Charge Generation
in Morphology-Controlled
Organic Photovoltaic Materials

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for the degree of Doctor of Philosophy
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School of Chemistry

April 7, 2017
Declaration of Authorship

This is to certify that:

(i) the thesis comprises only my original work towards the PhD except where indicated in the Preface,

(ii) due acknowledgement has been made in the text to all other material used,

(iii) the thesis is fewer than 100,000 words in length, exclusive of tables, maps, bibliographies and appendices.

Kyra Noelle Schwarz
April, 2017
Organic photovoltaics have attracted significant interest due to their potential low cost of production and fabrication as thin films on flexible substrates. The efficiency of organic photovoltaic devices is intimately linked to the nanoscale donor-acceptor morphology of the photoactive layer. However, the successful scale-up of devices and further improvements in efficiency will rely on active layer optimisation and the rational design of new materials. These advances hinge on the understanding and control of the complex effects of active layer morphology on charge photogeneration.

Strategies to gain greater control and tunability over bulk heterojunction nanomorphologies are increasingly being employed to optimise device efficiencies, using a wide range of methods. Recent developments in the mechanistic understanding of charge transfer have revealed its interconnection with morphology of donor and acceptor components. Despite recent advances, charge generation in specific morphological strategies and newly developed high performing materials is not yet fully understood.

In this thesis, alternative approaches to morphological control are investigated, and their consequences for charge photogeneration are explored spectroscopically. Charge photogeneration in organic photovoltaic materials occurs on ultrafast timescales, and requires time-resolved experiments, such as high sensitivity transient absorption spectroscopy, that can resolve the relevant processes. Using these techniques, the examined morphological approaches include: solvent vapour annealing, composite nanoparticles and block copolymers.

Solvent vapour annealing is an ambient temperature process that is used post-deposition to subtly alter bulk heterojunction morphology. This method results in a four percentage point efficiency increase for blends comprising the recently developed electron donor,
benzodithiophene terthiophene rhodanine (BTR). An important loss mechanism, the formation of BTR triplet excitons through sub-nanosecond bimolecular recombination, was identified in untreated blend films, and was significantly suppressed after solvent vapour annealing. This indicates that morphology and spin share a closely interconnected role in mediating triplet loss channels and hence, influence device efficiency.

Preparations of composite semiconducting nanoparticles provide a strategy for nanoscale morphological control and permit the use of polar, non-toxic solvents suitable for large-scale printing. Poly(3-hexyl thiophene): phenyl-C$_{61}$-butyric acid methyl ester (P3HT: PCBM) composite nanoparticles were prepared using two different methods, with contrasting outcomes for internal morphology, P3HT free exciton bandwidth and charge generation. Notably, the mini-emulsion nanoparticle fabrication process resulted in aggregates exhibiting charge generation dynamics similar to thermally annealed bulk heterojunction films of these materials, despite the lack of any elevated temperature processing.

Block copolymers that synthetically link donor and acceptor units within their molecular structure have the potential to simultaneously control morphological assembly and interfacial properties. The characteristics of the intramolecular interface were examined in a triblock copolymer comprising a (poly(9,9-diocetylfluorene-co-bis-N,N'-
(4-methylphenyl)-bis-N,N'-phenyl-1,4-phenylenediamine)) (PFM) electron donor and a (poly[(9,9-di-n-octylfluoren-2,7-diyl)-alt-(benzo[2,1,3]thiadiazol-4,8-diyl)] (F8BT) electron acceptor, forming PFM-F8BT-PFM. Donor excitation exhibited minor interfacial interactions, apart from energy transfer which was observed in non-polar environments. In contrast, excitation of the F8BT acceptor resulted in delayed fluorescence behaviour mediated by a charge transfer state at the interface of the blocks.

Collectively, this thesis presents a spectroscopic insight to the consequences of different morphological strategies on charge generation in organic photovoltaic materials. A greater understanding of charge generation in these systems will lead to improved and informed morphological and molecular design choices, with the goal of aiding the future advances for efficient, processable organic photovoltaic materials.
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A considerable number of people have supported me in this work and I would like to extend my appreciation and acknowledgement to some of them here.

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I am immensely grateful to my completely wonderful friends and family for their support, and especially my parents, Rodney and Natalie, for their constant love and encouragement over the years. Finally to Jonathan, for his unwavering support, love and partnership, and for the thousands of caffeinated beverages, without which this thesis would not have been completed. You are the best.

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Poster entitled ‘Suppressed sub-nanosecond bimolecular recombination and efficient hole transfer in a nematic liquid crystalline donor for organic photovoltaics’ Australian Centre for Advanced Photovoltaics (ACAP) Annual Conference, Australian National University, Canberra, December 2016

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<td>BC</td>
<td>Block Copolymer</td>
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<tr>
<td>BHJ</td>
<td>Bulk Heterojunction</td>
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<tr>
<td>BTR</td>
<td>Benzodithiophene Terthiophene Rhodanine</td>
</tr>
<tr>
<td>CT</td>
<td>Charge-Transfer</td>
</tr>
<tr>
<td>cw</td>
<td>continuous-wave (laser)</td>
</tr>
<tr>
<td>F8BT</td>
<td>(poly[(9,9-di-n-octylfluorenyl-2,7-diyl)-alt-(benzo[2,1,3]thiadiazol-4,8-diyl)])</td>
</tr>
<tr>
<td>GSB</td>
<td>Ground State Bleach</td>
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<tr>
<td>GVD</td>
<td>Group Velocity Dispersion</td>
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<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
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<tr>
<td>IR</td>
<td>Infra-Red</td>
</tr>
<tr>
<td>ICBA</td>
<td>Indene-C₆₀ bisadduct</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>ND</td>
<td>Neutral Density</td>
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<tr>
<td>NOPA</td>
<td>Non-collinear Optical Parametric Amplifier</td>
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<tr>
<td>NP</td>
<td>Nanoparticle</td>
</tr>
<tr>
<td>OPA</td>
<td>Optical Parametric Amplifier</td>
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<tr>
<td>OPV</td>
<td>Organic Photovoltaic</td>
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<tr>
<td>P3HT</td>
<td>Poly(3-hexylthiophene-2,5-diyl)</td>
</tr>
<tr>
<td>PA</td>
<td>Photo-induced Absorption</td>
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<tr>
<td>PCBM</td>
<td>Phenyl-C[61]-butyric acid methyl ester</td>
</tr>
<tr>
<td>PC₇₁BM</td>
<td>Phenyl-C[71]-butyric acid methyl ester</td>
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<tr>
<td>PCE</td>
<td>Power Conversion Efficiency</td>
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<tr>
<td>PFM</td>
<td>(Poly(9,9-diocetyl fluorene-co-bis-N,N’-(4-methylphenyl)-bis-N,N’-phenyl-1,4-phenylenediamine))</td>
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<td>PL</td>
<td>Photoluminescence</td>
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<tr>
<td>SC</td>
<td>Supercontinuum</td>
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<tr>
<td>SE</td>
<td>Stimulated Emission</td>
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<tr>
<td>SHG</td>
<td>Second Harmonic Generation</td>
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<tr>
<td>SLM</td>
<td>Spatial Light Modulator</td>
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<td>TA</td>
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<tr>
<td>TCSPC</td>
<td>Time-correlated Single Photon Counting</td>
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<td>THF</td>
<td>Tetrahydrofuran</td>
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Dedicated to my Mum, Natalie
- for keeping me curious
Chapter 1

Introduction

1.1 Broader context of the study

The amount of solar radiation that reaches the surface of the earth each year is $\sim 90,000$ terawatts, over 6000 times more than total annual global energy usage.[1] The efficient conversion of this solar energy into electricity would provide a viable solution to the current energy crisis,[2, 3] yet cost-effective technology to rival that of fossil fuels is necessary to make this economically viable.

The manufacture of current silicon-based photovoltaics requires large amounts of energy, where the payback of the energy used for manufacturing demands at least three to four years of continuous device operation.[2] This represents a serious obstacle, and intensive research is pursuing the prospect of efficient solar cells with low energy, low cost fabrication.

Organic semiconductors are materials that offer low-temperature processing and synthetic variability to modify their optical and electronic properties. Therefore, organic photovoltaics (OPVs) made from these conjugated organic materials show great promise for producing easily manufacturable, mechanically flexible, large-area solar cells. Perhaps their most important prospect is the potential to provide low-cost solar energy through high-throughput printing techniques, that result in relatively short energy payback times.[4–6]

Activities in the research and development of this technology have led to substantial increases in power conversion efficiencies from around 2% in 2001,[7] to recently greater than 11.5%.[8] Despite this, improvements are required for meaningful technological progress towards commercial viability.[9]
The current knowledge of molecular level processes in organic photovoltaics is far from complete, and hinders the rational design of new materials and strategies required to improve efficiencies further.

1.2 Motivation for the study

The challenges in understanding the details of light harvesting in organic photovoltaics are attributed to the complexity of the fastest primary processes in the chain of events that convert optical into electrical energy. The understanding of these processes has seen substantial developments in recent years. However, the complete mechanisms are still being fully unravelled, particularly with respect to questions surrounding free charge generation.

The series of events involved in photocurrent generation occur spatially at the nanoscale, in a photoactive layer consisting of a complex and disordered interpenetrating network of donor and acceptor materials.[10, 11] This donor-acceptor morphology has been identified as a key parameter in the efficiency of all of the primary events that occur in the photoactive layer of an organic solar cell. Recently, the basic understanding of the relationship between morphology and charge separation has been under discussion.[12–14] The driving force with which electron-hole pairs escape from their Coulomb well at the interface has been linked to the details of local donor-acceptor structure.

Concurrently, various approaches have been employed to modify donor-acceptor morphology in order to improve device efficiency. Beyond trial-and-error approaches such as annealing and solvent choice, in recent years more strategic methods have been employed. These include preforming morphology using composite donor-acceptor nanoparticle suspensions, and synthetically prefixing donor and acceptor domains prior to deposition in the case of block copolymers.

Large-scale device manufacturing of organic photovoltaics presents the challenge of maintaining micro- to nanoscale morphological control of the photoactive layer, over millimetre to metre printed areas. For industrial applications it is desirable that the optimal microstructure be easily and safely obtained using high throughput printing techniques.

The connection between morphology and its consequences for the events of charge photogeneration is of key importance to the development of more efficient devices. It is still not fully clear which microstructural features are important for optimising the range of optical and electrical processes necessary for efficient photovoltaic performance, which occur over a large distribution of length and time scales. Different strategies to controlling morphology will manifest in various outcomes for the charge generation process.
In light of recent developments in the mechanistic understanding of charge transfer, approaches to controlled morphology should be examined with more scrutiny. In particular, a focus on less established and more strategic approaches to the control of morphology is lacking with regard to understanding charge photogeneration. These approaches may be designed to address one issue in the charge photogeneration pathway, but their rational design must satisfy all criteria for successful devices.

1.3 Aim and scope

This thesis aims to understand the dynamics of charge generation in organic photovoltaics in the context of different approaches to controlled donor-acceptor morphologies. In particular, a focus on strategic morphological approaches is required to assess their ability to provide improved device efficiencies. These morphological strategies should also be compatible with large-scale solution processing techniques. Exploration of charge generation in these material systems will take place in the context of recent advances in the understanding of charge transfer and separation with respect to interfacial bulk heterojunction morphology.

The consequences of specific morphological strategies will be explored spectroscopically. In order to elucidate some of the fastest primary processes involved in light harvesting for organic photovoltaics, time-resolved techniques such as ultrafast transient absorption spectroscopy will be utilised (described in Section 3.5). Other complementary photo-physical techniques will also be used including time-correlated single photon counting, steady-state absorption and steady-state fluorescence spectroscopy.

This study aims to advance design rules for the interconnection of morphology and charge generation, using recently implemented processes and materials that infer morphological control. On a practical level, a further intended outcome is to clarify the possibilities and limitations of transient absorption spectroscopy to investigate donor-acceptor systems for organic photovoltaics.

A greater understanding of charge generation in these systems would infer new research directions and provide useful guidelines for the further development of efficient, processable semiconducting materials for organic photovoltaic applications.

1.4 Overview of the study

This thesis consists of seven chapters with three main avenues of research. Following this introduction, Chapter 2 situates the study within the current literature, including
a critical review of recent developments in the mechanistic understanding of charge transfer. A special focus is given to those developments within the context of bulk heterojunction morphology. Established and more nascent strategies for modifying and controlling bulk heterojunction morphology are outlined.

In Chapter 3, key steady-state and time-resolved methodologies are discussed with a focus on the primary experimental technique, transient absorption spectroscopy. This method is discussed in detail, including its advantages and limitations in elucidating charge photogeneration processes in the context of organic photovoltaic materials.

In Chapters 4, 5 and 6, charge photogeneration is investigated in the context of three different morphological strategies, and the consequences are explored spectroscopically.

Firstly, charge photogeneration in a high performance molecular donor is investigated (Chapter 4). Results indicate that a solvent vapour annealing treatment, which gives subtle changes to bulk heterojunction morphology and dramatically improves device performance, modifies charge generation dynamics and suppresses the formation of a triplet exciton loss channel.

Chapter 5 explores the approach of fixing morphology prior to film deposition using composite donor-acceptor nanoparticle preparations. Morphology is assessed optically using a model of weakly coupled H-aggregates, and charge generation is contrasted in two different preparation methods.

Chapter 6 examines the charge generation consequences of covalently joining donor and acceptor components directly, in the form of a semiconducting block copolymer. This approach has the advantage of maintaining morphological control of domain size following the demixing process. The consequences of the intramolecular donor-acceptor interface for charge generation are investigated and delayed fluorescence behaviour is observed, mediated by an interfacial charge transfer state.

Finally, Chapter 7 contains the conclusions and a reflective evaluation of further research approaches and directions.
Chapter 2

Background

2.1 The electronic structure of organic semiconductors

Conjugated organic molecules and polymers are characterised by their $\pi$-conjugated systems, which can give rise to semiconducting properties in these materials. Utilising these attributes, the field of organic electronics has grown rapidly since the 1970s,[15, 16] and conjugated materials have found application in a variety of areas, including light emitting diodes for displays and lighting,[17] biosensing,[18] field-effect transistors[19, 20] and organic solar cells.[5, 21, 22]

Organic semiconductors have several properties that make them relevant for the use in photovoltaic cells to convert sunlight into electricity. The unusually broad and intense nature of absorption bands in many organic conjugated materials makes them suitable for the absorption of a wide range of the solar spectrum.[24] The electronic absorption for $\pi$-conjugated materials can span the peak of black-body radiation from the sun as illustrated in Figure 2.1. Organic semiconductors also generally have impressive absorption coefficients, as high as $10^5 \text{ M}^{-1}\text{cm}^{-1}$, which is one to two orders of magnitude greater than that of silicon. Therefore, only a thin layer of the material (~200 nm) is required to absorb the majority of incident sunlight.

The semiconducting properties of organic semiconductors are mediated by their networks of $\pi$ bonds. The principle building block of organic conjugated systems is carbon, with the electronic configuration $1s^22s^22p^2$. Networks of $\sigma$ bonds are formed by the hybridisation of the $s$ and two $p$ orbitals of the valence shell into $3sp^2$ orbitals. The remaining $p$–orbital, which does not participate in the $\sigma$ bonding overlap, creates a system of $\pi$ molecular orbitals that are split into bonding and anti-bonding types. This conjugation is generally represented as alternating single and double bonds. It is these
Figure 2.1: Spectral solar irradiance above the earth’s atmosphere (orange) and of the earth at sea level (red). The range of possible electronic absorption for organic semiconductors is also shown. Data from NREL[23].

$\pi$ electrons that can be delocalised over the material, and that determine the molecule or polymer’s semiconducting properties.

The optical properties of these materials can be tuned by the variation of their chemical structure. This sets organic materials apart from other materials classes used for photovoltaics, where the semiconducting properties are generally restricted to the specific identities of the active components. Therefore, many of the main improvements in the field of organic photovoltaics (OPVs) have come about through tailoring the intrinsic optical and semiconducting properties of these materials by means of molecular and macromolecular modification.[25] For example, the conduction and valence band edges are designable molecular components, routinely modified by chemists to improve energy level alignment.[26] In addition to the conjugated backbone, side groups can be modified to influence various characteristics including solubility, crystallinity and regioregularity of the material.

As well as chemical structure, physical structure can also influence the optoelectronic properties of organic semiconducting materials. While in theory, a long molecular or polymeric organic semiconductor can exist as a one-dimensional chain of delocalised
Chapter 2. Background

Figure 2.2: Chromophore units in a conjugated polymer chain (poly-3(hexylthiophene)), separated by torsional breaks due to twists and bends in the polymer backbone.

**π**-electrons, structural disorder dictates that this electron density is broken up into sub-units known as chromophores.[27] Backbone flexibility, including bending and torsion, will divide the chain into these chromophore units (shown in Figure 2.2), affecting the material’s overall electronic properties. This is especially apparent in longer chained conjugated materials with inherent flexibility, such as polymers. The consequence is an intimate relation between the physical arrangement of the molecule, and its optical and semiconducting properties.

The aggregation behaviour of organic materials can also influence their optoelectronic properties. Intermolecular interactions formed through aromatic **π**-**π** stacking or Van der Waals forces can play important roles in the solid state. This behaviour can be explained in terms of the coupling of transition moments in adjacent materials. Despite the complex nature of excitons in solid state assemblies, aggregate photophysics can often be described using the concepts of J- and H-aggregation.[28, 29] In H-aggregates, molecules are aligned parallel and polymers can undergo interchain **π**-stacking interactions. J-aggregates occur when head-to-tail packing dominates, and can manifest in polymers where adjacent chromophore units on the same chain are well-aligned and couple via through-bond interactions.

A full understanding of the photophysical properties of organic semiconductors remains an active area of research. This is particularly relevant for polymers, and for materials in the solid state, where the complexities of multichromophoric systems pose challenges for physicists, chemists and materials scientists alike. This understanding is particularly important for the application of these materials for effective light harvesting in photovoltaic devices.
2.2 The operation of organic solar cells

Organic photovoltaic devices use organic semiconductors as their active component. They generally consist of a light absorbing electron donor (D) and electron acceptor (A) semiconductor blend, sandwiched between electron and hole extracting contacts.[30] The primary photoexcitations in organic solar cells are excitons, neutral bound electron-hole pairs, rather than free charge carriers as is the case in silicon solar cells.[11, 27, 31]

The term ‘charge photogeneration’ is used here to describe the overall process of light absorption through to the formation of free charges. The general process of light harvesting in an OPV donor-acceptor blend is comprised of a series of four steps as follows (also see Figure 2.3):

(i) A photon is absorbed by the electron donor (or acceptor), and an electron is excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) creating an exciton, a bound electron-hole pair.

(ii) The exciton diffuses, where it may reach a donor-acceptor interface.[24]

(iii) At the interface, the exciton is quenched by transfer of an electron from the donor to acceptor component (or in the case of acceptor excitation, a hole from the acceptor to the donor component) and charges may become separated.

(iv) Following charge dissociation, the free electron and hole can travel through the acceptor and donor materials respectively to device electrodes under the influence of the internal electric field,[21, 30] where photovoltage and photocurrent are generated.

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**Figure 2.3:** The steps required for charge photogeneration in an organic solar cell consisting of donor and acceptor components, describing: (i) photon absorption, (ii) exciton diffusion to the interface, (iii) charge separation and, (iv) charge migration to respective electrodes.
The first examples of OPV devices employed only a single organic semiconductor[32] layered between two dissimilar metal contacts which created an in-built electric field in the device. However, these solar cells exhibited a very poor performance, largely due to an inefficient field-dependent generation of free charge carriers. This issue was overcome by using two materials in the active layer, a donor and acceptor material as illustrated in Figure 2.3.[33] At the interface, a downhill energy offset between donor and acceptor LUMO (and HOMO) energies results in more effective electron (and hole) transfer. The requirements for the energy offset are discussed in more detail within Section 2.3.

Excitons are an important distinguishing feature of organic photovoltaics, often termed ‘excitonic solar cells’. Because excitons are neutral species, their motion is not under the influence of an electric field and singlet excitons migrate based on the principles of Förster resonant energy transfer. If an exciton does not reach an interface within its excited state lifetime, it will recombine (radiatively or non-radiatively) or combine with another exciton in a process known as exciton-exciton annihilation.[30]

Figure 2.4 summarises the basic photophysical processes following exciton formation, including exciton ($S_1$) recombination to the ground state. Following exciton dissociation, electrons and holes can also be subject to loss pathways. After the initial electron transfer step, ideally, free charge carriers are transported to electrodes under the influence of the device’s internal electric field. However, two main mechanisms of recombination may compete with photocurrent generation. The first, termed geminate recombination, is recombination of the initially bound electron-hole pair at the interface. Alternatively,
dissociated free charges can compete with charge transport to the electrodes and recombine in a process known as bimolecular recombination. These processes are discussed in further detail in Section 2.3.

### 2.2.1 Evolution in materials and device architecture

A major development in the evolution of organic photovoltaics came with the advent of the bulk heterojunction cell. Exciton diffusion lengths are reported to be relatively short (<10 nm) in organic semiconductors deposited from solution, and an active layer thickness of at least 100–200 nm may be required in order for the solar cell to absorb all incident sunlight. Therefore, in bilayer devices, as illustrated in Figure 2.5 (A), this generally results in a large proportion of excitons created away from an interface where they will recombine before they can reach a donor-acceptor heterojunction. An intermixed and ideally interpenetrating layer of donor and acceptor components, a bulk heterojunction (BHJ) morphology, results in a much greater interfacial surface area and smaller domain sizes (Figure 2.5 (B)). This means that excitons are more likely to reach the interface in their lifetime where they can dissociate.

![Figure 2.5: Evolution of device architecture showing (A) a bilayer device and (B) a bulk heterojunction. Insets illustrate exciton formation upon photon absorption and (A) exciton recombination when the exciton does not reach an interface, and (B) an exciton that reaches a nearby interface and undergoes charge transfer.](image)

The bulk heterojunction was developed in 1995,[30, 34] and since then has become the standard device structure in OPV research. In addition to exciton dissociation, the BHJ also has an influence on charge recombination due to the change in morphology. Charge collection requires percolating pathways within the blend film of a BHJ structure, with channels for electrons and holes to reach their respective electrodes. The morphological properties of BHJ D:A blends have long been realised as critical for producing optimised...
devices, and the relationship between morphology and charge photogeneration remains an active topic of research. This will be discussed in more detail in Section 2.4.

A second important development in recent years for improvements in efficiency was the synthetic development of low-band-gap polymers and molecular materials. Low-band-gap materials use the approach of an in-chain donor-acceptor motif with partial electron donating and electron acceptor moieties, shifting the absorption to lower energies. A significant advance in OPV device efficiencies has come with the development of these low-band-gap materials, giving better overlap with the range of maximum irradiance of the solar spectrum.

### 2.3 Charge carrier generation

In spite of significant advances in device efficiency, fundamental issues relating to the operation of organic solar cells remain unclear or hotly debated. Arguably the most significant of these is the full understanding of charge separation, step (iii) in Figure 2.3.

There have been major challenges in probing the details of charge separation for a number of reasons. Firstly, the influence of a complex BHJ morphology on the fate of charges can be difficult to disentangle from electronic properties of the materials that are being investigated. Secondly, the numerous processes involved have multiple contributions on overlapping timescales. This includes the processes of exciton diffusion, relaxation and dissociation; charge transport and recombination; and the collection of charges. These elements can be difficult to disentangle. Thirdly, although efforts have been made to provide a clear set of rational design parameters for organic photovoltaic materials in general, this task is difficult, especially when the finer differences in BHJ morphology are ignored.

While some consensus has been reached, the exact mechanism and driving force of charge separation at the donor-acceptor interface remains an active topic of research. A discussion of the issues surrounding charge generation will be included here, followed by a review of the current understanding of the morphological influence on charge separation.

#### 2.3.1 Exciton quenching

The first step required in the charge generation process is exciton quenching at the donor-acceptor interface. The simplest picture of charge generation involves electron transfer from excitons leading to the generation of positive and negative polarons. Simplistic
models of charge separation assume unity efficiency of charge separation if the donor-acceptor LUMO-LUMO gap is at least 0.3 eV.[26]

If quenched excitons lead directly to free charges, then a direct correlation between exciton quenching and the yield of photogenerated charges is to be expected. However, there is now extensive evidence that quenching does not show this correlation, nor does it act as a reliable measure of device performance.[37–42]

Excitons in organic semiconducting materials generally exhibit significant fluorescence quantum yields (with an exception of most fullerene-based materials), providing a convenient manner with which to monitor their lifetime and fate. Photoluminescence studies are often employed to monitor the competition between the electron transfer process and the luminescence decay of unquenched species as they recombine to the ground state.

Though almost all reasonably performing OPV donor:acceptor systems exhibit excellent (>90%) exciton fluorescence quenching when blended, the yield of photogenerated charges can vary significantly between blend films, with no quantitative link between the two.[41, 43, 44] This observation implies that there must be a pathway following exciton quenching at the interface that competes with the generation of long-lived charges.[14]

2.3.2 Mutual Coulomb attraction

Electron (or hole) transfer associated with exciton quenching results in the electron primarily localised on the acceptor LUMO and the hole on the donor HOMO. Despite being located on different materials, these charges can still experience a mutual Coulomb attraction, \( V \), given by:

\[
V = \frac{e^2}{4\pi\varepsilon_r \varepsilon_0 r}
\]

where \( e \) is the charge of an electron, \( \varepsilon_r \) is the dielectric constant of the surrounding medium, \( \varepsilon_0 \) is the vacuum permittivity and \( r \) is the separation between electron and hole. The dielectric constant of organic semiconductors is low, \( \varepsilon_r \approx 2–4 \), compared to other inorganic semiconducting materials e.g. silicon (\( \varepsilon_r \approx 12 \)).[45] A high dielectric constant can help in effectively screening the charges from each other, reducing their Coulombic attraction, resulting in the direct generation of free carriers.[46] In contrast, in organic semiconductors this lower dielectric constant can result in Coulomb binding energies that are \( \gg k_B T \) at room temperature and thereby lead to a bound electron and hole at the interface.

These Coulombically bound charges have been extensively studied, and will be referred to here as ‘charge-transfer’ (CT) states, without consideration of whether these states
will remain bound until recombination, or later dissociate into free carriers. Alternative nomenclature describing the same species can include terms such as: charge-transfer exciton, bound polaron pair, bound radical pair, bound electron-hole pair, geminate pair, interfacial dipole and exciplex. The latter, exciplex, is derived from the sub-bandgap exciplex-like emission that can be observed from bound CT states in some material combinations.[47, 48]

The existence of the CT state has been demonstrated experimentally in a number of BHJs by observation of its absorption or emission.[49–51] Such states generally have very low absorption coefficients (relying on a small wave function overlap of the donor HOMO and acceptor LUMO), and absorptions that are red-shifted with respect to pristine donor and acceptor components. CT state recombination that gives rise to photoluminescence is usually identified by finding emission that is absent in the fluorescence spectra of individual donor and acceptor components. Similarly, electroluminescence uses injected charges from an electric current to induce the radiative recombination of a charge transfer state.

Experimentally, CT states have been observed to undergo relatively rapid recombination, which can occur on time scales reported from picoseconds to $\sim 100$ ns.[43, 48, 52–56] This geminate recombination pathway can potentially provide a key limitation on charge separation, and therefore the efficient operation of OPV devices.[11, 51, 57, 58]

2.3.3 The charge separation process

The existence of the CT state and its significant Coulomb attraction has been outlined above. However, despite many efforts, the manner in which this CT state dissociates has been difficult to understand.[14, 31, 59–61] Nevertheless, in certain OPV systems charge separation proceeds with remarkable efficiency.[14, 31] In this section, the main observations and interpretations surrounding the driving force for charge separation are discussed.

The role of an energy level offset

The relative energy levels of the donor and acceptor have long been considered crucial to ensuring that excitons are fully separated into electrons and holes. A routine assumption in device efficiency models is that charge separation will proceed with 100% efficiency when a LUMO-LUMO energy offset between the donor and acceptor is at least $\sim 0.3$ eV.[26, 62, 63]

In a number of systematic studies by Durrant et al., a strong correlation was observed between the yield of free polarons, and the energy difference between the exciton and
polaron pairs. However, they did not determine clear correlations in all cases, indicative of other factors influencing the efficiency of separation, such as differences in film microstructure. They also noted that the magnitudes varied significantly between materials series, questioning the widely used assumption that a 0.3 eV energy offset is necessary for efficient charge generation.

**Ultrafast generation of free carriers**

A large proportion of charge generation in highly efficient blends has been observed to occur on ultrafast timescales. The technique of transient absorption spectroscopy (discussed more in Chapter 3) is often used for observing the timescales of charge generation, with time resolution as short as 15 femtoseconds (fs). However, there can be some difficulty with this technique in distinguishing between free and bound charges. As early as 2001, transient absorption spectroscopy was used to observe charge generation within <45 fs of initial photoexcitation. Ultrafast generation of free carriers was later confirmed to occur on timescales of less than 100 fs in a number of efficient material combinations, an observation that has subsequently been confirmed with THz spectroscopic techniques.

Although there is now a reasonable consensus surrounding the ultrafast generation of free carriers, it should be noted that there is some suggestion in the literature that the transient spectra of these carriers could instead be attributed to an interchain excimer species, formed on femtosecond timescales within aggregates of one component.

**The role of hot CT states**

Following electron transfer, a newly formed CT state is generally generated with some inherited excess energy due to the energy difference between the exciton and the CT state. When this state has not relaxed and still possesses excess energy, it is referred to as a hot CT state. There has been a long-standing debate whether free charge carriers are preferentially generated from this hot CT state directly, or whether relaxation occurs, and carriers are primarily generated from its relaxed state.

It has been proposed (though sometimes controversially) that excess photon energy contributes to the generation of hot CT states which then aid in long range charge separation. This mechanism primarily involves the kinetic competition between thermalisation (~100s of femtoseconds) and dissociation. This picture has been supported by work described above by Ohkita et al. using polaron yields calculated from femtosecond transient absorption. This photon energy dependence seems to be clearly observed for some blend systems with particularly small energy offsets.
Though femtosecond transient spectroscopy has shown the existence of higher energy, faster dissociating pathways at organic/organic interfaces,[41, 77, 79], there is now significant evidence to infer that this is not the only efficient or probable pathway for free carrier generation. A growing body of work supports the hypothesis that free charge separation can occur just as well following absorption from lower energy photons i.e. without excess energy inherited from the exciton.[52]

Internal quantum efficiency (IQE measurements), that show photon energy independence for photocurrent generation, strongly support the notion of efficient relaxed CT state dissociation.[80, 81] While energy independent IQEs have provided the most straightforward source of evidence that charge separation can proceed through relaxed CT states, other techniques have supported their conclusions in different materials combinations,[72, 74, 82, 83] often by proving that sub-bandgap excitation can contribute to photocurrent generation.

**Driving force of dissociation via the relaxed CT state**

Although hot CT states would explain ultrafast charge generation very well, evidence outlined above suggests that efficient free charge generation can proceed through the relaxed CT state. In this case, the driving force for dissociation of the Coulombically-coupled CT state requires further clarification.[13] The first quantitative descriptions of geminate charge separation and recombination were made by Braun and Onsager.[84–86] Braun-Onsager (BO) theory describes the dependence of the electron-hole dissociation rate on the electric field, temperature, and electron and hole mobility.

While this model has been successfully applied to homogeneous systems where no interface is present, its application to CT state dissociation in organic donor/acceptor heterojunctions has been less consistent, and unable to predict the absolute yields of charge photogeneration. BO theory has been used to simulate J-V characteristics for devices, giving reproducible results for less efficient blends, but has not been able to reproduce parameters for highly efficient donor-acceptor combinations.[87–89]

Several considerations that are not included in the theory are important features of organic photovoltaic interfaces. Disorder is not accounted for in BO theory, and is present in bulk heterojunctions and intrinsic to materials such as conjugated polymers. A combination of entropy and energetic disorder at the interface may be sufficient to significantly modify the dissociation rate and reduce the Coulombic barrier to charge separation.[31, 59, 90, 91] It is also noted that local morphology of the CT state and surrounds is not included in the theory, and will be discussed in more detail in the following Section.
2.4 Recent developments in the understanding of morphology and charge generation

The importance of BHJ morphology on device performance has long been recognised in the field of organic photovoltaics. The OPV operation model as described in Section 2.2 and Figure 2.3 includes the standard ‘textbook’ style description of a BHJ, where film morphology is described as a two component bicontinuous blend. However, donor-acceptor morphology is generally much more complex than this description suggests, and can include ordered and disordered regions of: neat donor, neat acceptor, intermixed donor and acceptor as well as a variety of interfaces.

In the key events describing light harvesting in an organic solar cell, as outlined in Figure 2.3, a consensus has emerged that every step can be affected by the donor-acceptor morphology. To summarise, device performance can be influenced by: light absorption and oxidation potential (altered by aggregation); exciton diffusion (influenced by local molecular order); exciton dissociation and charge separation (affected by domain size and blending); charge transport properties (affected by local molecular order); charge collection (influenced by percolating pathways); and electrode selectivity (altered by the vertical segregation of domains). Attaining the most suitable morphology is therefore a challenging task as it involves optimising processes over different length and time scales.[12]

This Section specifically focusses on the effect of morphology on charge generation properties. This has received a considerable amount of attention, as current work looks to clarify the microstructural factors that determine why some donor-acceptor combinations have such good free carrier generation and some do not. While early spectroscopic studies began to elucidate the mechanistic details of charge generation in different materials, the effect of local microstructure was often ignored. There is now sufficient evidence to indicate that film morphology plays a key role in the efficiency of the charge separation process. Here, the most important recent developments in the understanding of the relationship between morphology and charge generation are summarised, an area which remains an active topic of research.[12, 13]

2.4.1 Interfacial energetic landscape

Details of the molecular structure at the donor-acceptor interface can have a significant effect on the dynamics, energetics and efficiency of charge separation.

The energetic landscape of electron–hole attraction at the interface can be influenced by a number of factors. These include local structural order and alignment, electronic
Chapter 2. Background

polarisation, packing, and local dielectric constant.[11, 92, 93] Calculations and experimental studies have revealed that microstructural factors such as the mutual position, orientation, aggregation, and packing of donor and acceptor molecules have a significant impact in defining the energies of CT states.[12, 92] It should be noted that experimental approximations for determining the CT energy (from the difference in energies of the donor HOMO and acceptor LUMO), and bulk dielectric constant, often do not adequately capture these differences at the molecular level.[12, 92]

While the details of orientation and distance effects of molecules at the interface has been examined theoretically (most recently summarised by Few et al. [92]), it remains difficult to probe this experimentally. These difficulties persist mainly due to disorder, the nanometre spatial scales involved, and the similar (carbon rich) nature of donor and acceptor species.[12] However, useful methods to probe these effects are beginning to emerge.[94]

These interfacial energetics also relate to observations of free charge generation in neat semiconducting polymer films when no acceptor is present.[76, 95] While the generation of free charges in neat materials is sometimes ignored, evidence supports the hypothesis that long-lived free charges are generated at the interface between amorphous and crystalline domains.[95] In this scenario, the hole is transferred to the crystalline phase due to lower site energies provided by the elongated, aggregated domains present in these films. This work also demonstrates the key importance of microstructure in describing the photophysics of organic semiconducting films.

2.4.2 Delocalisation

The driving force for relaxed CT states to escape their mutual Coulomb attraction has yet to be fully resolved. However, some recent reports have revisited the basic assumption of a 1-2 nm distance between hole and electron when calculating the CT binding energy (as outlined in Equation 2.1). An emerging view is that free charge carrier generation is mediated by short-lived, spatially delocalised states, due to a strong reduction in the Coulomb binding energy caused by a greater effective separation of electron and hole.

The effect of hole delocalisation has been demonstrated by push-pump photocurrent experiments by Bakulin et al.[52] This illustrated the importance of hole delocalisation along the polymer chain. Longer, more delocalised conjugation lengths at the interface result in a greater probability of charge separation, as illustrated in Figure 2.6 (A). The effect of conjugation length on free charge generation has subsequently been investigated by others in a wider range of material combinations.[96, 97] Similarly, polymers and
molecular semiconducting donors with crystalline domains have also been shown to have better hole delocalisation in the presence of a greater proportion of intermolecular aggregates, and hence show improved charge separation efficiency at the interface.\cite{72, 98, 99}

More recently, experimental evidence has also been obtained that demonstrates electron delocalisation over fullerene or other acceptor aggregates.\cite{100–105} Electrons delocalised over fullerene clusters, as illustrated in Figure 2.6 (B), have been attributed as a key driving force for charge separation in a number of materials combinations, particularly those where devices are efficient despite the use of amorphous donor polymers that do not form crystalline domains or elongated conjugation lengths.\cite{59, 106}

### 2.4.3 Three phase morphology

Another plausible driving force for charge separation is described by a BHJ morphology that consists of three phases which can provide a cascading energetic landscape. It has been determined that bulk heterojunction structure is more complex than the 2-phase donor-acceptor morphology previously considered.\cite{12} In addition to the pure amorphous or crystalline nanoscale domains of donor and acceptor, recent investigations
have identified a third, intermixed phase present in a wide range of material blend systems.\cite{107-110}

Initial reports of a third phase by Mayer et al. used pBTTT (Poly(2,5-bis(3-tetradecyl thiophen-2-yl)thieno[3,2-b]thiophene)) and PCBM, notable because this particular material combination forms an intercalated co-crystal of acceptor molecules arranged between the polymer electron donor’s side chains.\cite{107} Following this report, material combinations with intermixed phases, which did not exhibit such ordered intercalation, were also reported and it was concluded that amorphous intermixed phases can show similar effects in assisting charge separation.

![Diagram](image)

**Figure 2.7**: (A) An illustration of a possible bulk heterojunction morphology consisting of three phases, including pure and intermixed regions of donor and acceptor. (B) A schematic of a cascading energy landscape at the interface between these phases, and how this may assist charge separation. Adapted from Burke et al. and Kesava et al.\cite{102, 111}

Pure crystalline phases are well known to have energy levels that are shifted relative to that of the amorphous material, with polymers such as P3HT showing a 300 meV lowering of bandgap when in its crystalline (compared to amorphous) form.\cite{112, 113} Similarly, PCBM, the most commonly used OPV electron acceptor, has aggregates with a 100-200 meV shift in electron affinity upon aggregation.\cite{100} As illustrated in Figure 2.7, this three phase structure provides an energetic cascade for either the electron or hole, increasing spatial separation and the probability that a bound pair of charges can
escape Coulombic attraction at the interface. Investigation of charge photogeneration using transient absorption spectroscopy has demonstrated that the highest yield of free charge carriers and suppression of geminate recombination occurs when three phases are present within blend films.[114, 115] Energetic cascades afforded by these morphologies may provide the driving force to assist charge diffusion and explain why some bulk heterojunction morphologies are able to generate free charge carriers so efficiently.[102, 111, 114]

2.5 Triplet states as a loss pathway

Triplet excitons (spin one) have long been observed in organic semiconducting materials,[116] and can be a terminal loss mechanism in standard OPV heterojunctions. These species can be generated by intersystem crossing from photogenerated singlet excitons. Alternatively, charge recombination has also been shown to lead to the generation of triplet states. The charge transfer state can either have singlet ($^1$CT) or triplet ($^3$CT) spin character, which are almost degenerate in energy.[117] Unlike singlet states, the recombination of $^3$CT states to the ground state is spin-forbidden. Relaxation processes are therefore very slow, however, if energetically accessible, the $^3$CT state can relax to the lowest lying triplet exciton state ($T_1$). Pathways to triplet exciton formation are shown in Figure 2.8.

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**Figure 2.8**: State diagram of basic photophysical processes including triplet exciton formation in organic photovoltaics. Black solid arrows show steps for free charge generation. Loss pathways are shown in grey dashed arrows, including those causing triplet exciton formation via geminate or bimolecular recombination. Spin states are indicated by small paired arrows for each intermediate species, where free charge carriers have spin states that are uncorrelated.
While dissociated singlet excitons can only form singlet charge transfer states, inter-system crossing of these states to $^3\text{CT}$ while the CT state is geminately bound can lead to appreciable yields of triplet CT states, and hence triplet excitons. A number of reports exist of significant donor triplet exciton generation occurring in polymer D:A heterojunctions as the result of geminate charges at the interface.[118–121]

While reports of this geminate mechanism have been discussed for some time, more recently, experimental evidence for triplet generation through bimolecular recombination has been observed.[122–125] The spin states of free charges are uncorrelated, and so recombination of these charges will give a ratio of singlet $^1\text{CT}$ to triplet $^3\text{CT}$ states of 1:3, as dictated by spin statistics. This is similar to the mechanism in organic light emitting diodes (OLEDs), where the recombination of electrically injected charges leads to singlet and triplet states in this same ratio. The importance of spin has long been considered in OLEDs, where the formation of non-radiative triplets has been a limitation to better performance. However, the generation of triplet excitons in this manner has been largely neglected in organic solar cells until recently.[126]

Triplet excitons are generally regarded as a terminal loss mechanism in organic photovoltaics, with the potential, even in high performance materials, to be the primary limitation on device performance.[122] Recent reports indicate that there is an important role played by bulk heterojunction morphology in mediating triplet exciton formation, the details of which are still being clarified.[122–125, 127]

### 2.6 Different strategies for morphological control

The key importance of morphology on the operation of BHJ organic solar cells has led to a variety of strategies to influence donor-acceptor structure in order to improve device efficiencies.[128–130] The molecular solids which comprise a BHJ have both micro- and nanostructures that are dependent on the self-organising tendencies of both donor and acceptor components. This can be influenced by the molecular structure of the components and the processing conditions to which a film is subjected. As such, this structure can be complex and difficult to control, especially when films are solution processed.[9]

The most common approach to film deposition is to cast a film from donor and acceptor components dissolved in a solvent in which they are both soluble. This solvent is then evaporated during the deposition process, and film formation will generally ‘lock’ the donor-acceptor blend into a non-equilibrium morphology upon drying.
Film deposition methods that are commensurate with solution processing include roll-to-roll printing, doctor blading and spin coating. While the latter, spin coating, has been regularly employed for fabricating and optimising efficient devices in the laboratory setting, it has received criticism for not being compatible with scaled-up device fabrication.[131]

Strategies to control bulk heterojunction nanomorphology include several approaches. During deposition, molecular differences can impact upon self-assembling behaviour, and different solvents or additives can impact on the arrangement and crystallisation of the BHJ on the micro- and nanometre scale. Following film deposition, heat or solvent treatments can be used to modify the BHJ. More strategic approaches can employ tactics to pre-fix donor-acceptor morphology prior to the deposition process. These methods are described in more detail in the following Sections.

2.6.1 Intrinsic modification

Various attempts have been made to manipulate the chemical structure of individual donor and acceptor materials to consequently influence self-assembly and blend microstructure. Intrinsic factors that can be tuned include backbone planarity, and the location and type of solubilising side chains. If the material is polymeric, other tunable parameters include molecular weight, regioregularity and polydispersity. Whilst outside the scope of this thesis, the reader is directed to comprehensive examinations of chemical design approaches to morphology in the following reviews.[9, 132, 133]

2.6.2 Heat and solvent treatments

Routes to controlling nano- and microstructure in an extrinsic manner are often routinely employed during device optimisation. The ease of adjusting parameters during the deposition process (donor:accepter ratio, solvent choice), or afterwards (annealing treatments) can give rise to modifications in BHJ morphology and hence, potentially improved device efficiencies. It should be noted that these increases in efficiency come despite the fact that these techniques can lack fine control and rational design over the morphological changes they produce.

The ratio of donor:acceptor is a routinely implemented adjustment which can affect morphology of the BHJ. The optimal D:A ratio can vary between material combinations, and is usually reported in wt% rather than in molar or volume ratio. Beyond optimising interfacial area, an optimal donor:acceptor ratio can promote the crystallisation of one
component, and the formation of bicontinuous percolating pathways, beneficial for the transport of charge carriers and reduction in bimolecular recombination.[130]

The solvent used in the deposition process can greatly impact the final arrangement of the active layer. The relationship between solvent choice and active layer morphology has been extensively investigated, and its ease of implementation has made it one of the first choices for manipulating BHJ structure.[134, 135] The demixing process during film formation will ultimately determine the morphology of the donor-acceptor heterojunction. Features that develop in the demixing process are then kinetically trapped when drying stops. Therefore, the evaporation rate, solvent viscosity, and the miscibility and relative solubility of components in a solvent have a significant influence on micro- and nano-structure.[9] Low vapour pressure solvents, such as chlorobenzene and dichlorobenzene have in general given higher power conversion efficiencies (PCEs) in many materials systems than highly volatile solvents like chloroform.[112, 136] While organic semiconductors are usually readily soluble in chlorinated solvents, these solvents’ toxicity and environmental impact present an issue for the conversion to industrial scale roll-to-roll printing processes. Deposition from solvent mixtures have also been used to successfully influence active layer nanomorphology.[135]

Annealing treatments are widely used to influence blend microstructure, and often involve heating a film above its melting or glass transition temperature. This treatment was first successfully applied to P3HT:PCBM blends which showed a substantial improvement in PCE with thermal annealing at 140°C.[137] This resulted in increased phase segregation and crystallisation of P3HT, and allowed some PCBM molecules to diffuse out of polymer regions to form larger aggregates. The BHJ was determined to contain crystalline P3HT regions, PCBM clusters, and amorphous P3HT:PCBM intermixed regions. Ultimately it was found that this morphology has led to better charge transport and improved charge pair separation efficiency, reducing geminate recombination and hence enhancing overall charge photogeneration efficiency.[138, 139] While the success of the thermal annealing treatment has been well-exploited in the P3HT:PCBM active layer, its use in other material combinations can lead to the overgrowth of domain sizes, leading to inefficient exciton quenching and poor device efficiencies.[140] It is therefore unclear to what extent these detailed studies can be extrapolated to other materials systems.[130]

Solvent vapour annealing is another approach to modifying blend crystallinity that takes place at ambient temperatures. Exposure to a solvent atmosphere under controlled conditions induces a swelling of the film with solvent molecules, causing an increase in molecular or polymer-chain mobility, similar to the process of temperature annealing.[141] A key advantage of this technique is that it does not require the heightened temperatures
of annealing with heat, which can interfere with the stability of the material or the deposition of other layers in the device manufacturing process.

### 2.6.3 Molecular additives

Molecular additives (also referred to as solvent or processing additives) can be added at low concentrations to the donor and acceptor in solution to control morphology during the solution deposition process. Additives typically have a much higher boiling point than the active layer components, and show a preferable solubility in one active material over the other, which can lead to better nanoscale phase separation and domain purity.

The molecular addition approach has received a great deal of interest since first reports in 2006,[142] where the most intensively investigated additives have been 1,8-di(R)octanes and alkanedithiols.[135] Studies have determined that a superior device efficiency can be obtained for some material combinations when processed with additives. This has been attributed to enhanced demixing, more favourable domain sizes and better donor-acceptor interfacial density.[135, 143] Initial reports found that when an alkyl thiol additive was included, hole transport was increased in the P3HT donor material when combined with PCBM, due to better structural ordering.[142] However, in other cases with a PCBM acceptor, no improvement in donor crystallinity was reported, and instead the increased performance was attributed to the formation of three phases and the improvement of electron mobilities.[144] These three phases, (i) PCBM and additive, (ii) crystalline donor, and (iii) intermixed donor and acceptor, are equivalent to those that are potentially beneficial for efficient charge separation as discussed in Section 2.4.3.

### 2.6.4 Nanostructured approaches

Organic semiconductors can be dispersed in poor or marginal solvents under controlled conditions to form aggregate nanostructured suspensions. The motivation for this approach is two-fold.

Firstly, colloidal suspensions permit the use of alternative solvent systems. Traditionally, solvents are chosen for their ability to readily dissolve organic semiconductors and to give the best morphologies and efficiencies upon deposition. These are usually toxic, halogenated organic solvents, which present issues for the development of safe and cost-effective large-scale printing, and also question the eco-friendly premise of this type of technology.

Secondly, nanostructured suspensions allow for aggregate structure tunability and control. Large-scale device manufacturing presents the challenge of maintaining micro-
to nanoscale morphological control of the photoactive layer, over millimetre to metre printed areas. The nanoscale pre-aggregation of the donor and/or acceptor domains has been shown to persist through processing.[145] This approach allows bulk heterojunction morphology to be influenced and tuned during a nanoparticle or nanowire preparation process, decoupling nanoscale morphology from the specific coating operation.

Nanoparticles or nanospheres are a method of developing controlled morphologies[146] that allows the use of polar, non-toxic solvents for deposition. Colloidal nano-suspensions of active layer materials can be prepared using water or other polar solvents, where the size and composition of particles can be controlled.

The two approaches to assembling a bulk heterojunction using this nanoparticle approach are illustrated in Figure 2.9 (C) and (D). The first requires donor and acceptor nanoparticles to be prepared separately. Mixed together upon deposition, this allows nanoparticle size, a controllable parameter, to be mediated in order to control domain size (Figure 2.9 (C)). In principle, deposition techniques such as spray coating also allow the possibility of creating graded heterojunctions by modifying the ratio of particles layer by layer.

**Figure 2.9:** Strategies for influencing bulk heterojunction morphology prior to deposition. (A) illustrates the standard approach of donor and acceptor dissolved in a good solvent prior to deposition, (B) shows a triblock copolymer approach with two donor polymers covalently attached to a central acceptor polymer unit. (C) illustrates a nanoparticle approach with separate donor and acceptor nanoparticles, and (D) a composite nanoparticle approach.
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The second approach uses composite particles that contain both donor and acceptor, where the structure can be fixed prior to the deposition process (Figure 2.9 (D)). Hence the development of nanoscale morphology can be somewhat decoupled from the specific coating operation, and the distribution of donor and acceptor on the nanoscale can be fixed during nanoparticle preparation. Using this strategy, it is possible to optimise the intrinsic characteristics of a given nanoparticle formulation for the best photovoltaic performance and then optimise the coating process to yield a set of extrinsic film properties.[147]

Preaggregated nanowires of organic semiconducting polymers (also known as nanofibres, nanoribbons, nanowhiskers) have been implemented to control donor domain structure and BHJ crystallinity with some materials.[148] By using a marginal solvent or adding a poor solvent to the dissolved polymer in solution, high-aspect-ratio nanostructures with good crystallinity can be prepared. These nanowires can then be added in controlled quantities to unaggregated donor and acceptor in solution prior to active layer deposition. Berson et al. have shown that for P3HT:PCBM, adding P3HT nanowires in a ratio of 75% preformed nanowires to 25% amorphous P3HT gave the optimal photoconversion efficiencies when combined with the PCBM acceptor.[149]

2.6.5 Covalently attached donors and acceptors

Another strategy for manipulating the assembly of BHJ systems is to synthesise covalently attached donor-acceptor dyads or block co-polymers (BCPs). Dyads have been used as an additional third component along with donor and acceptor in deposition solutions to increase the stability of the active layer, and mediate phase separation to small, pure domains.[129] Alternatively, the entire BHJ can consist of an all-conjugated block copolymer, enforcing a particular domain size by building it directly into materials’ synthesis. Covalently-jointed donor and acceptor units allow the control of different block lengths through the molecular weight of polymer subunits to directly manipulate the length scales of domains. For an all-polymer solar cell, the standard approach for solution phase deposition is illustrated in Figure 2.9 (A). The arrangement of a triblock copolymer, with two donor polymers covalently attached to a central acceptor polymer is illustrated in Figure 2.9 (B).

These materials have a unique self-assembling behaviour, and can also produce donor and acceptor domains with an alternating lamellar arrangement, and bicontinuous pathways suitable for the percolation of charges. Approaches to covalently linking donor and acceptor components, while often synthetically challenging, have received attention for
producing films with well-controlled phase-separation on the 20–30 nm scale, a domain size ideal for maximising exciton collection at the donor-acceptor interface.\cite{150,151}

This approach can also be used to correct for the fact that generally, bulk heterojunction phases are not in their thermodynamic minima, and may change over time. This has the potential to influence charge generation and extraction, and ultimately, device performance. Block copolymers offer a solution to this issue of stability, and can also potentially offer solvent independent deposition, advantageous for the processing of other layers within a device.

While these approaches can be extremely strategic in terms of their morphological control of domain size and lamellar structure, there have been limited reports on the relation of BCPs and their charge generation properties.\cite{152,153} Importantly, BCP formation provides an additional, intramolecular donor-acceptor interface to consider in addition to the intermolecular interfaces that are formed upon BHJ formation.

### 2.7 Conclusion and outlook

Organic semiconducting materials have a unique relationship connecting their structural and optoelectronic properties. This is of key importance for their application in organic photovoltaics where active layer morphology continues to be integral for the optimisation of device efficiencies. OPV heterojunctions are structurally complex and their morphology has been shown to influence every event in the pathway from photon absorption through to the collection of charge carriers.

The understanding of charge transfer and separation has developed in recent years, though a full comprehension, particularly in relation to BHJ morphology, is still to be resolved. Even in this sometimes controversial area, some consensus is emerging of the requirements for efficient carrier generation.\cite{13,14} Recent reports have indicated that a large amount of charge generation is ultrafast in highly efficient blends, and the existence of CT states at the interface has been observed experimentally. Free charges can be generated through hot CT states, although relaxed CT states also seem to efficiently produce free carriers in many blends. Several possibilities are outlined for the origin of the driving force required to overcome the Coulombic attraction between electron and hole in the relaxed CT state. Entropy and disorder may be responsible, and/or morphology at the donor-acceptor interface could play an important role.

For the best BHJ solar cells, there seems to be a consensus that an optimal morphology consists of at least some crystalline domains of donor and/or acceptor components, but these domains should not be large enough to inhibit efficient exciton quenching.
Furthermore, some reports show the benefits of also having a third intermixed donor-acceptor phase to enhance long range charge separation.

As outlined above, blend microstructure is controlled by the chemical structure of component molecules and by the processing route used. Strategies to gain greater control and tunability over these nanoscale morphologies are increasingly being employed to optimise device efficiencies, using a wide range of approaches. Despite recent advances, charge generation in specific morphological strategies and newly developed high performing materials is not yet fully understood. The question can be posed: do these morphological design principles align with positive outcomes for charge separation?

Strategies to increase OPV device efficiency for the past decade have been dominated by the central strategy of energy level tuning, and to great effect.\cite{25} Ratner et al., have recently argued that future OPV efficiency gains will likely come not from completely empirical combinatorial synthesis of new materials with optimum energy levels. Instead, they will come from novel design criteria that include, but go beyond, energy levels allowing for the development of systematic understanding-based protocols to control active layer morphology and optimise processing techniques.\cite{25}

If morphology is central to the efficient spatial separation of charges, as it is for optimal exciton quenching and charge transport, then understanding the timescales and influence of bulk heterojunction structure on these processes will be vital in developing rules of rational design for the next generation of efficient OPV materials.
Chapter 3

Experimental Methods

3.1 Introduction

The design and optimisation of materials for efficient organic photovoltaic cells requires a detailed understanding of the processes that occur between photon absorption and photocurrent generation. Events occurring after photoexcitation happen very quickly, and span orders of magnitude in timescale, from femtoseconds to the microseconds. In order to investigate these (ultra)fast phenomena, it is necessary to prepare and measure excited state systems with an optical perturbation that is shorter in time than the dynamics of interest. While a number of optical techniques to probe molecular photophysics are useful for full characterisation, a particularly useful tool has been demonstrated in ultrafast transient absorption (TA) spectroscopy. This technique is capable of probing non-radiative states, and over the timescales associated with charge photogeneration.

In this chapter, technical details of sample preparation, steady-state and time-resolved optical techniques employed during this project are described and fundamental concepts introduced. Particular emphasis is given to sub-picosecond transient absorption spectroscopy.

Several challenges exist for the investigation of photoinduced dynamics in OPV materials with TA spectroscopy, which will also be addressed here. These include the requirements of extremely low excitation densities, high sensitivity measurements, and the identification and interpretation of spectrally and temporally overlapping signals due to separate phenomena.
3.2 Sample preparation

3.2.1 BTR films

Benzodithiophene terthiophene rhodanine (BTR) was synthesised according to literature procedure.[140] The preparation of samples is credited to Mr. Paul Geraghty.[127]

In order to prepare substrates for spincoating, glass strip substrates with dimensions of 2.5 cm × 2.5 cm × 0.1 cm were cleaned by sonicating sequentially in NaOH (1M), distilled water, acetone, isopropanol and dichloromethane. Substrates were kept in isopropanol until further use, and dried with nitrogen and then subjected to UV/ozone treatment for 30 minutes prior to coating.

For neat films, solutions of BTR and PC_{71}BM (Nano-c, 99 %) were prepared by dissolving respective samples in HPLC grade chloroform to a concentration of 1 mg/100 μL. For blend films, solutions of BTR and PC_{71}BM were prepared by dissolving respective materials into HPLC grade chloroform at a concentration of 2 mg/100 μL. These solutions were then stirred for three hours in the dark under ambient conditions. Blend solutions were then prepared in a 1:1 weight % ratio by combining equal volumes of the PC_{71}BM and BTR solutions which were then stirred for a further hour. Thin films were cast onto glass substrates via spin coating (Laurell WS-650) at a rate of 1000 rpm (2000 acceleration) for 30 seconds.

The solvent vapour annealing (SVA) process involved exposing the deposited films to THF vapour for 20 seconds. A 30 mm glass Petri dish containing 1 mL of THF was first closed for 1 minute to let the vapour saturate the chamber. The lid was then quickly swapped with a Petri dish lid with an as-cast film attached on the backside. The film was around 1 cm above the solvent level during the SVA. All measurements were completed on thin films prepared on the same day.

3.2.2 Nanoparticles

The preparation of aqueous nanoparticle dispersions studied in Chapter 5 is described below, and is credited to Mr. Sam Farley.[154]

Aqueous nanoparticle dispersions of 50 kDa regioregular poly(3-hexylthiophene) (Merck) and phenyl-C61-butyric acid methyl ester (PCBM, technical grade, 99 %, Solenne BV) were prepared in 18.2 MΩ MilliQ water (Millipore Simplicity system).

Reprecipitation nanoparticles were prepared using 1 mg of a 1:1 P3HT:PCBM w/w mixture (or 1 mg of P3HT for neat particles) dissolved in 1 ml of tetrahydrofuran (THF)
(Sigma-Aldrich, Chromasolv(R) inhibitor-free), and stirred for 20 minutes at 40°C. The THF solution was transferred to a syringe and rapidly injected into 8 mL of MilliQ water under vigorous agitation. The remaining THF was then removed under reduced pressure using a rotary evaporator, and the solution filtered (0.45 μm PES filter) before characterisation.

Mini-emulsion nanoparticles were prepared using 60 mg of a 1:1 P3HT:PCBM w/w mixture (or 60 mg of P3HT for neat particles) dissolved in 1.12 mL chloroform (Sigma-Aldrich, Chromasolv(R) inhibitor-free) and stirred for 20 minutes at 40°C. The solution was sonicated (Unisonics FHP12DH) for 10 minutes and stirred again for 10 minutes at 40°C, then added to a 42 mM aqueous sodium dodecylsulfate (SDS, Scharlau, 95 % extra-pure) solution and stirred rapidly at 40°C for 1 hour to form a macroemulsion. The macroemulsion was sonicated with a 5 mm tapered microtip (Branson S450D) for 2 minutes at 60 % amplitude in pulse mode (0.5 s on, 1 s off). The subsequent mini-emulsion was slowly heated to 60°C while stirring for 3 hours to evaporate the chloroform and then centrifuged at 18,000 rpm for 16 minutes to concentrate the dispersion and remove excess surfactant (Sartorius Ultrafiltration centrifuge tube). Dispersions were filtered through a 0.2 μm PES syringe filter to produce the final mini-emulsion suspension in water.

Nanoparticles were characterised to determine their size and polydispersity index (PDI) using dynamic light scattering (DLS) (633 nm laser, Zetasizer Nano-ZS, Malvern Instruments). Nanoparticles produced by the two methods had similar average particle sizes: the mini-emulsion particles with average hydrodynamic diameters of 110 nm (P3HT) and 84 nm (blend), and the reprecipitation particles with diameters of 92 nm (P3HT) and 79 nm (blend). The PDI for all particle types was 0.23 ± 0.03.

3.2.3 Triblock copolymer

The PFM-F8BT-PFM block co-polymer discussed in Chapter 6 was synthesised by W. Tang and D. J. Jones according to the procedure described in detail by Holmes et al., and Yan et al.[155, 156] Briefly, the polymer F8BT, poly(4-(9,9-dioctyl-9H-fluoren-2-yl)benzo[c][1,2,5]-thiadiazole), electron-accepting block was synthesised by Suzuki condensation followed by end-capping with trimethylsilylphenyl groups and reaction with ICl. The block size was controlled by monomer ratio followed by removal of low molecular weight oligomers via Soxhlet extraction with ethyl acetate leaving a polymer with $M_n = 21,200$, $M_w = 32,000$ and $M_w/M_n = 1.51$. Chain extension with N1-(4-(7-(4-iodophenyl)-
9,9-dioctyl-9H-fluoren-2-yl)phenyl)-N₁,N₄-di-p-tolylbenzene-1,4-diamine under Buchwald-Hartwig conditions, followed by end-capping with bromotoluene, resulted in the formation of the triblock copolymer PFM-F8BT-PFM.

The triblock co-polymer has a weight ratio of PFM to F8BT of 1:1, and comprises approximately 60 F8BT monomers and 30 PFM monomers per chain ($M_n = 43,500$, $M_w = 56,400$, $M_w/M_n = 1.30$). Full synthetic and molecular characterization details are published elsewhere.$[155, 156]$

For further use, the homopolymers and triblock copolymer were dissolved in solvents as described in Chapter 6 at concentration of $1 \mu M$.

### 3.3 Steady-state measurements

#### 3.3.1 Absorption Measurements

Steady-state absorption spectra were recorded using a Varian Cary 50 UV-Vis spectrophotometer. Solution measurements were recorded at room temperature using quartz cuvettes of 10 mm path length unless otherwise stated. All absorption measurements were baseline-corrected using a solvent or film blank.

Steady-state absorption was also used to monitor sample integrity by performing measurements before and after laser exposure to detect photoinduced degradation.

#### 3.3.2 Fluorescence Measurements

Fluorescence spectra were recorded on a Varian Eclipse spectrofluorimeter. For solution state measurements, a $10 \times 10$ mm quartz cuvette was used unless indicated otherwise. All fluorescence measurements in solution employed sufficiently diluted samples with optical densities below 0.1 at the excitation wavelength, to allow both sufficient excitation light penetration and to minimise re-absorption of emitted fluorescence. Spectra were corrected for the detector wavelength response after acquisition, using a correction spectrum acquired with a light source of known intensity across the relevant wavelength range.

For film measurements, films were positioned (using a custom-built film holder) to avoid reflection of the excitation light towards the detector, and multiple measurements were averaged.
### 3.4 Time-correlated single photon counting

A standard method of determining chromophore emission as a function of time is time-correlated single photon counting (TCSPC), which can measure emission decays from tens of picoseconds to tens of nanoseconds. This technique can be useful for determining lifetimes of excited states which are radiatively coupled to the ground state. Conceptually, TCSPC is based on the probability distribution for the arrival time of the emission of single photons after repetitive excitation. Iterative sampling then yields a histogram of photon arrivals per time bin, which also represents the same dynamics as a single photon, by virtue of ergodicity.

A schematic of the experiment is shown in Figure 3.1. Briefly, an excitation pulse which excites the sample also produces a correlated electrical trigger pulse (usually using a photodiode). After passing through a constant fraction discriminator, this trigger serves as the ‘start’ input for a time-to-amplitude converter (TAC) which initiates the charging of a capacitor. When the excited sample emits a photon, this reaches the detector which
provides a suitable ‘stop’ signal for the TAC. The amplitude of this TAC signal is then proportional to the time delay between the start and stop signal, giving a numerical value which is stored through an analogue-to-digital converter (ADC). This process is repeated until a desired number of photon counts is generated in the predefined time ‘bins’ stored in computational memory. The generated histogram is then representative of the fluorescence decay, which has been obtained statistically from a large number of emitted photons over many iterations.

The excitation source was a mode-locked and cavity dumped Ti:Sapphire laser (Coherent Mira 900F/APE PulseSwitch) pumped by a Coherent Verdi-10 DPSS Nd:YVO4 laser. The laser output (880 nm wavelength, 5.4 MHz repetition rate) was frequency doubled to provide an excitation wavelength of 440 nm. Synchronisation of the laser pulses was achieved using a fast photodiode (Becker & Hickl, PHD-400-N) fed through a nanosecond delay box and constant fraction discriminator (Tennelec TC455) as the stop signal for the time-to-amplitude converter (Ortec model 457). The emission was collected at right angles relative to the excitation, spectrally selected using a monochromator (Jobin Yvon H20) and detected using a micro-channel plate (ELDY, EM1-132/100). Emission polarisation was collected at the magic angle (54.7°) relative to that of the excitation to remove polarisation artifacts. The instrument response function (IRF) was determined experimentally by measuring the response of excitation light from a non-fluorescent weakly scattering solution of colloidal silica (Ludox).

Photoluminescence decays were fit using the FAST software package (Edinburgh Instruments) with a sum of exponential decays by performing an iterative reconvolution with the instrument response function.

### 3.5 Principles of transient absorption spectroscopy

Processes of energy and electron transfer in light harvesting materials typically occur on < 0.1–100s of picosecond (10^{-12} s) timescales and hence relevant experimental techniques require at least this degree of time resolution. The advent of ultrafast laser systems in the 1990s, with pulse lengths on the order of femtoseconds (10^{-15} s), have since enabled the measurement of such dynamics.

While both TCSPC and ultrafast fluorescence-based techniques allow for the investigation of excited state decay profiles, they are inapplicable to the direct detection of transitions that are not radiatively coupled to the ground state. The direct detection of non-emissive transient species or ‘dark states’ can be achieved with time-resolved absorption experiments. This method is ideal for probing specific excitations, charge-transfer
states and free charges generated in light harvesting materials and for uncovering the dynamics of photoinduced processes.\textsuperscript{157–159} Ultrafast transient absorption spectroscopy is a pump-probe technique that uses short pulses of light to excite and subsequently measure absorption changes, and hence the excited state dynamics, in a solution or film sample of interest.

The pump and probe beams are generated by the same laser source (amplified Ti:Sapphire, described in detail in Section 3.6) to ensure synchronicity between pulses (which here are produced at a frequency of 92 kHz). The ultrafast excitation pulse or ‘pump’ is directed to the sample in order to promote a fraction of molecules to a chosen electronically excited state. A second, weaker probe pulse, then passes through the same volume of sample to measure the photoinduced transmission change. This probe can be comprised of either a single wavelength or a broad spectrum, so that an entire transient spectrum can be measured with each excitation event. A detector placed after the sample records the transmitted signal intensity of the probe pulses at each excitation event for a given time point. For the high repetition rate TA described here, the detector measures the recorded intensity over each batch of ten pulses (9.2 kHz), limited by the maximum detector readout rate. The pump beam is modulated using a chopper at half the probe detector frequency (4.6 kHz), meaning that ten probe pulses in a row experience pump pulses in the sample, followed by ten that do not.

The transient absorption signal is the pump-induced absorption change, $\Delta A$, normalised by the absorption of the ground state. The intensity of a pump-off probe pulse is given only by the ground state absorption of the sample ($A$), while the pump-on probe pulse is affected by the ground state absorption as well as those molecules that have been excited by the pump ($A + \Delta A$).\textsuperscript{158} The transient absorption ($\Delta A$) can thus in principle be derived from the difference between the pumped ($A_{\text{ex}}$) and non-pumped ($A_{\text{unex}}$) absorptions:

$$\Delta A = A_{\text{ex}} - A_{\text{unex}} = \left(-\log_{10}\left(\frac{I_{\text{ex}}}{I_0}\right)\right) - \left(-\log_{10}\left(\frac{I_{\text{unex}}}{I_0}\right)\right)$$

$$\Delta A = -\log_{10}\left(\frac{I_{\text{ex}}}{I_{\text{unex}}}\right)$$

(3.1)

where $I_0$ is the intensity of light incident on the material, $I_{\text{ex}}$ is the intensity of light transmitted when the sample has been pumped and $I_{\text{unex}}$ is the intensity of light transmitted for an unpumped sample.

From Equation 3.1 it is apparent that $\Delta A$ depends only on the pair of intensities, $I_{\text{unex}}$ and $I_{\text{ex}}$ needed to obtain the TA signal, and $I_0$ does need not be measured. The
magnitude of $\Delta A$ is then directly proportional to the transient population created by the pump, where the fraction of excited molecules is determined by the excitation power and absorption cross-section of the material. This is usually kept to a fraction of a percent of the molecules in the sampled volume.

For broadband measurements over a range of wavelengths, $\Delta A$ at a given time between pump and probe gives $\Delta A(\lambda)$. By changing the time delay between the excitation pulse and the probe pulse, and recording a $\Delta A$ spectrum at each delay point, $\Delta A(\lambda,t)$ is obtained, and the behaviour of excited states can be monitored in time. The temporal length of the pump and pulses, and the accuracy of the delay line, determines the time resolution of the experiment.

A typical transient absorption data surface is illustrated in Figure 3.2, where slicing through a particular wavelength gives the kinetic trace for that electronic energy, and slicing through at a certain time delay will give the transient absorption spectrum at that time. This can reveal the dynamic processes in light-absorbing systems, including energy migration, electron or proton transfer, intersystem crossing and isomerisation.

A transient absorption signal ($\Delta A$) is comprised of four general types of contribution as illustrated in Figure 3.3. Positive $\Delta A$ signals will arise from allowed transitions that are the result of a populated excited state, prepared by the pump pulse. Pump-induced absorptions can simply arise from transitions from the excited state itself (e.g. $S_1$) to higher energy states ($S_n$). Likewise, transient photoproducts can be formed when the
Figure 3.3: Possible transitions in a transient absorption experiment and corresponding experimentally observed signal varieties. (A) shows steady-state absorption and fluorescence spectroscopy for comparison. (B) illustrates transient absorption signals showing the ground state bleach (GSB), stimulated emission (SE), and photoinduced absorption (PA) of both the pumped excited state (here $S_1$) and a newly created photoproduct.

Pump excitation induces a photochemical reaction such as photoinduced electron transfer. These photoproducts (e.g. charge transfer states, triplet states or free charges) can absorb to higher lying states and possess their own absorption coefficients. Photoproducts can be detected if they absorb light within the wavelength range of the probe.

The two possible negative $\Delta A$ contributions are the ground state bleach (GSB) and stimulated emission (SE), both arising from an increase in the number of photons detected following an excitation event compared to an unexcited sample. The GSB signal appears as the sample’s steady state absorption signal inverted about the $\lambda$-axis and occurs due to the depletion of the ground state during excitation. This signal can give valuable information on the recovery of the ground state population, $S_0$, in time. If the probe pulse is resonant with a radiative electronic transition, it can stimulate the emission of a photon. This is known as stimulated emission (SE) and can occur in some samples, resembling the emission spectrum of the sample, again inverted about the $\lambda$-axis. The signal is negative as more photons are detected (rather than absorbed) at a given wavelength as the result of the pump pulse. This can only occur when the excited state is strongly optically coupled to the ground state. The kinetics of this signal describe the kinetics of the excited state population, e.g. $S_1$.
3.6 Experimental setup for transient absorption spectroscopy

The origin of laser light for the transient absorption setup was a mode-locked Ti:sapphire oscillator (Coherent, Mira Seed) pumped by a green (532 nm) cw diode-pumped laser (Coherent, Verdi V18). A pulse shaper using a spatial light modulator (SLM) (MIIPS Box 640, Biophotonic Systems) was used on the seed to adjust spectral phase and pulse shape. The SLM used the SHG spectrum for optimisation later in the beampath to create transform-limited pulses by pre-correcting the shape and dispersion of the seed. The oscillator output was then directed to a pulse expander (Coherent, EC9150) to stretch the pulses and reduce their peak power before they were used to seed a Ti:sapphire regenerative amplifier system (Coherent, RegA 9050). To compensate for some additional beam divergence produced by the long path length of the beam as the result of the MIIPS box, the pair of beam diameter expansion optics in the stretcher were reversed to instead compress the beam diameter prior to injection into the amplifier.

After typically 16 roundtrips, the pulses were ejected by the cavity dumper at a repetition rate of 92 kHz and a wavelength centered at 800 nm. The output was then finally compressed (Coherent, EC9150) to produce pulses of <50 fs duration.

Figure 3.4 schematically displays the basic optical and electronic elements of the pump-probe setup.

The output of the amplifier was split using a 50:50 beam splitter to direct half of the output to continuum generation for use as the probe pulse. The remainder was passed into an OPA (optical parametric amplifier) (Coherent, OPA9450) where the light was either frequency doubled with a BBO (barium borate) crystal or parametrically amplified to produce other pump wavelengths in the range from ∼490–750 nm. The resultant pump beam was mechanically chopped (Thorlabs, MC1000/MC1F60) at 4.6 kHz, between a pair of off-axis parabolic mirrors (Edmund Optics, NT47-097) to focus the beam through the chopper blades and ensure a small spot size to avoid the clipping of pulses.

The supercontinuum (SC) broadband probe was derived from the residual 800 nm beam focussed onto a 3 mm sapphire substrate (Crystal Systems) for measurements in the visible region (450–800 nm), and a 3 mm uncoated undoped YAG window (CRYSTECH) for the infrared region (800–1400 nm). Further information on supercontinuum generation can be found in Section 3.6.1.

The supercontinuum spectrum was still dominated by the 800 nm fundamental, so to avoid detector saturation and to limit the detected wavelength range to less than one optical octave, visible and NIR measurements employed an optical short pass filter (Asahi Spectra, XIS0780), and long pass filter (880 nm cut-off long pass) respectively. A
Figure 3.4: Schematic of the high repetition rate transient absorption optical setup showing basic components of the pump and probe optical paths, electronic triggering and computer-driven processes. BC: Berek compensator, for polarisation control.

notch filter (Semrock, NFDOI 785 nm) was also used for some visible measurements to omit only intense fundamental. Further adjustments to the visible SC’s spectral shape (to maximise uniformity across the wavelength region and optimise signal-to-noise) were made using an aqueous solution of CuSO$_4$ after the sample where the optical density could be adjusted via solution concentration.

The arrival time of the pump pulses relative to the probe was manipulated using a variable optical delay line (Newport, UTS150PP with ESP 300 controller). The uncertainty of positioning on this stage equates to a time uncertainty of $<5$ fs, meaning that the limit to time resolution is given instead by the length of pump and probe pulses (200 fs at the sample). The stage was controlled to move in a logarithmic distribution of time points over the desired range, so that large signal changes at short times could be mapped with more data points.

The relative polarisation of pump and probe was controlled by adjusting pump polarisation with a Berek compensator (New Focus, 5540) to the magic angle 54.7°. The versatility of the compensator means that it could be adjusted to alter to polarisation of a range of different pump wavelengths. Pump and probe beams were focussed on the
sample using a 100 mm off-axis parabolic mirror (Newport, 50332AU) to reduce further group velocity dispersion that would result from a lens.

For samples in solution, stoppered glass cuvettes (21/G/2, Starna) with a 2 mm path length were used, and were stirred with a magnetic stirrer bar (MSB/6x1.5, Starna) coupled to an externally motor-mounted magnet (magnetic stirring system, Ultrafast Systems). For film measurements, the sample was translated (x and y Oriel StepperMike, and Phidgets stepper controller 1602) with every movement of the delay stage to avoid photodegradation of the film that would occur after an entire experiment.

For the majority of measurements (unless otherwise noted) the pump beam was attenuated to a pulse power of 8 nJ/pulse with a spot area of $1.3 \times 10^{-3}$ cm$^2$, giving an excitation density of $6 \mu$J/cm$^2$, to reduce artefacts associated with exciton-exciton-[160] and exciton-charge annihilation.[161, 162] Nitrogen was blown over films for all measurements, except for those exposed to oxygen to demonstrate the quenching of triplet states.

After passing through the sample, the probe beam was analysed with fibre coupled-spectrometers, using a 1024 pixel CMOS detector for the visible region (9200 spectra/s for divide-by 10), and a 256 pixel InGaAs sensor for the IR region (both Ultrafast Systems), recorded at $\sim 7077$ spectra/s for divide-by 13. To achieve synchronised detection of the 92 kHz pulse train, timing electronics were employed to record spectra at 9.2 kHz (integrating over every 10 probe pulses) and chop the pump beam at 4.6 kHz. Using the master trigger signal from the laser amplifier, a divide-by circuit was employed for this purpose. This provided two outputs, firstly the master trigger divided by 10 (binary counter chip, 74HC193; and NAND gate, 74HC00) for spectrometer acquisition. This signal was then further divided by two (dual D-type flip-flop 74HC74) to achieve a division by 20 (4.6 kHz) and this trigger was applied to drive the chopper and to arm the spectrometer to ensure pump off/on were consistently recorded (see Figure 3.4). The two output signals from the division circuit were input into two individual 555 timer chip containing circuits, allowing the use of a pair of manually adjustable variable resistors to control the fine delay of each channel to optimise the timing.

The installation of a NIR spectrometer during the course of this project extended the probing capacity in principle from 350–800 nm to 350–1700 nm, however, the maximum read-out rate of this instrument was 7.5 kHz, rather than the 9.5 kHz which had allowed for the modulation of every ten laser pulses. Accordingly, the division circuit was adjusted to divide-by every 13 pulses, using the binary counter chip ($\sim 7.08$ kHz), with the chopper controller consequently driven at divide-by 26 ($\sim 3.54$ kHz). These settings were employed for all measurements in Chapter 4.
Software to interface user input with spectrometers, delay stage and film translation as well as data processing and storage was developed in-house using MATLAB. During an experiment, $\Delta A$ was calculated for each on/off pair, and an algorithm applied to discard pairs that deviated from the mode by more than two standard deviations. This approach gives better results from occasional large probe fluctuations, whereas using the mean would falsely bias outliers due to the asymmetrical qualities of laser and SC generation noise. Recorded spectra were then averaged for each time delay point, and several iterations (3-20) through the full time delay series were completed for a full experiment.

Following an experiment, data was processed using MATLAB routines, also developed in-house. Each iteration through the delay stage was inspected and compared with others to check for large fluctuations or photodegradation, before being averaged into a single data surface. An optional routine could be applied to compare each individual data point with the median value calculated from all adjacent points within the three-dimensional data set. A discrepancy beyond a certain threshold value would result in the exclusion of that data point. A transformation was applied to correct for the ‘chirp’ of the probe pulse, the wavelength dependent pump-probe delay that corresponds to the temporal overlap of pulses in the sample. This wavelength dependence is mainly due to the group velocity dispersion (GVD) of the broadband pump, and is more pronounced in the visible region than the IR. Chirp correction was implemented by examining the first few picoseconds of the experimental data. A cross correlation routine was applied and a 3rd order polynomial was fit to the chirped surface. The data is subsequently shifted by the appropriate temporal offset at each wavelength to produce the corrected dataset.

Further details regarding the development of the high repetition rate setup can be found in reference [163].

3.6.1 Generation of the supercontinuum probe

Supercontinuum (SC) (or ‘white’) light is extremely broadband coherent laser light that is generated in bulk media by a combination of non-linear optical processes. Supercontinuum light can be an invaluable tool for spectroscopy due to its compatibility with femto- to picosecond pulses and its very wide spectral coverage.

Widely used in transient absorption experiments as a broadband probe, a supercontinuum allows for the simultaneous determination of the transient signal at different wavelengths when coupled with a suitable spectrometer. As wavelengths from the UV up to the NIR are accessible, broadband probing dramatically decreases the amount
of time required to measure full spectra compared to monochromatic probing which requires scanning of the probe wavelength for each time delay. This technique is also especially helpful to identify spectral shifts, which undetected could lead to erroneous interpretation of excited state kinetics.

The processes and parameters involved in supercontinuum generation are non-trivial, and this section attempts to provide some clarification around this important experimental tool. The probe can also be a possible significant source of noise in transient absorption spectra, as will be discussed in Section 3.7. As such, the optimisation and stability of SC generation is of paramount importance to generating highly sensitive transient absorption measurements.

For a full description of the non-linear processes in supercontinuum generation, the reader is encouraged to seek a comprehensive review in references [164–166]. However, as an overview, SC generation begins with a physical effect known as self-phase modulation. When a pulse of high intensity laser light enters a medium, the refractive index of that material becomes intensity dependent due to the 3rd order nonlinear polarisability. The beam then effectively modulates its own phase as it propagates through the material. This results in new low frequency components being created in the leading edge of the pulse envelope, while high-frequency components are created in the trailing edge. The resulting phase and amplitude change can cause a frequency sweep of the carrier wave and self-focusing of the beam. A number of other non-linear and linear effects further broaden the spectra often extending over hundreds of nanometres of wavelength range. These other mechanisms can include electronic cloud distortion, reorientation, librations, and vibrational and molecular redistribution. The new frequencies are created inside the original pulse envelope, as self-phase modulation itself is not dispersive. However, they can become further chirped in time due to the GVD of the material.

For experimental application of the SC, several parameters are important. Bradler et al. have described many of these for generation in different bulk media in a comprehensive overview.[167] Different materials, seed wavelengths, intensity, beam shape, and pulse length strongly influence the generation process and can be employed to generate stable continua depending on the spectral range that is required. Supercontinua can be generated using ultrafast laser pulses propagating in many media including solids, liquids, gases, and various designs of optical fibres. Commonly used bulk materials for SC generation include single crystals of sapphire (Al₂O₃), calcium fluoride (CaF₂), yttrium aluminium garnet (YAG), yttrium vanadate (YVO₄), gadolinium vanadate (GdVO₄)
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Figure 3.5: A comparison of supercontinuum generation in (A) sapphire and (B) undoped YAG crystals over the visible and IR range. Visible and near-IR spectra were recorded separately using short- and long-pass filters respectively. The spectra are a convolution of the actual supercontinuum spectra with detector response and diffraction efficiency of the grating.

potassium-gadolinium tungstate (KGW), and D$_2$O:H$_2$O (7:1 mixture). Calcium fluoride (CaF$_2$) is able to reach the UV spectral range, but needs to be constantly translated in the beampath to prevent crystal damage. For continua extending to the near-infrared, YAG, sapphire and YVO$_4$ are more suitable, and the generation of the IR range can be optimised to a certain extent by using longer focal lengths (>60 mm) into the crystal.[167]

Figure 3.5 shows the visible and NIR supercontinuum spectra for two different media, a sapphire window and an undoped YAG crystal. The visible and NIR spectra were recorded separately using short- and long-pass filters respectively. The sapphire gives superior generation into the sub-500 nm region (but inferior to CaF$_2$). The YAG crystal was chosen for its stability in the IR region and ease of alignment due to its visible component, which is absent in some other materials.

Despite the high repetition rate of our system, more than adequate pulse energies were available for supercontinuum generation. Between 100 and 300 nJ per pulse was required of the 800 nm pulse for optimal supercontinuum generation with sapphire and YAG crystals. For optimisation of the continua, the SC seed was carefully adjusted with a continuous neutral density (ND) filter, so that single filament white light was generated. Iris apertures (some distance from the crystal) were also employed to control the beam profile, to eliminate non-fundamental modes from the seed laser. The ND wheel and
Irisises were adjusted iteratively to optimise the shape, spectral range and stability of the supercontinuum.

While an off-axis parabolic mirror had previously been used before the crystal for focussing, this was replaced with a 70 mm lens to ease the challenges of alignment for such a highly sensitive element. Good alignment was determined as imperative for the stability of the probe and the minimisation of noise in high sensitivity experiments. A parabolic mirror after the crystal was placed on translation stages to aid in the adjustments required for the collimation of the output beam, exacerbated by the power dependence of self-focussing in the SC generation. The intensity of the final SC was adjusted with a further neutral density filter wheel prior to the detector.

For supercontinuum generation, the seed power has a threshold level for the non-linear processes involved. Further increases raise the intensity and alter the shape of the white light spectrum, but beyond a certain energy level, spectral and spatial modulations of the beam can occur. This is thought to be caused by multiple filaments contributing to continuum generation at distinct locations within the crystal. [167] Irregularities and noise in the incident beam profile, even modest, can be rapidly reinforced and lead to a break-up of the beam in several hot spots which can act as nuclei for multifilament generation. [165]

Figure 3.6 shows the changes in the spectral output of a 3 mm sapphire crystal as the seed pulse energy is gradually increased while keeping all other parameters identical. Spectra are offset for clarity. At a seed pulse energy of 193 nJ, almost no spectral broadening is observed as the seed energy is below the threshold for generation. A slight increase to 212 nJ results in continuum generation and a spectral plateau in the visible region, with an energy of 232 nJ giving further spectral bandwidth. For seed energies of \( \sim 380 \) nJ and above, spectral oscillations or ‘wiggles’ [167] can be observed that are due to continuum generation at distinct locations within the crystal. If these continua are temporally separated at the crystal output, they may lead to spectral beating and interference between neighbouring filaments. At even higher pulse energies, the single filament quite obviously breaks up into many filaments, resulting in unstable, speckle-like colourful patterns within the SC, which can be easily noticed by eye.

Multifilamentation can also provide the source of unwanted artifacts within a transient absorption experiment. Non-optimal alignment of the pump and probe at the sample can result in some parts of the probe experiencing greater pump intensities (within its Gaussian distribution) than others. This is not ideal but not insurmountably detrimental to an experiment. However, if the probe is spectrally inhomogeneous, then this can result in significant artifacts in the transient spectra that cannot be easily removed.
Figure 3.6: Supercontinuum spectra in the visible region generated in a 3 mm sapphire window with increasing seed pulse energies (spectra are offset). A short-pass filter is employed at 800 nm. Inset photos show examples of the beam profile for (bottom to top): energy below the threshold for generation (193 nJ), a single filament (232 nJ) and multifilament generation (740 nJ).

Figure 3.7 (A) shows the transient absorption of the polymer PFM (at 3 ps), with the associated probe spectrum shown in grey. The spectrum is blocked with a short-pass filter at wavelengths greater than 750 nm. In (B), the same transient absorption spectrum is shown (at 3 and 100 ps), but with a different supercontinuum spectrum used for the probe, generated with a greater seed energy. The subtle oscillations in the probe spectrum evident between 650–750 nm are due to interference between neighbouring filaments in a multifilament effect. While not obvious in the probe spectrum, these oscillations are significant in the transient spectra, appearing after time zero, and persisting throughout the full range of time delays due to the pump’s interaction with the inhomogeneous probe. This illustrates that the transition between single and multifilament SC generation can be sometimes difficult to observe, and care should be taken to ensure that multifilaments are not inadvertently introduced into an experiment.
3.7 Considerations for transient absorption in organic photovoltaic materials

Transient absorption remains one of the most valuable techniques for observing photoinduced exciton and charge dynamics, offering a glimpse into the most important processes in organic solar cells. With broadband detection and sub-picosecond time resolution, a wealth of experimental information is provided. However, the dynamics of charge generation have often proven notoriously challenging to correlate with specific molecular and aggregate properties in direct relevance to organic photovoltaic device operation. One of the primary reasons is the highly complex nature of solid state blend morphology. Another is related to the complex and overlapping dynamics in these materials. Special considerations of relevance for transient absorption in OPV materials that have emerged are explored in this Section.

Figure 3.7: (A) The transient spectrum of PFM at 3 ps in toluene (red) with the spectra of the supercontinuum probe shown in grey. (B) Transient spectra of PFM at 3 ps and 100 ps, with the supercontinuum probe again shown in grey, but with a higher seed energy for SC generation. In (B), multifilamentation in the probe has resulted in the artifact in the TA spectra throughout all time delays due to inhomogeneity of the probe beam.
Firstly, for equivalence with OPV devices, TA measurements must be conducted of the BHJ itself, rather than separate materials or components in solution. In film samples, donor and acceptor materials are in close proximity to one another, and there can be a few additional challenges for measurements in the solid state. Film samples eliminate the option of stirring the sample, as is routine for solutions to avoid photo-damage and degradation. Generally, a combination of lower pump powers and translation of the film is implemented to avoid photo-damage and the build-up of heat in the sample.

A significant consideration for films in the solid state is the effect of excitation power, due to well-known coherent artifacts in transient spectroscopy, but also due to inherent non-linearities of the sample. At times corresponding to the temporal overlap of pump and probe pulses, coherent artifacts are possible due to the simultaneous action of photons in these pulses. These coherent artifacts are: two-photon absorption, stimulated Raman amplification, and cross phase modulation. All have a duration directly related to the temporal response function of the instrument and a linear dependence on pump pulse intensity.[168] While lowering pump intensity can minimise photodegradation and the appearance of these artifacts, solid state donor-acceptor materials have further concerns.

The significant non-linearities in the samples themselves with respect to excitation density have been demonstrated in a wide range of organic semiconducting materials in the solid state. The cause of these non-linearities are: exciton-exciton annihilation[160], exciton-charge annihilation[161, 162] and bimolecular recombination[31, 72], all resulting in strongly excitation-density dependent data.

It has now become apparent[76, 143, 169] that it can be difficult to avoid second order effects because of the photon density that is often required for sufficient signal-to-noise ratio in TA experiments, and the high peak power inherent to very short optical pulses. This is particularly true of some of the seminal literature. High excitation densities introduce second-order effects that can completely mask the relevant low excitation density processes, and have caused discussion in the literature over the correct assignment of transient signals.[76]

Recently, progress has been made both in understanding the threshold for second order processes and in performing experiments that avoid or account for this complication.[72, 169–172] The morphology of samples has even been found to determine the linearity (or otherwise) of excitation dependence.[72] Transient absorption signal intensity is proportional (within the linear regime) to the pump pulse intensity. Therefore to minimise second order effects, using much weaker excitation densities results in lower $\Delta A$ signals, and consequently, much greater sensitivity is required.
Organic solar cells under normal operation typically experience photon densities of approximately $10^{16}$–$10^{17}$ photons cm$^{-3}$, and accordingly, efficient devices have a similar number of charge carriers.[31, 173] Hodgkiss and coworkers have specifically outlined the requirement for highly sensitive experiments when investigating OPVs and make a direct assessment of the excitation density in comparison to solar radiation.[174] For example, using a pump energy of $\sim 2\, \mu$J/cm$^2$ gives approximately $10^{12}$ cm$^{-2}$ absorbed photons. If all of these photons are converted to charge in the BHJ (assuming a charge cross section of $10^{-16}$ cm$^2$), multiplying the number of excitations by the charge cross section gives a calculated TA signal of $10^{-4}$. By using the film thickness of $\sim 100$ nm, and the fluence, the excitation density can be determined as $10^{17}$ cm$^{-3}$, the upper end of the previously defined number of photons experienced by devices under solar AM 1.5 G illumination.

This is an extraordinarily low photon fluence for a spectroscopic measurement of this kind, and consequently, a sensitivity of better than $10^{-5}$ is required from the instrumentation. This regime is expected to avoid significant non-linear effects and experience bimolecular recombination similar to a working device. While transient absorption measurements have the potential to aid in the understanding of processes spanning the entire charge photogeneration process, its implementation as a useful tool depends on its ability to carry out measurements with this high sensitivity. Strategies to achieve such sensitive transient measurements, in our case the use of a high repetition rate laser, will be discussed further in Subsection 3.7.1.

The broad absorption bands of organic semiconductors give them a favourable absorption of the solar spectrum. However, the absence of well-defined signals may provide challenges for spectroscopic interpretation. Unisolated absorption bands can make it difficult to excite single components in a BHJ blend with available laser wavelengths and the overlap of transient signals can prevent the unambiguous separation of multiple components.

Structural disorder and aggregation in organic semiconducting films (as discussed in Section 2.1) can result in complex multiphasic dynamics which can potentially complicate transient data interpretation. Particularly in conjugated polymers, early relaxation can be caused by excitation energy transfer to lower-energy chromophores, and/or geometric changes in the polymer backbone.[175–177] This disorder presents complex, multiphasic dynamics which have been demonstrated in both the ultrafast fluorescence and transient absorption spectroscopy. Similarly, charged species may undergo relaxation and spectral shifts, and the rates of charge separation can depend on a distribution of different distances and orientations between the donor and acceptor.
Therefore the time evolution of transient signals can be influenced by multiple different processes, where for example, the unobstructed dynamics of charge separation may be entangled with that of exciton relaxation. Additionally, if charge transfer is mediated by the diffusion of excitons in pure domains, any time-resolved behaviour of the polaron signal will be blurred by the arrival time distribution of excitons to a donor-acceptor interface. Challenges relating to signal assignment will be discussed further in Section 3.7.2.

Despite the complexities of the solid state, transient absorption measurements on films have opened up new experimental possibilities. Film measurements of the BHJ in the absence of electrodes represents the case of open circuit voltage ($V_{OC}$), where there is no extraction and ultimately the recombination of all charges. The transient spectra of devices have also been measured under operating conditions and a proper device architecture.[71, 178] As this requires a metal back electrode, a transient absorption experiment must take place in reflective rather than transmissive mode, sometimes termed transient reflection spectroscopy. A typical active layer thickness of 200 nm is less than the wavelength of illuminating light, and the optical field must vanish at the reflective metal back electrode. This serves to create a significant spatial variation of the optical generation profile of pump and probe across the device, and therefore measures a non-uniform charge distribution.[179, 180] This optical cavity effect can add a strong wavelength dependence of spatial overlap between the pump and probe adding spectral distortion to measurements. However, this effect was exploited by Chow et al., who used it to extract both spatial and temporal information on the photogenerated hole distribution and charge transport dynamics for a device’s back electrode.[179]

Structural characterisation techniques cannot always generate the entire picture of BHJ morphology, with amorphous regions and interfaces proving particularly challenging for many techniques.[12] TA spectroscopy, while indirect, is capable of elucidating some of the details of the subtle morphological influence on charge separation.[181] While observing the charge photogeneration process directly, information regarding local morphology can be determined indirectly.[71, 72, 114, 171, 181, 182] For example, the evolution of the TA spectra from predominantly excitonic to polaronic signatures can offer information on the rate of exciton diffusion to the interface, and hence provide information on nanoscale morphology. With the assistance of other complementary techniques for BHJ characterisation, this can be a useful probe of the connection between phase morphology and photocurrent generation.
3.7.1 Sensitive transient absorption spectroscopy

In this Section, the primary experimental strategies for achieving high sensitivity transient absorption measurements will be discussed. Generally speaking, there are two types of transient absorption spectroscopy setup employed, those using a source laser with repetition rates of 40–250 kHz and those of 1–5 kHz. The former, high repetition rate systems, have the benefit of greater signal averaging. The latter, low repetition rate lasers, have the benefit of higher pulse energies (which can be used to drive multiple simultaneous non-linear processes) and can be used to excite a larger proportion of molecules in the sample. However, the relatively high peak pulse powers available are often not required for low pump energy measurements, discarding much of the power that comes with this type of system. Other benefits include longer relaxation times between excitation pulses, and the ability to sample each pulse individually.

In general, the primary sources of noise in a transient experiment are derived from: fluctuations in the probe pulse (which are wavelength dependent), fluctuations in the pump pulse, and readout noise contained in the detection system. While a number of parameters will affect pump and probe stability, the absolute first prerequisite for an experiment with good signal-to-noise is an extremely stable laser. A standard deviation of <0.3% is required and ideally <0.05 % is preferred for high sensitivity experiments.

Since the TA signal is derived from intensity differences between groups of sequential probe pulses (in this cases two pairs of ten), the sensitivity of the instrument will depend significantly on the fluctuations between sequential probe pulses. Bradler et al. assessed the correlation of energy fluctuations in supercontinuum generation (in a YAG crystal) with that of the seed laser, finding a slight, but not significant amplification during the generation process.[167] This is assuming optimised whitelight generation, but demonstrates that the large spectral broadening deterministically depends on the pump conditions and statistical processes are not involved. The non-linear processes that take place in SHG/OPA for the pump, and supercontinuum generation for the probe, are extremely sensitive to mode quality, beam alignment and environmental conditions, which if non-optimal can also introduce significant noise into the experiment. Noise originating in the detection system is also important. When conducting low excitation density measurements, the excited state population can only attenuate the probe transmission intensity by a relatively small amount compared to the shot noise on the signal. This demands probe light of a high enough intensity to fill photodiode bins and take advantage of the full dynamic range of the detector. Other possible noise sources that should be minimised can include fluctuations originating from the chopper, the stirrer bar and inhomogeneity in the film, as well as various types of environmental noise.
Apart from minimising noise from these sources, the best approach to improving sensitivity is by averaging and maximising the number of samples, $N$. In an ideal situation, the signal-to-noise ratio will be proportional to $\sqrt{N}$. This increased sensitivity through averaging is the main advantage of a high repetition rate instrument. While longer experiments can be conducted on laser sources with a lower repetition to improve averaging, laser drift is possible over many hours, and prolonged exposure of the sample to light (possibly in the presence of air and moisture) may lead to degradation.

High repetition rates TA spectrometers were once limited to single wavelength detection, where they can achieve sensitivities of up to $\sim 10^{-6}$ with the use of lock-in amplification.[159] Advances in the electronics of photodiode arrays have realised detectors that can largely keep pace (if not shot-to-shot) with the rate of pulses from a laser amplifier. This combines the averaging benefits of high repetition rate systems with broadband detection schemes. One additional consideration of a high repetition rate system is the shorter time between pulses, which is on the order of 10 $\mu$s for a 100 kHz system. This can potentially cause a build-up of extremely long-lived species though this issue is highly sample dependent.

Figure 3.8 illustrates a comparison of noise between a high and low repetition rate transient absorption instrument; a 92 kHz system (as described in Section 3.6 but using a white light probe, 500–760 nm), and a 1 kHz system at the University of Wisconsin, Madison.[‡]

Using the same carbon nanotube sample,§ and white light pump-probe setup, these experiments allowed a direct comparison of the same measurement taken on two separate setups. In Figure 3.8 averaged spectra are illustrated by the black lines, with coloured standard deviation across the spectral range. Transient spectra in (A) and (B) were taken using $6 \times 10^4$ shot pairs, where for the 92 kHz system in (A) the spectrometer read $6 \times 10^3$ times, each time integrating over ten pulses. The time taken for these measurements was $\sim 0.04$ s and 4 s respectively for the 92 kHz and 1 kHz systems. It is clear from the standard deviation in (A) and (B), which are compared in (D), that comparable levels of noise are achieved between the systems for the same number of shots. The spectrum in (C) illustrates a measurement on the 92 kHz system over the

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†These measurements were conducted at the University of Melbourne in collaboration with Nick Kearns and Martin Zanni from the University of Wisconsin, Madison.

‡A Ti:sapphire regenerative amplifier (Spectra Physics Spitfire 800 nm, 150 fs, 1 kHz) was focussed into each of two 4 mm YAG crystals to generate two white-light continua. The pump continuum was chopped at 0.5 kHz. After excitation with the pump, which was spatially filtered, the probe light was detected using a grating spectrometer (Acton SP2150i) and InGaAs photodiode array (Princeton Instruments OMA-V 512:1.7).

§Drop-cast carbon nanotube films from a 1:2 CNT:PFO solution were prepared on a substrate of indium tin oxide on glass. They were annealed at 150 °C for 30 min under a N$_2$ atmosphere to remove any residual solvent and encapsulated with an epoxied cover slip to exclude oxygen. Full details of carbon nanotube preparation and purification can be found in reference [183].
Figure 3.8: A comparison of noise in a high and low repetition rate transient absorption system showing transient spectra of carbon nanotube thin films with (A) a 92 kHz TA spectrometer, averaging $10^4$ shot pairs, the measurement taking 0.04 s (B) a 1 kHz TA, averaging $10^4$ shot pairs taking 4 s (C) a 92 kHz TA, averaging $10^6$ shot pairs taking 4 s. (D) illustrates the spectrally dependent standard deviation in (A), (B) and (C).

same time period as in (B), but with 100 times more shot pairs measured and averaged. As expected, this results in significantly improved signal-to-noise, approximately proportional to $\sqrt{N}$, where $N$ is the number of shot pairs. When even greater averaging is implemented in our 92 kHz system during a regular experiment, sensitivities better than $10^{-5}$ are easily attainable for experiments of modest duration.

There are several other strategies implemented that can be very effective at reducing noise for high sensitivity measurements. It should be noted that many of these are routinely implemented in the much more common low repetition rate systems, that do not have the benefits of averaging that a high-repetition rate system affords. A quantitative assessment of some of these approaches can be found in reference [184]. Many of these strategies could also be implemented on our high RR system for potential further improvements of signal-to-noise.

Referencing is a very commonly employed technique to cancel out shot-to-shot fluctuations in the probe pulse.[158] The probe beam is divided by a beamsplitter before the
sample, with the extra leg sent directly to a second ‘reference’ spectrometer. Each probe spectrum transmitted through the sample is then divided by the corresponding reference spectrum in order to correct for wavelength dependent noise in the probe. Similarly, this can also be applied to the pump pulse using a photodiode, to correct for pump intensity fluctuations, or to determine which individual shots to discard before averaging.

Often an amplified probe is employed to achieve better sensitivity using a NOPA (non-collinear optical parametric amplifier), which generates a greater intensity and potentially more stable probe light, with the ability to fill detector bins and increase the measurement signal-to-noise by using the full dynamic range of the detector. This method usually comes with some sacrifice in wavelength range compared to other probe sources, generally giving a range in the visible region from 520–760 nm.

A novel method that has recently been proposed by Barker, Hodgkiss and coworkers,[174, 184] is to deliberately enhance the probe chirp in order to decouple correlated noise in the wavelength domain from pump and probe fluctuations. A strongly dispersive element (such as a glass block) is inserted in the probe beampath, and chirp correction after an experiment proceeds as usual. With sufficient chirp (i.e. ~50 ps) the chirp correction gives values of ∆A where data points within each spectrum have been collected from separate laser shots, improving S/N by up to five times as demonstrated in reference [174], and theoretically by $\sqrt{x}$ when integrating over $x$ pixels.

### 3.7.2 Signal assignment

Transient absorption spectroscopy detects different spectroscopic signatures which can be categorised as illustrated in Figure 3.3. In the context of organic photovoltaics, signatures can be detected corresponding to the different primary species involved in the charge generation process: singlet excitons, charge transfer states, free polarons and triplet excitons. These signals can also show sensitivity to their surroundings, providing further clues on the local environment e.g. the effect of morphology or electric field.

However, unravelling these contributions can be challenging, and controversy surrounding the fundamental understanding of light harvesting in organic semiconductors is often linked to the interpretation of spectroscopic data. This section attempts to demystify at least some elements of signal assignment for organic photovoltaic materials and critically examine others to aid in the interpretation of transient spectra.
The exciton and stimulated emission

The exciton is the first species in the string of processes comprising charge photogeneration. In order to understand the spectroscopic signatures of excitons in organic photovoltaic materials, often the first step is to examine the spectra of donor and acceptor components individually. The kinetics and spectral signature of the exciton can then be used for disentangling spectra and dynamics in the blend.

In pristine materials, matching decay rates of a single photoinduced absorption signal with the ground state bleach can infer the presence of a single excited state species, where no additional excited state processes are occurring. The lifetime of these signals also gives the lifetime of the exciton.

A stimulated emission feature can also provide a direct measure of the population of the $S_1$ or exciton state, although often this negative signal can be overlapping with other transient signals. Spectral shifts in the stimulated emission or exciton PA likewise can provide information on exciton relaxation.

In blend films, the stimulated emission and exciton PA will still give information on exciton dynamics, while the ground state bleach will represent the contribution of all non-ground state species. In order for charge generation to proceed efficiently, its rate must compete with that of the exciton decay (usually 10–100s of picoseconds). Reduced exciton lifetimes can indicate quenching via energy or charge transfer, and may be accompanied by the appearance of another band, representing the species that results from exciton quenching.

Ground state bleach

The ground state bleach can be a valuable yet indirect marker of what is happening in an organic bulk heterojunction. It can provide potentially useful information on occupied non-ground state species of a particular material, its magnitude corresponding to the total of all excited state processes in a material.

The dynamics of the ground state depletion can give clues to the dynamics of other species in transient spectra. A partial decay of the GSB on the same timescale as the decay of another process can indicate its relaxation or recombination back to the ground state. When two or more materials are present, an increase in the GSB spectral feature of one component (if not accounted for by any overlapping signals), can indicate that energy or charge is being transferred to that material.

The magnitude of the initial GSB signal compared to its magnitude at delay times much longer than the exciton lifetime has been used as an indicator of the efficiency of charge transfer in blends. While this can be useful for some systems, the dynamics of
the GSB cannot be unambiguously assigned to a single photophysical process, since its recovery represents the sum of the dynamics of all excited states present in the blend. If, for example, in addition to excitons and charges, triplet excitons are generated in the blend, then they will also contribute to the rate of change of the GSB at delay times longer than exciton relaxation.

While steady-state absorption spectroscopy can often provide a measure of aggregate crystallinity in a film, transient spectroscopy can potentially yield information on the crystalline ordering in domains or in the vicinity of interfaces where charges are formed. The vibronic character of the ground state bleach can vary depending on the intra- and intermolecular coupling of chromophores occupied by excited state species at a particular time. The evolution of the spectral shape of the bleach can indicate the morphology (e.g. crystalline, amorphous) that is occupied by excitons or photoproducts at a particular time following excitation. The relationship between vibronic character and bleach appears to be common to the family of OPV materials.[184]

**Charges**

Signatures of charged species generated in organic photovoltaics are arguably the most important feature observed in a transient absorption experiment. Charged species are often initially identified by transient signals that are absent in individual donor and acceptor components, but present in a blend. They also exhibit transient signals that persist for often up to the microsecond timescale (much longer than excitons), and are quantitatively consistent with yields of charges in photocurrent experiments.[181]

The assignment of charged species in organic photovoltaics has not always been unambiguous. Central to this discussion are the many reports that argue that the transient absorption spectrum of the CT state is overlapping, if not completely indistinguishable from that of fully dissociated carriers.[13, 76, 185] Charge pair recombination usually occurs with very low fluorescence quantum yields, or completely non-radiatively, so luminescent techniques are usually not helpful for their quantification.

The primary method that has been utilised to tell populations of bound and separated charges apart is the power dependence of their transient signals. Charges in bound interfacial states are immobile and recombine by a monomolecular process. Therefore their dynamics should be independent of excitation fluence.[186] In contrast, free charges should undergo bimolecular recombination, therefore the rate will be non-linear with respect to charge density. The interpretation of polaron signal dynamics can have further challenges. As charge transfer is often mediated by the diffusion of excitons, any time-resolved behaviour of the polaron signal will be blurred by the arrival time distribution of excitons to a donor-acceptor interface.
Techniques to identify the transient spectral signatures of charges generally involves either chemical reduction/oxidation, or a spectroelectrochemical technique. To identify signatures of the electron on an acceptor, a reducing agent (such as cobaltocene[187]) may be used. For the hole polaron species, a donor may be oxidised in solution with an oxidising agent such as FeCl$_3$, or for films, iodine vapour.[125, 188–190] Spectroelectrochemistry can be used on films or in solution to identify the spectral characteristics of positive or negatively charged species. An incrementally increasing voltage is applied to ensure that a singly charged polaronic species is identified.

Another approach is to record any transient spectra (if one is present at all) at a negative time delay (~1 ms for a 1 kHz system), corresponding to a very long-lived species in the blend that was derived from the previous excitation pulse.[180, 191, 192] This method assumes that other transient features will be absent by this time (which could be problematic for blends with triplet species present) and only charge carrier absorption and its corresponding ground state bleaching remains.

**Electroabsorption**

A further consequence of charge generation in organic photovoltaic blends can be the appearance of an electroabsorption (EA) feature in transient spectra. In general, an electric field perturbs a molecule’s absorption spectrum by shifting the energy levels of the ground and/or the excited state. This is known as the Stark effect. A resulting electroabsorption signal is the difference between shifted and unshifted spectra, where changes in polarisability are related to the first derivative of the absorption spectrum.[101, 193]

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**Figure 3.9:** The origin of an electroabsorption feature in transient absorption spectra, illustrating (A) an electron-hole pair that generates a dipole-like electric field in its surrounding. (B) illustrates a ground state absorption spectrum, $S(0)$, and Stark-shifted absorption spectrum, $S(E)$, due to the local electric field $E$. The resulting electroabsorption (EA) signal shown (black line) is calculated from the difference between the shifted and unshifted spectra.
Devices under bias can show an electroabsorption (or photoinduced Stark effect) feature in their transient spectra due to the macroscopic electric field across the device. Alternatively, charged pairs at the donor-acceptor interface can act as dipoles and induce an electric field locally, as the result of charge separation. This is illustrated in Figure 3.9 (A) where an electron-hole pair generates a local electric field, and (B) illustrates the Stark-shifted absorption spectrum and resulting EA signal. If a Stark effect is caused in ground-state chromophores by charge pairs, then an EA contribution can be seen in the transient spectra, often contributing to the PA around the band-edge of the GSB.

As charge separation occurs and charges drift farther apart, their associated dipole moment can increase and the electric field inside the illuminated area is gradually screened, as reflected by the dynamics of the Stark feature.[193] The strength of electroabsorption is sensitive to the geometric configuration of chromophores relative to the electric field, as well as the sharpness of the ground-state absorption edge.

**Triplet species**

As described in Section 2.5, triplet states can be prevalent in organic materials and may provide a significant loss pathway in OPV devices.

The most direct and unambiguous way to spectroscopically detect states with a triplet character is to exploit their sensitivity to a magnetic field. One example of this is photoinduced absorption detected magnetic resonance (PADMR).[194–196] The PADMR technique measures the effect of spin-half magnetic resonance on the steady-state population of photogenerated polarons and triplets, measuring PA and PADMR under identical conditions.

To identify the triplet transient spectrum ($T_1 \rightarrow T_n$) of a given material directly may be difficult due to weak intersystem crossing from $S_1$ to $T_1$ states. Another option is to make use of a triplet sensitisation, to generate a high population of the triplet state passed over from the triplet population of the sensitisier, and hence identify the triplet spectrum of a given material. In a blend or mixture of a sensitisier and the molecule of interest, a triplet sensitisier is excited directly (or via energy transfer from the $S_1$ state of the molecule), and undergoes efficient intersystem crossing to its triplet state.[116] If the sensitisier’s triplet energy level is above that of the polymer or molecule of interest then triplet energy transfer can form large populations of the triplet exciton of interest, and the $T_1 \rightarrow T_n$ spectrum can be observed.[38, 189]

Widely used sensitisers include platinum(octaethyl)porphryin (PtOEP), palladium(octaethyl)porphryin (PdOEP), meso-tetraphenylporphryin (TPP), the fullerene derivative...
(porphyrin-C₆₀ dyad), tetracene, and pentacene.[38, 114, 125] Using a selection of sensitisers and detecting the success of energy transfer can also be used to provide an upper and lower limit for the triplet energy gap.

A further practical difference of a triplet compared to other species is the high sensitivity of the triplet state to quenching by oxygen (which is a triplet in its ground state). This sensitivity can accordingly be used to differentiate triplet species in transient spectra.

3.8 Summary

In this chapter, technical details of sample preparation, steady-state and time-resolved optical techniques employed during this project were described and fundamental concepts introduced. Time-resolved optical methods such as transient absorption spectroscopy remain some of the most valuable techniques for observing the charge photogeneration process and developing a fundamental understanding of the operation of organic photovoltaics. The principles and value of this technique were described, and details of the experimental system were provided. However, extremely low excitation densities, approaching that of solar radiation, are required to avoid non-linear effects which can distort the dynamics of charge photogeneration in donor-acceptor blends. In order to resolve such small changes in absorption, high sensitivity measurements are of key importance for these materials in the solid state. Specific strategies to achieving such sensitivities were outlined, in our case a high repetition rate transient absorption system. A comparison of this system to a low repetition rate TA was also reported. The generation of the supercontinuum probe was discussed, as a non-trivial yet integral part of the TA experiment, also important for the optimisation of high sensitivity experiments.

The highly complex nature of solid state blend morphology and overlapping timescales of the different processes involved can make it challenging to correlate specific molecular and aggregate properties with the processes relevant to device operation. Special considerations of relevance to transient absorption of OPV materials were explored, including those for solid-state measurements, reflection versus transmission experiments, and those relating to local morphology. A brief guide to signal assignment was also provided, given the potential challenges involved in the interpretation of spectrally and temporally overlapping signals due to separate phenomena.
Chapter 4

Charge generation in a solvent vapour annealed heterojunction

The following publication forms parts of this chapter:


4.1 Introduction

Section 2.6 discussed different approaches employed to modify BHJ morphology. Solvent vapour annealing (SVA) is a strategy to enhance molecular order, and one that can take place at ambient temperatures. Its low thermal budget also makes it attractive for processing on flexible substrates that may have low glass transition temperatures. SVA has been shown to facilitate the optimised processing of a number of ‘small molecule’ materials systems.[197–202] This is despite its limited success when first investigated for polymer systems in the late 2000s.[203–205]

The SVA technique was utilised on the recently developed benzodithiophene thieno-phenothiazine rhodanine (BTR), a donor-acceptor type molecular material. When used as an electron donor with a PC<sub>71</sub>BM electron acceptor this material produces devices with maximum power conversion efficiencies of 5.2%. The PCE is increased to 9.6% when SVA follows film deposition.[140] This treatment results in subtle changes to blend morphology, including an increase (though modest) in the crystallinity of the BTR component.[206] However, the exact causes of this impressive improvement are yet to be clarified.
Recently, interest has grown surrounding the loss channel of triplet excitons in BHJ solar cells, particularly those formed by fast bimolecular recombination (which was discussed briefly in Section 2.5). Curiously, this has almost exclusively been highlighted in donor-acceptor type donor polymers (also known as copolymers). These materials can often achieve very good efficiencies, but can see significant drops in efficiency when in a non-optimised morphology.

Veldman et al. have determined the CT and triplet energy levels of a wide number of materials.[38] They have identified the relative position of the triplet energy level relative to that of the CT state as an important parameter affecting device efficiencies, and thereby influencing the future design of new materials. Materials with donor-acceptor character appear to most often have low and accessible triplet energy levels compared to simpler repeating polymers such as P3HT. Recent work to explore the dynamics and details of the triplet loss mechanism have found that it is not just the energetics of materials, but the blend morphology that mediates the role of spin in OPV devices.[122, 123, 125] There is currently some debate around the generation of these triplet loss channels, particularly with regard to the role of bulk heterojunction morphology, however, understanding the mechanisms of triplet state formation is crucial for the optimisation of organic photovoltaic devices.

In this chapter, the effect of solvent vapour annealing as a successful morphological treatment will be outlined on the key steps in charge photogeneration. Presented here is a spectroscopic study of the newly developed, high-performing electron donor, BTR, providing a comprehensive picture of the different charge generation pathways and their relation to active layer morphology in blend films. The findings are related to the significant change in photovoltaic efficiency observed upon blend SVA, revealing that its influence on donor-acceptor morphology significantly suppresses the formation of BTR triplet excitons formed by the recombination of free charges on the sub-nanosecond timescale. The results also demonstrate that light harvesting from the PC$_{71}$BM acceptor component is an important factor in photocurrent generation.

### 4.2 BTR

While polymers have dominated the top OPV device efficiencies in recent times, molecular materials are receiving increasing attention for their ability to achieve high material purity in synthesis with positive repercussions for reproducible device fabrication. There has been enormous progress in solution-processed molecular materials in the past few years, with device power conversion efficiencies increasing from below 2% in 2008 to recently over 10%.
Benzodithiophene-terthiophene-rhodanine (BTR)\cite{140} is a recently developed molecular electron donor that has achieved power conversion efficiencies of 9.6 % with the fullerene acceptor, PC$_{71}$BM. In addition, even with an active layer that is $>300$ nm thick, SVA BTR:PC$_{71}$BM devices maintain a high fill factor (FF) of $\sim75\%$ along with a PCE of $>9.5\%$. This is a particularly promising property for conversion to roll-to-roll printing, where very thin films are prone to pinholes and can be difficult to precisely control.

The chemical structure of BTR is illustrated in Figure 4.1 (A) with a backbone consisting of a benzodithiophene unit, flanked by two terthiophenes and two rhodanine groups to form a coplanar structure. PC$_{71}$BM, a functionalised fullerene, is illustrated in Figure 4.1 (B). Figure 4.1 (C) and (D) illustrate the calculated HOMO and LUMO surfaces of BTR. HOMO wavefunctions are localised largely on the central benzodithiophene, and LUMO wavefunctions on the terthiophene and outer rhodanine moeities.

### 4.2.1 Nematic liquid crystallinity

BTR exhibits intriguing morphological properties including a high temperature nematic liquid crystalline phase. This liquid crystallinity has been demonstrated in neat films as a phase change at elevated temperatures, between 185–195°C.\cite{140} It is unclear whether the materials characteristics that lead to this liquid crystalline phase have any relevance at ambient temperatures and when blended with an acceptor. However, Engmann et al. have observed using AFM that the surface features of room temperature blend films
appear to be arranged in a liquid crystalline manner, with some apparent longer range order.\[206\] In the solid state, BTR has a coplanar structure to its conjugated backbone, facilitating crystal stacking, which is dominated by $\pi-\pi$ interactions.\[140\] It is this rigid rod-like shape that can maintain a directional long-range order with long axes aligned parallel, as evident in a nematic liquid crystalline phase. The BTR sidechains seem to be largely responsible for this planarity and consequently the liquid crystalline behaviour, which has not been observed in previous reports of molecular materials with a similar backbone.\[207, 208\]

There has been an interesting yet limited discussion surrounding the potential for liquid crystalline materials to have positive outcomes for OPV devices.\[209–211\] The liquid crystalline material properties that fuel this interest include the potential for high crystallinity, excellent carrier mobility and three dimensional charge transport. The relevance of liquid crystalline properties for charge transport has been discussed in the work of Hanna et al., where different types of liquid crystals would be expected to exhibit different carrier transport.\[212\] Discotic and smectic liquid crystals should exhibit one-dimensional and two-dimensional charge carrier transport respectively. However, conduction is three-dimensional in nematic liquid crystals, which could potentially provide a very beneficial properties for the generation of well-separated charges and for charge transport to electrodes.

Polyfluorenes also show liquid crystalline behaviour\[160\] though it is currently unclear how this is related to their photovoltaic performance in devices. The role or correlation of the interesting morphological properties of BTR with the device efficiency is still undetermined and is a subject for further research.

4.2.2 Solvent vapour annealing

In BTR:PC$_{71}$BM devices, solvent vapour annealing (SVA) with a moderately good solvent, tetrahydrofuran (THF), enhances performance from 5.2\% (as-cast) to 9.6\%. In contrast, thermal annealing significantly decreases device performance, through the pronounced coarsening of both the donor and acceptor phases.\[140\] SVA, which is conducted under ambient conditions, is a promising method of optimising active layer morphology, and is compatible with the roll-to-roll printing process. This treatment has been shown in other materials to increase the crystallinity of domains, and to enhance the performance of OPV devices.\[197, 198, 213\]

In order to understand the details of charge photogeneration in these blend films, it is necessary to first understand the details of BHJ morphology. BTR:PC$_{71}$BM blend films
have recently undergone a full characterisation before and after SVA, which is reported here to provide a basis for the interpretation of photophysical data.

Sun et al.,[140] have used atomic force microscopy to show lower surface roughness in the as-cast films following SVA. Following the SVA treatment, TEM tomography revealed interconnected percolating pathways and GIWAXS confirmed increased amounts of BTR crystallinity.[140, 206] X-ray crystal data revealed a co-planar, rigid, flat structure of the conjugated backbone, dominated by π-stacking between individual backbones of the molecule. GIWAXS measurements demonstrated that a random orientation of π-stacking evolves into both edge-on and face-on arrangements after SVA. The co-existence of π-stacking in both of these directions indicates that networks are available for three-dimensional charge transport. 3rd-order reflections in GIWAXS measurements are typical of long-range order, also beneficial for charge transport to device electrodes.

A recent study by Engmann et al. has used in-situ grazing incidence x-ray diffraction (GIXD) and small angle scattering (GISAXS) to reveal a picture of the evolution of crystallinity and phase purity during the solvent vapour annealing process.[206] They indicate that the vapour of the applied solvent can penetrate into a film, where BTR can undergo Ostwald ripening to form crystalline regions. Initially, as-cast films show a finely structured morphology with low contrast suggesting relatively impure domains of ~28 nm. Although the solvent annealing process only slightly increases the characteristic length scale (to 30 nm), the contrast is increased significantly, implying an increase in phase purity.

Using THF (a moderate solvent for BTR) for vapour annealing, films with high phase purity and desirable characteristic length scales of about 30 nm could be achieved, while the use of better solvents for SVA rapidly lead to excessive film coarsening and less preferable domain sizes on the order of 60 nm, too large for optimised charge separation. Unlike BTR, PC$_{71}$BM has very limited solubility in THF (<10 mg/mL). GIXD indicates that while BTR has some crystallinity in both as-cast and SVA samples, in both cases, PC$_{71}$BM remains in its amorphous state.[206] This is in contrast to other molecular materials where PC$_{71}$BM crystal size has been shown to grow during SVA with other solvents, and PC$_{71}$BM aggregation was thought to be significant in elevating the device performance.[213]

SVA was also found to have an effect on hole mobility, seen to increase by one order of magnitude following the treatment.[140] Another interesting property of the SVA BTR:PC$_{71}$BM blend is its significantly reduced Langevin recombination rate, recently demonstrated by Armin et. al.[214] The bimolecular recombination rate reported in this work is ~150 times lower that predicted by Langevin theory.
4.3 Steady-state absorption

Figure 4.2 (A) shows the steady-state absorption spectra of neat BTR and neat PC$_{71}$BM. Typical of π-conjugated materials, a red shift and formation of a new peak, at around 620 nm, results from the aggregation and crystallisation of the BTR donor material in the solid state compared to solution, where the absorption is structureless with an absorption maximum at 520 nm (not shown).[140]

![Figure 4.2: Steady-state optical absorption spectra of thin films cast from chloroform of (A) neat BTR (black solid line) and neat PC$_{71}$BM, (grey solid line) (B) shows the 1:1 BTR:PC$_{71}$BM blend film as-cast (blue circles), and the 1:1 BTR:PC$_{71}$BM blend film following treatment with SVA (green triangles). Traces are unnormalised.](image)

In Figure 4.2 (B), the spectrum of the as-cast 1:1 BTR:PC$_{71}$BM blend film largely resembles the superposition of individual component spectra in (A), with the exception of the low energy end of the BTR absorption around 620 nm. The aggregation apparent
in the neat BTR film is not as pronounced in as-cast D:A blends, as the addition of PC$_{71}$BM interferes with BTR molecular packing. In the SVA sample, however, the aggregate peak is more apparent where enhanced demixing leads to better molecular alignment and aggregation of BTR and an increase in absorption coefficient for the BTR portion of the spectrum. The prominence of the 0-1 peak compared to the more red-shifted 0-0 peak results from more H- than J-aggregate type crystal packing. These photophysical observations are supported by the full morphological characterisation as discussed in Section 4.2.2. This absorption enhancement at 620 nm directly translated to increased photocurrent in this spectral region, as reported by Sun et al., comparing the EQE of the as-cast and SVA samples as a function of wavelength.[140]

### 4.4 Emission quenching and morphology

As described in Section 2.3.1, exciton quenching does not necessarily act as a measure of charge photogeneration efficiency. Rather, photoluminescence quenching studies are more often used to show the success of D/A intermixing in blend films, where very high quenching levels are indicative of a highly intermixed BHJ, on the order of the exciton diffusion length.[108, 215–217]

Steady-state photoluminescence spectra of neat BTR and 1:1 BTR:PC$_{71}$BM blend films are shown in Figure 4.3. Thin films were excited at 630 nm (to only excite the BTR component) and emission was monitored.

Neat BTR films have a relatively broad emission with a maximum at 780 nm. With the inclusion of PC$_{71}$BM to BTR, 98.1% of BTR emission is quenched in the as-cast blend, indicating efficient exciton quenching at the interface between the two components. This implies that for the as-cast blend, BTR excitons are able to reach either a PC$_{71}$BM interface or an acceptor molecule in the intermixed BTR:PC$_{71}$BM region instead of relaxing back to the ground state.

The SVA film exhibits a reduced amount of exciton quenching at $\sim89.9 \pm 1.8\%$. This indicates that a higher proportion of donor domains must include regions of pure BTR which are larger than the BTR exciton diffusion length. These observations are consistent with the work of Sun et al. and Engmann et al., in which GISAXS measurements were used to identify domains of a similar size (30 nm) in as-cast and SVA blends, but of a much higher purity in the latter.[140, 206] Despite a reasonable proportion of BTR excitons ($\sim10\%$) remaining unquenched in the SVA samples, these devices still result in significantly improved device performance compared to non-SVA samples. This suggests other processes must be responsible for the superior efficiency of the SVA blend.
4.5 Charge generation pathways from donor excitation

4.5.1 BTR exciton dynamics

Transient absorption (TA) measurements were first performed with an excitation wavelength of 630 nm, a region where PC$_{71}$BM absorption is negligible, to predominately excite the BTR donor component. Therefore the transient signatures observed are considered to be solely from photophysical consequences of excitons generated within the BTR donor material.

The TA spectra (A) and kinetics (B) of a neat BTR film excited at 630 nm are shown in Figure 4.4. In the absence of an acceptor, the negative-going ground state bleach (GSB) region at 470–670 nm and the broad, positive-going signal from 850–1400 nm (PIA 1) show mirrored kinetics. This indicates that BTR exciton decay is the primary photophysical process that occurs in the neat film following excitation, with a lifetime of $\sim 110$ ps.
The vibronic peak at 630 nm (attributed to H-aggregation) is visible in the absorption spectrum and also in the ground state depletion of BTR. However, the relative magnitude of the 630 nm feature is greater in the GSB compared to the steady-state spectra. This indicates that from very short times following excitation, BTR excitons preferentially occupy the more crystalline regions of the film. This is evident despite a gap in the transient spectra around 630 nm, due to scattered excitation light from the pump.

It should be noted that while the bleach largely follows the dynamics assigned to the exciton, it does not completely recover within the 900 ps timeframe of the experiment. This could be due to small amounts of longer lived species, potentially charged species or triplet states that are generated in the neat blend, although a clear assignment is not possible from the positive photo-induced absorption also remaining at times $>800$ ps.

### 4.5.2 BTR blend dynamics

The TA spectra for as-cast and SVA BTR:PC$_{71}$BM blends are shown in Figure 4.5 (A) and (C) respectively, while the associated kinetics at indicated wavelengths are shown in (B) and (D). The steady-state absorption for each sample is shown for ease of comparison with the GSB. In neat BTR and blend films, enhanced vibronic transitions in the GSB relative to the ground state absorption spectrum of BTR indicate that, similarly to the neat films, excitons rapidly ($<1$ ps) collapse onto more ordered, crystalline regions of the BTR. The vibronic structure in these transitions is present throughout the time range.
Figure 4.5: Thin film transient absorption measurements with 630 nm excitation at 6 µJ/cm² of BTR:PC₇₁BM (A and B) as-cast, and BTR:PC₇₁BM after SVA (C and D). Spectral slices are shown in (A) and (C) at 1, 30, and 850 ps, with ground-state absorption spectra also shown for comparison (black dotted lines). Kinetic profiles are shown in (B) and (D) of the ground-state bleach (GSB) at 570 nm (open triangles), photoinduced absorption 2 (PIA 2) at 750 nm (closed diamonds), and photoinduced absorption 1 (PIA 1) at 1100 nm (open circles).

of the experiment and is enhanced following the SVA treatment where BTR is more crystalline.

In the blend films, the photoinduced absorption signal from the BTR exciton is still visible in the 850–1400 nm region (PIA 1) at early times, and is more pronounced in the SVA sample. However, at early times the BTR exciton signal decays faster in the blend compared to the neat film, indicating that some population of the exciton has been quenched. This is in agreement with the steady-state photoluminescence data and morphological information, which shows significant exciton quenching in both blend samples, though this is reduced in the SVA sample with its more pure crystalline BTR domains. The as-cast films show a decreased amount of exciton signal within the instrument response function (200 fs), and the reduced exciton lifetime suggests extremely fast charge transfer in the finely intermixed blend morphology where generated excitons are in close proximity to the donor-acceptor interface. The maintenance of the donor ground state bleach during this time also suggests that the BTR exciton has neither undergone energy transfer nor completely returned to the ground state.
The most striking new feature of both BTR blend spectra is an additional photo-induced (positive) signal stretching from 680–1000 nm (PIA 2). As this spectral signature is not present in either the donor or acceptor components, this suggests the formation of a new photoproduct as the result of BTR and PC_{71}BM interaction. Chemical oxidation of BTR films with I_{2} vapour, and BTR in chloroform with FeCl_{3}, gives rise to a new absorption signature in this same region, spanning the region between ~700–1100 nm (shown in Figure 4.6). This supports the assignment of the new transient signal to positive charge carriers, BTR hole polarons. Further evidence for charge pair generation at the donor-acceptor interface is the contribution of a positive electroabsorption feature at the band-edge, the result of the local electric field due to newly generated charge pairs.[218] This feature is more pronounced in the SVA sample.

Figure 4.6: (A) Steady-state difference spectrum of BTR film after chemical oxidation with iodine vapour, indicating the spectral shape of the BTR hole polaron (cation). (B) Steady-state difference spectrum of BTR in chloroform after chemical oxidation with FeCl_{3} (50 mM in chloroform), indicating the spectral shape of the BTR cation.

Figure 4.7 (A) illustrates the kinetics of polaron generation at a probe wavelength of
750 nm (where overlap is minimal with other transient signals) in as-cast and SVA samples. This signal is formed within the 200 fs limit of the experiment followed by an additional rise over ~5 ps. This indicates that some population of charges is generated on ultrafast timescales (<200 fs) and a further population is generated as BTR excitons diffuse to the D:A interface. The initial population and rise-time of BTR polarons is very similar between the as-cast and the solvent vapour annealed samples, which is maintained to the longest time delay in our experiment. Figure 4.7 (B) shows the work of Engmann et al., which demonstrates the very similar average size of BTR domains, though which have a higher purity and greater crystallinity in the case of the SVA blend. Efficient generation of charges is evident in both blend films, so the poorer performance of the as-cast devices must be explained through other means.

Charge transfer also generates negatively charged polarons residing on PC71BM, however, these species are not clearly resolved as they have an absorption at ~1350 nm with a low absorption coefficient compared to the donor species.[219]

![Figure 4.7](image)

**Figure 4.7:** (A) BTR hole polaron dynamics at 750 nm of BTR:PC71BM as-cast (triangles) and SVA in THF (squares). (B) Background corrected GISAXS scattering intensity showing the distribution of BTR domain sizes before and after annealing treatments. Reproduced from Ref. [206] with permission from The Royal Society of Chemistry.

### 4.5.3 Identification of a triplet species

A notable feature of the as-cast blend transient spectra is the growing photo-induced absorption (PIA 1) signal after 100 ps in the near infrared region, centred around 1100 nm (Figure 4.4 (B), red circles). This signal is apparent in a similar spectral region to the BTR exciton, though the dynamics of these species are very different. This feature is largely absent in the blend film treated with SVA, though a small amount of residual signal is present, which could also consist of BTR polaron signal overlap.
Figure 4.8: (A) TA kinetic profiles at 1100 nm of BTR:PC$_{71}$BM as-cast with 630 nm excitation. Measurements were conducted with exposure to N$_2$ gas (blue circles), followed by O$_2$ gas (red circles), and repeated (blue and red open triangles). (B) Transient spectra of a BTR film with 40 wt % triplet sensitizer Pd(OEP), indicating the BTR triplet spectrum (grey filled circles). The transient spectra of BTR:PC$_{71}$BM as-cast (blue line), neat Pd(OEP) (red unfilled circles), and neat BTR (black line) are also shown for comparison, all at 830 ps delay. The excitation wavelength for Pd(OEP) samples was 540 nm.
Upon exposure to an oxygen atmosphere, this rising signal could be reversibly quenched (Figure 4.8 (A)). Quenching was only observed in the region around 1100 nm, and any difference between oxygen and nitrogen exposure was not obvious for the rest of the transient signals. Triplet species can be effectively quenched by oxygen, a triplet in its ground state.[119, 220, 221]

The spectral signature of the BTR triplet exciton species was then defined by selectively populating the triplet state of BTR using the triplet sensitiser Pd(OEP),[116] as shown in Figure 4.8 (B) (grey circles). Since the sensitiser could not be selectively excited (BTR also absorbs at 540 nm) the relative magnitudes of the neat BTR and neat Pd(OEP) are shown at 830 ps for the same pump fluence. The much larger signal in the sensitised BTR indicates that a large population of the BTR triplet species is formed through sensitisation. The spectra of BTR:PC71BM as-cast film at the same time delay is shown for comparison (blue line, 830 ps). This includes the oxygen-quenchable spectral feature spanning the same region as the BTR triplet, as well as the overlapping BTR polaron component as described earlier, at 800-950 nm.

The question of how triplet species are formed in as-cast BTR:PC71BM blend films is now addressed. The absence of a triplet transient in the neat BTR film discounts the hypothesis that triplet excitons are formed via intersystem crossing from the S1 to the T1 state in BTR. In addition, triplet formation by direct intersystem crossing would be suppressed by the photoinduced charge separation that occurs in the blend films. Rather, the BTR exciton lifetime of ~110 ps is shortened in the presence of the acceptor, clearly a faster process than the BTR triplet exciton grow-in. Formation is more likely from a recombination process due to: (i) the triplet species’ prevalence in the blend compared to neat materials, and (ii) the concurrence of the triplet exciton rise (1100 nm) and BTR hole polaron decay (750 nm).

Charge recombination through a CT state to a triplet exciton is possible from a geminate process,[121, 222] where intersystem crossing of the 1CT to the 3CT is followed by relaxation to a lower lying T1 exciton. However, a number of recent reports show that triplet exciton formation on a sub-ns timescale can also be the result of bimolecular recombination.[122, 123, 125] The power dependence of the triplet exciton signal is shown in Figure 4.9, where a higher proportion of triplets are generated at earlier times with higher pump intensities. This result suggests a bimolecular rather than unimolecular process, whereas for geminate recombination, the proportion of bound polaron pairs at the interface should be unaffected by increases in charge carrier density. Although triplet formation is dependent on excitation density, the grow-in of the triplet signal is evident even at the lowest excitation densities measured (3 µJ/cm²), almost as low as photon densities experienced by devices under solar AM 1.5G illumination (see Section 3.7).
This suggests that this triplet loss mechanism is likely to be problematic even under solar illumination densities.

4.5.4 Morphology and triplet exciton generation

While the generation of triplets is significant in the as-cast BTR blends, notably the solvent vapour annealing treatment produces negligible or very low populations of BTR triplet excitons within the timescale of our experiments. This demonstrates that the generation of triplets, a loss pathway, is highly dependent on the morphology. The propensity for triplet excitons to be quenched by free carriers\cite{122, 123} makes it difficult to quantify their presence as a terminal loss channel throughout the course of the charge generation process. However, unlike transient absorption experiments of the active layer alone, an operating device has the rate of bimolecular recombination in competition with the extraction of free carriers. High fill factors in SVA BTR:PC\textsubscript{71}BM devices\cite{140} indicate that a significant proportion of charges are successfully extracted and are not lost to triplet generation on timescales greater than a nanosecond.

Because the relative absorption coefficients of the transient species are unknown, it is difficult to determine the exact population of triplets and polarons in each sample. Chow et al., determined quantitatively the amount of triplets generated in blend films,\cite{124} but the assumptions that were required to estimate the triplet extinction coefficient do not appear to hold for this system.
Triplet generation appears to be highly dependent on film morphology and a comparison of this process in the as-cast versus SVA blend films provides a useful scenario where the role of morphology can be considered without any other modification of blend composition. There are other recent reports in polymer donor:fullerene acceptor systems that have also demonstrated that bimolecular recombination causing triplet exciton generation can be significantly influenced by morphology. However, the relationship does not appear to be straightforward.\[123–125\]

Recent work has shown that greater phase separation leads to a reduction in the population of triplets generated,\[123, 125\] as has been demonstrated here. However, Chow et al., have shown that the additive, octanedithiol (ODT) in PCPDTBT:fullerene blends improves phase crystallinity and carrier mobility leading to better charge generation, but it also increases recombination to form more triplet excitons.\[124\]

It has been proposed that the relaxation of $^3\text{CT}$ states to $T_1$ states can be strongly suppressed by wavefunction delocalisation. As discussed in Section 2.4.2, charge transfer states formed at early times after excitation have their dissociation mediated by charge wavefunction delocalisation.\[52\] Rao et al., suggest that the same mechanism is also applicable to charge transfer states formed through bimolecular recombination. This means that greater delocalisation can drive the dissociation of $^3\text{CT}$ states back to free charges.\[223\] When this occurs faster than CT state relaxation to $T_1$, the population of triplet excitons will ultimately be affected.\[122, 126\] In this case, triplet exciton generation could be turned off, leaving only the possibility of recombination through the singlet channel.

It has been suggested that fullerene acceptor aggregation is the cause of this greater wavefunction delocalisation and decreased disorder, and hence the key driver of suppressed triplet formation in some systems.\[122, 224\] However, in the BTR blends studied here there is no clear evidence for PC$_{71}$BM aggregation in the SVA samples as observed by x-ray diffraction experiments.\[140, 206\] While this is not conclusive, and small PC$_{71}$BM domains that do not effectively diffract x-rays may be present, this demonstrates a departure from the attribution of this effect to fullerene aggregation alone. Instead, the increased donor domain purity (but not size) in the SVA blend, as demonstrated by Engmann et al., would increase delocalisation on the crystalline BTR donor and could also aid in the suppression of the triplet loss channel in the SVA films.

It is also possible that the connectivity of domains could explain the different effects of morphology on sub-ns triplet generation. As well as the coarsening of structure in the SVA blend, Sun et al. have shown that these larger domains of BTR are interconnected in three dimensions, forming percolating networks throughout the active layer.\[140\] Suppressed recombination in the SVA system could be due to this favourable
morphology, resulting in fewer triplet excitons formed through bimolecular recombination. In their work correlating non-geminate recombination with film structure, Shaoee et al. suggested that sub-ns bimolecular recombination dynamics observed for the BHJ films could be related to the confinement of charge carriers to the interface and the lack of interconnected pathways in some morphologies.

The relationship of morphology and triplet generation could also be explained by the concept of energy cascades\[12, 114, 226\] to drive long range charge separation, though this is an area still to be explored. It can be speculated that such energetic cascades, like those found in a three phase morphology, could play a role in the kinetics of $^3\text{CT}$ states and triplet exciton generation. While only two distinct phases (aggregate BTR and amorphous intermixed) have so far been identified during morphological studies on this blend, these phases may lead to a partial energy cascade for the hole from the intermixed phase to crystalline BTR. Larger separation distances caused by this effect may prevent fast bimolecular recombination which in this case suppresses the generation of triplet excitons. Further research will help to clarify the important and emerging role of morphology and spin in the performance of organic photovoltaics.

### 4.6 Charge generation pathways from acceptor and donor excitation

The contribution of photons absorbed by the donor or acceptor to the charge generation process can be investigated by selectively exciting each component and examining the subsequent dynamics. However, in many organic photovoltaic materials this is difficult due to broad and overlapping absorption bands. While the BTR donor could be exclusively excited at 630 nm, it was more difficult to selectively excite the acceptor. The shortest pump wavelength available in this experimental setup was 400 nm and this was used to excite as far into the PC$_{71}$BM absorption band as possible. This resulted in 68% of excitation light absorbed by PC$_{71}$BM and 32% by the BTR component for a 1:1 blend.

Because both donor and acceptor are absorbing the pump excitation, it can be difficult to disentangle individual contributions to transient spectra. To aid in the interpretation of blend film photophysics, Figure 4.10 (A) and (B) present the separate transient spectra of BTR and PC$_{71}$BM respectively when excited at 400 nm. Recorded at an identical pump fluence, it is apparent that the transient species of PC$_{71}$BM have lower absorption coefficients than that of BTR, due to the symmetry and non-planarity of this material.\[227\]
Figure 4.10: Thin film transient absorption measurements of (A) BTR, and (B) PC$_{71}$BM showing spectral slices at 1, 30 and 850 ps with 400 nm excitation at a fluence of 6 µJ/cm$^2$. (C) shows the linear addition of these components, corrected for their fractional absorption at the pump wavelength of 400 nm, a 68% contribution from PC$_{71}$BM and 32% from BTR.

Figure 4.10 (C) illustrates a construction of neat BTR and PC$_{71}$BM components, created by a linear addition of the transient spectra of the two neat films taken at the same delay times, and corrected for their relative fractional absorption at the pump wavelength. While the oscillator strengths of the PC$_{71}$BM transient species are low, they still have a reasonable contribution to the constructed spectra due to their significant proportional absorption at 400 nm relative to BTR. This reconstruction serves as a simulation of the BTR:PC$_{71}$BM blend film in the absence of any interaction between the two materials.

Figure 4.11 shows transient absorption spectra (A,C,E) and kinetics (B,D,F) of films excited at 400 nm. As described above, Figure 4.11 (A) and (B) represent the transient dynamics for the BTR + PC$_{71}$BM construction, observed in the absence of any relaxation processes that result from blending the two components. Figure 4.11 (C) and
Chapter 4. *A solvent vapour annealed heterojunction*

Figure 4.11: Thin film transient absorption measurements with 400 nm excitation at 6 µJ/cm² of (A and B) BTR + PC₇₁BM construction as described in Figure 4.10, (C and D) BTR:PC₇₁BM as-cast, and (E and F) BTR:PC₇₁BM after SVA. Spectral slices are shown in A, C, and E at 1, 30 and 850 ps, with the ground-state absorption spectra (black dotted lines) for comparison. Kinetic profiles are shown in B, D, and F of the ground-state bleach (GSB) at 570 nm (open triangles), photoinduced absorption 2 (PIA 2) at 750 nm (closed diamonds), and photoinduced absorption 1 (PIA 1) at 1100 nm (open squares).

(E) illustrate TA spectra for the as-cast and SVA blend films, respectively, where the dynamics are clearly different from that of the construction. In the blend films, a large positive photo-induced absorption signal is observed from 650–1150 nm (PIA 2), which is absent in the neat components. As shown previously, this is attributed to the BTR hole polaron, generated from charge transfer at the D:A interface. As with 630 nm excitation, some of this polaron signal is generated within the instrument response time (200 fs), and there is also a contribution to the signal with a rise time of several picoseconds.

The BTR exciton signal is again present as a broad photo-induced absorption in the constructed spectrum (A) due to the absorption of BTR excitons. It is clear in the unnormalised spectra in (C) and (E), that the SVA blend has a much larger contribution
from the exciton signal at short times. This signal can be observed at early times (kinetic trace at 1100 nm, PIA 1), but is quickly quenched in both systems, most significantly in the as-cast blend, which as determined earlier, is more intermixed. A small amount of signal rise is seen in this same region on the 100 ps timescale, and is attributed to some triplet exciton generation, as discussed previously.

An interesting component of the blend spectra excited at 400 nm is the increase with time of the negative-going signal at 570 nm (Figure 4.11 (D) and (F)). From the spectral shape and contribution, it can be assumed that the ground state bleach signal of BTR accounts for the majority of this signal. The slow rise cannot be explained by the overlapping signals of the BTR bleach with the negative signals of PC71BM bleach, nor overlapping dynamics of the positive BTR hole polaron. The increase of the BTR GSB signal indicates that non-ground-state BTR species are increasing in population over the 100s of picoseconds timescale. These dynamics can be explained by transfer of either energy or charge from PC71BM to the BTR donor. Energy transfer from acceptor to donor would be uphill and therefore not feasible. Hence, the most likely explanation is hole transfer, also referred to as photo-excited hole transfer or channel II charge transfer.[228, 229] This process describes the transfer of an electron from the donor HOMO level to the acceptor HOMO level, as opposed to photoinduced electron transfer, which occurs between LUMO levels of those species. Further evidence in support of this mechanism is provided by the dynamics observed in the growth of the hole polaron signal at 750 nm (orange diamonds, PIA 2), mirroring the rise of the BTR ground state bleach shown at 570 nm (purple triangles, GSB) (Figure 4.11 (D) and (F)). The HOMO-HOMO energy offsets between PC71BM and BTR are 0.76 eV,[140] favourable for transfer of an electron. As some population of the BTR donor is also being excited at 400 nm, ultrafast energy transfer from the BTR, followed by hole transfer to the PCBM cannot be ruled out.[189, 230] However, this type of behaviour was not observed when exciting only the BTR donor component in blends, and so is unlikely.

The rise time associated with the GSB signal has been previously explained by the diffusion of excitons in PCBM-rich domains.[231, 232] In PC71BM, excitons can diffuse and upon reaching an interface can be quenched by the hole transfer process. This causes a temporal recovery of the donor bleach signal due to the newly formed hole polaron species on the donor material, which then contributes to the ground state depletion of BTR. This signal then increases (becomes more negative) with time as more excitons reach the donor acceptor interface. It was observed that the grow-in is slower in the SVA sample (570 nm). Diffusion lengths in fullerenes have been determined by various methods to be around 6 nm,[231, 232] but a direct measurement of exciton hopping rates was not found in the literature. This slow exciton diffusion followed by hole transfer has been proposed in polymer:PCBM blends; the delayed yet efficient formation of charge
species at up to 75 ps following the excitation of PCBM has been observed in a number of materials.[143, 172, 229] This implies that exciton diffusion rates are an order of magnitude slower than that observed in the donor component.

It can be noted that the observation of slow hole transfer mediated by exciton diffusion in fullerenes requires at least small fullerene domains to be present in the blend. This contradicts measurements for both the as-cast and SVA blends, suggesting that the absence of any fullerene aggregates[206] may need to be confirmed with other techniques and the careful control of deposition. Alternatively, it is possible that hole transfer is not proceeding on ultrafast (fs) timescales. The ultrafast electron transfer described in Subsection 2.3.3 has been confirmed by many groups, but to our knowledge, these examples are all for LUMO-LUMO electron transfer. Hole transfer from fullerene-type materials is generally much more difficult to probe in isolation. It can be speculated that in the case that hole transfer is not ultrafast, the bleach rise time could instead be illustrative of the rate of the hole transfer itself, rather than the timescale of PC$_{71}$BM exciton diffusion to the donor-acceptor interface.

Internal quantum efficiency (IQE) measurements reported by Armin et al.[214] show that SVA devices have a quantum efficiency of 90% across the entire absorption range of donor and acceptor. This independence of charge yield across the spectrum demonstrates that photons absorbed in both donor and acceptor components contribute significantly to photocurrent generation.[214] This further supports our evidence for the importance of hole transfer in photocurrent production.

By comparing the amount of BTR bleach in the BTR + PC$_{71}$BM construction (Figure 4.11(A)) to the increased value of BTR bleach present in both blend films (Figure 4.11(C) and (E)), it is apparent that both prompt hole transfer and delayed hole transfer occur in significant yields. These dynamics associated with hole transfer occur over ~300 ps, a slower timescale than electron diffusion and subsequent transfer. This mismatch in the timescales for charge transfer (likely mediated by exciton diffusion) for donor and acceptor components may result in the charge generation process occurring over a longer period, thus smearing out the timescales of charge generation and reducing observed bimolecular charge recombination in the blend.

4.7 Summary

Solvent vapour annealing can be used to achieve significant increases to device efficiency compared to untreated blend films in BTR:PC$_{71}$BM BHJs. Photoinduced charge generation processes in blends of the high performing donor BTR, with a fullerene acceptor
(PC$_{71}$BM) were investigated by steady-state and time-resolved spectroscopic techniques.

SVA results in an increase of BTR crystallinity, confirmed by morphological studies which show high donor phase purity with desirable characteristic domain length scales of about 30 nm, which are interconnected. Exciton emission quenching determined that in the SVA films, over $\sim$10% of excitons are unquenched and lost to emission, suggesting that other mechanisms must be responsible for the large discrepancies in device efficiency.

Broadband femto- to picosecond transient absorption spectroscopy reveals both efficient hole and electron transfer in the bulk heterojunction blends. Differences in the dynamics of donor exciton migration and electron transfer, however, also do not appear to explain differences in device performance. Very efficient hole transfer is observed, on the $\sim$100 ps timescale.

BTR triplet excitons are formed due to sub-nanosecond bimolecular recombination in untreated blend films, though they are significantly suppressed after solvent vapour annealing. To our knowledge, this is the first report of this triplet loss mechanism in a molecular (non-polymeric) donor material demonstrating the important role of spin in high performance heterojunctions. This SVA treatment was shown to increase the purity of BTR donor domains and lead to three-dimensional percolating networks for charges. These fine morphological changes appear to affect charge recombination dynamics on the sub-nanosecond timescale and are linked to the significantly suppressed bimolecular recombination rates recently reported by Armin et al.[214] Both charge wavefunction delocalisation on BTR crystalline domains and percolating pathways in BTR may account for suppressed triplet exciton generation in SVA treated blends.

It is unclear whether the presence of a high temperature liquid crystalline phase in this material has any specific consequences relating to its OPV performance or dynamics; however, under the correct morphological conditions, the nanostructure of BTR in blend films has positive consequences for charge photogeneration, and possibly sub-ns bimolecular charge recombination, potentially related to BTR stacking in both face-on and edge-on orientations in the BHJ.

Solvent vapour annealing operates under ambient conditions and is an excellent candidate for modifying morphology in the roll-to-roll printing process for producing organic photovoltaics. Demonstrated to good effect in a high performance molecular material, BTR, these subtle morphological changes to the BHJ have a major effect on the processes of charge photogeneration. Spin and nanoscale morphology appear to have a significant and interconnected role in the prevention of triplet loss channels that, with careful control, can lead to superior device performance in promising new photovoltaic materials.
Chapter 5

Semiconducting Nanoparticle Photophysics

The following publication forms parts of this chapter:


5.1 Introduction

The previous chapter described the effect of a post-deposition treatment, solvent vapour annealing, on BHJ morphology, and determined the consequences of this treatment for charge photogeneration. In this chapter, the strategy for nanoscale morphological control is via the formation of semiconducting composite nanoparticles (NPs). In this approach, the morphology of the nanoscale donor-acceptor architecture is controlled previous to any deposition process. This is achieved by creating a composite donor-acceptor colloidal dispersion in a non-toxic polar solvent, providing a potentially eco-friendly and scalable approach for morphological control in organic solar cells.

The nanoparticle approach looks to address a principal challenge for organic photovoltaics, transferring the technology from the laboratory to large-scale production.[4, 233] Despite improvements in reported power conversion efficiencies, there remains significant process-dependent performance issues in controlling active layer nanomorphology across large device areas.[145, 147] Control of this parameter is necessary for the effective translation of this technology to larger commercial scales.
Donor-acceptor morphology over the nanometre scale can be influenced and tuned during the nanoparticle preparation process. Uniquely, the NP approach confines the device morphology to two different length scales: the nanoscale structure within the particle, and the arrangement of NPs within the active layer film. Hence the development of nanoscale morphology, which is of key importance to performance, can be somewhat decoupled from the specific coating operation, and the distribution of donor and acceptor can be fixed prior to deposition. Using this strategy, it is possible to optimise the intrinsic characteristics of a given nanoparticle formulation for the best charge photogeneration characteristics and then optimise the coating process to yield a set of extrinsic film properties.\[147\] This pre-aggregation of donor and acceptor domains during nanoparticle formation has been shown to persist throughout processing,\[145\] with the exception of NP films that are exposed to high temperature annealing treatments to further influence morphology. Nanoparticulate dispersions can also allow the use of multi-pass deposition techniques to build-in donor and acceptor compositional gradients for improved carrier percolation pathways to electrodes.\[234, 235\]

The use of significant volumes of toxic chlorinated solvents presents further barriers for the development of the industrial-scale printing of OPVs.\[4\] Both environmental and occupational health and safety concerns discourage the use of these solvents for high throughput printing in a commercial setting. Nonetheless, specific toxic chlorinated solvents, often dichlorobenzene or chloroform, are routinely used to produce the highest efficiency devices in laboratories with only a few exceptions. The nanoparticle method, while using organic solvents to dissolve the materials initially, allows for the total elimination of chlorinated solvents from the printing process, replaced by safer, polar solvents such as water or alcohols.

In recent years, various approaches to processing using low toxicity, eco-friendly solvents have been making progress. Efforts have been made to intrinsically modify materials to enhance their solubility in polar solvents. Side chain modification has been used for some time to overcome the original solubility limitations of organic semiconductors. The further development of soluble analogues using side-chain modification has provided options for improved processability in solvents like alcohols or water.\[236\] Yet modifications to enhance the solubility of materials may well impact on their performance, and device efficiencies have been limited to date.

Alternatively, nanoparticle suspensions of active-layer materials in water or alcohol have gained increasing attention and allow the use of existing, well-developed hydrophobic donors and acceptors.\[146, 237–240\] Despite a modest beginning, composite donor-acceptor nanoparticle photovoltaic devices have made noteworthy improvements. The efficiency of a nanoparticle poly(3-hexylthiophene) (P3HT):indene-C\(_{60}\) bisadduct (ICBA)
A device has reached > 4% PCE,[234, 240] comparable to the photoconversion efficiencies of 4-6% for similar bulk heterojunction devices cast directly from chlorinated solvents.[241] Despite the majority of reports focusing on P3HT:fullerene derived systems, this approach is beginning to expand to new materials,[242, 243] which in principle should be processable by the same routes.

There are two main approaches to preparing composite donor-acceptor nanoparticles; the additive-free reprecipitation method and the surfactant-based mini-emulsion method.

The reprecipitation approach[238] requires the organic semiconductor to be dissolved in a good solvent and then quickly injected into a poor solvent that is being rapidly stirred.[238] The good and poor solvents employed are usually THF and water respectively, due to their miscibility. Removal of the original solvent yields nanoparticle dispersions where particle size can be controlled within the range of 5–400 nm diameter. Devices made using this method have reached PCEs of 4.1% (P3HT:ICBA in methanol), although following deposition, nanoparticle films were subjected to high-temperature annealing.[240] Despite the use of a fairly standardised methodology for particle preparation (see Section 3.2.2), variations have since been reported that allow further control and manipulation over the NP’s internal morphology.[244]

The mini-emulsion approach[146] uses a combination of surfactant and sonication to produce dispersions of stable nanoparticles with diameters ranging 30–500 nm depending on surfactant concentration and sonication conditions.[245] Mini-emulsion nanoparticles of conjugated polymer donors and fullerene-based acceptors typically adopt a core-shell type distribution during formation,[145, 147, 246] with bulk heterojunction devices reaching photo-conversion efficiencies (PCE) of 2.5%. It has been demonstrated that by manipulating the processing conditions of these nanoparticles, it is possible to form a wide variety of different structures with a diverse range of internal morphological heterogeneity.[147]

The work presented in this chapter aims to investigate the two main methodologies for preparing composite donor:acceptor nanoparticles, and their differing outcomes for morphology and, subsequently, charge photogeneration. Nanoparticles of poly(3-hexylthiophene) (P3HT):phenyl-C_{61}-butyric acid methyl ester (PCBM) were prepared using the reprecipitation and mini-emulsion methods, producing composite nanoparticles of the same relative donor:acceptor composition and approximate size, but different internal morphologies.

To examine morphology in these particles, steady-state optical absorption was employed to determine parameters related to the P3HT aggregate morphology in the blend, which is reported to have important consequences for device performance.[9, 12] Morphology
was analysed using a model of weakly interacting H-aggregates, using vibronic peaks to define quantitatively the free exciton bandwidths and relative amounts of crystalline and amorphous P3HT component in each nanoparticle type.

Exciton dynamics and charge generation within the nanoparticles were investigated with transient absorption spectroscopy. While both particles contained crystalline polymer and intermixed domains, beneficial for charge generation, those produced by the mini-emulsion method contained greater amounts of crystalline P3HT domains with charge generation resembling that observed in phase-separated annealed films.

5.2 Nanoparticle morphology

5.2.1 Existing morphological characterisation

The aggregate behaviour of organic semiconducting materials and the chain conformation of polymers has a significant impact on OPV device performance. An understanding of the relationship between morphology and performance in bulk heterojunction organic solar cells has been developing over the past decade.\cite{9, 12, 247} P3HT in particular has been extensively studied. Upon film formation or aggregation, regioregular P3HT can self-assemble into 2D $\pi$-stacked lamellar structures, which can result in a significant improvement in charge mobilities,\cite{248} and charge generation,\cite{12, 102} especially when accompanied by intermixed regions.

Figure 5.1 demonstrates the molecular arrangement of P3HT in its aggregate form. $\pi$-stacking is the primary driver of P3HT aggregation, followed by the crystallisation of alkyl side chains. The length of planarised interacting segments is also shown, which may be interchain or intrachain in nature, due to the flexibility and high molecular weight of the polymer.

Enhancing the crystallisation of P3HT in a P3HT:PCBM blend has been a common route to improved device efficiency for this material combination.\cite{137, 138} In particular, following film deposition, annealing the blend at 140$^\circ$C has been shown to result in increased phase segregation and crystallisation of P3HT, where PCBM aggregation can also be partially induced. The resultant three-phase structure consists of crystalline P3HT regions, PCBM clusters, and amorphous P3HT:PCBM intermixed regions. This type of nanomorphology, with its three phases and low degree of intra- and interchain disorder, has been the cause of significant improvement in the PCE of these devices; in early reports annealing increased device efficiencies from 1% to 3.5%.\cite{137, 138}
In order to realise efficient nanoparticle devices, the particle’s internal structure will determine many of the nanoscale BHJ properties that ultimately determine the efficiency of charge generation in the device. Figure 5.2 illustrates the proposed internal structure of 1:1 P3HT:PCBM blend nanoparticles prepared by (A) reprecipitation and (B) mini-emulsion methods.

Previous studies have examined the structure of P3HT:PCBM reprecipitation nanoparticles using optical techniques.\cite{250, 251} They are reported to consist of intermixed donor and acceptor components, which incorporate a number of smaller crystalline P3HT nanodomains within the particle structure. Mini-emulsion nanoparticles of conjugated polymer donor and fullerene-based acceptors have been well characterised. P3HT:PCBM mini-emulsion nanoparticles have been reported by a number of groups and in contrast to the reprecipitation approach, appear to consistently adopt a core-shell distribution of components during formation, with a PCBM core and P3HT polymer chains surrounding the core to form a shell. This has been confirmed using small angle neutron
scattering\cite{147} and scanning transmission X-ray microscopy.\cite{145, 246, 252} Using the latter technique and radially averaging compositional particle cross-sections, the core composition has been determined as 80\% pure PCBM, and the P3HT shell comprising 67\% pure polymer for particles with an average diameter of \(\sim 120\) nm.\cite{252} Interestingly, the interface between core and shell was estimated to comprise around \(\sim 50\%\) of the total particle radius, inferring that a significant amount of intermixed region also exists within the nanoparticle.

### 5.2.2 Steady-state absorption

The absorption spectra of organic molecules are usually considered to be determined by their individual chemical structure, however, the nanostructure of aggregates can also have a large influence on a species’ absorption. This is especially the case for regioregular P3HT, and its aggregate properties (a spectral red-shift of almost 0.5 eV from its amorphous form\cite{253}) have been used as an opportunity to improve the match between its absorption and that of the solar spectrum. The physical features of optical absorption spectra can provide important information about the physical conformation and aggregation of molecules or polymer chains.

Figure 5.3 (A) shows the absorption spectra of reprecipitation and mini-emulsion P3HT nanoparticle suspensions. These spectra can be interpreted as the coexistence of two distinct populations of different P3HT molecular states. These are firstly, a higher energy region dominated by contributions from disordered chains, and secondly, a lower energy region attributed to crystalline P3HT. The population in the higher energy region contributes a single broad absorption peak from amorphous chains in their flexible coil formation. This is similar to P3HT in solution which has a featureless spectrum with an absorption maximum of 446 nm in THF. The lower energy absorbance features a distinct
Figure 5.3: (A) Normalised absorption spectra of P3HT nanoparticles prepared in water by the reprecipitation (black) and mini-emulsion (red) methods. Emission spectra of P3HT reprecipitation (black) and mini-emulsion (red) nanoparticles are shown with dashed lines. (B) Normalised absorption spectra of P3HT:PCBM 1:1 blend nanoparticles in water prepared by the reprecipitation (black) and mini-emulsion (red) methods.

Vibronic progression arising due to weakly interacting H-aggregate states formed in self-assembled 2D π-stacked lamellar structures (as illustrated in Figure 5.1).[254]

The absorption spectra of both nanoparticle types are significantly red-shifted compared to P3HT in solution, and both display some vibronic character. The shoulders at 610 nm and 556 nm correspond to the 0-0 and 0-1 transitions within P3HT crystalline domains,[254] and are indicative that both particles contain some aggregated P3HT. The vibronic shoulders are more pronounced for the mini-emulsion particles, which have greater P3HT aggregate character than the reprecipitation particles. Figure 5.3 (A) also compares the emission spectra of reprecipitation and mini-emulsion P3HT nanoparticle suspensions. Amplitudes of fluorescence vibronic progressions also indicate the presence
of H-aggregates,[251, 255] with disorder preventing pure H-aggregate type behaviour, where the 0-0 transition should be completely suppressed.[29]

Figure 5.3 (B) shows mini-emulsion and reprecipitation composite 1:1 P3HT:PCBM nanoparticle absorption spectra in solution, where particles are of a comparable size (∼80 nm diameter). Emission from blend nanoparticles was very weak, and is not shown in Figure 5.3, indicative of effective quenching of exciton emission in the composite particles of both types.

The composite absorption spectra appear as a superposition of the PCBM absorption component, which absorbs most strongly at wavelengths shorter than 400 nm, and neat P3HT absorption as seen in (A). The vibronic aggregate character is again apparent in both particle types, indicating that some amount of P3HT is in its crystalline form in the presence of the acceptor. However, slightly less vibronic character is evident in the reprecipitation particles, inferring that PCBM molecules have interrupted some of the P3HT crystalline π-stacking. The absorption of composite nanoparticles closely resembles that of P3HT:PCBM thin films, which contain both amorphous and aggregate P3HT in ratios dependent on processing conditions.

5.3 Quantitative analysis of polymer aggregates

In order to realise efficient nanoparticle devices, it is necessary to understand the composite particles’ internal morphology in more detail, and how this may affect photocurrent generation.

X-ray techniques are regularly employed to determine the crystallinity of organic semiconductor materials. While these techniques provide a good deal of useful morphological information, it should be noted that the fraction of aggregate species determined with this method does not necessarily correspond to the amount that interacts with light. If an aggregate is not significant enough to diffract x-rays, it will not produce a clearly discernable diffraction peak[256, 257] despite possessing an aggregate optical signature. Photophysical techniques therefore may be able to more accurately identify amorphous and crystalline components of blend microstructure.

The absorption spectrum can provide a facile way to investigate the influence of different treatments and preparation routes on the morphology of a BHJ. The quality of aggregates and the fraction of amorphous to aggregate material can be determined both in pure components and in donor-acceptor blends.[12] This is particularly useful in simple polymeric semiconductors, where Spano et al., have built on the earlier work of Kasha to describe aggregate photophysics using the concepts of J- and H-aggregation.[29, 254, 255]
An analytical model of weakly interacting H-aggregates was developed by Spano,[254, 255] and allows for a quantitative analysis of polymer aggregate species by examining their excitonic coupling. Consequently, the morphology of polymer species can be determined using absorption or emission spectroscopy. It should be noted that the model of weakly interacting H-aggregates has been widely applicable to many conjugated polymers.[258–260] However, it is not yet clear if a similar model can also be applied to the more recently successful push-pull donor materials to gain an insight into their condensed phase microstructure.[12]

Here, the model is applied to absorption spectra and allows for a quantitative description of the aggregate component as a progression of Gaussian functions. This modified Franck-Condon fit describes absorbance, \( A \), as a function of photon energy, \( E \), to determine the relative intensities of the individual vibronic transitions, \( m \):

\[
A \propto \sum_{m=0} \left( e^{-S_{m}} \frac{m!}{m!} \right) \left( 1 - \frac{W e^{-S}}{2E_p} \sum_{n \neq m} \frac{S^n}{n!} \frac{(n - m)!}{(n-m)!} \right)^2 \Gamma \left( E - E_{0-0} - mE_p \right) \tag{5.1}
\]

where \( S \) is the Huang-Rhys factor, \( W \) is the free exciton bandwidth, \( n \) is the vibrational quantum number, \( E_{0-0} \) is the 0-0 transition energy, \( E_p \) is the energy of the main intramolecular vibration, and \( \Gamma \) describes the Gaussian line shape. \( \sigma \) gives the RMS width (standard deviation) of the Gaussian line shape and the same linewidth is used for each vibronic transition in a sample. The free fitting parameters are \( \sigma \), \( E_{0-0} \), and \( W \), and it was assumed that the Huang-Rhys factor was unity and the coupling to the electronic transition is dominated by the C=C symmetric stretch at 0.179 eV.[112, 254]

To apply this model to the P3HT component of P3HT:PCBM blend nanoparticles, the PCBM spectral component was subtracted, following the method of Turner et al.[112] For this analysis, the composite nanoparticle absorption spectra were first normalised to the sharp PCBM absorbance peak at 336 nm. Then, 90% of the normalised spectrum was subtracted from each composite NP spectrum to account for the small amount of P3HT absorbance present 336 nm. Following this procedure, the NP spectra closely resembled the pristine P3HT spectra in the higher energy region. These spectra were then used to model the P3HT component aggregate behaviour in the following analyses.

Figure 5.4 presents the absorption spectra and P3HT vibronic structure best fits obtained using equation 5.1 for the P3HT component of (A) the reprecipitation and (B) the mini-emulsion blend nanoparticle suspensions. While the spacing and width of the Gaussians used to fit the vibronic progressions are constant, the Gaussian amplitudes vary, and a distinction can be observed between the particle types. The aggregate (blue circles) and amorphous (red triangles) components of P3HT are now clearly visible,
Figure 5.4: Absorption spectra of the P3HT component (thick black line) of (A) re-precipitation and (B) mini-emulsion 1:1 P3HT:PCBM blend nanoparticle preparations. Best fits using equation 5.1 for the aggregate component are shown (thin black lines) with the sum (blue circles) and sum subtracted from the measured absorption spectrum (red triangles) to indicate contributions of the aggregate and amorphous components, respectively. The aggregate region consists of the best fit of the low energy absorption region from 1.9–2.25 eV (550–650 nm). The amorphous region is the result of the subtraction of the aggregate region from the total P3HT absorption. The absorption spectrum of P3HT within the P3HT:PCBM blend nanoparticles was generated by subtracting a normalised spectrum of PCBM prior to analysis, using the method of Turner et al.[112]
where the amorphous component is given by the subtraction of the vibronic fit from the P3HT absorption spectra, as shown in Figure 5.4.

The H-aggregate model can use the dissection of the vibronic progression to determine further information about the aggregates. Spano’s model also provides a quantitative estimation of the aggregate free exciton bandwidth, $W$. This parameter is inversely related to the conjugation length of chains within the aggregate, assuming similar inter-chain order in the films, where an increase in conjugation length and order will lead to a decrease in $W$.

Using the ratio of the 0-0 ($A_{0-0}$) and 0-1 ($A_{0-1}$) vibronic transition intensities, the free exciton bandwidth, $W$, can be calculated:

$$A_{(0-0)}/A_{(0-1)} = \left(\frac{(1 - 0.24W/E_p)}{(1 + 0.073W/E_p)}\right)^2 \tag{5.2}$$

Using the fits from Figure 5.4, and equation 5.2, the free exciton bandwidth, $W$, for reprecipitation blend nanoparticles in solution was determined as $194 \pm 0.7$ meV. This value is comparable i.e. displaying a similar amount of disorder, to the value of $197$ meV reported by Turner et al.,[112] for P3HT:PCBM unannealed blend films cast from chloroform. While there is still a crystalline P3HT component to these films, these values of $W$ are indicative of larger free exciton bandwidths, and therefore shorter average conjugation lengths and lower crystalline quality.

In contrast, mini-emulsion composite nanoparticles gave a significantly lower free exciton bandwidth of $114 \pm 1.5$ meV, the result of more crystallinity and order. Films annealed at $160^\circ$C cast from chloroform and dichlorobenzene gave values of $135$ meV and $92$ meV respectively,[112] These lower values of $W$ are indicative of higher crystalline quality and larger conjugation lengths relative to the reprecipitation type particles.

The primary driving force for nanoparticle formation is the hydrophobic effect. The donor and acceptor components undergo rapid aggregation, and chain collapse in the case of a polymer, upon formation to avoid contact with water.[242] The agreement of free exciton bandwidth values between nanoparticles and annealed films is unexpected, as formation of nanoparticles occurs at room temperature. However, as pointed out by Clafton et al. in their analysis of particle domain size, the exclusion of water from P3HT chains during NP formation appears to have a similar effect on polymer morphology to thermal annealing the blend film.[251]

The free exciton bandwidth can also be related to the length of the planarised interacting chain segments that take part in an H-aggregate. The model developed by Gierschner et al., describes this relationship using non-nearest neighbour interactions in a 1D stack
of thiophene oligomers,[261] and has been used to determine the average conjugation lengths of aggregates in P3HT blend films.[112, 249] Conjugation lengths can also be described by the number of interacting monomer repeat units within the aggregate, \( N \), as illustrated in Figure 5.1. Using the simulation data of Gierschner et al., an exciton bandwidth of 194 ± 0.7 meV, as found for the reprecipitation particles, is equivalent to ~16 interacting repeat units, an interacting chain length of 6.4 nm.

In the much more ordered mini-emulsion sample, 114 ± 1.5 meV corresponds to an average H-aggregate conjugation length of ~32 units. This number of monomer units is equivalent to an aggregate length of around 12.5 nm, a significant length scale in a nanoparticle of ~80 nm in diameter.

The relative proportion of the nanoparticle consisting of P3HT aggregates compared to amorphous P3HT can also be determined. This is possible by using the fractions of the absorption spectra assigned to amorphous and aggregate P3HT absorbance,[134, 149] and the relative increase in oscillator strength when a polymer chain goes from twisted amorphous to planar aggregated state.[262] The relative increase of oscillator strength for a chain going from amorphous to aggregated has been determined by Clark et al. as 

\[ \varepsilon_{\text{aggregate}} = (1.39 \pm 0.10) \varepsilon_{\text{amorphous}}. \]

Using this relation and the percentage of absorbance attributed to aggregated chains (see Figure 5.4), the fraction of P3HT in an aggregated and non-aggregated states were determined.

Reprecipitation nanoparticles were found to have ~45% of their P3HT component as aggregated material, whereas mini-emulsion blend particles have ~57% aggregated P3HT phase. This adds to present morphological information on the structure of mini-emulsion nanoparticles that are reported to have an 80% pure PCBM core surrounded by a P3HT shell.[145]

5.4 Charge generation photophysics

Following the analysis of nanoparticle morphology, transient absorption spectroscopy was used to explore the excited-state dynamics within neat P3HT particles and the composite particles of each preparation type in solution.

5.4.1 Transient absorption of P3HT nanoparticles

In order to decipher the dynamics in composite nanoparticles, it is first necessary to examine the dynamics of P3HT without the presence of an acceptor to understand P3HT exciton dynamics. Transient absorption spectra and dynamics of P3HT nanoparticles
Figure 5.5: Transient absorption spectra of P3HT nanoparticles in water prepared using (A) the reprecipitation and (B) the mini-emulsion methods. The steady-state absorption spectrum is shown for each particle type (black dashed lines). Pump excitation was 400 nm, with a fluence of 9.75 &mu;J/cm^2.

Ground-state bleaching is evident from 480–630 nm in the same region as the ground state absorption (black dashed line). For both particle types, the bleach almost entirely recovers within the experimental time frame of 750 ps. This indicates that excitons have returned to the ground state, and have an exciton lifetime of ~200 ps consistent with that previously reported.[263] Negative-going peaks at 530 nm, 565 nm and 620 nm represent the 0-2, 0-1 and 0-0 vibronic progressions respectively, and are clearly visible in neat P3HT nanoparticles of both preparation types. While the steady-state absorption has some vibronic structure in both particles (H-aggregate character as described in Section
5.3), this structure is much more pronounced in the ground state depletion for both particle types. This observation is indicative of P3HT excitons preferentially occupying the planarised H-aggregate P3HT regions rather than the amorphous polymer.[71] It should be noted that both samples display transient signatures typical of a neat P3HT film.[71]

While the ground state depletion is the main feature of these spectra, a small amount of positive signal, a photoinduced absorption, can also be observed. This feature is attributed to a small population of charge pairs. These charges have been found to be directly photogenerated,[264] rather than formed from the decay of the singlet emissive species, and they are thought to be generated at the interfaces between aggregate and amorphous polymer domains.[265] While the role of the nanoparticle’s external interface as a location for trap states cannot be discounted, the small amount of this charge species feature (no more than what is observed in P3HT films), suggests no major differences from film-deposited P3HT. Potentially a very small amount of stimulated emission signal (700-750 nm) is also evident in the mini-emulsion sample, occurring in the same region as the P3HT fluorescence. This signal is also clear evidence of the P3HT (S_1) singlet exciton.

5.4.2 Transient absorption of composite nanoparticles

Now that the signature and dynamics of the P3HT exciton have been considered, charge generation in composite particles can be examined. Transient absorption spectra of P3HT:PCBM blend nanoparticles are shown in Figure 5.6 for (A) reprecipitation and (B) mini-emulsion suspensions in water.

The negative signal between 480–630 nm again represents the ground-state bleach of P3HT, occurring in the same region as the steady-state absorption signal. The ground-state depletion signals in both nanoparticle types are long lasting, particularly in the mini-emulsion sample, indicative of the formation of a long-lived species that delays the repopulation of the ground state. This is in contrast to neat P3HT nanoparticles, where both preparation types exhibit a ground-state depletion with a lifetime of \( \sim 200 \) ps, that of P3HT excitons.[263]

Negative-going peaks at 530 nm, 565 nm and 620 nm which represent the 0-2, 0-1 and 0-0 vibronic progressions, respectively, are again clearly present in the bleach, though are only pronounced for the mini-emulsion blend particles in Figure 5.6 (B). As the bleach is much longer lived in the blends than the P3HT-only particles, this indicates that excitons and the longer-lived free charges (discussed below) both preferentially occupy the planarised H-aggregate P3HT regions rather than the amorphous polymer.[71]
also indicates that the PCBM acceptor molecules in mini-emulsion particles have not significantly disrupted the P3HT chain planarity and lamellar structure that is observed in both varieties of neat P3HT nanoparticle. In contrast, reprecipitation nanoparticles (Figure 5.6 (A)), have a much less structured ground state bleach. This indicates that the short-lived excitons and long-lived charges largely do not occupy planarised chain segments, further evidence that PCBM has somewhat disrupted the formation of P3HT aggregates, and that charge generation is preferentially occurring in more intermixed donor-acceptor regions of the particle.

A broad positive signal from 680–900 nm (limited here by the probe range) has been previously attributed to the photo-induced absorption of the P3HT hole polaron.}[71,
the product of charge transfer. This same broad photo-induced absorption was similarly observed in ultrafast transient absorption spectroscopy performed by Kee et al.,\cite{251} in P3HT:PCBM reprecipitation nanoparticles, also attributed to P3HT hole polarons and with a maximum at 1000 nm. Under sufficiently low excitation densities (<30 µJ/cm²) this signal has been shown to persist for microseconds as the result of free charges generated within the BHJ.\cite{267}

Charge separation will consequently produce not only a hole polaron, but an electron on the acceptor material, PCBM. The absorption for this species has been reported at 1.2 eV (1030 nm)\cite{268} and is outside the wavelength range for this experiment. However, for similar reports, the contribution of this signal is often not observed or discussed, probably due to the low absorption coefficient of this transient species compared to that of P3HT and other donor materials. The broad, featureless characteristics of these signals also make it difficult to assign individual species where there are large amounts of overlap.

In the mini-emulsion sample, at early times (∼1 ps), a dip in the PA at 720 nm can again be attributed to small amounts of stimulated emission. This feature is apparent only at short times, and after a few picoseconds the spectral shape evolves with the loss of the SE contribution consistent with the completion of electron transfer or recombination of excitons to the ground state.

The kinetics of the polaron signal at 690 nm and GSB at 530 nm are shown in Figure 5.7 for the reprecipitation and mini-emulsion blend nanoparticles. The photoinduced absorption trace at 690 nm (top), assigned to P3HT hole polarons, was chosen specifically in this wavelength region to avoid any possible overlap from the negative-going stimulated emission signal, and to avoid the area directly around the band-edge of P3HT (discussed below). The P3HT hole polaron signal is present in both samples at times < 100 fs after excitation, within the 200 fs response time of the instrument. The reprecipitation particles exhibit all of their polaron signal generated in this short time window, reaching its maximum value within the instrument response time. This is consistent with finer phase separation and more intermixed regions indicating that excitons do not need to diffuse significant distances to reach a donor-acceptor interface. This same charge generation behaviour is similarly observed in unannealed P3HT:PCBM blend films shown in other work.\cite{71, 72}

The mini-emulsion particles exhibit a population of charges (approximately 60 %) formed promptly within the instrument resolution. This again is typical of charge generation occurring in intermixed donor-acceptor regions of the BHJ. For the mini-emulsion particles, a further delayed phase of charge generation occurs with a half-maximum rise-time
of 5 ps, with complete charge generation within ~30 ps. This type of behaviour is indicative of excitons generated in the P3HT phase that must diffuse through regions of highly pure P3HT to an interfacial or intermixed region in order to dissociate.\cite{71, 269}

Dynamics of charge generation are observed where charges are separated in intermixed regions, yet long-lived charges (as seen in the persistence of the GSB) reside on aggregate structures. This aligns with the three-phase energy cascade picture of charge separation discussed in Section 2.4.3, (although here only the pure donor and intermixed phases are discussed) which is consistent with the suppression of geminate recombination and the generation of high yields of free charges.

For both samples, the GSB exhibits a short initial decay of 3 ps, with a greater magnitude in the reprecipitation sample. However, this decay does not match with the dynamics of polarons for either sample, so requires further explanation. In the case of charge recombination, the ground state recovery should be matched to a similar drop in polaron signal as charges recombine to the ground state. As this is not the case, other explanations include exciton relaxation, for excitons that decay before they reach a donor-acceptor interface, exciton-charge annihilation, or overlap with the positive P3HT polaron signal.
Figure 5.8: Power dependence of P3HT:PCBM mini-emulsion nanoparticle transient absorption kinetics of (A) the photoinduced absorption at 690 nm (P3HT hole polaron) and (B) the photoinduced absorption signal at 650 nm. Pump excitation was at 400 nm at excitation densities of 5 µJ/cm², 10 µJ/cm², 30 µJ/cm², and 200 µJ/cm².

The large proportion of bleach and polaron signal remaining after hundreds of picoseconds provides good evidence for the successful generation of free charges and a higher number of those charges surviving on longer timescales. More GSB and polaron signal are present at long times in the mini-emulsion sample compared to the reprecipitation particles. This has similarly been observed in annealed P3HT films, already shown to be morphologically similar to the mini-emulsion particles.

It is also important to consider the effects of excitation density on the dynamics under investigation. High excitation densities can introduce additional decay mechanisms that are particularly prevalent in solid state systems where excitations are not isolated on individual molecules as they are in solution phase experiments.

The effects of an increasing excitation density are illustrated in Figure 5.8 (A) on the P3HT polaron signal at 690 nm. This fluence dependence demonstrates the contribution
of artefacts associated with exciton-exciton[160] and exciton-charge annihilation[161, 162] that are routinely reported in film samples of organic photovoltaic materials.[70] Similar effects were observed in the composite nanoparticle GSB signal. Higher excitation densities obscure the rise in the polaron generation signal, and can lead to misleading dynamics regarding exciton diffusion and charge generation.

The kinetics occurring in Figure 5.8 (B) are now addressed. Strikingly, the positive PA signal near the band-edge at 650 nm has distinctly different short decay dynamics compared to the low fluence measurements at 690 nm (shown in Figure 5.8) and those in the entire range of the hole polaron transient. In contrast to the rest of the transient kinetics, the short (1.2 ps) decay dynamics of the PA signal at early times has a clear independence of excitation fluence, even down to low excitation densities of 5 µJ/cm².

One explanation of this observation is that this signal corresponds to the absorption of hole polarons that are geminately bound at the interface. In contrast to the behaviour of free carriers, whose recombination should be excitation density dependent, the population of geminately bound charges at the interface should be independent of excitation intensity.[70, 195] The main support for this assignment is the excitation independent decay, though Korovyanko et al. also performed a polarisation memory decay (anisotropy) measurement on this signal, which decayed on similar timescales, leading them to believe that a more mobile species than geminate pairs was responsible.[195]

An alternative explanation is that this signal is a contribution of an electroabsorption (EA), also known as the Stark effect, from ground-state chromophores. Electroabsorption, as described in this case, is not produced by a macroscopic electric field across the device, but by the field induced locally by charged pairs acting as dipoles. This local electric field results in a shift in the absorption spectrum, where the resulting electroabsorption signal is the difference between shifted and unshifted spectra. As the charges drift farther apart their associated dipole moment increases and the electric field inside the illuminated area is gradually screened, as reflected by a reduction of the Stark feature.[193] The signal in Figure 5.8 (B) has dynamics, shape and proximity to the GSB that suggest that it could be the result of an electroabsorption effect.[71] If this is the case, the signal provides information on the kinetics of spatially separating electron-hole pairs, which appears to occur in the mini-emulsion sample over 1.2 ps. Signals at the band-edge have since been assigned to electroabsorption in a variety of material combinations.[114, 115, 143, 187, 270] It should be noted that when using high excitation intensities, (e.g. 200 µJ/cm²) the difference between the band-edge signal and the polaron signal in the rest of the visible range can not be differentiated from each other and the difference between the 650 nm decay and the rise of the hole polaron signal is completely obscured.
The spectroscopic dynamics described here for the composite mini-emulsion particles are similar to that of annealed P3HT:PCBM blend films, indicating some prompt charge generation associated with an intermixed morphology, and some delayed charge generation mediated by exciton diffusion within the P3HT donor phase.[71] In contrast, the reprecipitation particles exhibit dynamics of a more finely mixed donor-acceptor blend, consistent with that of unannealed P3HT:PCBM blend films.

### 5.5 Further work

Annealed blend films have properties advantageous for efficient charge generation,[40, 72] and have distinct similarities in their free exciton bandwidths and charge generation dynamics to P3HT:PCBM mini-emulsion nanoparticles. However, these nanoparticles have additional compositional factors that should be considered, including the presence of surfactant on the particles’ surface and a core-shell structure.

Despite concerns that surfactants in mini-emulsion particles may produce an insulating effect when incorporated into BHJ films, Venkataraman et. al., have demonstrated that surfactants present in mini-emulsion blend devices do not significantly impede charge transport.[271] This is provided that the excess surfactant is removed during particle preparation.

Other work suggests that the donor-rich shell makes it more difficult for photogenerated electrons to be transported out of the particle, leading to higher rates of internal recombination and subsequently lower measured photocurrents and device performance.[147] However, moderate annealing of films to sinter nanoparticles together have recently provided evidence that it is possible to form ‘nano-pathways’ between the PCBM cores of these nanoparticles if conditions are optimised.[243] Previous reports have shown that by manipulating processing conditions, it is also possible to form variations on the typical core-shell composition.[147, 244] Pozzo and coworkers have demonstrated the potential to create composite mini-emulsion nanoparticles that have a much more uniform distribution of conjugated polymer and fullerene throughout the nanoparticle volume such that electrons and holes are easily transported out of the particle.[147] In their study, these particles produced the best performing devices in comparison to other core-shell structural variations.

An alternative approach is to introduce processing variations that can assist in making reprecipitation type nanoparticles more crystalline to improve their intrinsic charge photogeneration properties, rather than relying on elevated temperature processing following nanoparticle deposition.[244]
The refinement and development of new NP preparation routes to influence internal particle structure may play a role in developing successful printable NP devices. Reports of nanoparticles prepared from higher performance materials are now emerging,[242, 243] and efforts are being made to develop alternative preparation and deposition methods using these nanoparticle suspensions.

5.6 Summary

In this chapter, steady-state and sub-picosecond transient absorption spectroscopy has been applied to compare the morphology and excited state processes in P3HT:PCBM nanoparticles prepared by mini-emulsion and reprecipitation methods. The absorption spectrum can be used as a simple indicator of excitonic coupling, intrachain order and the fraction of P3HT crystallinity within the samples. The composite reprecipitation particles, while exhibiting some degree of P3HT crystallinity, are the more amorphous particle type with an average free exciton bandwidth of $194 \pm 0.7\,\text{meV}$ corresponding to 16 interacting monomer units of P3HT, and $\sim 45\%$ of P3HT in its crystalline phase.

In contrast, the mini-emulsion preparation method gave an average of 32 monomer units of extended P3HT within aggregate domains, and a free exciton bandwidth, of $114 \pm 1.5\,\text{meV}$. With a higher proportion of crystalline P3HT, 57%, this morphology with its low degree of intra- and inter-chain disorder has been strongly linked to an increase in hole mobility and a concurrent overall improvement in charge carrier generation and extraction efficiency in P3HT:PCBM photovoltaic devices.[12] This indicates that the mini-emulsion particles, with longer average P3HT conjugation lengths and a greater average crystalline component compared to the reprecipitation particles, should present a favourable internal nanoscale morphology despite the lack of any high boiling-point solvents or elevated temperatures used in processing.

Transient absorption studies highlight the consequences these morphological differences can have on charge photogeneration within the nanoparticles. Probed on the picosecond timescale, efficient charge generation was observed in both nanoparticle types, with charges in the reprecipitation particles generated promptly within 200 fs, and having similarities to highly intermixed unannealed P3HT:PCBM blend films.

In contrast, charges in the mini-emulsion particles were generated on both the 100 fs and 10s of picosecond timescales, the latter mediated by exciton diffusion to the interface. With their higher crystalline quality, charge generation dynamics in these particles more closely resemble annealed films cast from chlorinated solvents, a morphology where geminate recombination is suppressed. Despite the favourable charge separation properties
of mini-emulsion particles, the typical core-shell structure may inhibit efficient charge
collection in devices fabricated from these particles, unless NP preparation routes or
device processing can be refined.

Differences in the charge generation dynamics between differently prepared particles of
similar size and composition highlight the importance of understanding how the crys-
tallinity and internal distribution of materials affects device performance. The nanopar-
ticle fabrication process can result in aggregates that exhibit features similar to thermally
annealed bulk heterojunction films of these materials, despite the lack of any elevated
temperature processing.\[145, 251\] This work provides a deeper insight into charge gen-
eration in nanoparticle dispersions which serve as a strategic morphological approach
for controlling BHJ structure.
Chapter 6

Block Copolymer Photophysics

The following publication forms parts of this chapter:


6.1 Introduction

As described in Chapter 2, the processes of exciton diffusion, charge generation, and carrier percolation all have morphological requirements which must be carefully balanced for efficient bulk heterojunction solar cells. Bulk heterojunctions comprised of donor and acceptor mixtures lack the precise control of critical interfaces[272] and it remains unclear how to control their interfacial orientation and self-assembly.[12]

A ‘block copolymer’ describes a polymer that consists of covalently linked component homopolymer blocks of different composition, in this case an electron donor and acceptor. All-conjugated block copolymers provide a strategy for morphological control that simultaneously incorporates a functional interface within the organic semiconducting molecule itself, and the potential to control the assembly of bulk heterojunction morphology. There are several advantages of this elegant approach which make block copolymers attractive candidates for the rational design and control of electron donor and acceptor moieties in optoelectronic active layers.

Firstly, morphology can be tuned in shape and size by altering the molecular weight (the length) of individual blocks, where films with well-controlled phase separation on the 10–100 nm length scale have been reported.[150, 273–280] Periodic nanostructured
morphologies of alternating donor and acceptor domains can be produced, with a tunable size on the order of a typical exciton diffusion length. These are characteristics that represent a proposed ideal structure for BHJ morphology to optimise exciton diffusion and charge collection.[152]

Secondly, specific control is gained over the donor-acceptor interface between blocks, providing a unique opportunity to tune charge and energy transfer processes by rational design. Block copolymers may also offer an opportunity to examine fundamental questions relating to the interfaces of organic semiconductors.

Thirdly, blocks are known to self-assemble into thermodynamically stable equilibrium structures. This is in contrast to standard approaches to BHJ formation that depend upon demixing from a common solvent, forming non-equilibrium donor-acceptor structures that are optimised empirically. Consequently, the block copolymer approach can potentially provide very stable, well-ordered nanostructures once in the equilibrium ordered state, stable over the lifetime of a device. Utilising a thermodynamically stable structure can also provide solvent independent morphologies, a welcome characteristic for application to large scale printing.

Although many block copolymers have produced ordered nanoscale morphologies,[274–280] until recently,[281] almost all have also displayed comparatively low power conversion efficiencies in organic photovoltaic devices. Progress in synthetic and morphological design has lead to the development of new block copolymer materials, but reports may neglect to consider how charge separation could be affected in the development of these new, complex polymer systems.[150, 272, 282] However, some work has begun to address these issues for particular materials.[153, 283–285]

The linking group between blocks serves to covalently join donor and acceptor, but may have consequences beyond this fundamental role. Whereas regular BHJ devices operate only with interchain phase separation between electron donor and acceptor, the donor-acceptor interface between blocks presents a new intramolecular interface for charge separation or other photophysics to occur. Therefore it is important to understand the electronic and photophysical behaviour that occurs at this junction, whether this be the limitation of significant interactions at this interface, or the control of optimised charge separation.

In this chapter, the examined approach for nanoscale morphological control goes a step further than strategies in previous chapters by synthetically linking the donor and acceptor blocks for the potential of simultaneous morphological and optoelectronic control. In the work presented here, a PFM-F8BT-PFM triblock copolymer is investigated to probe the photophysics of the intramolecular donor-acceptor interface that is introduced with
this strategy. This block copolymer has been used in devices, with modest performance, yet has power conversion efficiencies that outperform that of the equivalent material combination by a factor of three.\textsuperscript{[156]} Steady-state and time-resolved fluorescence and absorption techniques reveal distinct dynamics at the block copolymer donor-acceptor interface compared to individual components, including energy transfer as the result of donor excitation, and delayed fluorescence due to interfacial charge separation by excitation of the acceptor. These results aim to extend the understanding for design criteria necessary for targeted morphological strategies of all-conjugated block copolymer solar cells.

\section*{6.2 Triblock copolymer PFM-F8BT-PFM}

The conjugated polymer electron donor PFM (poly(9,9-diocetylfluorene-co-bis-N,N'-(4-methylphenyl)-bis-N,N'-phenyl-1,4-phenylenediamine)) and electron acceptor F8BT (poly[(9,9-di-n-octylfluorenyl-2,7-diyl)-alt-(benzo[2,1,3]thiadiazol-4,8-diyl)], comprise the novel triblock copolymer PFM-F8BT-PFM (see Figure 6.1).\textsuperscript{[155, 156]} The A-B-A triblock copolymer has been shown to phase separate on the 20–30 nm scale, a domain size ideal for maximizing exciton collection at the donor-acceptor interface. Polymer-polymer solar cells have the advantage of significant and complementary light absorption from both donor and acceptor components (a property lacking in fullerene-based acceptors), though polymers have traditionally been outperformed as acceptors by fullerenes for a number of reasons including their decreased carrier mobility and poor phase separation.\textsuperscript{[286]} These are issues that the block copolymer approach could address.

![Figure 6.1: Semiconducting triblock copolymer PFM-F8BT-PFM](image)

Recent work has examined the single molecule properties and emission of this triblock copolymer, observing interactions as the result of the interface in a single chain.\textsuperscript{[285]} Yan et al. has explored the morphological, optical and device properties of this triblock copolymer in the solid state.\textsuperscript{[156]} They find a greater deal of intermixing in the block
copolymers compared to a blend of its components. However, the triblock copolymer (and to a lesser degree the PFM:F8BT blend) exhibits significant exciplex emission, caused by a strongly bound geminate polaron pair which leads to triplet generation. This study aims to probe the photophysics that occurs specifically at the intramolecular interface of PFM-F8BT-PFM by conducting emission and time-resolved transient absorption measurements in dilute solution. This discounts intermolecular effects which occur in the solid state and can complicate the understanding of these materials.

### 6.3 Block copolymer absorption

An initial photophysical characterisation of the individual homopolymers and block copolymer was undertaken using steady-state absorption spectroscopy. Figure 6.2 illustrates the absorption spectra of the individual components, PFM and F8BT in (A), and the PFM-F8BT-PFM triblock copolymer in (B).

The absorption spectrum of F8BT (Figure 6.2 (A)) is comprised of two distinct peaks in contrast to the broad, single peak absorption spectra of many conjugated polymers. The two dominant transitions consist of the blue transition at \( \sim 330 \text{ nm} \), assigned to the excitonic \( \pi - \pi^* \) transition, typical in conjugated polymers.[287, 288] The other band at \( \sim 450 \text{ nm} \) represents a localised transition to a charge transfer state within F8BT itself, where the electron resides on the benzothiadiazole acceptor and the hole on the fluorene unit of the conjugated backbone.[288] PFM exhibits a single absorption band with a maximum around 380 nm.

The shape of the PFM-F8BT-PFM absorption spectrum (Figure 6.2 (B)) can be described as the linear superposition of the absorption spectra of the two homopolymer blocks that comprise the copolymer, with their respective contributions proportional to their stoichiometric ratio. The lack of change or additional features in this absorption spectrum compared to its PFM and F8BT components indicates there is little to no ground state interaction observed in the copolymer i.e. the block copolymer can be regarded as its separate donor and acceptor components due to a lack of significant mixing of the electronic wavefunctions in the ground state.

All spectra were measured in three different solvents of increasing polarity (given by the solvent polarity parameter ET(30)[289] and also increasing dielectric constant); toluene, tetrahydrofuran (THF), and dichloromethane (DCM). As apparent in Figure 6.2, absorption spectra do not show any significant solvent dependence for the PFM-F8BT-PFM block copolymer and the component homopolymers, typical of a vertical Franck-Condon transition.
Figure 6.2: Normalised absorption spectra of (A) PFM (blue) and F8BT (red) polymers, and (B) the PFM-F8BT-PFM block copolymer (black). Absorption is shown for each polymer in different solvents: toluene (solid lines), THF (dashed lines) and DCM (dotted lines). The triblock copolymer’s absorption spectrum resembles a linear superposition of the component polymers, and no obvious spectral shifts occur between the spectra taken in different solvents.

6.4 Block copolymer steady-state emission

While homopolymer and block copolymer absorption spectra do not show significant solvent dependence, quite different behaviour is observed in the emission spectra. A shift in fluorescence emission as a function of solvent polarity can determine the magnitude of the excited state dipole moment compared to the ground state. If the excited state dipole moment is larger than that of the ground state, it will be stabilised by a polar solvent, reducing the energy gap and leading to a red-shift in the emission maximum.

Figure 6.3 (A) first outlines the effect of solvent on PFM emission alone. PFM shows a significant red shift with increasing solvent polarity and dielectric constant, indicating that the excited state has a large dipole moment. Toluene is a reasonably non-polar solvent with a dielectric constant of 2.4, while PFM in benzonitrile, with dielectric constant of 25.2, in comparison exhibits an emission red-shifted by 60 nm. This is consistent with the emission of other polyfluorenes which also show pronounced solvatochromism.[290] F8BT emission is also moderately red-shifted with increasing solvent polarity (Figure 6.6 (B)).
Figure 6.3: (A) Absorption and emission spectra of the PFM homopolymer. Emission spectra are excited at $\lambda_{exc} = 380$ nm, and shown in solvents of increasing polarity: toluene (solid thick line), THF (dashed line), DCM (dotted line) and benzonitrile (solid thin line). (B) Absorption and emission spectra of the F8BT homopolymer. Emission are excited at $\lambda_{exc} = 470$ nm, and are shown in solvents of increasing polarity, toluene (solid thick line), THF (dashed line), DCM (dotted line) and benzonitrile (solid thin line).

Figure 6.4 represents a map of the triblock copolymer photoluminescence intensity plotted as a function of excitation and emission wavelengths, taken in (A) toluene and (B) DCM, a more polar solvent. The wavelength of maximum emission was found to vary with the excitation wavelength, characteristic of the two separate components that comprise the block copolymer.

The photoluminescence intensity is found to exhibit two maxima. In toluene, a maximum of $\lambda_{em} = 530$ nm corresponds to $\lambda_{ex} = 330$ nm and 445 nm. These are the two absorption maxima for F8BT, indicating that emission resulting from the two absorption features does not depend on excitation wavelength. The second, weaker, local maximum at $\lambda_{em} = 460$ nm, is the result of excitation at 370 nm, corresponding to absorption from the PFM component.
In DCM, a similar picture is apparent, where the broad emissions are much closer together, as is characteristic of the emission of PFM and F8BT illustrated in Figure 6.3 (A) and (B) in this solvent. The emission maximum $\lambda_{em} = 545$ nm is attributed to the F8BT block and $\lambda_{em} = 515$ nm is attributed to PFM.

In both solvents, there is no appearance of any emission other than from the component polymers. In some other block copolymers, an interfacial charge transfer state has been identified as a result of the intramolecular interface, evident by its steady-state emission.[153, 283] For PFM and F8BT, a strong exciplex emission is evident in solid state blends with a broad red-shifted emission from 600–700 nm,[285, 291] acting as a terminal loss mechanism in solid state devices for recombination. No such exciplex emission is apparent here as a result of the triblock copolymer intramolecular interface.

The primary difference for block copolymer emission in solvents of different polarity (Figure 6.4) is the relative intensities of emission from the two blocks. Emission in toluene is dominated by the F8BT emission, whereas DCM exhibits more equal emission between the blocks, with significant PFM donor emission. This is explored in more detail below by examining fluorescence quenching in the block copolymer versus comparable blends of the homopolymers in a range of solvents (Figures 6.5 and 6.6).

### 6.4.1 F8BT block excitation

A straightforward, initial analysis of behaviour resulting from the block’s intramolecular interface is based on fluorescence quenching. Figure 6.5 illustrates emission spectra of the block copolymer excited at 470 nm. Exciting at this wavelength allows the exclusive...
excitation of this component, without any overlap from the PFM donor. To provide a direct comparison to the behaviour of the unattached PFM and F8BT components, a mixture of 2:1 PFM:F8BT with an identical absorption profile was also measured, so that approximately the same number of photons were absorbed at 470 nm for the components in each solvent, as confirmed by a measurement of optical density. To aid in interpretation, individual PFM and F8BT emission spectra in each solvent are shown below for comparison.

The PFM:F8BT mixture (Figure 6.5), as expected, exhibits only F8BT-type emission in all solvents, due to its excitation at 470 nm, where PFM does not absorb. Minimal quenching is expected, as the proximity is low between separate polymer chains in solution at low concentrations. This results in the vast majority of excited chains relaxing without other effects, such as energy transfer.

Covalently bonded block copolymers, however, are expected to have different outcomes, due to their enforced proximity. The block copolymer also solely exhibits F8BT emission, showing that some of the F8BT block is not completely affected by the intramolecular interface, however, this emission is quenched relative to the mixture. This indicates that the block interface does have some influence on excitations within the F8BT block.

The same result is observed in solvents of increasing polarity, THF in (B), DCM in (C), and benzonitrile in (D) where quenching increases with a increasing solvent dielectric constant.
For the block copolymer, increased quenching in more polar solvents indicates that charge transfer rather than energy transfer is occurring at the two intramolecular interfaces between acceptor and donor blocks. More polar solvents are able to stabilise a CT state and make this process more efficient.\cite{38, 290, 292} As this proposed charge transfer is the result of acceptor rather than donor excitation, hole transfer or channel II transfer appears to be occurring as a result of the intramolecular interface, and will be discussed more below.

It is well-established that the lowest energy excitons in push-pull type polymers like F8BT and PFM have significant charge transfer character.\cite{288, 290} However, to clarify the nomenclature used in the subsequent discussion, ‘CT state’ will refer to the intramolecular state at the block interface, unless otherwise stated.

### 6.4.2 PFM block excitation

In Figure 6.6, the block copolymer emission is investigated by exciting predominantly the PFM donor block at the peak of PFM absorption, 380 nm. This is not as straightforward as the case shown in Figure 6.5, because some of the F8BT is also excited (roughly 20\%), however, some valuable information can be gathered from the subsequent emission spectra.

![Figure 6.6: (A), (B), (C) and (D) illustrate emission from the PFM-F8BT-PFM triblock copolymer (black solid lines), exciting predominantly the PFM block, but also a small component of the F8BT block at $\lambda_{\text{exc}} = 380$ nm. BC stands for block copolymer. The emission mixture of 2:1 PFM:F8BT (green dashed lines) with an identical absorption spectrum is shown for comparison, and typical PFM (blue dashed lines) and F8BT (red dashed lines) emission in each solvent are also shown below. The block copolymer and mixture comparison is shown in solvents of increasing polarity: toluene (A), THF (B), DCM (C) and benzonitrile (D).](image)
Again comparing triblock copolymer emission with that of its equivalent 2:1 PFM:F8BT mixture, the least polar solvent, toluene, is initially discussed (Figure 6.5 (B)). PFM and F8BT emissions are well-separated in this solvent, and the mixture shows similar amounts of emission from both blocks. However, in the block copolymer, a clear increase in the contribution of the F8BT emission is observed. The PFM emission in toluene has a maximum of 452 nm and F8BT an absorption maximum of 455 nm (see Figure 6.3). The strong overlap of PFM emission and F8BT absorption is assumed to result in a fast and rapid Förster resonant energy transfer (FRET) of PFM excitons to F8BT.\cite{293, 294} As well as spectral overlap, FRET also depends upon the relative distance of donor and acceptor ($\propto r^{-6}$) and their relative orientation. The conditions given by PFM and F8BT chromophores within the block copolymer would likely satisfy at least the distance requirement, if not both of these conditions.

In contrast to observations of the F8BT block excitation, for majority PFM excitation, no significant increase in quenching is observed for the block copolymer in solvents of increasing polarity. This is good evidence to support the hypothesis that while energy transfer may be occurring between the blocks (and is significant in toluene due to spectral overlap), charge transfer is not a major outcome for excitations originating in the PFM block. No CT state stabilisation and increase in the efficiency of quenching with solvent polarity is observed. Coupling through the F8 unit on either side of the central acceptor prevents electronic interaction of the donor and acceptor across the interface and therefore appears to largely maintain the regular electronic properties of the donor moiety.

As the solvent dielectric constant increases and PFM emission further red-shifts, it becomes more difficult to differentiate between the overlapping PFM and F8BT emission profiles. The conditions for PFM emission and F8BT absorption spectral overlap also decrease, as the PFM emission red-shifts with increasing polarity. Consequently, in the more polar solvents, no significant evidence of energy transfer is observed, with the PFM component of emission (the higher energy side of mixture emission) maintained with only a moderate decrease in intensity compared to the mixture. For THF, DCM and benzonitrile, (Figure 6.6 (B), (C) and (D)), it is the F8BT side of the emission for block copolymers that is decreased. This may infer that the phenomenon observed when exciting the F8BT block in Figure 6.5 is also being observed in the small component of excited F8BT at 380 nm. If this is the major effect, then PFM excitation has little apparent consequence at the block interface for interaction unless environmental polarity allows a large overlap of the donor emission and acceptor absorption spectra.
6.5 Time-resolved emission

To further investigate the quenching observed from the F8BT emission of the block copolymer, time-correlated single photon counting (TCSPC) was employed to determine the dynamics of these processes. Figure 6.7 illustrates the fluorescence decays of F8BT and the block copolymer while exciting the F8BT component at 440 nm. This is shown in (A) toluene, and (B) the more polar DCM.

For both solvents, F8BT shows a monoexponential decay, with a fluorescence lifetime of 3.075 ns in the more polar solvent, DCM, compared to 2.153 ns in toluene. In contrast, the block copolymer has biexponential dynamics in both solvents, which can be fit by a sum of exponential decays ($I(t) = a_i \exp(-t/\tau_i) + a_j \exp(-t/\tau_j)$). The results of these fits are shown in Table 6.1. The two exponentials of the block copolymer in toluene gave lifetimes of 0.671 ns and 2.707 ns respectively, the longer of the two, notably, is greater than the monoexponential lifetime of F8BT in the same solvent (2.153 ns).

The shorter lifetime apparent in the block copolymer is indicative of a charge transfer process from F8BT, supported by the solvent-dependent emission quenching. The biexponential behaviour has also been observed in single molecules of the same PFM-F8BT-PFM triblock copolymer in other work, in solution and the solid state, where this behaviour was also attributed to intramolecular charge transfer.[285]

![Figure 6.7: Fluorescence decays of F8BT (red) and PFM-F8BT-PFM (black) excited at 470 nm in (A) toluene and (B) DCM. Emission was measured at 530 nm. Solid lines illustrate fitted functions for each decay.](image-url)
### Table 6.1: Fluorescence decay fits for 2:1 PFM:F8BT mixtures and the PFM-F8BT-PFM triblock copolymer in toluene and DCM.

<table>
<thead>
<tr>
<th></th>
<th>mixture ($\lambda_{exc} = 440\text{ nm}$)</th>
<th>block copolymer ($\lambda_{exc} = 440\text{ nm}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>toluene</td>
<td>2.153 ns (100%)</td>
<td>0.671 ns (13%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.707 ns (87%)</td>
</tr>
<tr>
<td>DCM</td>
<td>3.075 ns (100%)</td>
<td>0.635 ns (43%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.323 ns (57%)</td>
</tr>
</tbody>
</table>

#### 6.6 Transient absorption spectroscopy

Fluorescence quenching is not necessarily a complete indicator of efficient charge generation in organic photovoltaic materials.[37–42] Transient absorption measurements can potentially provide further details on photophysical processes that may be occurring. Using transient absorption spectroscopy, the spectra of the PFM donor and F8BT acceptor were studied individually and compared to that of the block copolymer.

Transient spectra of individual homopolymers, a homopolymer mixture and block copolymer in DCM are illustrated in Figure 6.8, following excitation at 400 nm. The inability to excite individual blocks in isolation with the available pump wavelengths resulted in the simultaneous excitation of both the PFM and F8BT components.

Transient absorption spectra of PFM in DCM are shown in part (A) of Figure 6.8. Due to the wavelength range available for the probe beam, neither ground state bleach or stimulated emission signals were observable for this polymer. However, the positive photo-induced absorption signal is consistent with a transition from the $S_1 \rightarrow S_n$ energy levels with a maximum around 515 nm. The rapid blue shift to shorter wavelengths with time of this $S_1$ photo-induced absorption signal is thought to arise from solvent relaxation of this excited state, which has significant CT character. As the $S_1$ level of PFM relaxes, this corresponds to a greater energy transition to a higher excited state, hence the blue-shifted signal over time. While the shift could arise from torsional relaxation processes or energy transfer within the polymer chain, there was a much greater shift observed in DCM than in less polar solvents such as toluene and THF (not shown). Due to the significant solvent dependence, it can be suggested that the substantial solvatochromism is largely the result of solvent relaxation. This behaviour and explanation has also been given for other polyfluorenes in polar solvents.[290]
The transient absorption spectra of F8BT in DCM, is shown in (B) of Figure 6.8. A negative transient absorption signal at \(\sim 470\) nm is assigned to the ground state bleach, as it has the characteristic wavelength and spectral shape of the absorption spectrum in this region. Another negative signal with a peak at \(\sim 575\) nm is assigned to stimulated emission originating from the first excited singlet state, since its spectral position matches the fluorescence of F8BT. The stimulated emission feature undergoes a significant red shift, likely due to the same solvent relaxation processes that were seen in the transient absorption of PFM, but for the transition that corresponds to the energy gap between the \(S_1\) and ground state. For wavelengths > 620 nm, a broad photoinduced absorption
band extending into the near infrared is attributed to the \( S_1 \rightarrow S_n \) state absorption, because the SE and PA bands share the same dynamics. This is in agreement with the transient absorption spectra of F8BT reported in similar solvents.[295, 296]

The transient absorption spectra of a 2:1 mixture of PFM and F8BT are shown in Figure 6.8 (C) adjacent to spectra of the triblock copolymer, (D). The spectrum of the component mixture resembles the linear superposition of the transient absorption spectra of PFM and F8BT alone, though the F8BT component dominates. Interactions between the separate polymer chains are unlikely at the concentrations and timescales employed here, so the vast majority of the excited chains relax unperturbed by molecular interactions.

The inability to excite individual blocks in isolation with the available pump excitation wavelength results in the simultaneous excitation of both the PFM and F8BT block components. This, combined with significant spectral shifts make global quantitative analysis of data a challenging endeavour.

Preliminary analysis of this data shows two key differences between the mixture and block copolymer transient spectra. These differences can be attributed to interactions at the interface between the donor and acceptor blocks in solution. Firstly, the \( S_1 \rightarrow S_n \) signal of F8BT (700–900 nm) in the block copolymer exhibits different dynamics to that of the F8BT and the mixture transient spectra, with a more rapid decay. A reduction in the stimulated emission and ground state bleach features of F8BT can also be observed, but this is more difficult to clearly resolve due to overlapping signals.

No additional photoinduced absorption features are apparent in the block copolymer compared to the mixture, indicating (at least in the wavelength range investigated) that there is no clear spectral signature of moieties directly representing charge transfer products. It is clear that there is extensive spectral overlap of various species in the copolymer and assigning one species to a particular wavelength region is difficult.

Figure 6.9 illustrates the transient decay at 870 nm for F8BT (red triangles), 2:1 PFM:F8BT mixture (green diamonds), and the block copolymer (black circles). This wavelength was chosen for its minimal PFM absorption contribution, allowing for the dynamics of the F8BT component to be examined largely in isolation. The signal at this wavelength corresponds to the F8BT \( S_1 \) PA, and as it represents the population of the F8BT \( S_1 \) state, it should have equivalent dynamics to the fluorescence decays in DCM which are illustrated in Figure 6.7.

In Figure 6.9 it is clear that the transient decay dynamics of the F8BT homopolymer are similar to that of the mixture. The F8BT component was fit by a sum of two exponentials, and due to the short time window available in the transient absorption
experiment, the longer decay component of 3.2 ns was fixed, obtained from fluorescence decays reported in Section 6.5. An additional shorter component was required to describe short timescale relaxation of F8BT, not resolved in TCSPC experiments. The F8BT S$_1$ signal in the PFM:F8BT mixture shows almost the same behaviour as F8BT alone, with very similar dynamics, but required a small contribution from a third exponential decay (9%), presumably to account for some PFM overlap.

![Figure 6.9: Transient absorption kinetics at 870 nm of F8BT (red), 2:1 PFM:F8BT mixture, and the PFM-F8BT-PFM block copolymer, all in DCM. Excitation was at 400 nm.](image)

<table>
<thead>
<tr>
<th></th>
<th>F8BT</th>
<th>2:1 PFM:F8BT mixture</th>
<th>block copolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_1$ (ns)</td>
<td>3.200 (36%)</td>
<td>3.200 (30%)</td>
<td>2.323 (5%)</td>
</tr>
<tr>
<td>$\tau_2$ (ns)</td>
<td>0.486 (64%)</td>
<td>0.404 (61%)</td>
<td>0.635 (56%)</td>
</tr>
<tr>
<td>$\tau_3$ (ns)</td>
<td>0.018 (9%)</td>
<td>0.021 (39%)</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.2: Time constants (and relative amplitudes) from exponential fits to transient absorption data of F8BT, a 2:1 PFM:F8BT mixture and the block copolymer at 870 nm. Underlined values were fixed during fitting, and obtained from the fluorescence decay fits for the same materials in DCM in Figure 6.7 and Table 6.1.

As expected from TCSPC results, the triblock copolymer shows different time-resolved dynamics. Using the decay fits from TCSPC data for the longer time constants, a sum of three exponentials were used to describe this data, as outlined in Table 6.2. It is possible that a small amount of energy transfer could be occurring from the PFM to the F8BT blocks, although this is not significant in DCM compared to less polar solvents like toluene, where spectral overlap is favourable for this process. Additional photophysics
Chapter 6. Block Copolymer Photophysics

due to PFM block excitation would complicate dynamics on short timescales, although a reasonable fit is observed for the block copolymer’s dynamics that matches those from the fluorescence decays.

A more detailed understanding of this system’s short timescale dynamics would be facilitated by TA pump energies that could selectively excite the individual components of the block copolymer. In the transient absorption data presented here, an explicit spectral signature of a CT state was not observed. However, the transient absorption dynamics, in addition to solvent polarity-dependent fluorescence quenching and TC-SPC decays have together suggested that a charge transfer state is a likely intermediary following F8BT acceptor excitation.

6.7 A kinetic model of delayed fluorescence

A possible explanation for the block copolymer decay behaviour observed with TCSPC and transient absorption is a contribution due to delayed fluorescence behaviour from the F8BT block. Delayed fluorescence is a term generally used to describe thermally activated $S_1$ emission, which often occurs from reverse intersystem crossing from $T_1 \rightarrow S_1$ when the energy difference between these two states is small and the $T_1$ lifetime is sufficiently long to make this process competitive with other deactivation pathways. Delayed fluorescence can also occur as the result of interactions between a locally excited state and a charge transfer state. While charge transfer is usually an efficient mechanism for fluorescence quenching, in some circumstances where energy levels are appropriately matched and states suitably coupled, a locally excited and charge transfer state equilibrium can lead to a delayed emission (kinetic scheme shown in Figure 6.10).

Figure 6.10: A kinetic model of delayed fluorescence.
The result is the observation of two fluorescence lifetimes: a shorter, prompt fluorescence decay and a longer, delayed decay component.\cite{297, 298} Fluorescence from the longer component occurs with the same spectral distribution as the regular emission but with a longer decay constant. This type of behaviour has been observed previously in molecular materials\cite{298–301} and polymers.\cite{48, 302}

Fitting biexponential fluorescence decays with \( I(t) = a_i \exp(-t/\tau_i) + a_j \exp(-t/\tau_j) \) gives \( \tau_i, \tau_j, (\lambda_i = 1/\tau_i, \lambda_j = 1/\tau_j) \) and pre-exponential factors \( a_i, a_j \). With these values, along with the fluorescence lifetime of an unquenched acceptor, \( \tau_{flu} \), it is possible to calculate the rate constants of charge separation \( k_{fwd} \), the back reaction \( k_{rev} \), and the rate of recombination to the ground state \( k_{CR} \)\cite{298, 299}:

\[
\lambda_i = \frac{(X + Y) + [(X - Y)^2 + 4k_{fwd}k_{rev}]^{\frac{1}{2}}}{2} \tag{6.1}
\]

\[
\lambda_i = \frac{(X + Y) - [(X - Y)^2 + 4k_{fwd}k_{rev}]^{\frac{1}{2}}}{2} \tag{6.2}
\]

\[
\frac{a_i}{a_j} = \frac{(\lambda_i - Y)}{(Y - \lambda_j)} \tag{6.3}
\]

where \( X = k_{flu} + k_{fwd}, Y = k_{CR} + k_{rev} \), and \( k_{flu} \) is the reciprocal of the fluorescence lifetime, \( \tau_{flu} \), in the absence of delayed fluorescence.

By calculating the equilibrium constant of the forward and backward reaction, the driving force, \( \Delta G \), for the charge separation reaction can be calculated:

\[
K_{eq} = \frac{k_{fwd}}{k_{rev}} \tag{6.4}
\]

\[
\Delta G = -RT\ln K_{eq} \tag{6.5}
\]

where \( R \) is the gas constant and \( T \) is the temperature.

The emission observed from the block copolymer is consistent with this type of kinetic scheme, with all emission having the spectral characteristics of F8BT emission, rather than that of a charge transfer state (which here must be non-emissive). The two fluorescence lifetimes described in Section 6.5 therefore arise from quenching of the excited state by charge transfer (shorter lifetime), and the thermal regeneration of the excited state as a result of the time spent in the charge transfer state (longer lifetime).
A similar intramolecular CT state has been reported by Petrozza et al. for a F8BT-TFB random copolymer, and by Hooley et al in the same PFM-F8BT-PFM triblock material. Using the fluorescence decays of the F8BT acceptor block, and block copolymer presented in Section 6.5, the rate constants for the above kinetic scheme were calculated and are presented in Table 6.3.

The forward rate constants for charge transfer, $k_{fwd}$, in toluene and DCM were found to be $3.206 \times 10^8$ s$^{-1}$ and $5.700 \times 10^8$ s$^{-1}$ respectively. The slower rate for $k_{CR}$ than $k_{rev}$ in both solvents indicates that the main channel for CT state relaxation is through emission of the exciton, rather than direct recombination to the ground state. Together $k_{fwd}$ and $k_{rev}$ allow for the calculation of the equilibrium constant $K_{eq}$ and therefore the determination of $\Delta G_{CS}$ for charge separation.

The free energy change for charge separation, $\Delta G_{CS}$, was calculated as +0.108 eV in toluene and -0.003 eV in DCM. The energy separation between the locally excited and charge transfer state is relatively small, and the position of the equilibrium is dependent on the local environment, with solvent polarity controlling the energetics. While in toluene, the charge separation process appears to be endothermic, and delayed fluorescence can occur that is facilitated by thermally activated back transfer from the charge transfer state to the emissive excited state at room temperature. In the more polar solvent, DCM, the CT state is stabilised, and the $\Delta G_{CS}$ of -0.003 eV indicates that the CT state would be energetically accessible by this route. This type of ‘dielectric switching’ has also been described by Petrozza et al., in another polyfluorene copolymer. In both cases, the environment is responsible for switching between a neutral singlet exciton to a charge transfer state depending on the polarity of the solvent.

### Table 6.3: Rate constants for delayed fluorescence in PFM-F8BT-PFM triblock copolymer, in toluene and DCM, and the calculated driving force for charge separation, $\Delta G_{CS}$

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$k_{fwd}(\text{s}^{-1})$</th>
<th>$k_{rev}(\text{s}^{-1})$</th>
<th>$k_{CR}(\text{s}^{-1})$</th>
<th>$\Delta G_{CS}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>toluene</td>
<td>$3.206 \times 10^8$</td>
<td>$3.220 \times 10^8$</td>
<td>$1.024 \times 10^8$</td>
<td>+0.108</td>
</tr>
<tr>
<td>DCM</td>
<td>$5.700 \times 10^8$</td>
<td>$5.699 \times 10^8$</td>
<td>$5.060 \times 10^8$</td>
<td>-0.003</td>
</tr>
</tbody>
</table>

#### 6.8 Film studies

The intramolecular interfaces in block copolymers are of great interest for their potential to mediate charge separation and create a fundamental study of the donor-acceptor
interface. However, the solid state properties of the PFM-F8BT-PFM triblock copolymer are most relevant to their operation in organic photovoltaic devices. This has previously been investigated by Yan et al. and Hooley et al., and therefore is not repeated in this work.[285, 291]

The device efficiencies of PFM:F8BT solar cells reported by Yan et al. were three times greater for block copolymer blends compared to mixtures of the corresponding homopolymers.[156] They also observed a greater degree of intermixing in the triblock copolymer compared to the analogous blend of PFM and F8BT. Upon thermal annealing Yan et al. also detected enhanced microphase separation with diameters of around 10 nm, characteristic of block copolymer films. This should help promote the efficient quenching of excitons upon photoexcitation. However, both films exhibited significant exciplex emission, due to a geminate polaron pair which was long-lived and remained tightly bound at the interface. The Coulomb binding energy of this exciplex, by virtue of its shorter electron-hole separation distance, was proposed to be too great to allow dissociation into the free charge carriers. These states could then undergo intersystem crossing and resulted in significant triplet generation in devices, here a terminal loss channel. Triplet state formation was reported as approximately 20 times more efficient in films of the triblock copolymer when compared against a representative bulk heterojunction blend of the constituents.

Exciplex emission is characterised here for comparison with solution measurements, illustrating the absorption spectrum of a PFM-F8BT-PFM film, and the emission spectra of: the homopolymers, a 2:1 PFM:F8BT blend and block copolymer film (Figure 6.11). The block copolymer film has a very similar absorption spectrum to the solution absorption. However, quite different emission behaviour is observed compared to solutions.
In the block copolymer and PFM:F8BT blend, a broad red-shifted emission is indicative of the formation of a new emissive state between 600–700 nm, identified as a charge transfer or exciplex state.[285, 291] The lack of red-shifted emission in solution suggests that emissive exciplex formation requires close interchain interaction, and is not the result of photophysics occurring at the intramolecular interface.

Both the greater observation of exciplexes and the greater triplet yield in block copolymer blends is the result of a more finely intermixed blend morphology and a greater interfacial area, compared to the representative blend of constituents. This work suggests that the issue with exciplex and triplet formation is a function of the inherent material combination and/or its domain size[303] due to the finer phase separation caused by the block copolymer. The primary exciplex loss mechanism is not attributed to specific interactions at the intramolecular block interface.

6.9 Summary

The PFM-F8BT-PFM triblock copolymer has been investigated in solution and its photophysical properties compared to mixtures of component homopolymers to determine the effect of the intramolecular interface. Results from steady-state and time-resolved fluorescence and absorption measurements indicate that excited state interactions take place which occur at the block copolymer interface with differing consequences depending on which component is populated by excitons.

When examining PFM donor excitons, synthetic coupling through the F8 unit on either side of the central acceptor prevents electronic interaction of the donor and acceptor across the interface and so largely maintains the regular electronic properties of the donor moiety. PFM donor excitation resulted in only minor interfacial interactions, predominantly energy transfer from PFM to F8BT which occurred in environments where donor emission and acceptor absorption were overlapping.

However, a different case is encountered when examining channel II interactions where the acceptor was excited. Hole transfer occurred at the interface, resulting in the formation of an intramolecular charge transfer state. The similarity of energy levels of the locally excited state and CT state lead to delayed fluorescence from the F8BT group, affected by the polarity of the environment. The kinetics of delayed emission could be interpreted in terms of an equilibrium between a locally excited and a charge transfer state at the interface. The importance of examining both donor and acceptor excitation pathways for charge transfer in block copolymers has been highlighted in this work.
In the case presented here, the conjugated linkage facilitates hole transfer yet does not provide a low energy charge transfer complex or exciplex as a pathway for significant charge recombination, as has been demonstrated in some other attempts at all-conjugated block copolymers.[152, 153, 283] In these cases, strong coupling and electronic mixing at the interface resulted in a significant loss pathway. An exciplex species, however, is present in significant population in PFM:F8BT blend films with higher populations in block copolymer films, as the result of a greater interfacial area due to a more intermixed morphology. The exciplex operates as a terminal loss mechanism in PFM:F8BT and block copolymer blends, but this issue is not the result of the intramolecular interface in the block copolymer.

The conjugated coupling at the interface, while not detrimental to device performance, could potentially be further tuned to improve the efficiency of charge generation. Inspiration could be taken from the mechanisms of efficient charge transfer in bulk heterojunctions; by the formation of a cascading interfacial energetic landscape, or through the formation of a delocalised CT state to facilitate longer range charge separation. In practice there are a number of shortcomings and complexities that need to be addressed for block copolymers, however, their simultaneous potential for controlling donor-acceptor morphology and functional interfaces makes them an attractive future prospect for rationally designable materials for organic photovoltaics.
Chapter 7

Overall Summary and Conclusions

Advances in the efficiency and scale-up of promising low-cost organic solar cells hinge on the control and optimisation of active layer morphology combined with the rational design of new materials. These factors are reliant on an understanding of the complex effects that nanoscale donor-acceptor morphology have on charge photogeneration. Concurrently, various approaches have been employed to modify donor-acceptor morphology in order to improve device efficiency, with varying levels of control.

The overall goal presented in this work was to investigate specific strategies for controlled donor-acceptor morphologies and understand how solid-state microstructure affects photoinduced charge generation in these materials. As a result, the study aimed to advance design rules for the interconnection of morphological control and charge generation in the context of recent advances in the understanding of the charge separation process.

Chapter 2 situated the study within the current literature, including a critical review of recent developments in the mechanistic understanding of charge transfer. A special focus was given to those developments within the context of bulk heterojunction morphology. Established and more nascent strategies for modifying and controlling bulk heterojunction morphology were outlined. From this, the question was posed: do these morphological design principles align with positive outcomes for charge separation?

In Chapters 4, 5 and 6, charge photogeneration was investigated in the context of three different morphological strategies, and the consequences explored spectroscopically.

The morphological strategies investigated here are all methods that are amenable with a large-scale printed processes. This aligns with the objectives of organic photovoltaics in the first instance; that they are solution processable and facile to manufacture. For
example, in Chapter 4, solvent vapour annealing is an ambient temperature process compatible with high-speed printing. This was conducted on BTR heterojunctions, a newly developed material with thick active layers, a promising property for large-scale manufacturing (Chapter 4). In Chapter 5 and 6, the nanoparticle and block copolymer approaches are compatible with eco-friendly solvents.

7.1 Experimental Methods

The design and optimisation of materials and morphologies for efficient organic photovoltaic cells requires a detailed understanding of the processes that occur between photon absorption and photocurrent generation. Charge photogeneration in organic photovoltaic materials occurs on ultrafast timescales, and requires time-resolved experiments that can resolve the relevant processes. The primary experimental technique used in this study, transient absorption spectroscopy, has the ability to do so.

However, as is discussed in Chapter 3, extremely low excitation densities, approaching that of solar radiation, are required to avoid non-linear effects which can distort the dynamics of charge photogeneration in donor-acceptor blend films. This requires very sensitive transient absorption measurements, and specific strategies to achieving such sensitivities were outlined, in our case a high repetition rate transient absorption system. While a comparison of a high and low repetition rate system illustrated clearly the benefits of this setup, further potential improvements for high sensitivity TA were also outlined. The generation of the supercontinuum probe was discussed, as a non-trivial yet integral part of the TA experiment, also important for the optimisation of high sensitivity experiments.

The highly complex nature of solid state blend morphology and the overlapping timescales of different processes can make it challenging to correlate specific molecular and aggregate properties with the processes relevant to device operation. Special considerations of relevance for transient absorption of OPV materials were explored, especially those relating to signal assignment and interpretation in bulk heterojunctions.

7.2 Charge generation in a solvent vapour annealed heterojunction

In Chapter 4, the modification of a bulk heterojunction via solvent vapour annealing, an ambient temperature processing technique, was investigated spectroscopically. This
approach to morphological control has been used to achieve significant increases in device efficiency compared to untreated blend films in BTR:PC$_{71}$BM BHJs.

SVA results in an increase of BTR crystallinity, although exciton emission quenching determined that over $\sim 10\%$ of excitons were unquenched in the SVA films and lost to radiative processes. Multiple efficient charge separation pathways were revealed by transient absorption spectroscopy where both hole and electron transfer contributed to photocurrent generation.

However, differences in the dynamics of donor exciton migration and electron transfer did not explain efficiency differences in device performance. The most significant discrepancy between untreated and solvent vapour annealed films was a BTR triplet exciton loss channel, formed due to sub-nanosecond bimolecular recombination. Triplet generation was significant in untreated blend films though was substantially suppressed after solvent vapour annealing, an effect solely attributed to the morphological change. It is suggested that both charge wavefunction delocalisation on BTR crystalline domains and percolating pathways in BTR may account for suppressed triplet exciton generation in solvent vapour annealed blends.

To our knowledge, this is the first report of this triplet loss mechanism in a molecular (non-polymeric) donor material, demonstrating the important role of spin in high performance heterojunctions. The materials characteristics that lead to the presence of a high temperature liquid crystalline phase warrant further investigation into their potential role in creating optimal morphologies for charge photogeneration in these devices. Subtle morphological changes such as those induced by solvent vapour annealing appear to have a significant role in the interrelation of spin, charge generation and morphology. These factors may require significant attention in the future design and optimisation of new generation low-bandgap materials.

### 7.3 Semiconducting nanoparticle photophysics

Chapter 5 explored the approach of using donor-acceptor nanoparticle suspensions to allow nanoscale aggregate structure tunability, and the decoupling of nanoscale morphology from the deposition process in eco-friendly solvents.

Different preparation routes for P3HT:PCBM nanoparticles were revealed to have a significant impact on their morphology and charge generation character. By dissection of the absorption spectrum, morphology was assessed optically using a model of weakly coupled H-aggregates, determining excitonic coupling, intrachain order and the fraction
of crystalline P3HT within the samples. Using transient absorption spectroscopy, morphology and excited state processes were examined in particles of comparable size and composition, but differing preparation methods.

Nanoparticles prepared by the reprecipitation method presented a more intermixed donor-acceptor morphology resulting in charges generated promptly within 200 fs, with similarities to highly intermixed unannealed P3HT:PCBM blend films. In contrast, the mini-emulsion preparation method gave larger average P3HT conjugation lengths, higher crystalline P3HT proportions, and charge generation that was mediated by exciton diffusion in pure P3HT domains. The nanoparticle fabrication process was found to result in aggregates and charge generation dynamics that exhibited features similar to thermally annealed bulk heterojunction films cast from chlorinated solvents, despite the lack of any elevated temperature processing.

These results highlight the importance of understanding how crystallinity and the internal distribution of materials can impact on performance in this strategic morphological approach to controlling BHJ structure. Expansion of this work would involve the exploration and refinement of preparation methods that lead to micro- and macrophase structure for both optimised nanomorphology and microstructure for device processing. The fabrication and investigation of nanoparticles of low-bandgap and higher performance solar cell materials also warrants further attention.

7.4 Block copolymer photophysics

Chapter 6 examined the charge generation consequences of covalently attaching donor and acceptor components, in all-conjugated block copolymers. Block copolymers provide a unique opportunity to control the assembled morphology of a bulk heterojunction, while having the potential to simultaneously tune photophysical interactions at the interface. Synthetically joining donor and acceptor moieties for morphological control introduces a new intramolecular donor-acceptor interface, and the consequences of this linkage were investigated in this work.

Two PFM chains linked to a central F8BT chain, forming the triblock copolymer PFM-F8BT-PFM, and different consequences were observed at the intramolecular interface depending on which constituent was excited. PFM donor excitation resulted in only minor interfacial interaction, apart from energy transfer which occurred in non-polar environments. F8BT acceptor excitation resulted in delayed fluorescence behaviour mediated by a charge transfer state at the block interface. In this case, the conjugated linkage did not provide a significant pathway for charge recombination at the interface,
as has been demonstrated in other block copolymers. While in this particular materials combination, exciplex formation in blends is a primary loss mechanism, this was found to be unrelated to the block copolymer intramolecular interface.

This work highlights the importance of examining the consequences of both donor and acceptor excitation in block copolymers, and the complexity associated with such systems. Despite the challenges of these materials, their simultaneous potential for controlling donor-acceptor morphology and functional interfaces makes them an attractive future prospect for rationally designable materials for organic photovoltaics. Further work in this area could focus on the optimisation of the charge transfer process across the block, potentially utilising known charge separation mechanisms as design strategies, including energetic cascades and charge delocalisation.

7.5 Outlook

OPV heterojunctions are structurally complex and their morphology has been shown to influence every event on the pathway from photon absorption through to the collection of charge carriers. Strategies to gain greater control and tunability over these nanoscale morphologies will need to be employed in order to further optimise device efficiencies and successfully transition to large-scale manufacturing.

Organic semiconductor materials have a unique relationship connecting their structural and optoelectronic properties. However, this role is not straightforward, especially in the solid state, and tools to monitor the key steps of charge photogeneration must be able to incisively investigate these processes. Further improvements in techniques will facilitate a detailed understanding of the underlying photophysics in these systems.

This work has highlighted a few research opportunities for morphological design criteria. From the work presented here it is apparent that strategies for morphological design may sometimes come with unexpected photophysical consequences. For example, subtle changes to bulk heterojunction morphology can induce significant changes in the interrelationship of spin with charge generation dynamics (Chapter 4). Also unexpectedly, room temperature donor-acceptor nanoparticle formation can exhibit morphologies and charge generation properties that are reminiscent of those observed in high temperature processed films cast from chlorinated solvents (Chapter 5).

Strategies to increase OPV device efficiency for the past decade have been dominated by energy level tuning, and to great effect. However, future gains will likely require the development of systematic understanding-based protocols to control active layer morphology and optimise processing techniques.[25] This design must take place within the
context of the intimate relationship that is now becoming clearer between morphology and charge photogeneration, and has now been demonstrated to go beyond the simple picture of exciton diffusion lengths and percolating charge carrier pathways.

Morphological properties cannot be easily predicted a priori, therefore understanding the timescales and influence of bulk heterojunction structure upon key photophysical processes will be vital in developing the next generation of efficient OPV devices. As strategies for rational molecular and morphological design progress, a spectroscopic insight to the consequences for charge generation must continuously inform these approaches. A greater understanding of charge photogeneration in these systems will lead to improved and informed design choices, with the goal of aiding future advances in processable and efficient organic photovoltaic devices.
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31.

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