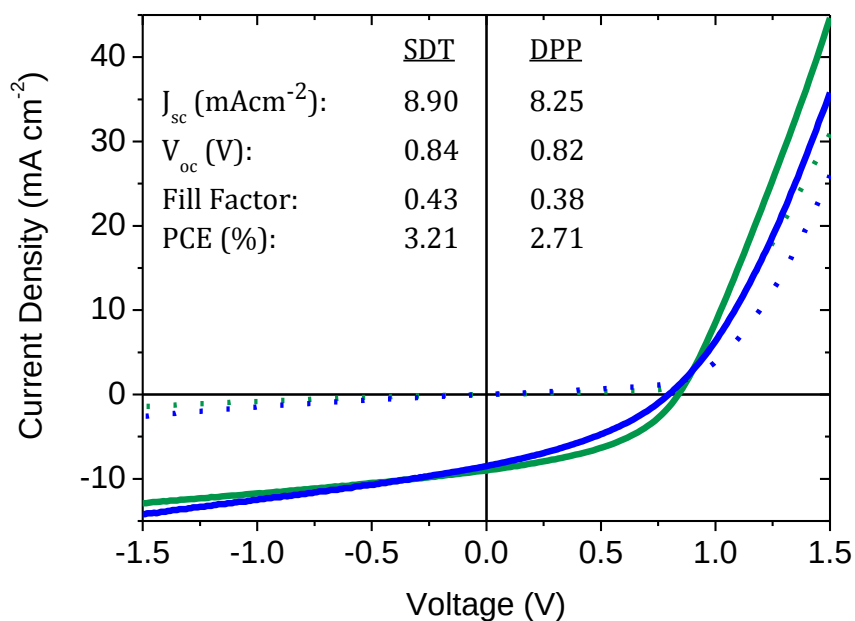


Figure 6.12 – The J-V characteristics for SDT(TDPPTBFu)₂:PC₇₀BM (blue) and DPP(TBFu)₂:PC₇₀BM (green) devices at 1 sun light intensity with the corresponding dark curves (dashed lines).

The device characteristics, including the efficiency, FF, J_{SC} and V_{OC} for SDT(TDPPTBFu)₂:PC₇₀BM (blue) and DPP(TBFu)₂:PC₇₀BM (green) devices are shown in Figure 6.12, corresponding with previously reported efficiencies for these blends.⁴⁹ The V_{OC} for these two blends is higher than that of the PCPDTBT devices reported above by ~ 200 mV, at ~ 0.84 V, however, J_{SC} in both of these devices is smaller than that of the two most efficient PCPDTBT blends. These small molecule blend devices exhibit only modest FFs (0.38 and 0.43), and both exhibit relatively large gradients through zero bias. Following the analysis presented above for PCPDTBT:PC₇₀BM and APFO-3:PCBM blends, the same approach was applied to these small molecule / PC₇₀BM blend devices, initially starting with TAS spectra and decay analysis.

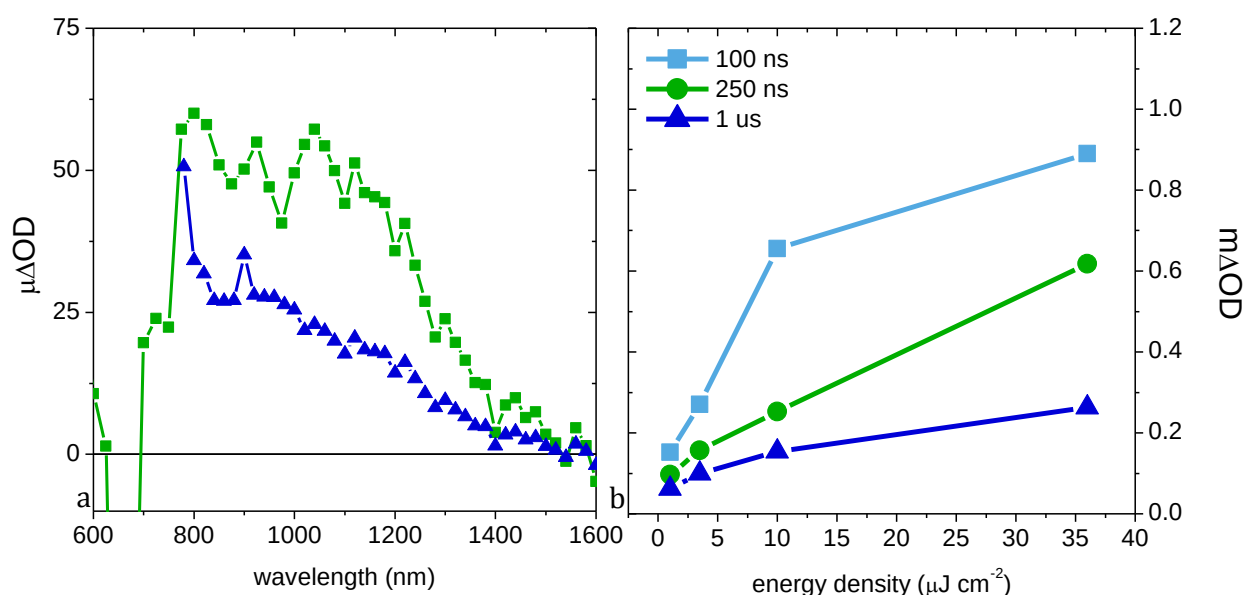


Figure 6.13 – a) Transient spectra of SDT(TDPPTBFu)₂:PC₇₀BM (green squares) and, DPP(TBFu)₂:PC₇₀BM (blue triangles) devices at 1 μs, following excitation at 600 nm, and b) excitation density dependent measurements for DPP(TBFu)₂:PC₇₀BM probed at 980 nm as a function of time after excitation, following excitation at 600 nm, at 100 ns, 250 ns and 1 μs.

The transient spectra at 1 μs are shown in Figure 6.13a for both SDT(TDPPTBFu)₂:PC₇₀BM (green squares) and DPP(TBFu)₂:PC₇₀BM (blue triangles). Both of these blends show a broad transient absorption between 800 – 1200 nm, and all TAS kinetics were recorded at 980 nm for both blends. The excitation density dependence of the pump fluence on the magnitude of the ΔOD signal is shown in Figure 6.13b, at three different times (100 ns, 250 ns and 1 μs) for DPP(TBFu)₂:PC₇₀BM, probing the transient species at 980 nm. Excitation densities of 6 μJcm⁻² were used herein to minimise non-linear excitation processes. We now consider the possibility that charge dissociation in these blends may itself be field dependent, thereby resulting in field

dependent geminate recombination losses. For this purpose TAS measurements of polaron dynamics were conducted, as previously, as a function of applied bias.

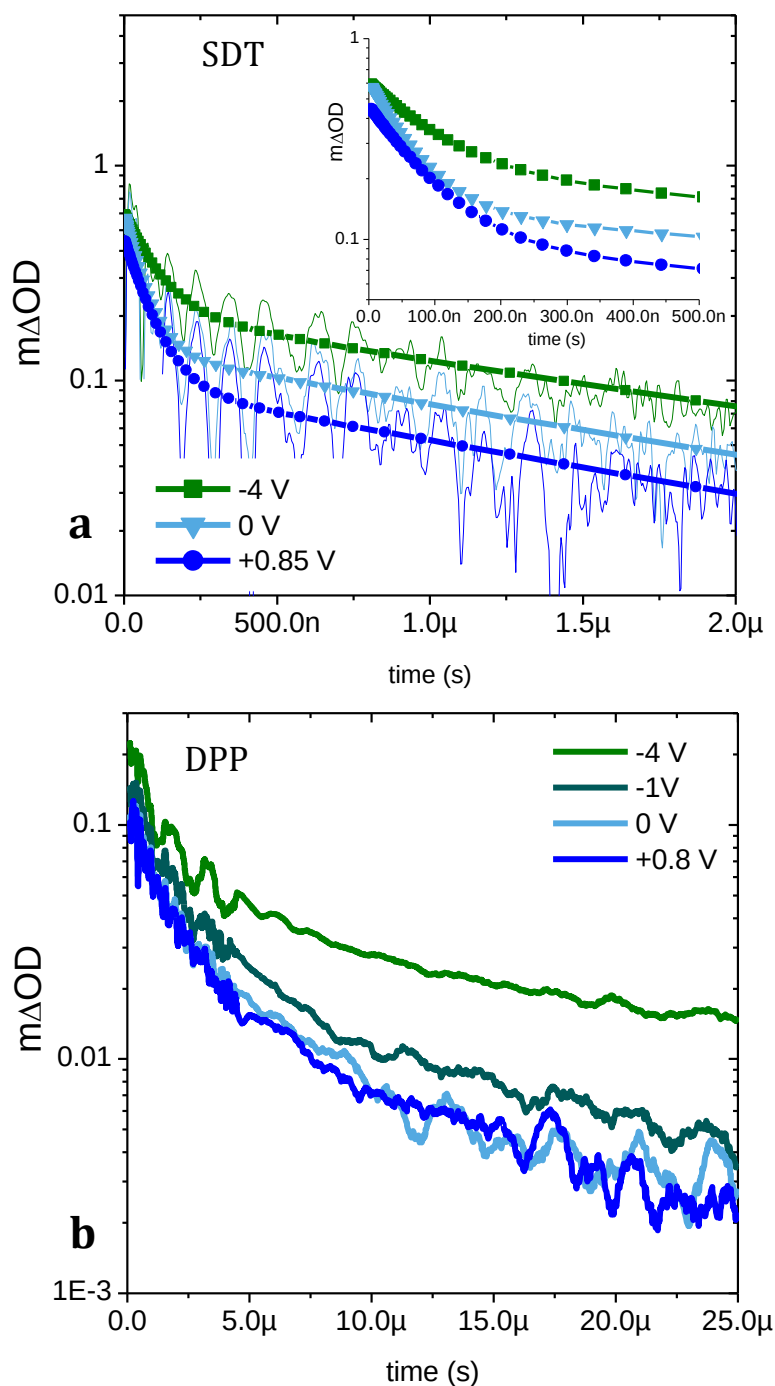


Figure 6.14 – Transient decay kinetics as a function of applied bias for a) SDT(TDPPTBfu)₂:PC₇₀BM and b) DPP(TBfu)₂:PC₇₀BM devices at 980 nm.

The TAS decay kinetics for both (a) SDT(TDPPTBfu)₂:PC₇₀BM and (b) DPP(TBfu)₂:PC₇₀BM devices are shown in Figure 6.14 as a function of applied bias and time. Devices were excited at

600 nm, and the resulting photoinduced absorption monitored in the near-infrared on ns – μ s timescales. Both these devices show a significant acceleration of the signal decay dynamics towards forward applied bias, which is apparent as the bias voltage approaches V_{OC} . This acceleration cannot be assigned to sweep-out of carriers to the device electrodes, as we would expect this process to become slower towards open circuit. Rather, this acceleration in kinetics is assigned to enhanced recombination losses. The transient signals for both DPP(TBFu)₂:PC₇₀BM and SDT(TDPPTBFu)₂:PC₇₀BM could be fit to a biphasic decay, as seen from the overlaid solid lines in Figure 6.14a, with a fast (~ 100 ns for SDT(TDPPTBFu)₂:PC₇₀BM and ~ 400 ns for DPP(TBFu)₂:PC₇₀BM), mono-exponential decay phase followed by a slower power-law decay. The fast phase has been assigned to geminate recombination of charges and as previously, we assign the power-law decay, on the longer timescale, to the non-geminate recombination of dissociated charges in both devices. The amplitude of the fast decay phase was observed to be strongly bias dependent, and is assigned to an early-time field dependent recombination process. Due to this field dependent recombination, we observe the amplitude of the power-law decay phase, and therefore the yield of dissociated charge carriers, to increase substantially between V_{OC} and reverse bias. To further investigate the effects of a macroscopic field on the these blends, we plot in Figure 6.15 the charge generation yield as a function of applied bias at different timescales for SDT(TDPPTBFu)₂:PC₇₀BM

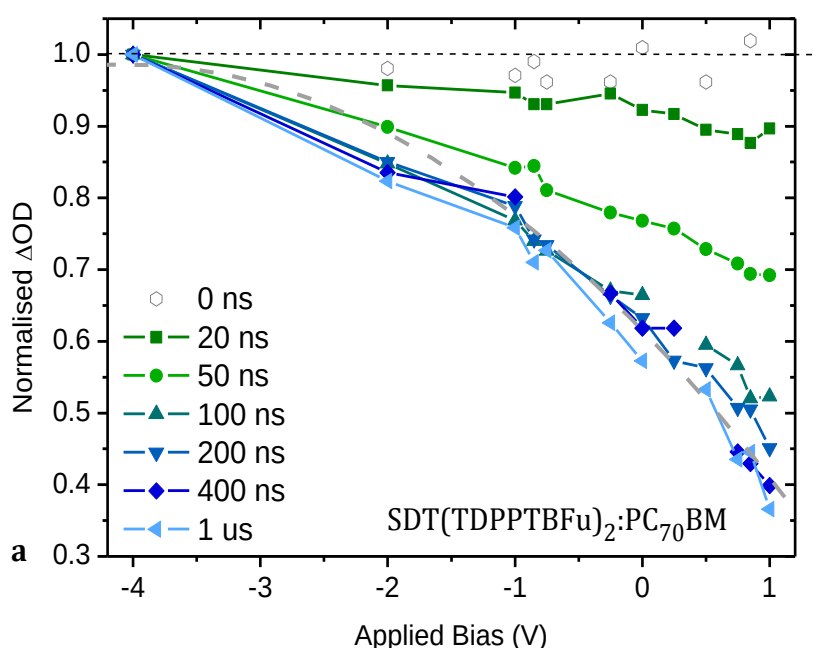


Figure 6.15 – Normalised ΔOD signal as a function of applied bias (between +1 V to -4 V) for SDT(TDPPTBFu)₂:PC₇₀BM between 20 ns and 1 μ s. 0 s time data was taken by extrapolating back the fast phase fit to $t = 0$ s. A quadratic expression has been fitted to the data at 400 ns, shown by the grey line.

The bias dependence of this dissociated polaron yield can be accurately characterised (close to the power-generating quadrant) by a simple quadratic function, illustrated by the fit to the signal at 400 ns (grey dashed line), shown in Figure 6.15 for SDT(TDPPTBFu)₂:PC₇₀BM. It is apparent that this variation in early-time geminate recombination results in an approximate halving of the yield of dissociated charges between -4 V and +1 V bias, and ~30 % reduction in the yield of charges between biases corresponding to short-circuit and open-circuit conditions. For APFO-3:PCBM, the magnitude of these losses between -4 V and +1 V is comparable to that described for SDT(TDPPTBFu)₂:PC₇₀BM, with a 50 % decrease between short and open circuit conditions, at 100 ns. The DPP(TBFu)₂:PC₇₀BM devices follow the same trend as the SDT(TDPPTBFu)₂:PC₇₀BM devices, showing a 40 % reduction in the yield of charges between open and short circuit.

For the SDT(TDPPTBFu)₂:PC₇₀BM device the initial signal amplitude, extrapolated to $t = 0$ ns, was not strongly bias dependent, indicative of only minor field dependent losses prior to our instrument-limited time resolution (~ 20 ns). Following this timescale, the charge generation yield is affected by the presence of the macroscopic electric field generated by the applied bias. Our observation that the yield of dissociated charge carriers increases under reverse bias conditions is strongly indicative of field-assisted splitting of geminate charge pairs. The fraction of geminate pairs lost to recombination increases over the first ~ 100 ns, beyond which time the bias-dependence of the transient signal converges to a single profile for SDT(TDPPTBFu)₂:PC₇₀BM from 100 ns, and for APFO-3:PCBM between 100 – 400 ns. We suggest that this convergence represents the situation whereby the majority of field dependent geminate recombination events have occurred, and the transient signal therefore correlates with the yield of dissociated polarons which are available for collection, as is discussed in more detail below.

6.4 Discussion

The role of device electrodes upon the charge generation has been investigated as a function of applied bias in three series of OPV devices and has shown two different outcomes. Three different PCPDTBT:PC₇₀BM blends showed no change in the charge generation yield with an applied bias, whereas APFO-3:PCBM and two small molecule / PC₇₀BM blends did show a change in the transient optical signals with applied bias, indicative of a change in the charge generation yield.

6.4.1 Electric field independent charge generation

For the PCPDTBT:PC₇₀BM devices, both the initial ΔOD signal and J_{sc} increase in the order C < C + ODT < Si. This correlation is in agreement with previous studies and provides further confirmation that our ΔOD assay is an effective measure of the efficiency of charge photogeneration in these devices. The lower charge photogeneration observed for the C-PCPDTBT:PC₇₀BM device is assigned to geminate recombination of interface CT states on the picosecond / nanosecond timescales, as has been discussed previously.^{20,63} From the J-V data presented in Figure 6.3, it may be suggested that C-PCPDTBT:PC₇₀BM devices have the greatest tendency to show a field dependence of charge generation, if using established device models that consider the FF of the device to be determined by the electric field dependence of charge generation. The analysis presented in Figure 6.5 and Figure 6.6 indicate that the transient absorption signals observed correspond to the photoinduced absorption of dissociated polarons, and that the decay dynamics we observe correspond to non-geminate recombination. The excitation density comparison between the two yields shows that the magnitude of the transient signal increases approximately linearly with excitation density (10 fold with the 10 fold increase in excitation density), confirming the transient signal is not saturated. Therefore the initial signal magnitude, corresponding to the polaron absorption prior to the onset of non-geminate recombination, is a direct assay of the yield of dissociated polarons following photoexcitation. However, the data presented in Figure 6.6 suggests that none of the devices studied here have a significant contribution from electric field dependent geminate recombination and therefore do not show a field dependence of charge generation despite the differences in FF observed between the blends.

We must highlight that there was no observed sweep out of the charges, or change in the decay dynamics of these transient spectra with applied bias for any of the PCPDTBT:PC₇₀BM blends tested here. The origin of this effect has not been extensively investigated, but may arise from a difference in the background and photogenerated charge densities as TAS measurements such as these are large perturbation measurements. This method of investigating the charge dynamics employs relatively high charge densities, but these may not correctly reflect the nature of the charge dynamics in a PV in which the deepest trap states have been filled. Therefore, in the dark the photogenerated charges may occupy the deepest traps and non-geminate recombination or collection of the charges may occur on longer timescales than typically observed in devices. However, this hypothesis has not been tested here, and the effects of an applied bias were not recorded in the light. We note that the bias independent observations we report herein are distinct from those drawn by Marsh *et al.* from analogous studies of P3HT:PCBM based solar cells using TAS.⁹ In this regard, it is important to appreciate

that the experiments reported herein, and by Marsh *et al.*, are ‘large perturbation’ experiments, where the optical excitation generates a significantly greater polaron density ($\sim 10^{17} - 10^{18} \text{ cm}^{-3}$) than that present in the device under normal operation ($10^{15} - 10^{17} \text{ cm}^{-3}$ under one sun solar irradiation). As such, caution should be exercised in relating such measurements directly to device performance. In particular it is difficult to use such data to analyse any potential electric field dependent transition between geminate and non-geminate recombination losses under device operation (as proposed by Marsh *et al.*) due to the strongly nonlinear dependence of non-geminate recombination upon polaron density. Instead, true quantification of non-geminate losses requires small perturbation measurements, such as transient photovoltage analyses, as reported elsewhere.²⁵ Rather, the focus of the analysis reported herein is on the initial yield of dissociated charges, expected to be less strongly dependent upon charge carrier density, consistent with the approximately linear excitation density dependence of charge generation, as reported in Figure 6.13.

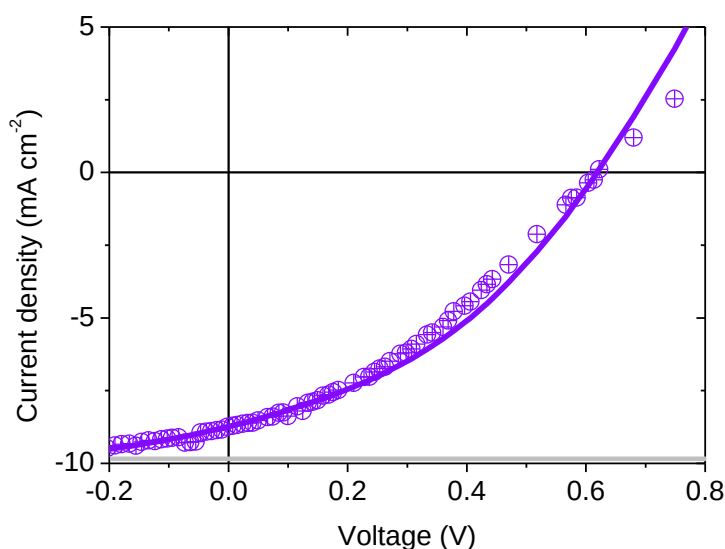


Figure 6.16 – J-V reconstruction for PCPDTBT:PC70BM + ODT (circles) considering a flat generation profile (grey line) and no significant contribution arising from geminate recombination, compared with the experimentally derived J-V curve (solid line). Data reconstructed and analysed by Dr. Andrea Maurano.

To further demonstrate that the TAS data presented in Figure 6.5, showing no significant geminate recombination in C-PCPDTBT:PC₇₀BM + ODT blends, may be used to describe the J-V in these blends, the J-V curve has been reconstructed using a flat generation profile. The method and analysis have been described previously,²⁸ involving no fitting parameters but considers either a flat generation profile, if there is no field dependence of geminate recombination, or, a varying profile if geminate recombination varies with macroscopic field. As the TAS data

showed no change in the charge generation yield with an applied bias, a flat generation profile has been employed in this analysis. Figure 6.16 shows the experimental J-V (solid line) and the reconstructed J-V (circles) employing the flat generation profile. From these data it is possible to see that there is a good agreement between the experimentally derived data and the reconstructed data considering only non-geminate recombination across the J-V. The agreement between the measured and calculated photocurrent around J_{sc} suggests that our calculation of the reconstructed of the J-V curve is valid when describing this device and that the non-geminate recombination has a primary role in determining device behaviour around J_{sc} in these devices. However, it must be highlighted that this analysis did not work well for all of the devices tested and analysed in this series. In particular some problems were encountered when attempting to reconstruct the J-V in far reverse bias, where the photocurrent continues to change with bias, which was unable to be fit to this model.

We also note that the data presented here regarding the field independent charge generation in PCPDTBT:PC₇₀BM devices is inconsistent with literature reports, including alternative measurements by Blom and co-workers employing space charge limited current analysis³⁰ and Neher and co-worker using a time delayed collection field (TDCF) technique.⁶⁴ Neher and co-workers have compared the bias dependence of charge generation in C-PCPDTBT:PC₇₁BM devices with and without ODT, both of which have been shown to exhibit field dependent charge generation. This technique shows a significant ($\sim 25\%$) change in the geminate pair splitting with an applied field between open short circuit, that was not observed in measurements presented in this chapter. Whilst the observed variations in the two (TDCF and TAS) field dependent generation measurements are obvious, the significance of non-geminate recombination in these devices is not so clear. The apparent contradiction between the results presented here and those discussed in literature may arise from the differences in materials employed and the fabrication techniques used. As discussed previously in Chapter 4 and elsewhere in literature,^{59,65,66} the active layer morphology plays a key role in determining the magnitude of the effect of geminate recombination and the charge generation. Therefore the use of different batches of each of the materials employed, accompanied by differences in the fabrication may be responsible for the different observations. The materials and device properties which may determine the relative importance of electric field dependent geminate recombination losses are discussed below.

6.4.2 Electric field assisted charge generation

Three blend compositions investigated in this chapter, APFO-3:PCBM, DPP(TBFu)₂:PC₇₀BM and SDT(TDPPTBFu)₂:PC₇₀BM, have all exhibited electric field dependences on charge generation, as monitored using TAS as a function of applied bias. These three blends all showed an increase in the amplitude of ΔOD with the application of a reverse bias compared to the yield recorded at voltages corresponding to 1 sun V_{OC} , indicating that the yield of dissociated charges increases with the application of a reverse bias. The increase in charge generation yield and of an applied bias in APFO-3:PCBM blends presented here are in agreement with previous reports in literature that also demonstrate a change in the dissociation of bound states with an applied bias.^{10,17}

Following the J-V analysis presented for C-PCPDTBT:PC₇₀BM + ODT devices, and again consistent with the method previously reported used to analyse the J-V curve for P3HT:PCBM devices,²⁸ the same analysis was employed here. Initial J-V reconstructions were performed for SDT(TDPPTBFu)₂:PC₇₀BM considering a flat generation profile, and are shown in Figure 6.17a for four different light intensities. These show a poor correlation between the experimentally measured J-Vs (dashed lines) and the reconstructed J-Vs (triangles). Considering the poor J-V analysis considering a flat generation profile, the experimentally derived bias dependence of charge generation at 400 ns, as observed from the quadratic fit in Figure 6.15, was used to reconstruct the J-V curve with complementary transient photocurrent measurements. These measurements and analysis were performed by Dr. Dan Credgington. A varying generation profile is assumed, indicated by the black dashed line, which has been experimentally derived from the field dependent TAS measurements described above and shows the field dependence of geminate recombination in this device. As discussed previously, this biphasic behaviour is assigned to the presence of an additional, relatively fast (~100 ns) exponential decay phase assigned to a geminate recombination process, in addition to the power law decay phase of dissociated charges at longer timescales. We do note that it is not possible to completely rule out some contribution of polymer triplet exciton absorption to this 100 ns exponential decay phase, however these are unlikely to make a significant contribution to the signal amplitude. The reconstructed J-V is shown by the blue diamonds, using the experimentally derived data and fits very well to the experimentally measured J-V (black line) in Figure 6.17. This J-V reconstruction demonstrates the application of field dependent measurements, such as bias dependent TAS in further understanding the charge generation mechanisms that may occur in OPV operation.

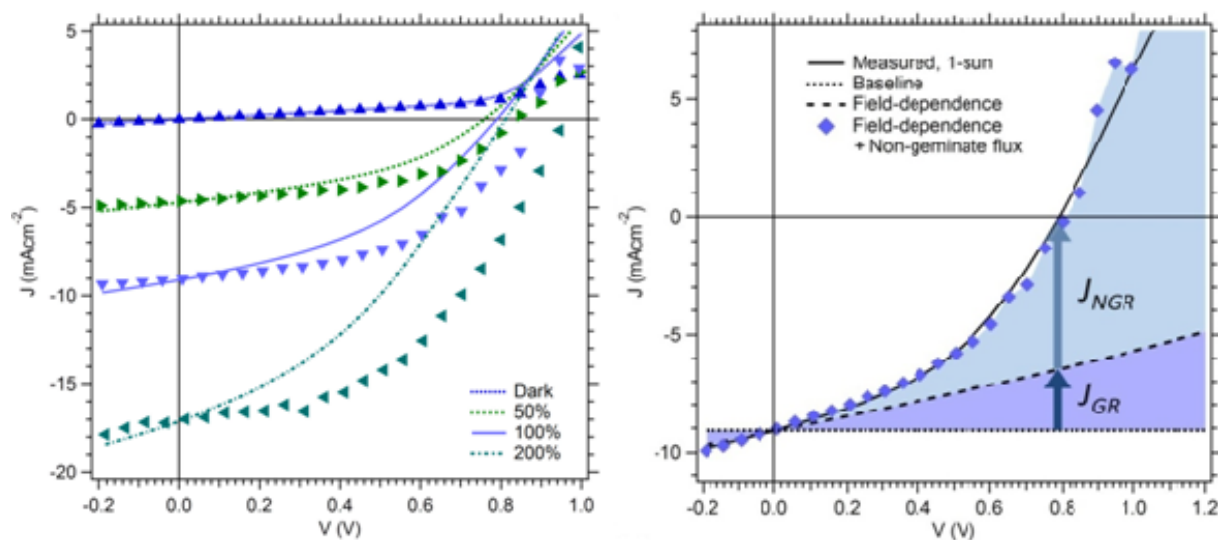


Figure 6.17 – Reconstruction of the J-V curve for SDT(TDPPTBFu)₂:PC₇₀BM considering a) a flat generation profile, shown at different light intensities and b) variable generation profile (black dashed line), arising from the contribution of the field-dependence of geminate recombination at 1 sun. The measured 1 sun J-V for this device is shown in black. Data reconstructed and analysed by Dr. Dan Credgington at Imperial College London using the bias dependence of charge generation at 400 ns, using a quadratic fit to the data in Figure 6.15.

The short circuit current in the PCPDTBT:PC₇₀BM devices tested in this chapter have shown to correlate with the TAS charge generation yields presented in Figure 6.6 and are in agreement with the analysis by Clarke *et al.*⁶⁷ showing the correlation between ΔOD at 1 μs and J_{sc} . Whilst the charge generation yields for many polymer:PCBM blends have shown a good correlation with J_{sc} in devices, there are some blends that do not follow this trend. This includes the polymer poly[2,8-(6,6,12,12-tetraoctylindenofluorene)-co-5,5-(40,70-di-2-thienyl-20,10,30-benzothiodiazole)] (IF8TBT), which when blended with PCBM, yields a higher J_{sc} than predicted from TAS analysis. These materials form a highly amorphous mix⁶⁸ and show very little tendency to crystallise. Both of the small molecule blend systems investigated in this chapter have also been shown to be very amorphous and not to form domains of the neat materials, as verified by atomic force microscopy of the active layer.⁴⁹ The C-PCPDTBT:PC₇₀BM devices tested by Neher and co-worker show the greatest electric field dependence of charge separation in the devices fabricated without ODT, which they show to be highly amorphous in structure.⁶⁴ This shows that there may be a correlation in these devices between the active layer morphology and the electric field dependence.

The device electric field dependence on charge generation has been investigated here in only a very narrow range of materials but it would appear from these analyses that amorphous blends with a highly intermixed morphology of the donor and acceptor, such as APFO-3:PCBM, DPP(TBFu)₂:PC₇₀BM and SDT(TDPPTBFu)₂:PC₇₀BM show the greatest electric field dependence

of charge generation. These data suggest it that the role of that the blend morphology plays a significant role on the degree of geminate recombination in certain blends. The PCPDTBT:PC₇₀BM series exhibit a higher degree of crystallinity than the other materials investigated here and also show the smallest electric field dependence on charge generation and suggest that the electric field dependence of charge generation is dependent on the active layer crystallinity.

6.5 Conclusions

The charge generation yield, as monitored by TAS, in six donor / acceptor blend BHJ devices have been studied as a function of an externally applied electrical bias. We have found that charge photogeneration in three different PCPDTBT:PC₇₀BM devices studied, C-PCPDTBT:PC₇₀BM, C-PCPDTBT:PC₇₀BM + ODT and Si-PCPDTBT:PC₇₀BM, is independent of electric field (to within $\pm 10\%$), at least over the range of bias conditions applied in this investigation. As such, differences in the fill factors and ‘photoshunt resistances’ observed between these three compositions cannot be assigned to differences in their electric field dependence of charge photogeneration or the competing geminate recombination.

In contrast, APFO-3:PCBM, SDT(TDPPTBFu)₂:PC₇₀BM and DPP(TBFu)₂:PC₇₀BM devices all showed a significant electric field dependence of charge photogeneration, as inferred from an increase in ΔOD with increasing reverse bias. APFO-3:PCBM devices have shown not only an increase in charge generation yield with increasing reverse bias, but also exhibited an increase in the lifetime of the monitored charges on this timescale. The two small molecule / PC₇₀BM blend devices investigated both showed $\sim 30\%$ change in the charge generation yield between open and short circuit. This field dependent charge generation is attributed to the splitting of geminate charge pairs by the field, which may account for the low FF in these devices. This experimental data has then been used to successfully re-create the J-V curve, with consideration of a bias dependent generation profile. The varying gradient generation profile, employed to reconstruct the J-V curve in Figure 6.17b, may also be used to describe devices, such as the two small molecule blends discussed in Section 6.3.3 along with APFO-3:PCBM devices, that do show a significant electric field dependence on charge separation. The degree to which the generation profile is dependent on the electric field is experimentally derived from TAS measurements and varies for each of the materials systems. These data on these DPP based small molecule / PC₇₀BM and APFO-3:PCBM devices show that, for some BHJ systems, there is a significant change in the charge generation yield with the application of an external bias.

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Chapter 7

Conclusions and Further Work

This thesis has focused upon investigating the charge generation in donor / acceptor blends considered for use as the photoactive layer in OPVs, in particular upon polymer / PCBM blends. We have specifically considered the role of blend composition, morphology and macroscopic electric fields upon the charge photogeneration. Following these investigations, a functional model has been proposed to understand the role of morphology and phase segregation in organic blend materials.

7.1 Conclusions

The degree of mixing between the donor and acceptor in organic BHJs has been shown in Chapter 3 to have a profound effect on the device performance, as observed for the PCPDTBT:PC₇₀BM blends, with the addition of ODT which has been shown elsewhere to increase the phase segregation between the donor and acceptor, in turn leading to increased device performance. The increased device performance has been correlated with an increase in charge generation, as monitored using TAS, demonstrating the use of TAS in investigating device efficiencies.

The role of PCBM crystallisation appears to be critical for charge generation in pBTTT:PCBM blends. This has been shown by an increase the electron affinity of crystalline PCBM that forms upon the addition of excess of this material to the blend, compared to that of PCBM in the bimolecular co-crystal that is formed upon intercalation of PCBM into the pBTTT side chains. TAS studies in Chapter 4 have shown the requirement for a high (> 66 %) weight fraction of PCBM is required for dissociated charge formation. However, efficient exciton formation and quenching has been shown through PLQ spectroscopy, indicating that it is not the initial bound charge pair formation that is hindering device performance at low PCBM concentrations. Electrochemical analysis has indicated that upon the addition of excess PCBM to the blend, that there is a change in the electron affinity of the PCBM, indicating a change in PCBM crystallinity. It would appear that crystalline regions of PCBM are required to facilitate geminate pair splitting and assist the formation of free charges. Following this assignment, a functional model has been proposed considering the different materials structures present in these blends. This study has considered the unique nature of PCBM as an electron acceptor, investigating two alternative fullerenes that show less of a tendency to crystallise than PCBM, as determined by CV. This model proposes that the crystallisation of one material is desired to retard the recombination of free charges.

Following the observation of the change in E_A with the presence of a crystalline material in the blend, the analysis in Chapter 5 has demonstrated that it may be possible to change the PCBM crystallisation onset using methyl ester additives in pBTTT:PCBM blends, or by altering the side chain position on the polymer backbone. The addition of the short chain esters to the blend hinders the intercalation of PCBM into the polymer side chains, lowering the PCBM crystallisation onset, as determined by CV, leading to an increase in dissociated charge generation in blends with a lower PCBM fraction. Modification of the side chain position again impacts the intercalation of PCBM, and the formation of neat domains is observed by the incomplete PLQ in blends with PCBM.

Finally, the role of macroscopic electric fields in assisting charge generation has been shown in Chapter 6 to have a differing impact on the materials systems investigated. The impact of an applied bias in three different PCPDTBT:PC₇₀BM blends showed negligible effect on the charge generation yield measured in TAS. Geminate recombination of bound charges, appears not to be significantly limiting the device performance. Therefore, these data indicate that Onsager's theory of dissociation and formation of free charges may not be applicable in these materials. However, two small molecules systems, DPP(TBFu)₂:PC₇₀BM and SDT(TDPPTBFu)₂:PC₇₀BM, both shown significant geminate recombination losses that have been suppressed by the application of an electric field. The physical basis for the substantial geminate recombination has not been investigated here, but has been suggested to arise from an unfavourable nanomorphology, as these blends exhibit poor phase segregation. This may hinder the formation of free charges from separation of the Coulombically bound states, however, when a field is applied, effects of this unfavourable morphology may be overcome.

7.2 Suggestions for further work

The role of the PCBM crystallisation has been investigated in pBTTT:PCBM and pATBT:PCBM blends, however, the study presented here has not been extensively investigated further for its applicability in other polymer / fullerene systems. Therefore, investigating the role of crystallisation of one, or both, of materials used in organic solar cells may provide further insight into how critical the role of crystallisation, and the effects on the blend morphology, is on charge generation in BHJ devices.

In addition to the limitations arising directly from the morphology, geminate recombination has been shown to be a significant loss mechanism in two small molecule / PC₇₀BM blends investigated in Chapter 6. Finding a route to suppress geminate recombination, and thereby reducing the effects of macroscopic electric fields, may be significant in improving device efficiencies of blends that are significantly hindered by these losses. A more detailed morphological analysis, potentially investigating the degree of mixing between the two materials, the formation of neat domains or the electrochemical properties of the materials in the small molecule / PC₇₀BM devices, may be a useful method for identifying strategies for improving the charge generation in these blends.