Spectroscopic investigation of excitonic and charge
photogeneration processes in organic photovoltaic cells

by

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I always start these events with very lofty goals,
like I'm going to do something special. And after a point
of body deterioration, the goals get evaluated down to
basically where I am now – where the best I can hope for is
to avoid throwing up on my shoes.

— **Ephraim Romesberg**

*Nuclear engineer and ultra-runner
65 miles into the Badwater Ultramarathon*

Abstract

Organic photovoltaic (OPV) cells show significant promise as a renewable energy resource capable of meeting the world's large and growing energy needs. Increasing device efficiency is central to achieving an economically viable option for widespread applications. To this end, a better understanding of the structure and dynamics of the electronic excited states is needed. In particular, the mechanism by which excitons (electron-hole pairs) escape their Coulombic attraction and generate photocurrent is yet to be established. In this thesis ultrafast laser spectroscopy, in particular transient absorption and time-resolved photoluminescence, are used to study: exciton relaxation, morphological effects on charge separation, and the pathway leading to triplet exciton states.

In Chapter 3, a series of oligothiophenes are synthesised with well-defined conjugation lengths to act as molecular models of polymer backbone sub-units, and thereby probe exciton relaxation processes. Time-resolved photoluminescence (TRPL) and transient absorption (TA) spectroscopy measurements presented in Chapter 4 reveal emission signatures evolve from a mirror image of absorption - which lacks vibronic structure - towards a spectrally narrower and vibronically structured species on the hundreds of femtosecond to early picosecond timescale. Analysis of this spectral evolution shows that a broad distribution of torsional conformers is driven to rapidly planarize in the excited state, including in solid films. This provides evidence that both torsional relaxation and energy migration could contribute to the non-mirror image absorption-emission spectra observed in polymer thin films.

Recently, long lived TA signatures have been attributed to triplet excited states with the suggested formation pathway being similar to organic light emitting diodes, whereby non-geminate (bimolecular) charge recombination leads to the formation of both singlet and triplet states. Isolated oligothiophenes in solution provide an ideal model system to investigate the role of structural relaxation on triplet exciton formation. Through analysis of TA spectral dynamics in Chapter 5, singlet and triplet exciton populations were tracked. Restriction of the torsional relaxation

increased triplet yield suggesting vibrational hot states could drive triplet formation. This model could aid in understanding triplet exciton formation in polymer-based solar cells via spin-mixing instead of non-geminate recombination.

In a series of polymer:fullerene blends, the link between the nature of polymer:fullerene intermixing and charge generation pathways was investigated. It is shown in Chapter 6 that free charge generation is most efficient in a 3-phase morphology that features intimately mixed polymer:fullerene regions amongst neat polymer and fullerene phases. Distinct spectroscopic signatures made it possible to determine whether holes occupy disordered or crystalline polymer chains. TA spectral dynamics reveal the migration of holes from intermixed to pure polymer regions in 3-phase morphology blends, which contrasted with observations in 2-phase blends. The energy gradient between the intermixed and phase-pure regions may be sufficient to drive efficient separation of charge pairs initially generated in intermixed regions, with free charges subsequently percolating through these phase-pure domains.

The photophysics of a high performance polymer:polymer blend is studied in Chapter 7 in an effort to elucidate how these blends can rival their polymer:fullerene counterparts. Optical spectroscopy reveals incomplete exciton dissociation and rapid geminate recombination in the blends. This is shown to result from a largely phase-separated morphology with domains greater than the exciton diffusion length. Significant loss of charge carriers on early timescales highlights increasing polymer:polymer solar cell efficiency requires optimizing blend morphology to realise facile charge separation.

Taken together, this thesis presents a valuable spectroscopic insight into the pathway of efficient charge separation and the importance of both blend morphology and polymer structure.

Publications

Work carried out during this thesis has contributed to the following publications:

Chapter 3

Chen, K.; **Gallagher, J. K.**; Barker, A. J.; Hodgkiss, J. M. “Transient Grating Photoluminescence Spectroscopy: An Ultrafast Method of Gating Broadband Spectra”, *J. Phys. Chem. Lett.* **2014**, 1732–1737 DOI: 10.1021/jz5006362.

Chapter 4

Gallagher, J. K.; Chen, K.; Huff, G. S.; Prasad, S. K. K.; Gordon, K.; Hodgkiss, J. M. “Evolution of Nonmirror Image Fluorescence Spectra in Conjugated Polymers and Oligomers”, *J. Phys. Chem. Lett.* **2016**, 6, 3307–3312 DOI: 10.1021/acs.jpcllett.6b01185.

Chapter 6

Reish, M. E.; Huff, G. S.; Lee, W.; Uddin, M. A.; Barker, A. J.; **Gallagher, J. K.**; Hodgkiss, J. M.; Woo, H. Y.; Gordon, K. C. “Thermochromism, Franck-Condon Analysis and Interfacial Dynamics of a Donor-Acceptor Copolymer with a Low Band Gap”, *Chem. Mater.* **2015**, 28 (8), 2770–2779 DOI: 10.1021/cm504655f.

Gallagher, J. K.; Prasad, S. K. K.; Uddin, M. A.; Kim, T.; Kim, J. Y.; Woo, H. Y.; Hodgkiss, J. M. “Spectroscopically Tracking Charge Separation in Polymer : Fullerene Blends with a Three-Phase Morphology”, *Energy Environ. Sci.* **2015**, 8 (9), 2713–2724 DOI: 10.1039/C5EE01713K.

Chapter 7

Deshmukh, K. D.; Qin, T.; **Gallagher, J. K.**; Liu, A. C. Y.; Gann, E.; O’Donnell, K.; Thomsen, L.; Hodgkiss, J. M.; Watkins, S. E.; McNeill, C. R. “Performance, morphology and photophysics of high open-circuit voltage, low band gap all-polymer solar cells”, *Energy Environ. Sci.* **2015**, 8, 332–342 DOI: 10.1039/c4ee03059a.

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List of abbreviations

4T	3,3''-dihexylquaterthiophene
6T	3,3''-dihexylsexithiophene
8T	3,3'',3''''',4''''-tetrahexyloctithiophene
10T	3'',3''''''',4,4''''''-tetrahexyldecithiophene
BHJ	bulk-heterojunction
BSF4	dithienyl-benzo[1,2-b:4,5-b]dithiophene:5-fluoro-2,1,3-benzothiadiazole co-polymer
CB	chlorobenzene
COSY	correlation spectroscopy
CT	charge-transfer
DCM	dichloromethane
DIO	1,8-diiodooctane
EET	excitation energy transfer
ESI-MS	electrospray ionisation mass spectrometry
FC	free charges
GSB	ground-state bleach
HMBC	heteronuclear multi-bond correlation
HOMO	highest-occupied molecular orbital
HRMS	high resolution mass spectrometry
HSQC	heteronuclear single quantum coherence
IR	infrared
LUMO	lowest-occupied molecular orbital
m	multiplet
MeTHF	2-Methyltetrahydrofuran
NIR	near-infrared
NMR	nuclear magnetic resonance
ODT	1,8-octanedithiol
OPA	optical parametric amplifier
OPV	organic photovoltaic
P(NDI2OD-T2)	poly([N,N-9-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-bithiophene)
P3HT	poly(3-hexylthiophene-2,5-diyl)

PCBM	phenyl-C[61]-butyric acid methyl ester
PCE	power conversion efficiency
PDTBT	poly(5,6-bis(tetradecyloxy)-4-(2,2'-bithiophen-5-yl)-benzo[c][1,2,5]thiadiazole)
PIA	photoinduced absorption
PL	photoluminescence
PTBO	poly(5,6-bis(tetradecyloxy)-4-(thiophen-2-yl)-benzo[c]-[1,2,5]oxadiazole)
PTBT	poly(5,6-bis(tetradecyloxy)-4-(thiophen-2-yl)-benzo[c][1,2,5]thiadiazole)
PTTBT	poly(5,6-bis(tetradecyloxy)-4-(thieno[3,2-b]thiophene-2-yl)-benzo[c][1,2,5]thiadiazole)
q	quartet
SC	separated charges
SE	stimulated emission
SEM	scanning electron microscopy
SVD	singular value decomposition
t	triplet
TA	transient absorption
TEM	transmission electron microscopy
TGPL	transient-grating photoluminescence
THF	tetrahydrofuran
TRPL	time-resolved photoluminescence
UV-Vis	ultraviolet-visible spectroscopy

Chapter 1

Introducing the fundamentals of organic photovoltaic cells

1.1 Background

Of the numerous applications where conjugated polymers are employed as a fundamental component (*e.g.*, light emitting diodes, lasers, displays, sensors, and transistors), one particular interest is that of organic photovoltaic (OPV) devices.¹ Traditional inorganic and novel organic semiconductors are used in many of the same applications, but the underlying mechanisms are very different. Due to the properties of conjugated polymers being between conventional (inorganic) and molecular semiconductors, the properties and photophysics of conjugated polymers are highly complex, and in many cases far from being understood.²

The classic description of charge generation in OPVs allows for an appreciation as to the challenges associated with charge generation. Upon photoexcitation of a conjugated polymer, an electron-hole pair is formed which is bound through Coulombic attraction. In order to generate free charge carriers, this binding energy must be overcome, typically through the use of a donor/acceptor interface. However, recent studies suggest that this model is too simplistic and that the excited states of polymers evolve over a broad range of time scales and involve exciton relaxation, localisation, and energy transfer processes that are influenced by dynamic polymer chain conformations.³ These reports have contributed to a revived focus on the nature of primary photoexcitations in organic photovoltaic blends because of their importance to resolving significant questions posed by recent developments.

There are several notable discrepancies between the simple description of an OPV device operation and experimental evidence. First, the appearance of charges in efficient heterojunction blends within 100 fs.⁴⁻⁸ With domain sizes on the order of 10 nm, this timescale is much shorter than the time it would take for an exciton to diffuse to an interface.⁹ Second, free charges can be generated in neat polymer films which lack a donor/acceptor interface.¹⁰ Third, recent investigations suggest that free charge carrier generation in OPVs is influenced by short-lived delocalised states.² These reports highlight that the question of how charge pairs overcome their mutual Coulomb attraction is far from resolved.^{11,12}

This chapter provides a brief overview of the properties of conjugated polymers and the properties of the excited states they form. The implication this has on the operation of an organic photovoltaic (OPV) device is reviewed through a summary of the basic model used to describe photocurrent generation in these devices. The emerging theories regarding how excitons escape their Coulombic attraction and generate photocurrent. Whereby understanding the nature of the initial excitations in conjugated polymers, the importance of higher lying excited states on charge transfer, and the efficiency of morphology on charge separation have all recently received considerable attention. In spite of these recent developments the interplay of these factors in the mechanism of photocurrent generation in OPV devices, and design principles towards increased device efficiency is yet to be established.

1.2 Properties of conjugated polymers

Organic semiconductors rely on the presence of π -orbitals for their electron transport and optical properties. The electronic conduction in π -conjugated polymers originates from the sp^2p_z wave functions of the carbon atoms in the repeating unit.¹³ The σ bonds (from sp^2 hybridisation) between carbon atoms provides the structural component of the polymer, whilst the orthogonal π -bonds (formed from p_z orbitals) creates the chain of delocalised electron density, giving rise to the conductivity.¹⁴

Photoexcitation of a conjugated polymer results in electronic excitation, which is typically delocalised over a variable number of monomer units.³ The primary photoexcitation in conjugated polymers are not free charge carriers, but rather a singlet excited state in which the electron and hole are still influenced by a strong Coulomb attraction.¹⁵ This bound electron-hole pair is known as a singlet exciton. One important feature of π -conjugated systems is the strong electron-phonon (vibration) couplings, most commonly a C=C stretching vibration (0.17 eV), and a lower frequency

torsion.¹⁶ As a result, following photoexcitation, the electronic excited state relaxation is accompanied by a perturbation of the molecular structure.¹⁷ This structural relaxation results in bond length changes and to local planarisation.¹⁵ Therefore, the term exciton encompasses both the electronic excitation and the local structural deformities it induces.

Although in theory a conjugated polymer can form a linear one dimensional π -conjugated chain, structural disorder results in a distribution of subunits that can act as effective chromophores.^{3,18} This is schematically shown in Figure 1.1. Each of these conformational subunits are able to act as individual chromophores. The electronic excitation of a chromophore is able to be transferred to nearby chromophores by a process of electronic energy transfer, providing two key conditions are met.¹⁹ Firstly, there must be an electronic coupling between the two chromophores, often described by a Coulombic dipole-dipole interaction of transition dipoles.²⁰ Secondly, the donor fluorescence spectrum must overlap with the acceptor absorption spectrum, thereby ensuring conservation of energy.^{3,21} Although all of these units can absorb light, electronic energy transfer processes funnels the excitation energy to the lowest energy site (Figure 1.1). This energy transfer can occur intramolecularly when polymer chains are in an open chain conformation, or intermolecularly in a more aggregated polymer conformation.

Figure 1.1 Conformation of a polymer showing conjugation breaks from structural disorder create chromophoric subunits which vary in conjugation length. Intra- and interchain energy transfer funnels the excitation to the lowest energy subunit. Figure reproduced from Collini *et al.*¹⁸

The optical band gap of the absorbing chromophore is governed by the degree of delocalisation. Therefore, the degree of π -conjugation (*i.e.*, the length) of each chromophore determines the energy of the lowest electronic excited state. Through application of the particle in box model the more delocalised the electron density in a chromophore, the lower the energy required for excitation. Typically conjugated polymers exhibit a broad structureless absorption spectrum, whilst the emission spectrum is narrow and exhibits vibronic structure. The energy distribution (*i.e.*, broadness) can be rationalised by noting that photoexcitation results in absorption from effectively all conformational subunits, whereas the energy funnelling results in emission by a select subset of units. Therefore, subunits can be excited with a broad energy distribution, whereas the distribution of emission energies is much more narrow.³ Excitation energy transfer (EET) processes occurring following photoexcitation of a conjugated polymer have also been employed to explain the signatures of steady-state optical absorption and emission spectra.²² Emission from an excited chromophore subunit is typically lower energy than the absorption (Stokes shift). If a short subunit is in close proximity to longer (and hence lower in energy) subunit, large spectral overlap integral between the emission of a short unit and the absorption of the longer unit allows this energy transfer process to be energetically favourable.

The time scales of EET processes are shown in Figure 1.2 and show that there are two distinct modes of EET that occur, a fast ('downhill') component, and an iso-energetic process.²³ Reports in the literature show that the rate of energy transfer is dependent on the energy of the excitation. If the polymer is excited at higher energy than the red edge of the absorption spectrum, predominately chromophores with blue-shifted absorption are excited, corresponding to short conjugation lengths.²⁴ Emission from such a chromophore will have good spectral overlap of red-shifted (longer) chromophores, and provided that two subunits are in close proximity and have favourable geometrical factors, Förster-type EET can occur. Such a situation leads to fast excitation transfer and to migration of the exciton towards sites with the reddest possible absorption.^{23–25} These red-shifted states are often called 'trap states' since they are of the lowest energy, and the EET process referred to as 'downhill'.

If the excitation energy is close to the red edge of the polymer absorption spectrum, chromophoric segments with the largest conjugation length (red-shifted) are predominately excited. The excited state is already energetically close to a trap state (or a trap state is directly excited) and therefore the conditions after light absorption resemble those at the completion of downhill EET. The formation of a low energy state surrounded by high energy states means EET is unlikely.²³ However,

Figure 1.2 Time scales of excitation energy transfer in conjugated polymers. Figure adapted from Scheblykin *et al.*²³

thermal fluctuations can cause spectral broadening of states (through structural relaxation) which may allow for significant overlap and result in energy transfer. Since states involved in this process are very similar in energy, the transfer can be considered iso-energetic (see Figure 1.2). This type of energy transfer is sensitive to the structural order of the polymer, *e.g.*, well-ordered polymer chains may have sites of similar energy in close proximity to one another, so this process occurs on longer time scales.

Recent studies suggest this model is too simplistic due to the excited states of conjugated polymers evolving over a broad range of time scales, and involving multiple process influenced by the dynamic polymer chain.^{3,26} Time-resolved spectroscopic measurements on conjugated polymers have attributed relaxation dynamics following photoexcitation to a combination of conformational relaxation and excitation energy transfer.²⁷⁻²⁹ However, these studies lacked intrinsic oligomer inputs in order to investigate the relaxation processes. Indeed, theoretical studies have suggested that the non-mirror image absorption-emission spectra are an intrinsic property of oligomer chromophores.³⁰ This highlights the need to further investigate the processes that occur after photoexcitation. In particular, how does structural relaxation effect the observed spectral dynamics in conjugated polymers? What are the intrinsic exciton relaxation processes of sub-units? And are these dependent on sub-unit conjugation length?

1.3 Organic photovoltaic devices

1.3.1 From excitons to charge separated states

Due to the formation of excitonic states upon photoexcitation of π -conjugated polymers, photocurrent generation in OPVs relies on overcoming the binding energy of the exciton to generate free charge carriers. This needs to occur before relaxation to the ground state and is a critical component of efficient OPV cell operation. Early OPV cells that had an active layer comprised of pure conjugated polymers yielded power conversion efficiencies (PCEs) on the order of 0.01%.³¹ A breakthrough in device performance was realised through the measurement of efficient quenching of polymer photoluminescence via the photoinduced electron transfer from a conjugated polymer to C₆₀-fullerene.^{32,33} This led to the design principle that OPV cells consist of an interface between an electron-donor material and an electron-acceptor material, known as a heterojunction.^{2,34} The structure of the heterojunction has recently been revealed to be more complex than initially proposed, with the specific details of film morphology in OPV blends reserved for discussion later in this chapter.

The classic description of photocurrent generation in a donor-acceptor polymer based OPV blend are shown in Figure 1.3, and outlined as follows: (1) The absorption of a photon in the donor component promotes an electron from the highest occupied molecular orbital (HOMO) into the lowest unoccupied molecular orbital (LUMO) of the donor, to yield a bound electron-hole pair (*i.e.*, an exciton). (2) Relaxation occurs whereby the exciton is driven to lower energy sites in the donor *via* excitation energy transfer processes. (3) This relaxation causes the exciton to diffuse through the donor phase and could result in the exciton reaching a donor-acceptor interface. (4) The energy offset between donor and acceptor LUMO levels can promote electron transfer into the LUMO of the acceptor, resulting in the formation of a charge transfer (CT) state. This occurs providing the energy offset ($E_{\text{donor LUMO}} - E_{\text{acceptor LUMO}}$) is greater than the Coulomb binding energy of the exciton resulting in the electron transfer being energetically downhill.³⁵ (5) The charge pairs in the CT state may subsequently overcome the Coulombic attraction and fully dissociate to yield free charges (also termed separated charges). These can then undergo transport through the respective components to electrodes and contribute to extractable photocurrent.

One important feature of this model is the formation of a CT-state following electron transfer. Owing to the close physical proximity of donor and acceptor molecules,

Figure 1.3 Energy level diagram showing a simplified viewpoint of charge photocurrent generation in polymer-based OPV cells. (1) Photoexcitation generates an exciton, (2) relaxation to low energy states, (3) exciton migration to a donor-acceptor interface, (4) electron transfer across the interface, and (5) separation of the electron and hole which can be extracted and photocurrent.

electron transfer only yields a moderate spatial separation of the electron and hole, typically the same order of magnitude of the size of the molecules involved.^{2,15} This small spatial separation maintains some Coulomb attraction between the electron and hole known as the CT-state binding energy, and in principle can be a source of energetic barrier towards charge separation.³⁶ If the electron-hole pair recombine before separating, the process is termed geminate recombination.^{37,38} It is also worth noting that the formation of separated charges does not necessarily promise extractable photocurrent due to the possibility of free charge carriers reaching a different donor-acceptor interface during migration to the electrodes. Such an event would yield non-geminate (bimolecular) recombination of charges, decreasing the population of charges able to contribute to extractable photocurrent.³⁹

Additionally, energy migration itself could be hindered through the formation of exciton traps. The common trap site in organic semiconductor polymer films occur through exciton self-trapping. This is where localised conformational relaxation decreases the torsional disorder between two short chromophore sub-units, which increases the electronic coupling between them. This results in two high-energy sub-units being converted into a single sub-unit which has a longer conjugation length. This lowering in exciton energy can cause a trap site whereby the energetic landscape alters to have a low energy sub-unit surrounded by sub-units of higher energy, thereby preventing energy migration.

1.3.2 Morphology dependent device efficiency

The active layer of OPV cells consists of a blend of donor and acceptor materials in order to promote separation of excitonic species. The first devices made of this nature involved a simple bilayer structure, schematically represented in Figure 1.4A. This layer architecture has limitations such as a small surface area between donor-acceptor interfaces, and also the requirement of facile diffusion in order for excitations to reach an interface within the exciton lifetime.^{40,41} Owing to the limited lifetime of excitons, loss of charge carriers before migration to an interface is a main contributor to bilayer devices suffering from poor PCE values. A step forward in device performance was realised through the introduction of a bulk heterojunction (BHJ) structure, first reported independently by Heeger *et al.* and Friend *et al.* using polymer:fullerene and polymer:polymer blends.^{33,42} A BHJ morphology, Figure 1.4B, involves mixing of donor and acceptor molecules in the bulk of the OPV active layer to create a bicontinuous interpenetrating network. This increases the surface area of donor-acceptor interfaces thereby increasing the probability of an exciton diffusing to an interface to undergo separation within its lifetime. Free charge carriers are then able to migrate through the donor or acceptor domains (known as percolation pathways) to the electrodes for extraction.

Figure 1.4 Schematic representation of donor:acceptor blend morphologies, in a bilayer morphology (A) excitons may decay before reaching an interface. In the interpenetrating donor:acceptor network of a bulk heterojunction morphology (B) the exciton is able to diffuse to an interface and undergo separation.

Although modern OPV active layers adopt this general BHJ structure, early research revealed that the donor-acceptor phase separation (morphology) plays a critical role in free charge yield.^{43–45} The finite exciton lifetime means the diffusion length is approximately 10 nm in these materials.⁴⁶ Thus, the domain size of both donor and acceptor components should be small enough to optimise exciton migration to an interface. However, if the domains are too small the probability of bimolecular recombination between charge carriers increases. The balance of these factors leads

to a rule-of-thumb that BHJ domain size should be 10–20 nm to enable efficient charge generation.⁴⁷

Fine-tuning the arrangement of donor and acceptor components in a BHJ morphology has received considerable interest in the journey towards improving device efficiency.^{47–49} One common approach is the use of solvent additives during the spin casting of the polymer-based active layer. The first report of this utilised a small amount of 1,8-octanedithiol (ODT) added to a polymer:fullerene blend, yielding a PCE increase from 2.8% to 5.5%.⁵⁰ It was found that ODT is able to solubilise the fullerene component in the host solvent (*e.g.*, chlorobenzene). The ODT additive has a higher boiling point and evaporates slower than the solvent. This results in the fullerene being dissolved in the host solvent for longer, compared to without additive, and in particular staying in solution longer than the polymer component. This leads to improved crystallinity of the polymer as well as control over the phase separation during the spin-casting process.^{47,51} It is these two factors that are optimised through selection of particular solvent additives in order to improve device efficiency.

Another approach to improving polymer crystallinity and phase separation is to anneal the OPV blend after the spin-coating process. This can be achieved via thermal or solvent vapour approaches.^{44,47,52,53} In general, thermal annealing requires heating the film above the glass transition temperature of the polymer to allow a self-reorganisation to promote ordered crystalline polymer domains. In a similar vein, solvent vapour annealing is achieved by placing the spin-cast film in a closed chamber filled with solvent vapour which can partially dissolve the film components to alter the crystallinity and phase separation morphology.

With the improvement of structural characterisation techniques the complexity of the morphology in a BHJ has been realised.⁴⁸ The basic view outlined here has the BHJ consisting of interpenetrating pure donor phases and pure acceptor phases, known as a 2-phase BHJ. However, this view has been revealed to be too simplistic with recent investigations having identified the presence of an intermixed donor:acceptor phase in addition to the pure phase domains.^{54–63} The details of this 3-phase BHJ morphology, and its importance to device performance will be discussed in further detail in the subsequent sections when reviewing the emerging theory of free charge photogeneration.

1.4 Emerging theory of free charge photogeneration

The pathway to free charge photogeneration in OPV devices is receiving considerable attention owing to several significant discrepancies between the classic mechanism obtained through considering the heterojunction and experimental results. First, Brabec *et al.* showed in 2001 that the yield of generated charges in efficient heterojunction blends can occur within 100 fs, with the formation of charge-transfer (CT) states in ~45 fs.⁷ This is supported by several subsequent studies on other high-efficiency blends.^{4–6,8} Applying point-like excited state diffusion and measured exciton diffusion coefficients, in 100 fs these states can only migrate on the order of 0.1–0.2 nm.^{9,46} Yet free charge carriers are found to be generated with significant yields in polymer blends with 10 nm polymer domain sizes, which cannot be explained simply through excitons diffusing to reach an interface. Secondly, it has been observed that charges can be photogenerated on these timescales even without the presence of donor:acceptor interfaces to separate excitons.¹⁰ Third, recent theoretical and experimental studies were published spanning 2009–2013 suggesting that short lived delocalised excited species may provide the driving force for exciton separation.^{2,64–66} A key study in the literature regarding the mechanism of charge generation (and its divergence from what was previously thought) was published in Science by Bakulin *et al.* in 2012.⁶⁵ This result provided experimental evidence that delocalised excited states could provide a driving force for charge separation. Fourth, the complex nature of the donor:acceptor phase morphology has been revealed and its role in charge generation cannot be overlooked.^{54–63} Taken together, these raise the questions: how do charge pairs overcome their mutual Coulomb attraction to separate? How do the complex conformational dynamics of a conjugated polymer chain affect this process? And what is the exact role of mixing morphology on the efficient pathway to free charge photogeneration? This section provides an account of some emerging theories in the literature aimed toward addressing these questions, and highlights the challenges that lie ahead.

1.4.1 Ultrafast exciton localisation

There is extensive experimental evidence that show relaxation processes in conjugated polymers after photoexcitation occur within tens to hundreds of femtoseconds.^{12,64} One such example was reported by Banerji *et al.* who investigated the excited state photophysics of poly-3-hexyothiophene (P3HT) using time-resolved photoluminescence spectroscopy.²⁸ Figure 1.5 presents the steady-state optical absorption

and photoluminescence (PL), overlaid with the reported time-resolved PL spectral slices. The time resolution of the experiment was 200 fs, however, even at the earliest measurement the PL spectral position is already strongly red-shifted compared to the absorption, and overlaps with the steady-state PL spectrum. The authors also noted that the PL spectrum at 200 fs is relatively narrow compared to the mirror image of the absorption spectrum, and lacks the lower energy vibronic (0-1) peak, which is apparent in longer delay PL spectra.²⁸

Figure 1.5 Normalised time-resolved PL spectra of a P3HT thin film overlaid with the steady-state optical absorption and photoluminescence spectra. The PL time slices correspond to 200 fs, 500 fs, 2 ps, 50 ps after photoexcitation. Figure reproduced from Banerji *et al.*²⁸

The overlapping spectral position of the PL at 200 fs compared with the steady-state indicates that a large component of the structural relaxation following photoexcitation must occur within this ultrafast timescale, since no Stokes shifting dynamics are resolved. These spectral features suggest either a different nature of the emitting state, and/or a reduction of conformation inhomogeneity on the ultrafast time scale.²⁸ Moreover, the earliest PL spectrum in the P3HT film is similar with either 400 or 500 nm excitation, even though amorphous (high energy) or aggregated (low energy) regions of the polymer are excited with these wavelengths. From this Banerji *et al.* proposed that ultrafast relaxation results from either migration of excitation from amorphous to crystalline segments, or a conversion of amorphous to aggregated chains via conformational dynamics such as torsional motion.¹² These conclusions rely on the classic description of OPV photocurrent generation (see Section 1.3.1) being correct, and that the energy transfer must happen faster than what can be resolved.

A tool that is often used when probing relaxation of electronic excited states is that of polarisation anisotropy. When a randomly oriented sample is illuminated with polarised light, the chromophores with absorption transitions aligned parallel to the vector of the polarised excitation have the highest probability of excitation. Therefore, a population of excited chromophores which are aligned close to the axis

of polarisation is obtained. The extent of polarisation of the emission is described in terms of the anisotropy (r), which is calculated using the following:⁶⁷

$$r = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}} \quad (1.1)$$

Where $I_{\parallel}$ is the intensity when the detector polariser is oriented parallel ($\parallel$) to the excitation polariser. Likewise, when the polarisers are perpendicular ($\perp$) the intensity is called $I_{\perp}$. PL anisotropy is independent of the total intensity of the sample because the difference ($I_{\parallel} - I_{\perp}$) is normalised by the total intensity ($I_{\parallel} + 2I_{\perp}$). A reduction in the degree of the polarisation of the PL will occur when the orientation of the chromophore changes before re-emitting a photon. This makes the technique a good probe of excited state dynamics because relaxation processes may cause the nature of the excited species to change, in particular the orientation of the excitation during relaxation. The maximum theoretical value of anisotropy for a dipole absorption in the absence of any relaxation processes is 0.4.⁶⁷

A commonly observed feature of relaxation processes is the decay of anisotropy (loss of polarisation) in time-resolved measurements.^{68–70} The PL anisotropy of a P3HT thin film measured in the study by Banerji *et al.* previously mentioned showed that at the earliest possible measurement (200 fs) the anisotropy is 0.2, significantly below the value expected in the absence of relaxation processes. This shows that an ultrafast relaxation process has already occurred within the time resolution of the experiment. Although the anisotropic decay was unresolved by those authors, other reports show a anisotropic decay component of <100 fs for other polymer systems.^{25,70}

This ultrafast relaxation occurs too fast to be explained by the Förster-type excitation energy transfer processes. This has provoked the suggestion that a primary excitation is initially delocalised and spans a distribution of polymer chain orientations.³ This is schematically shown in Figure 1.6. Immediately after photoexcitation the formation of a delocalised excitation samples multiple subunits, each with a dipole moment, yielding a range of dipole orientations contained in the excitation. During the localisation, only one (or some subset) of the subunits initially excited will be involved in the excitation. Therefore, the reduced anisotropy arises since only emission from the localised excitation is detected, rather than the distribution that were initially excited.

The nature of this primary, delocalised, excitation was recently investigated by Chen *et al.* using broadband time-resolved PL spectroscopy on polymer thin films.⁶⁴

Figure 1.6 Immediately after photoexcitation a broad distribution of polymer backbone subunits are excited, each with a dipole transition moment. As the exciton localises, there is a loss of anisotropy since emission is only detected from this localised excitation, not the distribution initially excited.

This resolved high-energy emission on the sub-picosecond timescales before energetic relaxation. Coupled with theoretical calculations, it was confirmed that excitons initially extend along the polymer chain prior to the localisation. The authors were able to probe the volume of this excitation by exploiting annihilation effects at high excitation intensity and resolved that the volume of the delocalised exciton was 17 nm^3 within 100 fs.⁶⁴ Put into perspective, if the interchain stacking in a polymer network is 0.8 nm, and a cylinder is a representative geometric shape, then the delocalised exciton spans 9 nm in length.

This localisation is a complex processes and is thought to be caused by a number of combined processes and is still a matter of debate in the literature.¹² Theoretical studies have suggested that quantum coherent energy transfer processes in the intermediate coupling regime may be significant in the localisation process.^{18,68} This implies that electronic relaxation to a localised lowest-energy state occurs through a series of delocalised states. However, structural distortion through nuclear relaxation needs to be considered since the excited state transitions of conjugated polymers are strongly coupled to nuclear modes, in particular the C=C stretching vibration and torsion. Structural relaxation following photoexcitation could cause exciton self-trapping. This occurs if the conjugation between two subunits reaches a point where they become a single unit, thereby reducing its overall energy and causing an apparent localisation.³

Theoretical studies have shown that the conformational disorder present in the electronic ground state is responsible for breaking the polymer chain into chromophores subunits.^{71,72} Following photoexcitation the Franck-Condon molecular conformation relaxes towards a new equilibrium geometry which has more rigid torsional modes resulting in the thermally equilibrated excited (thexi) state having a planar geometry.^{73,74} Therefore, the excited state photophysics may not be explained solely

through energy migration processes, and instead structural relaxation has an important contribution to relaxation pathways in conjugated polymer systems. The relevance to charge photogeneration has recently been highlighted by Grancini *et al.* who showed the formation CT states can occur within 50 fs in donor:acceptor blends.^{5,75} This is the same timescale as exciton localisation and structural relaxation, suggesting that a crucial aspect of charge photogeneration is the nature of the polymer excited state immediately after excitation. Investigating the intrachain localisation is difficult in a polymer system owing to the diverse range of sub-units present, with no simple way of only sampling a defined subset. Insight to the relaxation photophysics, and testing the proposed models in the literature, could be obtained via molecular model compounds which represent the polymer backbone subunits.

1.4.2 Delocalised states and charge separation

As discussed earlier, the generation of photocurrent in an OPV device requires the dissociation of the bound excitonic excited states of the polymer. The previous section highlights how above band-gap excitation of conjugated polymers results in Franck-Condon excited states (termed ‘hot’ states) which are delocalised in nature, which then undergoes exciton localisation before exciton migration. A recent study by Bakulin *et al.* investigated the role of above band gap excitation of polymers in OPV devices, demonstrating delocalised states play an important role in free charge generation.⁶⁵ The results are summarised in the energy level schematic in Figure 1.7. After initial excitation, excitons localise at the donor:acceptor interface to form a charge transfer (CT) state. The excess energy provided by the excitation populates CT states which are 0.3–1 eV above the lowest lying CT₀ state.⁶⁵ This charge-pair undergoes relaxation which is evidenced by a red-shifted CT state emission.⁷⁶ To repopulate these, the authors selectively excited the CT₀ to CT_n transition using an infra-red (IR) ‘push’ pulse, which is too low in energy to form additional singlet exciton states of the conjugated polymer. The re-excitation of CT₀ to CT_n states was confirmed using pump-probe-push transient absorption (TA) spectroscopy, which showed fewer CT₀ states were occupied by excitation after the push pulse.

To probe the role of CT_n states on OPV device performance, Bakulin *et al.* performed an electro-optical pump-push experiment on working OPV devices to measure the photocurrent as a function of time.⁶⁵ The repopulation of hot CT states caused an increase in photocurrent within 200 fs of the push pulse arrival. Such a short timescale suggests that the species formed immediately after re-excitation was involved in the formation of separated charges. Computational studies on the

Figure 1.7 Energy diagram illustrating the energy pathways involved in generating separated charges (SC) through repopulating hot CT states (CT_n) after initial relaxation. Figure adapted from Bakulin et al.⁶⁵

nature of the CT states reveal that the CT_0 states are more localised than the higher-lying CT_n states.⁶⁵ The authors proposed that hot CT states have a strong energetic driving force for separation owing to their delocalised nature reducing the energetic barrier through a greater spatial separation between the electron and hole. By re-exciting thermally relaxed CT states to hot delocalised CT states, the charge pairs are provided a further chance to separate.

The standard model of photocurrent generation in heterojunction based OPV devices predicts that upon above-band-gap excitation the excess photon energy is rapidly lost through internal conversion type processes, resulting in wasted energy.^{15,77} Reports in the literature propose that the excess energy of the CT state contributes to long range charge separation,⁷⁸ while other reports question this interpretation.⁷⁹ Bakulin *et al.* probed this by investigating the effect of the push pulse experiment using an initial below-band-gap excitation which populated CT states directly at the interface, rather than *via* exciton dissociation.⁶⁵ The re-excitation of hot CT states again increased the photocurrent of the device, demonstrating that excess energy associated with the exciton is not a requirement for charge separation, but rather the delocalised nature of the CT states could provide the energetic driving force.⁶⁵

CT states can form within 50 fs after photoexcitation in donor:acceptor blends which is similar timescales as the relaxation of the polymer excited state immediately after excitation.^{5,75} This means after photoexcitation there are several plausible explanations to the nature of the excitation. First, rapid formation of CT delocalised states at an interface which can undergo separation immediately. Second, highly delocalised excitons are formed which could have a reduced energetic barrier of

separation owing to the spatial separation between charge pairs. Or third, excitons formed are delocalised such that they sample across a donor acceptor interface. The relevance of delocalised excitations to charge photogeneration is supported by a report from Chen *et al.* which shows delocalised hot excitons formed immediately after photoexcitation can separate to form charges without passing through the CT manifold.⁶⁴ Furthermore, it was proposed that the delocalised hot excitons could account for the ultrafast time scale of charge generation observed in efficient OPVs.

A recent study by Barker *et al.* has highlighted the need to understand the relaxation of initial excited states through the revelation that long range charge separation occurs within the thermalisation (state cooling) timescales of CT states.¹¹ The authors were able to measure the distance distributions of thermalised charge pairs by freezing them (at 10 K) following the primary charge separation, resulting in recombination only via monomolecular tunnelling. A summary of the findings are presented in Figure 1.8. TA spectroscopy was used to examine the charge recombination for a range of OPV blends and showed evidence of 2 different populations recombining with different tunnelling rates (upper right panel in Figure 1.8). This is consistent with the different populations corresponding to CT states and separated charges (SCs).¹¹ Fitting tunnelling recombination rates it was shown that free charge generation occurs via CT states which have a separation distance between charge pairs of 3–4 nm.¹¹

Figure 1.8 Charge pair distances measured by freezing charge pairs after thermalisation such that recombination occurs via tunnelling dynamics. Two populations were identified in the recombination, which related to charge transfer (CT) states and separated charges (SC). It was proposed that free charge yield is determined within the thermalization time scale. Figure reproduced from Barker *et al.*¹¹

Further to this, Barker *et al.* also observed that the yield of separated charges in the low temperature regime is strongly correlated with the yield of free charges at room temperature.¹¹ This relationship was observed for a wide range of polymer:fullerene blends studied by the authors. This supports a model whereby the fate of charges is determined during the thermalisation of CT states. On this timescale, charge pairs which achieve the critical separation distance (3–4 nm) will separate, whilst

all others will be lost to recombination. This suggests that it is hot CT states which are able to contribute to extractable photocurrent in an OPV cell.¹¹ This highlights that the relaxation of hot excited states is a critical aspect of free charge photogeneration.

It is noteworthy that the method of freezing charge pairs following the primary charge separation step and following their recombination is useful to test current models of charge separation; however, this method is unable to provide information on the process leading up to charge separation. The question still remains regarding the delocalised nature of the primary excitation and if it promotes direct long range charge diffusion and charge separation. Indeed, the authors found that the yield of free charges was dependent on the formation of fullerene crystalline domains.¹¹ This highlights that the role of donor:acceptor phase morphology, and how this impacts the pathway toward efficient charge separation is far from understood.

1.4.3 Morphologically driven charge separation

The importance of polymer:fullerene blend morphology on device power conversion efficiency is reflected by charge separation at a heterojunction not necessarily generating useful photocurrent, that is, extractable charges.^{80–83} Early studies on polymer:fullerene systems have highlighted the importance of balancing exciton diffusion with the percolation of free charge carriers through the nanoscale morphology.^{34,84} Indeed, the charge generation photophysics was shown to be sensitive to blend morphology in a range of polymer:fullerene systems.^{6,85–87} However, in spite of this knowledge the question of how charge pairs overcome their mutual Coulomb attraction to separate was not completely resolved.^{11,65,88,89}

As mentioned earlier, the heterojunction structure has recently been revealed to be more complex than the 2-phase morphology initially proposed. Not only can polymer and fullerene blends form either phase-pure amorphous or crystalline domains, recent investigations have identified an intermixed phase being present in a wide range of polymer:fullerene blends.^{55,56,58–63} The first report of an intermixed phase was identified in a blend of poly(2,5-bis(3-hexadecylthiophen-2-yl)thieno-[3,2-b]thiophene (pBTTT) and [6,6]-phenyl C₆₀ butyric acid methyl ester (PCBM), whereby the two components formed an ordered intercalated co-crystal.⁵⁴ The crystallinity of this intermixed phase allowed its composition to be probed using X-ray scattering techniques, which revealed the structure to involve PCBM molecules intercalated between the side-chains of ordered polymer domains. This co-crystal morphology was also shown to be sensitive to processing conditions during film preparation.⁹⁰

It can not be overlooked that the highest device performance in polymer:fullerene blend OPVs is typically obtained with a three-phase microstructure consisting of neat domains as well as intermixed regions.^{54,57,91} This has led to the proposal that this 3-phase morphology is able to improve yields of charge separation and collection, and could present as a solution to the problem regarding what drives charge pair separation.^{56,62,63,92,93}

Recently, Scarongella *et al.* investigated the role of morphology on the pathway of charge generation in the pBTTT:PCBM blend using transient absorption (TA) spectroscopy.⁹⁴ In a 1:1 blend of pBTTT:PCBM, a fully intercalated co-crystalline domain was formed yielding a one phase morphology (Figure 1.9A). In this morphology most charge pairs generated after charge transfer recombine geminately within 100's of picoseconds, and only a small fraction are able to overcome their mutual Coulomb binding energy.^{54,90,95} This is consistent with the low power conversion efficiency (PCE) observed in a device using this blend. With a 4-fold excess of PCBM the co-crystalline regions were accompanied by neat PCBM clusters, resulting in a two phase morphology (Figure 1.9B). This suppressed the rate of geminate recombination, evidenced by a longer lifetime of TA spectral signatures associated with charge pairs. It was proposed that this is explained by favourable spatial separation of charge pairs formed in the co-crystalline domains,⁹⁴ owing to the higher electron affinity of pure PCBM clusters creating an energy cascade.⁹⁶ This could provide a driving force to remove electrons from the co-crystal phase at a rate that competes with geminate recombination. For comparison, a fully phase separated (simple 2-phase BHJ) morphology (Figure 1.9C) has a greater charge yield than the fully intercalated morphology, but less than the morphology containing pure PCBM clusters.⁹⁴

Solvent additives allowed Scarongella *et al.* to control the formation of a 3-phase morphology (Figure 1.9D) whereby co-crystalline regions, PCBM clusters and neat pBTTT domains were present.⁹⁴ In the presence of this 3-phase morphology, they resolved an electro-absorption signal in TA spectra that arises in the specific electrostatic environment of the co-crystal. The photogeneration of charges in a polymer:fullerene blend results in a localised electric field which can perturb the energy levels of molecules in close proximity.⁸⁸ This causes a change in dipole moment or polarizability between the ground and excited states, known as the Stark effect.⁹⁷ The electro-absorption signature in TA spectroscopy was exploited by Scarongella *et al.* to determine in which phase of the blend the charges reside, and probe their spatial separation. The decay of this electro-absorption signature occurred on the sub-picosecond timescale, and is indicative of hole transfer from co-crystal domains into pure pBTTT crystals.⁹⁴ Charge pairs are also found to be more localized

Figure 1.9 Schematic representation of four investigated microstructures for a pBTTT:PCBM blend obtained *via* changes in processing conditions. Figure adapted from Scarongella *et al.*⁹⁴

and short-lived in co-crystals compared with pure phases.⁹⁸ Importantly, transfer of charges out of the intermixed co-crystal domains was found to suppress geminate charge recombination.

In other high efficiency polymer:fullerene blends the intermixed phase is generally more amorphous rather than crystalline, often making its role in charge generation harder to directly resolve.^{55,57,59–63} However, owing to fullerene crystals exhibiting >100 meV higher electron affinity than dispersed fullerene,⁹⁶ combined with holes which may be stabilized by >300 meV in pure polymer phases compared with amorphous intermixed phases,⁹⁹ the energetic landscape formed from coexisting pure and intermixed amorphous phases may provide the driving force for charge separation. This has resulted in the theory that charge pairs generated in the intermixed region may be driven into pure phases via this energetic bias, as well as diffusion to account for the improved device efficiencies in these blends. Spectroscopic investigations have shown that central to device efficiency is the yield of long-lived free charges, as these are the only charges which are able to contribute to extractable photocurrent.⁹⁶ However, if the pathway of charge generation is morphologically driven, then it must be occurring on much earlier timescales. Therefore, the proposed energy cascade caused by amorphous and intermixed domains is yet to be directly tested. Additionally, if the morphology is central to efficient spatial separation of charges, establishing the time scales of this process could be vital for improved design principles for efficient OPV active layer microstructures. A major difficulty in probing the morphologically driven charge separation results from the timescales

in question having possible contributions from numerous processes, such as exciton relaxation, exciton separation, or geminate recombination on the femtosecond to nanosecond timescale; and on slightly longer timescales (nanosecond-to-millisecond timescale), charge migration, and bimolecular recombination of free charges. This requires a structure-property investigation whereby the morphology can be tuned without changing the electronic properties of the material, since that could alter the energetic driving force of photoelectron transfer between donor and acceptor components.

1.4.4 Triplet states as a limit on efficiency

Considerable efforts toward improving OPV device efficiency have relied on increasing the understanding of charge transfer (CT) state dynamics, as this is a critical component of photoconversion efficiency. In an OPV device the power conversion efficiency is affected by the open circuit voltage, which is determined by the CT state energy.^{100,101} CT state energy is defined as the difference between donor ionisation potential energy and the acceptor electron affinity, plus a CT state binding energy of 0.1–0.5 eV. In the quest for improved device efficiency, conjugated polymer design has led to the synthesis of low-band gap polymers which absorb lower energy photons of the solar spectrum. In high-band gap polymers, such as poly-3-hexylthiophene (P3HT), the lowest lying polymer triplet (T_1) state is higher in energy than the CT state. In contrast, Veldman *et al.* have shown that in low-band gap polymers the polymer T_1 state is actually lower in energy than the CT state.¹⁰² Importantly, the relaxation of triplet CT states to triplet excitons is emerging as a major loss mechanism in OPV cells.^{103–107}

Understanding CT state dynamics typically involves studying the photophysics of CT states formed directly from photogenerated excitons. The properties of CT states formed via electron-hole encounters during charge migration has received far less attention. Recently, it has been proposed that bimolecular recombination of free charges in OPVs could be analogous to the underlying mechanism in organic light-emitting diodes (OLEDs), whereby recombination of electron and holes can lead to the formation of charge transfer states with spin-singlet (^1CT) and spin-triplet (^3CT) characteristics.^{102,103} Since low band-gap polymers have a T_1 state lower in energy than the CT state, the formation of CT states in the triplet manifold could activate a relaxation pathway to form triplet exciton traps, which would normally be spin-forbidden for ^1CT states, and energetically unfavourable in high-band gap polymers.

Figure 1.10 shows the bimolecular recombination pathways in OPVs taking into consideration the spin characteristics of free charges.¹⁰³ As free charge carriers migrate through the device active layer, there is a chance that charges will encounter one another at a donor:acceptor interface. According to spin statistics, the recombination of these spin-uncorrelated charges (*i.e.*, a non-geminate pair) should lead to the formation of both ^1CT and ^3CT states, which are almost degenerate in energy.¹⁰⁸ The fate of these states is then determined by the competition between free charge re-formation and other energy loss pathways. While spin-singlet states can recombine directly to the ground state,¹⁰⁹ this is spin forbidden for ^3CT states and hence both radiative and non-radiative process are slow. However, in order to maximise the open circuit voltage of an OPV cell, the energy of the triplet exciton (T_1) is less than the CT state energy.^{76,102} This means the relaxation of ^3CT into the T_1 manifold of the polymer is energetically favourable, and could result in ^3CT being trapped in the lower energy triplet state. These triplet excitons are subsequently able to relax to the ground state through triplet-charge annihilation which is detrimental to device efficiency.¹¹⁰ The decay of both CT states are therefore allowed transitions and directly compete with charge separation. The emerging theory is that the formation of triplet states is a dead-end with regards to charge carrier generation which are able to contribute to extractable photocurrent.

Figure 1.10 Schematic of bimolecular recombination pathways of free charge carriers in OPVs. Spin-uncorrelated charges can form charge transfer (CT) states with both spin-singlet (^1CT) and spin-triplet (^3CT) characteristics. ^1CT states can recombine directly to the ground state. Meanwhile, ^3CT cannot and instead relax to the lower-lying polymer triplet exciton (T_1) which can then relax to the ground state, which is detrimental to device efficiency. Figure adapted from Chow *et al.*¹⁰⁴

The mechanism of triplet exciton formation in polymer:fullerene blends, and their role in charge generation pathways, was recently brought to the fore by Etzold *et al.* who used transient absorption spectroscopy to probe the timescales of triplet exciton formation, and found that this can occur on the order of 100's of picoseconds.¹⁰⁵

The authors found the triplet exciton formation was dependent on the concentration of charges, as evidenced by intensity dependence experiments. However, this timescale is an order of magnitude faster than is typically observed for bimolecular recombination.^{11,111} Meanwhile, Dimitrov *et al.* proposed that on the ns-timescale recombination of charges could occur at the interface, whereby the hole undergoes spin-state mixing to form a triplet state, which then repopulates the donor.¹¹² This suggests triplet exciton formation in polymer:fullerene blends could occur through bound electron-hole crossing into the triplet manifold. Therefore, intersystem crossing (ISC) of excitons or charge transfer states could be of fundamental importance to the formation of triplet excitons in polymer based OPV's. However, the mechanism of triplet exciton formation, and their role in limiting the generation of extractable photocurrent, is not fully resolved.

1.5 Challenges ahead for improved device performance

Many of the outstanding questions regarding photogeneration processes in OPV cells relate to the mechanism by which excitons (electron-hole pairs) escape their Coulombic attraction and generate photocurrent. What is the kinetic competition between exciton relaxation and charge photogeneration? With the relevance of delocalised states having a role in efficient charge photogeneration, it remains to be resolved the role of blend morphology on this process. Further, what are the timescales of the morphologically driven charge separation? With the potential limit of efficiency being impacted by the formation of triplet excitons, the discrepancy between experimental evidence concerning their formation certainly warrants elucidation. This thesis presents a valuable spectroscopic insight into the pathway of efficient charge separation and the importance of both blend morphology and polymer structure.

Chapter 2 of this thesis provides an overview of spectroscopic methods utilised and data analysis methods used to answer the questions posed. In Chapter 3, a series of oligothiophenes are synthesised with well-defined conjugation lengths (from 4 to 10 monomer units) which act as molecular models of the sub-units found in a π -conjugated polymer backbone. These are used to probe exciton relaxation processes. The results presented in Chapter 4 provide experimental evidence that both torsional relaxation and energy migration could contribute to the spectroscopic inhomogeneous broadening observed in neat polymer thin films. In Chapter 5, singlet and triplet exciton populations in oligothiophenes were tracked to probe the mechanism for the triplet exciton formation and investigate any length dependent

behaviour. Results presented suggest that in addition to charge recombination, vibrational hot states could drive triplet exciton formation via spin-mixing between singlet and triplet manifolds. Chapter 6 investigates the link between the nature of polymer:fullerene intermixing and charge generation pathways. It is shown that morphologically driven charge separation could be accounted for by the energy gradient between intermixed and phase pure regions. Finally, Chapter 7 investigates the photophysics of a high performance (BFS4:P(NDI2OD-T2)) polymer:polymer blend showing that optimizing blend morphology in this class of OPVs is required if they are to rival their polymer:fullerene counterparts.

Chapter 2

Optical spectroscopy to probe molecular photophysics

2.1 Introduction

Time-resolved optical spectroscopy techniques have found widespread application for the study of excited state dynamics in various materials.^{113–115} Indeed, the current understanding of the underlying photophysics governing OPV cell operation discussed in Chapter 1 have been driven by spectroscopic methods. A major difficulty in probing the mechanism of photocurrent generation results from the timescales in question having possible contributions from numerous processes, such as exciton relaxation, exciton separation, or geminate recombination on the femtosecond to nanosecond timescale; and on slightly longer timescales (nanosecond-to-millisecond timescale), charge migration, and bimolecular recombination of free charges. For the organic semiconductor polymers materials used in OPVs, optical spectroscopy is a valuable tool to probe the mechanism of relaxation following photoexcitation. The main relaxation of polymer excitons is through radiative decay to the ground state, allowing relaxation kinetics to be probed using time-resolved photoluminescence spectroscopy.¹⁵ Additionally, exciton dynamics can also be isolated due to their unique spectral signatures in transient absorption spectroscopy. Similarly, polarons (charge carriers) on conjugated polymers have been shown to exhibit distinct photoinduced absorption signatures from excitons.¹¹³ Charge recombination dynamics can be probed through intensity dependent measurements, whereby bimolecular recombination will exhibit power-dependent decay rates, which is absent in geminate recombination.

Identifying spectroscopic signatures throughout the visible-infrared regions associated with the variety of different optical excitations involved (*e.g.*, singlet and triplet excitons, charge-transfer states, and polarons/charge pairs) provides a useful probe of their local electronic environment (*e.g.*, polymer morphology). In addition to steady-state optical measurements, time-resolved spectroscopy techniques will be the main investigative tools used in this work. This chapter introduces the fundamental concepts behind transient absorption and time-resolved photoluminescence spectroscopy techniques. Additionally, a brief overview of the data analysis techniques are discussed. A case study is then presented demonstrating the data structure and analysis of transient absorption spectroscopy.

2.2 Transient absorption spectroscopy

Transient absorption (TA) spectroscopy is a pump-probe experiment involving two laser pulses, with an schematic representation of the experimental setup presented in Figure 2.1. A narrow-bandwidth (ideally monochromatic) laser pulse, referred to as the ‘pump’ pulse, is tuned to be resonant with an electronic transition of the material of interest. This is absorbed by the sample and excites a fraction of the molecules into an excited state *via* a vertical Franck-Condon transition. The percentage of molecules excited is dependent on the excitation power and absorption cross-section of the material, and is usually kept to a fraction of a percent of the molecules in the sampled volume (*i.e.*, the area excited by the pump).¹¹⁶ The pump pulse is typically narrow in the frequency domain to selectively probe a specific optical transition of interest, for example the ground state (S_0) to first excited singlet state (S_1).

Figure 2.1 Schematic of a transient absorption spectrometer set-up which is described in the text. Figure adapted from A. J. Barker *et al.*¹¹⁶

The dynamics of these electronic excited states are then probed by the second laser pulse to monitor the photo-induced transmission changes. This second pulse is referred to as the ‘probe’ pulse and can be either broadband (*i.e.*, contains multiple wavelengths) or ‘monochromatic’. The probe passes through a cross-section that has

been photo-excited by the pump pulse. If the probe pulse is not ‘monochromatic’, it is then spectrally dispersed and collected on either a photodiode array or camera. By varying the delay of the pump with respect to the probe, information about the excited species is obtained as a function of both time and wavelength. For femto-to-nanosecond time delays a mechanical delay stage is used, which alters the path length the pump pulse travels. For longer delays (up to microseconds) an electronic delay can be used to control the trigger rate of one of the pulses.

The signal from a TA experiment is the pump-induced transmission change (ΔT) normalised by the transmission of the ground state (T).¹¹³ This is calculated as shown in Equation (2.1), where T is the transmission spectrum, and ΔT is the difference in the absorption spectra with (T_{on}) and without (T_{off}) pump excitation. From the definition it is clear that in order to calculate a signal 2 probe pulses are required. This is achieved by blocking the pump pulse at a frequency of $\omega/2$, where ω is the probe pulse repetition rate. For each time delay the intensities of sequential probe pulses are collected. Alternate pump pulses are blocked using an optical chopper and multiple pulse-pairs are collected at each time delay in order to obtain an improved signal-to-noise ratio, which scales as $\sqrt{N}$ for the number of pulse-pairs (N).

$$\frac{\Delta T}{T} = \frac{T_{on} - T_{off}}{T_{off}} \quad (2.1)$$

The time resolution of the experiment is limited by the duration of the pump and probe pulses, whilst wavelength resolution comes from the broadband nature of the probe light. In this work the laser excitation source was a Ti-sapphire laser (Spectra Physics) which provides pulses of 100 fs pulse duration centred at 800 nm, at a repetition rate of 3 kHz. Pump pulses were generated using an optical parametric amplifier (OPA). Broadband probe pulses were generated as a result of non-linear modulation of refractive index when an intense femtosecond laser pulse is focused into a transparent medium.¹¹⁷

A TA data surface for an oligothiophene (dihexyl-sexithiophene, see Chapter 3 for chemical structure) in solution is presented in Figure 2.2A. This is used as an example material to illustrate the typical procedure used to interpret a TA measurement. The data is corrected for group velocity dispersion (‘chirp’) effects, which results from the frequency dependent speed of light in transparent media whereby longer wavelengths are delayed relative to shorter wavelengths.¹¹⁸ The temporal overlap (time-zero) of pump and probe pulses is given by the temporal overlap of pump and probe, and can be taken as 50% of the maximum signal intensity, with the signal

having a rise time of approximately 200 fs in duration due the instrument response function (IRF). This arises due to the convolution of the Gaussian-shaped laser pulse and underlying decay dynamics.¹¹⁴

At time delays when the probe arrives before the pump (*i.e.*, negative time) the differential signal ($\Delta T/T$) is zero, by definition. The composition of the TA surface, and an initial interpretation, is done through taking ‘slices’ in either the time domain (spectral slices, Figure 2.2B), or wavelength domain (kinetics traces, Figure 2.2C).

There are three effects on the transmitted pulse that can be present in TA spectral slices.^{114,115} First, if the probe pulse is resonant with ground state absorption of the material, *i.e.* resonant with the $0 \rightarrow j$ transition (for some excited state j), then the probe transmission will be increased after excitation since the pump pulse reduces the population of molecules in the ground state. This causes an increase in sample transparency and is known as a ground state bleach (GSB) which results in a positive $\Delta T/T$ signal (*e.g.*, centred at 410 nm in Figure 2.2B). Second, if the probe pulse is resonant with the $1 \rightarrow 0$ transition, it will stimulate the emission of a second photon, known as stimulated emission (SE). This occurs only when the lowest excited state is optically coupled with the ground state. This results in additional photons to be collected with the probe pulse and causes a positive $\Delta T/T$ signal (*e.g.*, 475–600 nm in Figure 2.2B). Third, if the probe pulse is resonant with a transition between excited states ($i \rightarrow j$, where $i \neq 0$) then the probe photons will be absorbed by the sample resulting in a photoinduced-absorption (PIA). This reduces the transmission of the probe pulse with respect to the instance without a pump pulse, thereby causing $\Delta T/T$ to be negative (*e.g.*, >700 nm in Figure 2.2B)

The integrated intensity of spectral features can be used to track excited state dynamics, and also provide information on lifetime. Figure 2.2C shows integrated kinetics over several wavelength regions. For example, integrating the intensity at 400 nm as a function of time tracks the GSB signature, which is proportional to the total excited state population. A discussion on the data structure and tools that aid in the analysis of relaxation photophysics are reserved for later in this chapter.

Figure 2.2 Transient absorption measurements of an oligothiophene in solution showing the TA data surface (A), spectral slices (B) and integrated kinetics (C).

2.3 Transient grating photoluminescence spectroscopy

Photoluminescence (PL) spectroscopy provides contrasts to transient absorption (TA) by measuring the intensity of light proportional to the population of emissive states only, compared with total excited state population for TA. Time-resolved PL is achieved by exciting the sample with a light source (e.g., short laser pulse) and then collecting the resulting PL intensity as a function of time. This requires the use of a shutter so as to only collect PL intensity on the detector at a specific time intervals after photoexcitation. Useful information is not derived just from PL kinetics, but also the evolution of PL spectra which provides information on the nature of the excited state.^{64,119,120} In the literature, the most commonly employed experimental setup is fluorescence upconversion spectroscopy.^{28,121,122} This method relies on upconverting (increasing the PL photon energy) by overlapping the PL signal with a second laser pulse inside a crystal. However, this method is unable to detect broadband PL spectra due to the phase matching in the upconversion process being wavelength specific, and obtaining spectra involves scanning the crystal angle to resolve different wavelengths and collecting each upconverted signal individually.

Recently, transient-grating photoluminescence (TGPL) spectroscopy was developed in our group at Victoria University of Wellington, which provides time-resolved, broadband PL spectra.¹²³ Figure 2.3 shows a schematic depiction of the TGPL experimental setup. A key aspect of this technique is the generation of an optical shutter through the formation of a transient diffraction grating via the interference of two short laser pulses (referred to as gate pulses). This occurs inside a gate medium which changes the refractive index through a non-linear optical effect (Kerr-effect).¹²⁴ Following excitation with a short laser pulse, PL from the sample is collected and passed through the gate medium. PL spectra at specific time delays after photoexcitation are sampled *via* diffraction off the transient grating. This separates the gated PL from the background PL signal, acting as an effective ultra-fast shutter. This spatial separation of gated PL is particularly important when dealing with samples with long-lived PL lifetimes, for example P3HT.^{64,123}

Time delay is achieved in the same manner as TA, changing the path length of the probe using an optical delay alters the overlap of the PL signal and the grating, controlling what time delay after photoexcitation the PL spectrum is sampled. Since the transient grating is only present at overlap of the two gate pulses, it is beneficial to have a delay line on the gate pulse path to tune the temporal overlap of the gate pulses. The time resolution of the experiment is governed by cross-correlation of the

Figure 2.3 Schematic depiction of transient grating photoluminescence experimental set up. Figure adapted from Chen et al.¹²³

pump and gate, in the same way as for TA spectroscopy. The gate medium material is fused silica owing to its favourable non-linear optical effects with amplified laser pulses, and the material transparency covering the ultraviolet-to-infrared wavelength range.

2.4 Data structure and analysis

Time-resolved spectroscopy measurements are comprised of a collection of spectra at various time delays. The resulting data structure is a 3-dimensional data set (*i.e.*, a matrix or table, $\mathbf{D}$), where each column corresponds to a full spectrum at a certain time and each row the variation of signal intensity as a function of time delay. For a measurement at m number of time points, the data matrix consists of m columns of spectra of length n , where n is the pixel count of the photodiode detector, this is shown in the first panel of Figure 2.4. In an ideal situation, the entire data surface ($\mathbf{D}$) would be described by a linear sum of r different photoactive species (*e.g.*, either absorbing or emitting), referred to as components, to yield $\mathbf{D} = \mathbf{K}^T \times \mathbf{S}$. Where the columns of matrix $\mathbf{K}^T$ are sized $m \times r$ and are the time-dependent concentrations (kinetics) of the r components at the m time delay values, the rows of $\mathbf{S}$ are sized $r \times n$ and are the spectral signatures at each time delay. $\mathbf{K}^T$ is the transpose of $\mathbf{K}$. Figure 2.4 shows how a data matrix can be decomposed into the individual contributions, in this example using 2-components (*e.g.*, $r = 2$).

In a general sense, the goal of data analysis is to determine the number of excited state species present, the time-independent spectral features of these, and the change in concentration/population of these states as a function of time. Assuming $\mathbf{D}$ can be described by a combination of a series of contributing components, this can be achieved by globally modelling the data matrix to decompose $\mathbf{D}$ into individual components. There are two approaches to this; hard and soft-modelling.^{113,125,126}

Figure 2.4 Simulated time-resolved spectroscopy data set showing how the data matrix ($\mathbf{D}$) can be decomposed using a linear combination of contributing species (components), in this case a 2-component decomposition. This yields a concentration of each component as a function of time, and the corresponding spectral signatures of each.

In hard-modelling, parametrised equations are used to form at least one component of the underlying model which describes the system dynamics. For example, the functional form of the decay (*e.g.*, an exponential) of all excited state species would provide a parametrised kinetic model describing the concentration of each species as a function of time. In contrast, a soft-modelling approach involves decomposing the system and then applying boundary conditions to obtain physically meaningful components (*e.g.*, non-negative concentrations). This yields a non-parametrised model which describes the system without a parametrised equation to describe the physical processes in the system. This is useful when the number of components or underlying model are unknown.

One method of soft-modelling is to use singular value decomposition (SVD) as an initial reduction of the data set, and then apply physical constraints to the result to reduce the mathematical ambiguity. SVD decomposes $\mathbf{D}$ into the product of three matrices: $\mathbf{D} = \mathbf{K}\Sigma\mathbf{S}^T$ where $\mathbf{K}$ is an $(m \times m)$ matrix, Σ is a diagonal $(m \times n)$ matrix, and $\mathbf{S}^T$ is an $(n \times n)$ matrix. The elements on the diagonal of Σ are square roots of the eigenvalues of $\mathbf{D}\mathbf{D}^T$ arranged in decreasing order. The number of significant values in Σ provides the rank of $\mathbf{D}$, which is the maximum number of linearly independent columns (or rows) of $\mathbf{D}$.¹²⁷ This is meaningful as it is equal to the number of components required to describe the data surface. The matrices $\mathbf{K}$ and $\mathbf{S}$ are the weightings (concentration kinetics) and the spectral line shapes, respectively.

Equation (2.2) shows the data ($\mathbf{D}$) is represented by the product of kinetics ($\mathbf{K}$) and spectra ($\mathbf{S}$) basis sets, as previously discussed. However, this decomposition solution is not mathematically unique, which can be proven by deriving a linear transformation on the solution space. Since any matrix multiplied by the identity matrix does not change (by definition),¹²⁷ it can be introduced into the linear decomposition, as shown in Equation (2.3). For some invertible matrix $\mathbf{R}$, the product of $\mathbf{R}$ and its inverse ($\mathbf{R}^{-1}$) is also equal to the identity. Therefore, it is valid to introduce this into the decomposition of $\mathbf{D}$, as shown in Equation (2.4). Since matrix multiplication is associative (*i.e.*, the order matters), the expression can be arranged as in equation (2.5). This means the kinetics basis set ($\mathbf{K}$) can be evaluated as the term in the first brackets ($\mathbf{KR}$), which is a new kinetics basis set altered by the elements of $\mathbf{R}$. The same holds for the spectra basis set, whereby ($\mathbf{R}^{-1}\mathbf{S}$) is a new spectra basis set which has been altered by the elements of $\mathbf{R}$. This yields two new basis sets $\mathbf{K}_{\text{new}}$ and $\mathbf{S}_{\text{new}}$ and the multiplication of these is still a valid (*i.e.*, equal) decomposition of $\mathbf{D}$ (see Equation (2.5)). This clearly shows the mathematical ambiguity of the decomposition and that there are an infinite number of choices for $\mathbf{R}$.

$$\mathbf{D} = \mathbf{KS} \tag{2.2}$$

$$= \mathbf{KIS} \tag{2.3}$$

$$= \mathbf{KRR}^{-1}\mathbf{S} \tag{2.4}$$

$$= (\mathbf{KR})(\mathbf{R}^{-1}\mathbf{S}) \tag{2.5}$$

$$= \mathbf{K}_{\text{Rot}}\mathbf{S}_{\text{Rot}} \tag{2.6}$$

This ambiguity in the mathematical decomposition of the data matrix is exploited in soft-modelling to constrain the solution to a physically meaningful result using knowledge of the system being studied. This is achieved by applying a linear transformation to the solution; in particular a rotation transformation. This rotation matrix ($\mathbf{R}$) will be an $r \times r$ matrix, where r is the number of components in the decomposition. Multiple types of information about the system could be used as constraints, such as rate of decay of components or spectral shapes. In the above 2-component example (see Figure 2.4), $\mathbf{R}$ will be a 2×2 matrix. In this example, assume the spectral information about component 2 is known, *i.e.*, $\mathbf{S}_2$, which provides physically meaningful information about the system of the spectral contributions of one component in a 2 component system. With the physical constraint of the system identified, it remains to calculate the rotation matrix. The formula for a 2-dimensional rotation matrix is shown in equation (2.7), for some angle of rotation

(θ). The matrix is calculated by performing a linear least squares fitting between the initial spectral components obtained and the spectral shape of the known species. Since the spectra of both components are incorporated into the least squares fitting, both spectral shapes change in order to accommodate for one component rotating to match the physical constraint. This evaluates the angle of rotation in the solution space that provides the best matching spectrum, in particular for spectral rotation this calculates the quantities on the right-hand side of the matrix (i.e., $-\sin(\theta)$ and $\cos(\theta)$). Thus, the corresponding rotation values can be calculated (based on the formula) and applied to the kinetic basis set to maintain a valid decomposition solution of the data matrix.

$$\mathbf{R}(\theta) = \begin{bmatrix} \cos(\theta) & -\sin(\theta) \\ \sin(\theta) & \cos(\theta) \end{bmatrix} \quad (2.7)$$

It is noted that this discussion focusses on ‘noise-free’ data; in reality the decomposition also contains an error matrix which contains the difference between the measured data and the decomposition. This information is critical in determining how well the decomposition model represents the data, and in an ideal case will consist of time-independent noise (*e.g.*, light instability or electronic noise) from the measurement. Analysis of the fitting residuals is used to guide the minimum number of components required to model the system of interest.

2.5 Case Study: Charge generation in a PTBO:PC[71]BM blend

To give an example of the results generated by a TA spectroscopy experiment, an investigation of poly(5,6-bis(tetradecyloxy)-4-(thiophen-2-yl)-benzo[c]-[1,2,5] oxadiazole) (PTBO) blended with [6,6]-phenyl C₇₁ butyric acid methyl ester (PC[71]BM) is presented as a case study. PTBO is a low-bandgap polymer recently developed by collaborators at Pusan National University, South Korea in the research group of Prof. H. Y. Woo, and the chemical structure is shown in Figure 2.5. An OPV cell comprised of PTBO:PC[71]BM blend (1:2 wt% ratio) as active layer shows only 1.1% PCE, which is a far cry from the >10% PCE obtained from state-of-the-art devices. TA spectroscopy of PTBO:PC[71]BM blends reveal the conversion of excitonic species to charges *via* charge-transfer between the polymer and fullerene components. The loss of charge population within 100's of picoseconds highlights morphology-dependent charge recombination as the main factor limiting device photocurrent of this OPV blend.

TA measurements of a pristine PTBO thin film (Figure 2.5) allows to first identify spectroscopic signatures associated with excitons of the polymer. This information is then able to guide the interpretation of TA measurements of the PTBO:PC[71]BM blend. Measurements were conducted at sufficiently low fluence in order to avoid non-linear recombination effects, such as exciton-exciton annihilation.¹¹¹ This was confirmed by the decay dynamics being independent of excitation intensity. Figure 2.5A shows the TA spectral slices for neat PTBO, which contains two features; a ground-state bleach (GSB) feature in the visible region of the probe, which has the same vibronic progression as observed in the steady-state absorption spectrum (not shown) at ~2.01 eV and ~1.85 eV, and a photo-induced absorption (PIA) which is peaked at ~0.93 eV. In this polymer no stimulated emission feature is observable. Integrating these spectral features provides the kinetic traces for neat PTBO shown in Figure 2.5B, which tracks the population of excited species. The equal decay rates of both spectral features confirms the presence of a single excitonic species with a half-life ($\tau_{1/2}$) of ~50 ps.

Having identified the spectrum and lifetime of excitons in PTBO, the dynamics of the PTBO:PC[71]BM blend can be considered. Following photoexcitation of the blend, the initial (200 fs) TA spectral slice (Figure 2.6A) resembles that of neat PTBO, *i.e.*, the PTBO exciton. This is clearly shown by the overlay of the 200 fs spectral slice of neat PTBO having a strong overlap with the early time spectral signatures of the blend. At longer time delays, the exciton PIA decays to yield

Figure 2.5 Transient absorption measurements of a neat PTBO film showing spectral slices at indicated time delays, (A) following 100 fs excitation at 660 nm. The spectral regions labelled GSB, PIA-1 refer to the wavelength integration regions shown in the kinetic traces (C). Kinetics are normalized by the average value within the first picosecond. Inset shows the chemical structure of PTBO.

a new PIA peak at ~ 1.15 eV (labelled PIA-2) which is distinct from the broad exciton band (PIA-1). PIA-2 appears as a shoulder after only 1 ps, and integrated kinetics (Figure 2.6C) shows this feature persists beyond the 3 ns timescale of the measurement. The new PIA-band is also accompanied by a long-lived GSB signature which significantly outlives the exciton lifetime. This new sub-band-gap PIA (PIA-2) and extended lifetime of polymer excitations are indicative of an additional species being formed. This pattern of visible and near-infrared (NIR) TA dynamics indicate charge photogeneration *via* charge transfer to yield hole polarons on the polymer, in line with numerous previous studies.^{11,37,128}

Figure 2.6 Transient absorption measurements of a PTBO:PCBM blend film showing spectral slices at indicated time delays (A) following 100 fs excitation at 660 nm. The spectral regions labelled GSB, PIA-1, and PIA-2 refer to the wavelength integration regions shown in the kinetic traces (C). Kinetics are normalized by the average value within the first picosecond.

Having identified that charges are generated in PTBO:PC[71]BM, discussion turns to probing the dynamics charge generation and how this relates to the observed device performance. Comparison of exciton kinetics (PIA-1) of the PTBO:PC[71]BM blend

with the neat polymer confirms a reduced exciton lifetime due to charge photogeneration in the polymer:fullerene blend. However, partial GSB decay within the first 1 ps shows that some excitons decay before generating charge pairs. This is supported by the ratio of the exciton PIA to the GSB peak intensity in the PTBO:PC[71]BM blend (40%) is less than that observed in the neat polymer (57%). Since polarons on the polymer would retain the GSB peak, it suggests that 30% of excitons are converted to charges within the first 200 fs, *i.e.*, promptly generated charges. This suggests that 70% of polymer excitons are not generated in immediate proximity to a PC[71]BM acceptor, and must diffuse to a polymer:fullerene interface in order to separate. Using the integrated intensity of PIA-2 to track the population of charges reveals recombination events after only 1 ps. This results in only 55% of the initial charge yield remaining at 3 ns. The integrated intensity of the GSB region is proportional to the total population of excitations, and matches the decay dynamics of charges. This confirms that the decay of charges is through rapid geminate recombination to the ground state.

The spectroscopic analysis of charge generation in a PTBO:PC[71]BM blend has identified inefficient exciton dissociation in the blend, as evidenced through severe geminate recombination on sub-nanosecond timescales. Such rapid recombination events halves the charge population available on longer timescales to contribute to extractable photocurrent. One possible cause of this is a highly phase-separated film morphology whereby the polymer and fullerene domains are larger than the exciton diffusion length. However, TA measurements show evidence of charge generation within the time resolution of the experiment (200 fs) which is consistent with some excitons being generated close to a heterojunction interface. To further elucidate the link of poor device efficiency to these charge generation dynamics, film morphology studies would be of great benefit. Nevertheless, the results presented here provide a useful example as to the analysis of transient absorption spectroscopy and how it can be used to gain insight on charge photogeneration pathways and the link to device efficiency.

Chapter 3

Synthesis of oligothiophenes as molecular models

3.1 Introduction

As discussed in Chapter 1 (Introduction), conformational defects (disorder) present in a conjugated polymer prevent the formation of a 1-dimensional π -conjugated chain, and break the polymer backbone into sub-units of varying conjugated size.³ Each of these sub-units can act as effective chromophores, and the number of monomer units comprising each unit (i.e., conjugation length) alters the delocalisation of π -electrons, which changes the optical band-gap. These sub-units are able to interact with one-another, and combined with the distribution of conjugation lengths, result in the complex relaxation dynamics observed in conjugated polymers.¹² In the drive for optimized organic photovoltaic device performance, a detailed knowledge of relaxation dynamics is required. In particular, separating the inherent relaxation dynamics of chromophore sub-units from the energy transfer processes in polymer systems has not yet been realised.

One of the most well-studied conjugated polymers for organic photovoltaic (OPV) applications is poly(3-hexylthiophene), P3HT, which has monomeric units comprising a single thiophene ring with a hexyl-chain substituents to aid in the solubility of the long π -conjugated backbone. Polythiophenes have favourable properties for application in organic electronics because of their efficient charge transport properties, low cost, and compatibility with flexible substrates.^{129–131} The optical and electronic properties of semiconductor polymers is effected by molecular ordering and self-assembly.¹³² Oligothiophenes exhibiting the same repeat unit as a polymer

have allowed the separation of the inherent properties of the semiconducting chromophore from the combination of structural defects, chain disorder, or aggregation which all contribute to the complex relaxation dynamics of a polymer system.^{133–135} Therefore, understanding the complex relaxation photophysics occurring in polymer photovoltaic devices requires isolating and studying well-defined systems.

In recent years a variety of methods have been reported for the synthesis of polythiophene derivatives.^{136,137} The synthesis of oligothiophenes with well-defined conjugation lengths are often based on these polymeric synthetic procedures. However, in general these often yield relatively short oligothiophenes of less than 8 monomer units.^{138,139} The continued interest in these materials has lead to the development of new synthetic strategies with a variety of catalyst types to yield mono-disperse oligothiophenes of longer conjugation length.^{133,134,140–142} These long oligothiophenes have been utilised to determine the effective conjugation length of polythiophene, *i.e.*, the longest sub-unit in the polymer chain.¹⁴³ This is found by tracking the optical absorption red-shift as a function of oligomer length and finding the point of saturation of this shift. Estimates using this method showed the effective conjugation length for P3HT was 11–20 thiophene units.^{144,145} Interestingly, oligothiophenes with 72 and 96 repeat units have been reported which exhibited a 1.9 nm red-shift between the absorption maxima,¹⁴⁶ with the authors of that study proposing that the effective conjugation length in P3HT may be longer than initially thought. However, it is noteworthy that the electronic absorption maximum in these very long oligomers were at lower energy than for P3HT. This suggests the 72-mer oligomer length may not be an accurate representation of P3HT sub-units.

In this chapter, the synthesis of a series of oligothiophenes with well-defined conjugation lengths are reported. These are of 4, 6, 8, and 10-thiophene units in length, and are a good representation of sub-units that could be present in P3HT, based on previous studies on effective conjugation length being 11–20 monomer units.^{144,145} Additionally, by avoiding steric interactions between alkyl-substituents on neighbouring thiophene units, these oligomers are good models of conformational sub-units which could be present in a polymer chain. The synthetic protocols employed are discussed, along with the structural characterization techniques used to confirm the identity of each oligomer.

3.2 Molecular design and synthetic strategy

The oligomers synthesised in this work were chosen to model conformational subunits of P3HT for 2 reasons; Firstly, understanding the excited state photophysics in P3HT has direct relevance to the research field of optoelectronic devices, owing to P3HT being extensively studied in OPV applications, and secondly, the relatively simple nature of the polymer backbone compared to low band-gap donor-acceptor co-polymers. In order for an oligothiophene to be a valid model of the conformational subunit, consideration needs to be given with regards to the effective conjugation coupling between adjacent thiophene rings. In particular, alkyl-substitution of the thiophene monomer present the possibility of steric interference between neighbouring monomers. Figure 3.1 illustrates the different side-chain substitution patterns possible between 2 thiophene units with alkyl-substituents at the 3-position of each ring. In a head-to-tail (H-T) orientation (Figure 3.1A), the alkyl substituents are positioned away from each other in every ring rotation orientation. This means the formation of unfavourable steric interactions are unlikely. Similarly, in a tail-to-tail (T-T) orientation (Figure 3.1B) the alkyl-substituents are far enough apart to not have unfavourable steric interactions. In contrast, with a head-to-head (H-H) orientation (Figure 3.1C) thiophene ring rotation can result in the alkyl-substituents pointing toward each other which will result in steric repulsion between side-chains.

Figure 3.1 Coupling orientations of adjacent alkyl-substituted thiophene rings.

The coupling orientation, or regiochemistry, of thiophene units in the backbone of polythiophenes controls conformation features which in turn governs the degree of π - π conjugation between adjacent rings. This manifests itself in the improved

electroconductivity, optical non-linearity, and crystallinity in regiospecific polymers, such as regioregular P3HT which has >99% H-T couplings.^{147,148} This is in comparison to regiorandom (or sterically hindered) polymers whereby H-H couplings in the polymer chain can cause conformational defects and reduce the desired physical and electronic properties of the material.¹⁴⁹ Thus, in order for an oligothiophene to be a valid model of a chromophore sub-unit in P3HT, H-H regiochemistry needs to be avoided.

Numerous synthetic strategies towards well defined oligothiophenes have been reported in the literature.^{133,134,140–142} A seemingly direct approach is to exploit the electron density at different positions of a thiophene ring and use oxidative coupling of thiophene rings by oxidising a thiophene derivative,¹⁵⁰ or deprotonating then dimerising a mixture of short α -oligothiophenes using copper chloride.¹⁵¹ In these reactions the coupling between monomer segments occurs at the position of the highest electron density.¹⁵² However, this site specific reactivity is reduced with increasing conjugation length of the precursor and this approach generally results in short oligomers.¹⁵⁰

An alternative synthetic strategy toward well-defined oligomers is to adapt the metal-catalysed cross-coupling reaction employed to obtain polythiophene derivatives.^{136,137} This can be achieved *via* a polymerisation reaction toward regioregular P3HT, and altering the monomer-to-catalyst ratio to obtain low-molecular weight polymers.¹⁵³ Although this method is easily adaptable to yield polymers of varying molecular weight, the chain-growth mechanism of the reaction results in a polydispersity is obtained. This method prevents single thiophene ring precision with regards to conjugation length. This would complicate the analysis of excited state dynamics between materials of similar conjugation lengths. Purification techniques such as size exclusion column chromatography could be employed to reduce this polydispersity, but the resolution on such techniques would be unlikely to allow single monomer unit resolution due to the small change in molecular weight. In order to obtain well-defined conjugation lengths of single thiophene ring precision, a different synthetic strategy needs to be employed.

Recently Mori *et al.* have developed metal-catalysed homocoupling of bromothiophene to obtain a short oligothiophenes with C—Br bonds at the terminal thiophenes, allowing for additional derivatisation.^{154–156} This synthetic strategy uses a stepwise lengthening of the oligothiophene, where the first iteration yields a bithiophene, which is converted to the terthiophene and then to the quaterthiophene as so on. However, so far reports have only yielded relatively short oligothiophenes, up to 8 thiophene rings, using this approach. Again, this is likely due to the diminishing

differentiation of reactive sites on the thiophene as the conjugation length increases.

Instead of performing a polymerisation reaction and altering reaction parameters, an alternative is to perform a functional-group selective carbon-carbon bond formation reaction, such as a Suzuki-Miyaura or Stille reactions.^{157,158} This provides a synthetic strategy toward coupling of two monomeric building blocks in a selective and discreet manner, yielding well defined extension of the oligomer. Recently, Stille coupling reactions were used by Zhang *et al.* to prepare oligothiophenes up to 24-thiophene units long.¹⁵⁹ While Koch *et al.* have utilised a similar approach to obtain oligothiophenes of 36 thiophene rings.¹⁶⁰

For the oligothiophenes synthesised in this work, the reports in the literature using metal-catalysed cross-couplings provides a synthetic strategy towards a series of oligothiophenes with well-defined conjugation lengths. With regards to the required regiochemistry of avoiding steric interactions of alkyl-side chains, it was decided that the building block would be 3,3''-dihexyl-2,2':5',2'':5'',2'''-quaterthiophene, which has been synthesised previously.¹⁶¹ In this structure, the H-H orientation of the two hexyl-substituted thiophene moieties is separated by an unsubstituted bithiophene motif. This results in any subsequent coupling of thiophene units will be attached in either a HT or TT fashion, thereby controlling the only instance of HH coupling as the oligomer length is increased. This prevents unfavourable steric interactions occurring in the oligothiophene series.

3.3 Synthesis and structural characterisation

The synthesis of dihexylquaterthiophene (4T) is shown in Scheme 3.1, and follows a similar procedure as reported in the literature.¹⁶¹ This first involved the bromination of both 3-hexylthiophene using N-bromosuccinimide (NBS) to yield 2-bromo-3-hexylthiophene (**2**) in 71% yield, and the bromination of bithiophene to yield 5,5'-dibromobithiophene (**3**) in 82% yield. Purification was achieved for **2** by vacuum distillation, and recrystallisation for **3**. Subsequently, a Kumada-coupling reaction was performed using the Grignard reagent **4**, which was then added to bithiophene **2** in the presence of a Nickel catalyst, Ni(dppp)Cl₂. This provided quaterthiophene (**4T**) in an excellent yield of 92% after purification by column chromatography.

The synthesis of longer oligomer is to be achieved through the Suzuki-Miyaura reaction, which is a selective carbon-carbon bond formation between, an aryl-halide and an aryl-boronic acid/boronic ester (in this case). Consideration was also given to

Scheme 3.1 Synthesis of quaterthiophene: i) NBS (1 eq.), THF, 0 °C, 1h, N₂ atm; ii) NBS (2 eq.), DMF, rt, overnight; iii) Mg, Et₂O, 1,2-dibromoethane, 2h, reflux, N₂ atm.; iv) Ni(dppp)Cl₂ (1.4 mol%), PhMe:Et₂O (3:2), overnight, reflux, N₂ atm. The numbering relates to the ring position notation referred to through the text.

the Stille reaction which also provides functional-group selective carbon-carbon bond formation.¹⁵⁸ However, such reactions involve the synthesis of organotin compounds which are highly toxic, and preference was to avoid these if possible. Therefore, the first derivatisation toward longer oligomers involved the bromination of 4T using NBS. The key ¹H NMR data used to characterise the products of the reaction are the chemical shifts of aromatic protons (~6.90–7.25 ppm) and the α-CH₂ protons (~2.65–2.90 ppm), shown in Figure 3.2. The bromination of 4T resulted in the isolation of 3 products, the 4T starting material, dibrominated 4T (4T-Br₂), and monobrominated 4T (4T-Br) as products. Structural identity of these products was confirmed using both 1- and 2-dimensional ¹H nuclear magnetic resonance (NMR) spectra, in particular 1-D ¹H and ¹³C NMR, HMBC (Heteronuclear Multiple Bond Correlation), HSQC (Heteronuclear Single Quantum Coherence), and COSY (homonuclear correlation spectroscopy) experiments (see Appendix).

The ¹H NMR spectra of 4T (Figure 3.2A) shows 4 signatures exhibiting doublet-multiplicity with chemical shifts indicative of aromatic protons, suggesting that each proton is coupling to one other proton. Additionally, a signature with triplet-multiplicity corresponding to the α-CH₂ protons based on chemical shift and the involvement of 3 protons in the coupling pattern. The aromatic signatures integrate for 2 protons each, and ¹H-¹H COSY experiments show a correlation between the peaks at 6.94 ppm and 7.18 ppm, which also have an HMBC correlation with the α-CH₂ protons at 2.77 ppm. Therefore, these signatures are assigned to the aromatic protons at the 4 and 5 position of terminal (i.e., alkyl-substituted) thiophene rings. Additionally, ¹H-¹H COSY experiments show a correlation between the peaks at 7.02 ppm and 7.12 ppm, which are assigned as the aromatic protons on the unsubstituted central bithiophene of 4T.

Bromine substitution was confirmed by the changes in ¹H NMR signatures from

Figure 3.2 ^1H NMR spectra showing the brominated products of quaterthiophene (**4T**). Three products were isolated, (A) **4T** (starting material), (B) mono-brominated **4T** (**4T-Br**), and (C) di-brominated **4T** (**4T-Br₂**). ^1H NMR spectra were collected in CDCl_3 show the spectral region containing aromatic protons (6.90–7.25 ppm) and $\alpha\text{-CH}_2$ protons (2.65–2.80 ppm) for each product.

4T starting material. The ^1H NMR spectrum of **4T-Br₂** (Figure 3.2B) shows the presence of 2 doublet signatures corresponding to the aromatic protons on the unsubstituted bithiophene (6.96 ppm and 7.10 ppm) and the triplet corresponding to $\alpha\text{-CH}_2$ protons, which has shifted up-field to 2.71 ppm. This chemical shift is caused by a change in electron density distribution upon substitution of a bromine atom. Additionally, the peak at 6.90 ppm exhibits singlet-multiplicity which is consistent with no proton-proton coupling interactions, *i.e.*, no near-by proton environments. Along with an expected mass-to-charge ratio observed in electrospray ionisation mass spectrometry (ESI-MS), this confirms a symmetric substitution of bromine on each thiophene terminus. For **4T-Br** (Figure 3.2C), the ^1H NMR spectrum shows additional complexity compared to the previous spectra discussed. This is owing to the loss of symmetry about the bithiophene which is present in **4T** and **4T-Br₂**. The ^1H spectrum shows the same peaks in unsubstituted-**4T** together with the peaks that are present in dibrominated-**4T**. The presence of both chemical environments is consistent with mono-bromination, with this product isolated in a near statistical yield of 44%.

It is noteworthy that the NMR spectra presented in Figure 3.2 exhibit second-order effects, in particular a phenomena known as ‘tenting’. This is observed when the ratio of the chemical shift difference ($\Delta\sigma$) and the coupling constant (J) gets small, *i.e.*, $\Delta\sigma$ is not ~ 10 times greater than J .¹⁶² This is caused by protons exhibiting strong coupling to each other, and results in altered line shape intensities giving the appearance of peaks leaning towards one another, as observed in each aromatic

proton doublet signature (6.90–7.25 ppm). This provides evidence of the aromatic backbone having strong through-bond coupling in the oligomer, and further confirms the structural assignment.

With the brominated **4T** obtained both symmetrically and asymmetrically substituted, the next focus was to synthesise the boronic-ester component for the Suzuki-Miyaura reaction. Initial borylation reactions utilised **4T-Br** as starting material with the idea that the site of bromination is more reactive than the protonated-terminus, providing a source of asymmetry. This was attempted by lithiating **4T-Br** using *n*-BuLi with subsequent additions of triisopropylborate and pinacol, similar to that reported in the literature for the borylation of 3-hexylthiophene.¹⁶³ However, all that was recovered was unsubstituted-**4T**. This suggested that the lithiated intermediate species was being quenched before borylation could occur. One source of this was thought to occur from the multi-step addition post formation of the lithiated intermediate, combined with the hygroscopic nature of pinacol introducing moisture to the reaction system. Reaction conditions were changed whereby dioxaborolane (2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane) was added to the lithiated **4T-Br** starting material, which allowed mono-borylated **4T** to be isolated (confirmed by ¹H NMR). However, the desired product was isolated in poor yield (<6%), even after multiple attempts, which made this route undesirable for additional reactions toward longer oligomers. To circumvent this, the conjugation length extension of **4T** *via* the Suzuki-Miyaura reaction (see Scheme 3.2) was performed using a diborylated-bithiophene (compound **1**) as the boronic ester component. Following optimization of catalyst loading (12 mol% over 2 additions), careful purification through column chromatography resulted in 3 products being isolated which were identified as sexithiophene (**6T**), octithiophene (**8T**), and decithiophene (**10T**).

The by-products aside from the targeted **10T** product arise through two ways. The carbon-carbon bond formation on one side of the bithiophene results in the asymmetric substitution (*i.e.*, **6T**), whereas homo-coupling between **4T-Br** (aryl-halide) omits the bithiophene (borylated-substrate) in the final structure (*i.e.*, **8T**). Figure 3.3 presents the ¹H NMR spectrum of **10T** collected in CDCl₃. There are two residual solvent peaks present, 7.26 ppm and 1.56 ppm which are assigned as CHCl₃ and H₂O, respectively. The molecular structure of **10T** has a plane of symmetry lying through the bithiophene core, resulting in equivalent proton environments for matching proton positions on either side of this plane. This reduces the number of separate chemical shift signatures by a factor of 2. The structural identity was confirmed by assigning each chemical shift environment in the proposed structure to the NMR spectra.

Scheme 3.2 Synthesis of a series of oligothiophenes of well defined lengths using the Suzuki-Miyaura reaction. This afforded the series: quaterthiophene (**4T**), sexithiophene (**6T**), octithiophene (**8T**), and decithiophene (**10T**).

Distinct signatures of the H_1 and H_2 protons (*i.e.*, the protons attached to C_1 and C_2 , as labelled in Figure 3.3) were identified as peaks at 6.95 ppm and 7.19 ppm due to two factors; first a ^1H - ^1H COSY correlations between the two protons showed they are spin-coupled (close enough for a proton-proton interaction), and second the chemical shift environment of the C_1 and C_2 carbons (identified through HSQC coupling) are the same as the terminal thiophene protons that were identified in **4T**. Additionally, each of these signatures integrated for 2 protons each, consistent with the chemical structure proposed. The observation of a ^1H - ^1H COSY correlation between the region of 7.00–7.10 (multiplet) and the chemical shift at 7.14 ppm (tenting doublet-multiplicity) and 7.23 ppm (doublet-of-doublet-multiplicity) confirmed that these peaks are composed of several overlapping aromatic-proton chemical environments. Definitive assignment of these peaks was not possible due to the chemical environments of protons H_6 – H_{19} being similar. However, the complex splitting pat-

Figure 3.3 ^1H NMR spectrum for decithiophene (**10T**) showing the full assignment of signatures providing confirmation of the structural identity, along with additional characterization as described in the text.

tern observed for the signature at 7.23 ppm is indicative of second-order coupling, and could be expected from H_{10} coupling to both H_7 and H_{11} , or similarly H_{18} in a similar coupling pattern. Nevertheless, the integration of all spectral features in the aromatic region (6.90–7.25 ppm) match the expected number of protons for the proposed structure.

For the aliphatic protons (0.8–2.80 ppm), the $\alpha\text{-CH}_2$ protons showed both HMBC and COSY correlations to the β - and $\gamma\text{-CH}_2$ groups, which in turn showed a COSY correlation to the methyl group at the terminus of the hexyl-chain. Although two hexyl-substituents are present in each symmetric half of the molecule, the chemical environments could be expected to be similar due to the distance from the position of carbon-carbon bond formation on the molecule in relation to the starting materials. The measured NMR data accounted for each chemical environment in the **10T** structure, and the structural identity was further supported by mass spectrometry data, which showed the expected mass-to-charge ratio for **10T**. This structural characterization analysis was performed to confirm the identity of each oligothiophene obtained, with data for all oligomers presented in Appendix II. In-line with studies of effective conjugation length, the conjugation length spanned in this series (4 to 10 thiophene units) is a good representation of P3HT sub-units. The photophysics of these will be discussed in detail in the subsequent chapters.

The effective conjugation length of chromophoric subunits in a P3HT chain is accepted to be between 11 and 20 monomer units.^{144,145} The library of oligomers synthesised in this work fall just short of this range. The synthetic pathway toward longer oligomers in this work proved unsuccessful. The methodology centred on adaptations of the same procedure utilised to obtain the series reported here. Firstly,

the symmetric bromination of **10T** using NBS was attempted, yet this yielded a mixture of products that could not be separated through column chromatography due to the bromine substitution being a relatively inconsequential change to the molecular polarity on such a large structure. The asymmetric borylation of **4T** was also unable to be obtained readily in a pure form; in spite of multiple reaction conditions commonly the symmetric borylated compound was often the major product isolated. This involved trials using the installation of bromine substitutions to add a source of asymmetry in the reactivity. Similar results were obtained using the other oligomers as starting substrates for the longer oligomers.

The difficulty surrounding the synthesis of long oligothiophenes is highlighted by the majority of oligomer synthesis in the literature yielding oligomers of 2–8 thiophene units in length.^{138,139,154–156} One possible explanation for the unsuccessful synthesis of longer oligomers is that the reactivity of the α -position of oligothiophenes decreases as conjugation length increases.¹⁵² This increases the competitive reactivity at the β -positions of thiophene rings, and could result in unfavourable kinetics in cross-coupling reactions. The synthesis of a 96-mer oligothiophene was achieved by Izumi *et al.* by blocking the β -position on the thiophene rings prior to chain lengthening cross coupling reactions.¹⁴⁶ However, this alters the inter-ring torsion of the molecule and decreases the suitability of the oligomer to act as a molecular model of P3HT, which only contains a single alkyl-substituent. A 24-mer oligothiophene with only alkyl-substituted thiophene rings was recently reported by Zhang *et al.* using Stille coupling in a step-wise chain growth reaction protocol.¹⁵⁹ Although the Stille cross coupling reaction used in that study is similar to the Suzuki-Miyaura coupling used here, the successful synthesis of long oligomers suggests that the installation of the organotin functional group (*i.e.*, stannylation reaction) required for a Stille cross coupling has better site selective reactivity compared to the borylation reaction used for Suzuki-Miyaura cross coupling precursors. Based on this it is proposed that the synthesis of oligomers longer than 10-monomers (obtained here) should be attempted through a Stille cross coupling reaction. This was not pursued in the current work and instead the optical and electronic length dependent properties of the current library was explored, and is the focus of subsequent chapters.

3.4 Optical properties

A summary of the optical properties of the series of oligothiophenes are presented in Table 3.1. The steady-state absorption and photoluminescence (PL) of the series of oligothiophenes in dilute solution show a progressive red-shift (toward lower

energy) with increasing oligomer length. This length dependent band-gap is consistent with the increased delocalisation of π -electrons as the number of thiophene units is increased. The π -electrons are mobile throughout the overlapping orbitals between thiophene rings and would spread out of this system in order to minimise electron-electron repulsion. Therefore, it is valid to assume that the π -electrons are non-interacting, and the energetics can be described by a series of one-electron energy levels, which is analogous to the simple quantum mechanics model of a particle in 1-dimensional box. The energy levels of an electron in a box of length L , is defined as:

$$E_n = \frac{h^2 n^2}{8m_e L^2} \quad (3.1)$$

where h is Planck’s constant, n is the principle quantum number, and m_e is the mass of an electron. In the model the potential energy of the electron is infinity at each end of the conjugated oligothiophene, and constant throughout the conjugation length.

The decreasing band-gap as a function of increased conjugation length is confirmed in Figure 3.4, which shows the absorption maximum linearly scales as a function of the inverse oligomer length, defined as the number of thiophene units. The linear behaviour suggests that the conjugation length is not at the limit of the sub-unit length in a polymer backbone, which is consistent with the expected conjugation length of P3HT being 11–20 monomer units long before a red-shifting saturation (non-linear relationship) is observed. The PL spectra show the expected length dependent red-shift, with a Stokes-shift of ~0.5 eV for each oligomer. A dilute solution ensures that the oligomers exist as isolated (non-interacting) chromophores, which prevents energy migration between π -conjugated chromophores. This means these spectral features are inherent properties of the oligomer chromophores.

Table 3.1 Summary of the optical properties of a series of oligothiophenes in a dilute solution of toluene. Q_{PL} is the photoluminescence quantum yield determined using an integrating sphere, and τ_{PL} is the PL lifetime obtained by TCSPC.

Oligomer Length (n)	Absorption Max (eV)	PL 0-0 Peak (eV)	Q_{PL} (%)	τ (ns)
4	3.28	2.73	14.6	1.71
6	2.95	2.42	35.6	1.67
8	2.83	2.29	23.0	2.10
10	2.70	2.25	35.0	1.43

PL quantum yields (Q_{PL}) were determined in dilute solutions (absorption maximum ~0.05) using an absolute method employing an integrating sphere,¹⁶⁴ and show PL yield in the range of 15–35% for the series, which trends upwards as the

Figure 3.4 Steady-state optical absorption maximum of a series of oligothiophenes as a function of $1/L$, where n is the number of thiophene units. The solid line is a linear fit based on a particle in a box model and confirms the length dependent band gap.

oligomer length increases. It is noted that the homo-coupled 8T is an exception to this trend as it is higher than 4T, but lower than either 6T or 10T. This could relate to the central unsubstituted bithiophene being absent in this structure, altering the rate of non-radiative pathways of relaxation. PL lifetime was measured through time-correlated single photon counting (TCSPC) with excitation of 452 nm. The lifetime constant (τ) was calculated from an exponential fit of the resulting TCSPC histogram. The lifetime of all oligomers are on the order of a few nanoseconds. The photophysics of this series of oligothiophenes will be discussed in subsequent chapters in this thesis.

3.5 Synthesis and characterisation of an oligothiophene dimer

The ability of π -conjugated materials to interact with each other through overlap of orbitals results in intermolecular coupling of π -conjugated systems. This interaction is highly sensitive to the relative orientation of the π -conjugated molecules. When a

high degree of molecular organisation is obtained, extended π -coupled networks can be formed. The series of oligothiophenes as model compounds appear ideally poised to probe the dependence of molecular distance and electronic coupling between chromophoric units of a conjugated polymer backbone, which would compliment the studies on isolated chromophores. To achieve this, it is useful to impart structural constraints to control both the distance and orientation between chromophores.¹⁶⁵ This concept has been shown to allow for the ‘construction of multi-chromophoric architectures through covalently linking chromophores together.’^{166–169} One example was reported by Giaimo *et al.* to examine the excited singlet states of co-facial dimers and trimers of perylene bisimide dyes using a rigid xanthene linker.¹⁷⁰ The authors showed the ability to induce strong electronic interactions between PBI chromophores by examining steady-state optical absorption and emission spectroscopy.

To investigate the effect of electronic coupling on the excited state dynamics of oligothiophenes, **4T** was covalently linked to a xanthene scaffold employing a Williamson ether synthesis as shown in Scheme 3.3. This was achieved by first derivatising **4T** via a Suzuki-Miyaura reaction with 4-hydroxyphenylboronic acid pinacol ester (**6**) and the brominated derivative of **4T** (4T-Br) to give a phenol-substituted quaterthiophene derivative (4T-PhOH) in 15% yield. Next, the 2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene scaffold (**7**) was functionalised to the 4,5-bis(chloromethyl) derivative (**8**) following literature procedures.^{171,172} Finally, the oligothiophene dimer (4T-Dimer) was obtained via a Williamson ether synthesis between 4T-PhOH and **5** in 40% isolated yield following purification using silica gel chromatography. The structural identity was confirmed through NMR and mass spectrometry, which can be found in Appendix III.

Intermolecular coupling of π -conjugated systems is sensitive to the local electronic environment, meaning steady-state optical absorption and emission spectroscopy is a useful probe to the state of coupling when the 4T oligomers are linked by the xanthene scaffold. Figure 3.5A presents overlaid optical absorption and emission spectra of 4T, 4T-PhOH, and 4T-Dimer in dilute tetrahydrofuran (THF) solution. The use of a dilute solution yields isolated chromophores in each case and allows for a direct measure of the xanthene linker. All compounds are characterised by a broad, featureless absorption and a vibronically structured emission. The vibronic structure in the PL spectra is attributed to the strong electron-phonon coupling during excitation. The change in spectral position of 4T and the dimerised derivative is a result of the extended conjugation length arising from the attachment of the phenol moiety. This is confirmed by the overlapping absorption spectral position between 4T-PhOH and 4T-Dimer, and consistent with the red shifted PL spectra.

Scheme 3.3 Synthesis of a quaterthiophene-dimer (4T-Dimer) through covalently linking the phenol-substituted 4T to a xanthene scaffold using a Williamson ether reaction.

Figure 3.5 Normalised steady-state optical absorption and photoluminescence spectra of the oligothiophene dimer (4T-Dimer), overlaid with those of the monomer (4T-PhOH) and starting oligomer (4T).

An important observation is that the PL spectra for the dimer and monomer (4T-PhOH) are very similar. However, if the xanthene scaffold was promoting electronic coupling between oligomer chromophores, the resulting excimeric state would be expected to exhibit a highly-quenched and red-shifted emission.¹⁷⁰ Since this is not observed it suggests that the orientation of the oligomer chromophores induced by the xanthene scaffold is not able to provide an efficient π - π -interaction. A detailed discussion of the features of 4T steady-state spectra are discussed in Chapter 4.

The controlled formation of various assemblies of π -conjugated materials depends on a variety of factors, such as temperature, concentration, solvent composition, and particular additives. Often it is through a delicate balance of these factors that leads to an ordered interaction between molecules. To investigate if an electronically coupled dimer could be obtained, a solvent titration experiment was performed in an attempt to force the assembly. This can be done by dispersing the molecule in a solvent known to provide isolated chromophores (*i.e.*, a “good” solvent), and then adjust the solvent composition to include a solvent which would not readily solubilise the π -conjugated chromophore (*i.e.*, a “poor” solvent).

In this study the solvent mixture chosen was THF:H₂O, whereby THF was chosen to be the good solvent, and water was selected as the poor solvent. The effect this has on the electronic states of the dimer can then be monitored as a function of solvent composition using steady-state absorption (Figure 3.6A) and PL (Figure 3.6B).

The absorption spectrum remains peaked at 400 nm until the solvent composition exceeds 60% H₂O, at which point there is an 8 nm red shift, and a slight broadening in the spectral shape. This is accompanied by a loss of vibronic structure in the PL spectra which develops into a red-shifted and broad emission, consistent with aggregation of chromophores.¹⁷³ However, this broad PL is also observed in the control measurement involving the same experiment performed on 4T-PhOH (Figure 3.6C). This suggests that the aggregation observed is most likely occurring intermolecularly involving multiple individual chromophores species, rather than a result of isolated and well-defined dimer formation induced by the xanthene scaffold. Unfortunately, such an aggregated system does not provide a valid molecular model to study the effect of electronic coupling on the excited state photophysics of ordered polymer segments. For this reason, further synthetic development, and a study of the oligothiophene dimer photophysics were not continued in this thesis.

3.6 Summary

In summary, this chapter presents the synthesis of a series of oligothiophenes of well defined conjugated lengths using the Suzuki-Miyaura reaction. Oligothiophenes were targeted due to their direct relevance to the well studied polymer P3HT in photovoltaic devices. These oligomers are good models of the chromophore sub-units that could be present in P3HT as they avoid unfavourable steric interactions between alkyl-substituents on neighbouring thiophene units. The conjugation lengths of 4–10 are in line with the conjugation lengths observed in P3HT systems previously reported. Steady-state optical absorption spectroscopy confirms a length dependent band-gap as the thiophene ring number is increased. Therefore, this series of oligomers provide access to a library of compounds to probe the relaxation photophysics present in conjugated polymers, which is addressed in subsequent chapters.

Additionally an oligothiophene dimer was synthesised by covalently linking **4T** to a xanthene scaffold. This was motivated by the possibility of yielding a molecular model to probe the effect of electronic coupling between chromophoric units of a conjugated polymer backbone on the relaxation photophysics. Unfortunately, the xanthene scaffold was not a suitable substrate in order to provide structural constraints that favoured the formation of a isolated dimer in solution, and this avenue would require an investigation outside the scope of the work presented here.

Figure 3.6 Solvent titration using THF and H₂O mixtures to promote aggregation probed through steady-state optical absorption (A) and photoluminescence (PL) spectra (B) of the oligothiophene dimer (4T-dimer) at the water composition indicated. The red-shifting absorption and broadening PL indicate aggregation. The observations of the same spectral dynamics in the PL of the control experiment involving 4T-PhOH (C) suggest the aggregation involves multiple chromophores, instead of well defined dimers.

Chapter 4

Torsional relaxation dynamics in a series of oligothiophenes

4.1 Introduction

In the optimization of devices, an understanding of the intrinsic electronic and conformation properties is required, as polymer excited states are influenced by the dynamic polymer chain conformations.²³ One important characteristic is the torsional dynamics of the backbone leading to conformation defects.^{3,68} This gives rise to inhomogeneous broadening due to a distribution of sizes (and therefore energies) of chromophores comprising the polymer backbone.^{30,174} All conformational sub-units are able to absorb light and act as chromophores. As a result, photoexcitation causes a broad distribution of chromophores to be populated, consistent with polymer absorption spectra which are typically broad and featureless. However, polymer emission spectra are typically narrow and contain vibronic structure. This has often been attributed to energy transfer funnelling excitation to lower energy (longer conjugation length) sub-units and therefore emission is only observed from a narrow distribution of energies.^{3,18,22,175}

Time-resolved spectroscopic measurements on conjugated polymers have attributed dynamics to a combination of conformational relaxation and excitation energy transfer.^{27–29} These relaxation features are identified through spectral red-shifting and a perturbation in the vibronic progression in polymer emission spectra, identified by comparing the kinetics at specific wavelengths. However, these studies lacked intrinsic oligomer inputs in order to investigate the relaxation processes. Theoretical studies have shown that for oligomers of well-defined conjugation length, the broad

absorption spectra arise due to a distribution of ground state torsional configurations at room temperature.^{30,176–179} Torsional modes in the excited state become more rigid which results in the thermally equilibrated excited (thexi) state having a planar geometry.⁷³ Structural relaxation is driven by the potential energy curve of the excited state being steeper than the ground state,^{180,181} resulting in a drastically non-equilibrium conformation distribution when the ground state potential is projected onto the excited state. This promotes rapid torsional relaxation to occur before emission, consistent with emission from a narrow distribution of conformations being observed.

Previous time-resolved spectroscopy shows torsional relaxation in oligomers occurs within tens of picoseconds after photoexcitation, as the molecular conformation relaxes towards the new equilibrium geometry.^{71,74,182,183} These results support the slow 10 ps dynamics observed in the dynamics of conjugated polymers.^{29,184} Recently, Busby et al. used pump-dump-probe spectroscopy to show that in polythiophene there are two phases of structural relaxation involving small-scale reorganisation (<10 ps) and a slow reorganisation involving large-scale planarisation of thiophene groups (~20 ps).¹⁸⁵ Furthermore, Raman spectroscopy on oligomers confirms this by showing the main torsional relaxation occurs on sub-picosecond – few picosecond timescales, which is also strongly coupled to the electronic properties.¹⁸⁶ These results show that the non-mirror image absorption-emission spectra in polymer systems are not solely explained through energy migration processes, and that torsional relaxation has an important contribution to relaxation pathways in conjugated polymer systems.

In this chapter, time-resolved transient grating photoluminescence (TRPL) and transient absorption (TA) spectroscopy are used to probe torsional relaxation dynamics in a series of oligothiophenes of well-defined conjugation length. The series of oligothiophenes (see Chapter 3) act as mimics for conformational subunits on a P3HT backbone. Optical spectroscopic signatures capture all phases of intrinsic oligomer relaxation. Modelling the dynamic photoluminescence spectra to a Franck-Condon progression of Gaussians, it is shown that the spectral dynamics are caused by a time-dependent narrowing of Gaussian widths and decreasing Huang-Rhys factor. Interestingly, no length dependent kinetics are observed over the series probed here. The implications of torsional relaxation on polymer films was probed by dispersing an oligomer in an inert matrix to provide isolated oligomers dispersed throughout the film depth. Tracking the relaxation photophysics reveals torsional dynamics are also present in the solid state. This provides evidence that both torsional relaxation and energy migration could contribute to the non-mirror image absorption-emission spectra in polymer thin films.

4.2 Vibronic progression in steady-state emission spectra

The steady-state absorption and photoluminescence of the series of oligothiophenes (see Chapter 3 for chemical structures) in dilute solution are shown in Figure 4.1. Spectral features exhibit a progressive red-shift with increasing oligomer length as discussed in Chapter 3. For all oligomers, the absorption is spectrally broad and unstructured, whilst the photoluminescence is narrow and contains clear vibronic structure. A dilute solution ensures that the oligomers exist as isolated (non-interacting) chromophores, which prevents energy migration (*e.g.*, Förster resonance energy transfer), resulting in these spectral features being inherent properties of the oligomer chromophores.

To obtain parameters that allow quantitative comparison throughout the library, the emission spectra were fit to a Franck-Condon progression of Gaussians, which has previously been applied to polythiophene steady-state emission spectra.^{184,187} This model is based on the assumption that the vibronic structure is caused from an electronic transition being coupled to a single vibrational mode (*e.g.*, C–C stretch).^{177,188} Subsequently, the PL spectra can be modelled by a progression of Gaussian line shapes displaced by the phonon energy of the stretching mode. This was achieved using Equation 4.1 for PL intensity (I) at optical frequency (ω):

$$I(\omega) \propto (\hbar\omega)^3 n(\omega) \times \sum_{m=0} \frac{S^m}{m!} \Gamma(E_{0-0} - mE_{ph}, \sigma) \quad (4.1)$$

Where $\hbar\omega$ is the Einstein coefficient of spontaneous emission, $n(\omega)$ is the refractive index at optical frequency (ω), m is the vibronic transition index, S is the Huang-Rhys factor, E_{0-0} is the energy of the 0-0 transition in eV, E_{ph} is the phonon energy for a C–C stretch, and Γ is a Gaussian line shape function with full-width half-maximum, σ . In the fitting procedure, the free parameters are S , E_{0-0} , and σ , while $n(\omega)$ is assumed constant across the frequency range, and E_{ph} was fixed as 0.17 eV.^{184,187,189}

The optimized fits for the series of oligothiophenes in this study are overlaid on PL spectra in Figure 4.1 (solid lines), and match well with the experimental data. Also presented are the Gaussian line shapes that compose each of the optimized fits showing the decreasing Gaussian amplitude as m increases. For the 0-0 vibronic transition (*i.e.*, $m=0$) the pre-Gaussian factor ($\frac{S^m}{m!}$) will be equal to 1. For higher

Figure 4.1 Normalized steady-state absorption and photoluminescence of a series of oligothiophenes in dilute solution (toluene) at room temperature: A. dihexyl-quarterthiophene (4T), B. dihexyl-sexithiophene (6T), C. tetrahexyl-octithiophene (8T), and D. tetrahexyl-decithiophene (10T). Each oligomers exhibits broad, unstructured absorption spectra and a narrow, vibronically structured PL. The PL spectra were fitted to a Franck-Condon progression of Gaussians (Franck-Condon model) with the resulting fit (solid black line) and the Gaussian components (grey dotted lines) overlaid.

vibronic transitions the Huang-Rhys factor (S) determines vibronic peak ratio scaling, and is a measure of the displacement between the ground and excited state equilibrium positions on the potential energy surface.¹⁹⁰ Optimized fits of oligomer PL yields a decreasing Huang-Rhys factor as the oligomer length is increased, representative of the 0-0 vibronic peak increasing in intensity relative to the 0-1 vibronic peak. This is consistent with parameters reported by Yang *et al.* for steady-state PL in a series of α -oligothiophenes of length 2–7.¹⁹¹ These data confirm the non-mirror image absorption-emission spectra as an intrinsic property of the isolated oligomers, along with the ability to model the PL spectra effectively using the Franck-Condon model.

4.3 Torsional relaxation photophysics

To probe length dependent relaxation, transient-grating photoluminescence spectroscopy (TGPL) was performed, which provides time-resolved, broadband PL spectra.¹²³ Data acquisition was performed by Dr. Kai Chen in the Hodgkiss research group,¹⁹² and the analysis and processing was performed separately as part of this investigation. TGPL spectra for the series of oligomers at various times are shown in Figure 4.2, along with the optimized fits obtained using the Franck-Condon model (described above). Immediately after photoexcitation (<0.5 ps) the spectra for all oligomers are broad and unstructured, reminiscent of the steady-state absorption spectra. On the order of a few picoseconds, the high energy edge of the PL spectra shift to lower energy, and clear vibronic structure becomes apparent. These spectral features are consistent with structural relaxation as the excited state is driven towards the thermally equilibrated excited (thexi) state which has a planar conformation. The timescale of this relaxation is on the order of a few picoseconds, consistent with the timescale of torsional relaxation reported by Zhou *et al.* using femtosecond stimulated Raman spectroscopy.¹⁸⁶ The red-shifting of the high energy edge continues on 10's of picosecond timescales which is consistent with the slow relaxation component reported by Wells *et al.* for conjugated polymers.²⁹

Owing to the broad distribution of conformational states accessible at room temperature, the initially broad PL spectra result from a broad distribution of excited states being populated immediately after photoexcitation. However, the subsequent narrowing could result from: 1) a red-shifting (decreasing) 0-0 transition energy induced by solvent reorganization as the molecule geometry relaxes, 2) a narrowing of the distribution of molecular conformations as the excited state molecular geometries are driven to a similar structure, or 3) a combination of these two effects.

To investigate the photophysics observed Figure 4.3 presents the optimized fitting parameters extracted from the Franck-Condon model applied to TRPL as a function of time. Figure 4.3A shows the Huang-Rhys factor increases for all oligomers over time, with the value at 100 picoseconds being ~ 1 , consistent with the steady-state value obtained for the oligothiophene series (see Appendix), and those reported for poly- and oligophenylenevinylenes.^{178,193} The Huang-Rhys factor is a measure of the displacement between the ground and excited state equilibrium positions on the potential energy surface.¹⁹⁰ Thus, this parameter provides a measure of the conformational relaxation energy of the excited state. Immediately after photoexcitation the majority of chromophores excited will be close to the equilibrium nuclear geometry of the ground state as minimal relaxation has occurred. This direct projection of the ground state geometry onto the excited state potential is called the Franck-

Figure 4.2 Normalized time-resolved transient grating photoluminescence (TRPL) spectra of (A) 4T, (B) 6T, (C) 8T, and (D) 10T showing a spectral red-shift at early time (<0.5 ps) of a broad spectrum which narrows and vibronic structure evolves on the picosecond timescale. PL spectra at each time point were modelled using the Franck-Condon model, with optimized fits overlaid (solid lines). Also included are the steady-state absorption and fluorescence spectra of each oligomer.

Condon geometry. As the molecule is driven toward planarity there is a required shift in the nuclear (torsional) coordinate in order to reach equilibrium of the excited state. At early time the spectrum is broad and contains contributions from an ensemble of excited state conformations and the increasing Huang-Rhys factor is explained through a relaxation of the overall excited state population to the thexi state. The timescale for this relaxation is within 2 picoseconds, and is likely a localised torsional relaxation between neighbouring thiophene rings in the oligomer backbone. This accounts for the evolution of vibronic structure in the PL spectra within a few picoseconds.

Figure 4.3 Optimized parameters extracted from the Franck-Condon model applied to TRPL of oligomers as a function of time. (A) The Huang-Rhys factor, (B) the position of the 0-0 transition, and (C) the full-width half-maximum of the Gaussians. The minimal change in 0-0 position suggests that the TRPL dynamics are not accounted for by a red-shifting spectrum, but instead by a narrowing of the initially broad distribution of excited states due to structural relaxation of isolated oligomers (decreasing FWHM, increasing Huang-Rhys factor).

Spectral red-shifting was investigated using the 0-0 transition energy (Figure 4.3B) and Gaussian full-width half-maximum (FWHM) values (Figure 4.3C) obtained from the Franck-Condon progression fitting. The length dependent band gap is clearly resolved in optimized E_{0-0} values extracted in the fit with $4T > 6T > 8T > 10T$, as expected. The energy of the 0-0 position for each oligomer is constant across the time scale of the experiment, suggesting minimal contribution from stabilization of the excited state energy, which would present as spectral red-shifting. Instead, the Gaussian FWHM decreases from ~400 meV to 150 meV for all oligomers within a few picoseconds. This is on the same timescale as the change in Huang-Rhys factor, showing that the spectral narrowing and vibronic structure evolution are linked.

In the optimized fitting, the Gaussian FWHM values represent the average transition 'width' of the total excited state population sampled. Since the ground state has a softer potential energy gradient than the excited state, photoexcitation leads to a distribution of overlapping excitation energies.¹⁹⁴ This is supported by the broad Gaussian FWHM values at early time delays (<0.5 ps), which results from a summation of overlapping excited state transitions. This is also consistent with the broad

steady-state absorption spectrum which is observed for all oligomers. These results show that the observed spectral dynamics have minimal contribution from red-shifting due to solvation effects and instead originate from dynamic narrowing of the Gaussian widths. This is consistent with the distribution of molecular conformations narrowing as the excited states funnel to a similar structure, owing to the steeper gradient of the excited state potential. Furthermore, the narrowing kinetics of FWHM is similar for all oligomers, suggesting there is no length dependence in the torsional relaxation.

To further investigate that the spectral features are caused by a dynamic narrowing of the molecular conformation distribution toward planarity, transient absorption (TA) spectroscopy was performed which provides high data density (time slices) compared to TRPL spectroscopy. TA spectral slices are shown in Figure 4.4A for 4T in dilute solution. The spectral slices are characterised by a ground state bleach (GSB) signature at probe photon energies >3.0 eV, which overlaps with the steady-state absorption spectrum, a dynamic stimulated emission (SE) signature (2.8–2.4 eV), and a photoinduced absorption (PIA) > 2.2 eV. The spectral dynamics of the SE region are reminiscent of those observed in TRPL, whereby at 200 fs the spectral feature is broad and unstructured, and vibronic structure develops in less than 5 picoseconds. TA spectral slices show similar dynamics for the other oligomers in solution (see Figure 4.4B–D), but are red-shifted owing to the extended conjugation length. These spectral features are consistent with rapid torsional relaxation to reach a thexi state with a planar excited state geometry.

It is noteworthy that the vibronic progression intensity differs between the PL spectra and the SE region in a TA spectral slice. Figure 4.5 shows the comparison of TRPL spectrum at 50 ps to the SE region of a TA spectral slice at the same time delay. This clearly shows the 0-1 vibronic peak is more intense in the TA spectral slice than the TRPL spectrum. This is explained through consideration of quantum theory related to spontaneous and stimulated electronic processes.¹⁹⁰ After photoexcitation the excited state population has a tendency to relax and lose the excess energy. Thus, the radiation of light from this process alone is spontaneous emission. In contrast, the stimulated emission feature observed in TA has an external stimuli (*i.e.*, a probe photon) in order to stimulate the transition to the ground state. Therefore, stimulated emission is similar to absorption in quantum theory of radiation. Importantly, the rates of these processes are related to Einstein coefficients, which are different for each process.¹⁹⁰ The Einstein coefficient for spontaneous emission is denoted as $(\hbar\omega)^3$ in Equation 4.1. Since this coefficient is not present in stimulated emission, normalizing the TRPL spectrum by this factor accounts for the differing vibronic intensity, as shown in Figure 4.5.

Figure 4.4 Transient absorption spectra of 4T (A), 6T (B), 8T (C), 10T (D) in solution at the times indicated following photoexcitation with 400 nm showing a dynamic stimulated emission feature with similar spectral features as observed in TRPL.

Having accounted for the spectral shape between TRPL and TA showing similar features, attention returns to the relaxation dynamics. Due to the spectral dynamics observed in TRPL being explained through Gaussian narrowing, the SE region could ideally be modelled using a similar method. However, the vibronic progression of the SE region cannot be modelled using a full Franck-Condon progression of Gaussians because there is a negative PIA which has some (unknown) spectral overlap with the SE spectral feature. To circumvent this, it is noted that the phonon energy separating the progression of Gaussians (0.17 eV), together with the Gaussian FWHM (from TRPL) being on the order of hundreds of millielectron volts, yields the high energy edge of stimulated emission being dominated by contributions from the 0-0 transition only (*i.e.*, minimal contribution from the 0-1 transition Gaussian). However, this high energy edge will have contributions from the overlapping tail of the GSB signature. To account for this overlap the steady-state absorption spectrum was used as a spectral mask for the GSB feature, allowing this feature to be

Figure 4.5 Transient absorption spectrum of the stimulated emission feature (black dots) for 6T in solution, overlaid with time-resolved PL spectrum (red line) for 6T, both at 50 ps time delay. A more intense 0-1 peak in stimulated emission is accounted for by normalising the PL spectrum by the Einstein coefficient for spontaneous emission (blue line), which is not present in the stimulated emission process.

subtracted from the data surface. Figure 4.6A shows the steady-state absorption spectrum overlaid with the TA spectral slices for 6T, which is representative of all oligomers. The effectiveness of this subtraction process was confirmed by the $\Delta T/T$ signature being at the baseline at probe energies related to the GSB (>2.7 eV), presented in Figure 4.6B.

The TA surface resulting from this process now contains a region of the SE which has no overlapping signatures and enough points to uniquely define a single Gaussian line shape. Using the amplitude and FWHM of a single Gaussian as free fitting parameters as a function of time, tracks the excited state transition narrowing in a similar way as achieved for TRPL. The FWHM values obtained for all oligomers using this method are shown in Figure 4.6C and show that a narrowing of Gaussians accounts for the spectral dynamics, consistent with the results from TRPL fitting. All oligomer TA spectra are characterized by a decreasing Gaussian FWHM from ~ 400 meV to ~ 200 meV within 3 ps, followed by a slower narrowing observed on longer timescales (>10 ps). The FWHM values are similar for all oligomers and exhibit the same narrowing dynamics. The FWHM dynamics extracted from TA spectroscopy are cropped at 100 ps due to the appearance of a PIA signature appearing on longer timescales, which overlaps with the SE region. The dynamics of this PIA growth are discussed in detail in Chapter 5.

Figure 4.6 Transient absorption spectra of 6T in solution at the times indicated (A) showing a dynamic stimulated emission feature (2.4 eV), overlaid with the steady-state absorption spectrum. This was used as a spectral mask in order to account for overlapping GSB and SE spectral features (B). Spectral dynamics were modelled by fitting the high energy edge of the SE to a Gaussian line shape (as described in the text) to provide FWHM values (C). The values obtained are consistent with FWHM parameters extracted from the TRPL data.

This length independent structural relaxation is consistent with the parameters obtained from TRPL spectra using a Franck-Condon fit, and confirms the same dynamics are observed in both TRPL and TA spectroscopy. These data show that the Gaussian narrowing occurs on the same timescale as a change in the torsional coordinate (i.e., Huang-Rhys parameter). Additionally, the two stage of torsional relaxation have been resolved through these methods. The excited state molecular geometry is funnelled to a narrow distribution *via* planarisation within 3 ps, and this accounts for the majority of the structural relaxation. This rapid torsional relaxation is likely due to a localised change in torsion angles between neighbouring thiophene in the conjugated backbone. A slower narrowing of the distribution is observed on longer timescales (>10 ps) which is attributed to large scale reorganisation of the backbone conformation.²⁹

To gain further insight into the torsional relaxation process, density functional theory (DFT) calculations (CAM-B3LYP functional)¹⁹⁵ were used to model the torsion of the ground and excited state oligomer structures. These were performed by Gregory S. Huff and Prof. Keith Gordon at University of Otago, Dunedin, New Zealand.¹⁹² The potential energy surfaces were calculated from optimized S_0 and S_1 molecular geometries using single-point and time-dependent DFT calculations. The hexyl-substituents were reduced to methyl-groups in order to minimise computational time. Fitting the energy versus average dihedral angle calculated for each oligomer to a harmonic oscillator model (quadratic) produces pseudo-force constants for torsional rotation (twisting) shown in Table 4.1.

Table 4.1 Summary of the pseudo-force constants (k) for twisting of the S_0 and S_1 states for the oligomers calculated by fitting the average dihedral angle to a harmonic oscillator model.¹⁹²

Oligomer length	k (eV/radian ²)	
	S_0	S_1
4	0.29	0.62
6	0.38	0.82
8	0.63	0.87
10	0.74	1.07

The force constants are larger in the S_1 state than in the S_0 state, consistent with spectral dynamics observed here, and with calculated potential energy surfaces for oligophenylenes.¹⁹⁶ The force constants also increase as a function of oligomer length, which results in a narrower potential curve (increased tightness). This suggests that oligomers should relax more quickly when excited. However, calculations predict that the ground states of the longer oligomers are more disordered because of a higher density of states and number of degrees of freedom. The counterbalancing of these two effects may be responsible for the length-independent relaxation dynamics which were observed in the time-resolved optical spectroscopy experiments discussed

here.

4.4 Molecular geometry relaxation in films

The link between spectral dynamics and torsional relaxation discussed above has so far focused on solution based measurements. To probe the role of torsional dynamics when in a film, 6T was dispersed in polystyrene and then cast into the solid state *via* spin coating. Polystyrene acts as an electronically inert matrix to suspend the oligothiophene. A thin film increases the apparent viscosity of the solvation environment, which could restrict the extent of torsional relaxation.¹⁹⁷ In order to isolate the role of torsional motion without contributions from energy transfer a large excess of polystyrene with respect to 6T (20:1 wt%, polystyrene:oligomer) was used. Figure 4.7 shows the steady-state optical absorption spectra of 6T in dilute toluene solution and in a polystyrene film. The spectra have similar broadness and only a small red-shift in peak position. The lack of aggregate artefacts present in the absorption spectra of the film (*e.g.*, H-/J-aggregate peaks),¹⁷³ confirms that the film contains isolated oligomer chromophores, owing to the high dilution with polystyrene.

Figure 4.7 Steady-state optical absorption spectrum of a 6T:polystyrene film compared to 6T in solution. The similar spectral shapes confirms the presence of isolated chromophores in the solid state.

To investigate torsional relaxation dynamics in a film TRPL and TA were performed on the 6T:polystyrene film, presented in Figure 4.8A and Figure 4.8B, respectively.

Initially the TRPL spectrum is broad and unstructured which narrows and vibronic structure evolves over a few picoseconds. TA dynamics are similar, with a shifting SE region over the same timescale. Although the vibronic progression of the PL is not well defined, the vibronic ratio ($[0-1]/[0-0]$) extracted from SE region in TA shows only a 4% difference between solution and solid state. The spectral dynamics in the solid state are similar to those observed in solution, confirming that torsional relaxation still occurs in the environment of a thin film.

Figure 4.8 Steady-state optical absorption spectrum of a 6T:polystyrene film compared to 6T in solution. The similar spectral shapes confirms the presence of isolated chromophores in the solid state.

To examine this further, Figure 4.8C tracks the Gaussian FWHM parameter of optimized fits obtained for both spectroscopic methods. As detailed earlier, this is achieved using a Franck-Condon progression of Gaussians for TRPL, and through fitting a singular Gaussian line shape to the high energy edge of the SE signature in TA spectra. The dynamics of the spectral narrowing are remarkably similar for both solution and solid state measurements. The difference of narrowing kinetics within the first picosecond between TRPL and TA for 6T:polystyrene could be

explained by the standard error obtained from each fitting method. Applying a 95% confidence interval provides errors of ~1–2% for TRPL fitting, whereas this value is ~5–10% for TA fitting. This shows that there is good agreement of narrowing kinetics between the two spectroscopic methods. The decreasing FWHM within 4 picoseconds identifies that the fast torsional relaxation component still occurs in the solid state, whereas the slower component of greater conformational relaxation appears to be less prevalent.

These results could have implications on understanding the relaxation processes occurring in conjugated polymer films following photoexcitation. Results discussed here have resolved all phases of structural relaxation in oligothiophenes in the solid state. The fast localised torsional relaxation (<4 ps) could compete with the energy transfer processes, suggesting that this aspect should not be overlooked when considering polymer relaxation dynamics such as exciton self-trapping. On longer timescales (>10 ps), the slow conformational relaxation is unlikely to significantly compete with excitation energy transfer in polymer films due to the increased lifetime of these dynamics.

4.5 Summary

In this chapter, the non-mirror image absorption-emission spectra often observed in conjugated polymers was investigated using oligothiophenes as molecular models of polythiophene sub-units. Using time-resolved photoluminescence (TGPL) and transient absorption (TA) spectroscopy all phases of structural relaxation were resolved. PL/SE spectral shapes immediately following photoexcitation were broad and unstructured, similar to the steady state absorption spectra. Within 4 ps the evolution of vibronic structure was observed, which was coupled by a spectral red-shift that continued onto 10's of picosecond timescales. TGPL spectra were modelled by a Franck-Condon progression of Gaussians which provided a link between spectral features and molecular geometry. This revealed that the spectral dynamics are caused by a time-dependent narrowing of Gaussian widths and decreasing Huang-Rhys factor. This is attributed to the structural relaxation funnelling the molecular geometry to a narrow distribution of conformations as the excited state planarises. Modelling the TA data using a single Gaussian line shape on the high energy edge of SE also confirmed these findings.

The dynamics of the planarisation revealed the majority of the torsional relaxation occurred within a few picoseconds, induced by a localised relaxation of the torsional

angle between neighbouring thiophene rings in the backbone. The slower structural relaxation (>10 ps) was attributed to a large scale conformational relaxation of the backbone. DFT calculations showed the excited state potential is steeper for longer oligomers, but at the same time the molecular geometries are more disordered. The interplay of these two effects is proposed to be the reason for length independent structural relaxation dynamics. The implications of torsional relaxation on polymer films was probed by dispersing an oligomer in an inert matrix, which revealed the 2-phase torsional dynamics were able to occur in the solid state. This provides evidence that both torsional relaxation and energy migration could contribute to the non-mirror image absorption-emission spectra in polymer thin films.

Chapter 5

Triplet exciton formation in a series of oligothiophenes

5.1 Introduction

Understanding relaxation dynamics in π -conjugated molecules following photoexcitation is of fundamental interest in OPV device optimization. Central to OPV device operation is the dissociation of excitons at a donor-acceptor interface to form charge-transfer (CT) states. The classic model of OPV device operation predicts that CT states either undergo geminate recombination, or separate to form free charge carriers.^{2,15} Recently it has been highlighted that free charges in an OPV could exhibit similar behaviour as observed in organic light emitting diodes, whereby non-geminate (bimolecular) recombination leads to the formation of both singlet and triplet CT states.^{103,104,198} A triplet CT state could subsequently relax into the lower-lying triplet exciton manifold of the donor component (*e.g.*, conjugated polymer).^{199–201} Since triplet states are much lower in energy in organic materials, relaxation of the triplet CT state within the triplet manifold would act as an energy trap by increasing the energy barrier to charge separation.²⁰² In turn this would lead to a decreased device efficiency through loss of free charges.

The potential role of triplet states in OPV devices was recently brought to the fore by Etzold *et al.* who used transient absorption spectroscopy to probe the photophysics of charge generation in polymer:fullerene blends, and reported that triplet formation in polymer:fullerene blends can occur on the order of 100's of picoseconds.¹⁰⁵ However, this timescale is an order of magnitude faster than is typically observed for bimolecular recombination.^{11,111} Furthermore, Dimitrov *et al.* have suggested

that triplet exciton formation in polymer:fullerene blends occurs through spin-state mixing of bound electron-hole pairs.¹¹² This implies that intersystem crossing (ISC) of excitons or charge transfer states could be of fundamental importance to the formation of triplet excitons in OPV's based on π -conjugated materials. However, the mechanism of triplet exciton formation, and their role in OPV blends, is not fully resolved.

In general for π -conjugated chromophores, photoexcitation leads to population of the first singlet excited state (S_1), and the rate of internal conversion (IC) and photoluminescence (PL) are much greater than intersystem crossing (ISC) to the triplet manifold.²⁰³ However, in oligothiophenes the non-radiative decay processes are dominated by ISC.²⁰⁴ In these systems, triplet formation and photoluminescence are the major relaxation pathways. These exhibit length dependent dynamics with PL quantum yield increasing and triplet quantum yield decreasing as the oligothiophene conjugation length is increased.^{204–207} Theoretical and spectroscopic studies concerning the energy state landscape show two or more triplet states are lower in energy than the lowest singlet state.^{208–210} In particular it has been proposed that the T_2 state (the second excited state in the triplet manifold) may have a major role in accounting for the high triplet yields in oligothiophenes.²¹¹ Furthermore, Siegert *et al.* have shown that these dynamics are linked to molecular geometry, whereby torsional disorder (non-planar conformation) is a requirement for ISC due to spin-orbit coupling between singlet and triplet manifolds.²¹² It is important to note that it is not just the presence of a twist that enables ISC, but motion along this coordinate, *i.e.* twisting, is critical to favourable spin-mixing.

Work presented in this chapter aims to probe the link between molecular geometry and triplet exciton formation *via* ISC. The oligothiophenes synthesised in this work (discussed previously) provide molecular models which allow the complex ISC dynamics of polythiophene to be isolated. Singlet and triplet exciton photophysics were probed by transient absorption (TA) spectroscopy on picosecond to nanosecond timescales. Through the identification of singlet and triplet signatures it was possible to track the singlet decay and triplet formation dynamics showing that restriction of torsional relaxation increased triplet yield. It is proposed that vibrational hot states in π -conjugated polymers help drive ISC through favourable spin-orbit coupling between the singlet and triplet manifold. This model of triplet exciton formation in oligothiophenes could aid in understanding triplet exciton formation in polymer:fullerene blends *via* spin-mixing instead of non-geminate recombination.

5.2 Tracking singlet and triplet exciton dynamics

The TA spectroscopy of **4T** in methyltetrahydrofuran (MeTHF) at 295 K is shown in Figure 5.1. The solvent was chosen as MeTHF forms a glass when frozen instead of crystallising like most common solvents. This glass formation prevents light scattering upon decreasing temperature, and also allows for measurements to be conducted in a vacuum-sealed cuvette since the frozen solvent will not expand which could crack the quartz cell. The TA spectrum at 10 ps (Figure 5.1A) is dominated by three spectral signatures; a broad ground state bleach (GSB) at ~ 3.26 eV, a stimulated emission (SE) at ~ 2.61 eV, and a broad photoinduced absorption (PIA) > 2.2 eV, which extends out beyond the spectral window of the measurement. The dynamics of these features (Figure 5.1B), omitting the first 10 ps to avoid the structural relaxation dynamics (see Chapter 4), show that the GSB does not fully decay within the 5 ns time delay window. In contrast, the SE feature decays within 100's of picoseconds and the integrated kinetics become negative. Spectral traces at these longer time delays reveal that the SE signature is replaced by a broad PIA (~ 2.0 – 2.9 eV), which has well-defined vibronic peaks at 2.11 eV and 2.24 eV, and accounts for the negative dynamics in the nanosecond timescale observed in the kinetics. This vibronically structured PIA forming on ~ 1 ns timescales has previously been attributed to the formation of triplet excitons in **4T** *via* intersystem crossing.^{186,204,211,213} Therefore, the TA dynamics presented for **4T** are consistent with a singlet state formed directly after photoexcitation, which decays in hundreds of picoseconds, with the formation of triplet states at longer delays.

For oligothiophenes longer than 3 units, theoretical calculations predict that the T_2 state is similar energy as the S_1 state.^{208–210} It is expected that internal conversion within the triplet manifold would be extremely fast and therefore the PIA is likely caused from the T_1 absorption. In order to gain insight into the photophysics of the relaxation processes, soft-modelling of the TA surface was performed using singular value decomposition (SVD). The minimum number of components required to model the TA surface was guided by the singular values obtained from SVD. This was shown to be 2 components, reflected by the residual surface (see Figure 5.2) which shows no time dependent signals. SVD provides component spectral shapes and time-dependent weighting for each of components. As already discussed, the solutions from this linear decomposition are not mathematically unique. This means the obtained spectra and weightings do not necessarily carry any physical meaning, only that their product is an accurate description of the initial data series.

Figure 5.3A shows the spectral components resulting after a linear rotation transformation applied to **4T** TA data. This transformation was discussed in detail in

Figure 5.1 Transient absorption measurements of 4T at 295 K showing spectral slices at indicated time delays (A) and kinetic traces (B) following 100 fs excitation at 400 nm. The spectral integration kinetics are of GSB (3.26 eV) and SE/PIA (2.61 eV) features. All measurements were performed in a cuvette sealed under vacuum using methyltetrahydrofuran (MeTHF) as solvent. Kinetic traces are normalized to the average value between 10 and 15 ps.

Chapter 2. Since singlet state decay occurs within hundreds of picoseconds, at late time delay (*e.g.*, 5 ns) the TA spectrum only has contributions from the triplet exciton absorption. This gives physically meaningful information about the system of the spectral contributions of one component in the 2-component system. The TA spectrum at 5 ns was used as the physical constraint, and overlaying with the SVD solutions shows a correlation between one of the extracted components (blue line). Since the TA spectral mask (5 ns slice) is solely from triplet exciton absorption the matching component is assigned as the triplet exciton, and the other component is assigned as the singlet exciton. The associated time-dependent weightings for singlet and triplet components are shown in Figure 5.3B, which fit well to mono-exponential decays (solid lines). This fitting procedure allows the lifetime parameters of singlet state decay and triplet state growth to be extracted from the original TA surface.

Additionally, converting singlet and triplet state dynamics to a normalized popu-

Figure 5.2 Residual TA surface from a 2-component global fitting of the TA data presented in Figure 5.1 using singular value decomposition. The absence of time-dependent signatures shows the entire TA surface can be accounted for by 2 components.

lation scale (as shown in Figure 5.3B) allows the relative yield of triplet states to be determined. This was performed based on the integrated intensity of the ground state bleach (GSB) which provide a useful probe of the total excited state population since both singlet and triplet excitons will bleach the number of chromophores available for photoexcitation. The total population (GSB) was normalized to 1 at 5 ps, which is the timescale after structural relaxation (see Chapter 4) but before decay from the singlet excited state. Scaling was achieved using a linear combination such that: $\text{GSB}(t) = x\mathbf{S}(t) + y\mathbf{T}(t)$, where x and y are scalars, singlet population $\mathbf{S}$, triplet population $\mathbf{T}$, as a function of time (t). Figure 5.3B shows the sum of singlet and triplet exponential fitted functions (dashed line), which tracks the total population dynamics, as expected. The triplet yield was subsequently calculated as the asymptote of the exponential fit to the triplet dynamics, *i.e.*, the exponential function was evaluated at infinity. The singlet and triplet photophysics will be discussed in further detail in the subsequent sections when comparing temperature dependent TA measurements and triplet yields as a function of conjugation length.

The extraction of singlet and triplet exciton dynamics for the longer oligothiophenes is validated by analysis of the TA data shown in Figure 5.4. Time slices at 10 ps (Figure 5.4A) and 5 ns (Figure 5.4B) show the progressive shift to lower energy (red-shift) of spectral signatures as the oligomer length increases. All 10 ps spectral slices contain a stimulated emission (SE) region, with a photoinduced absorption (PIA) that appears at probe energies >1.8 eV. The full PIA signature cannot be totally resolved for these oligomers due to overlap of the fundamental seed wavelength (800 nm, 1.55 eV) used for generation of the broadband probe. TA spectra

Figure 5.3 SVD components for **4T** at 295 K following rotation using the TA spectrum at 5 ns as a physical constraint showing the spectra basis set (A) and the component weightings (B). The component weightings have been normalized based on the integrated intensity of ground state bleach (GSB) extracted from the TA data in Figure 5.1 which is a measure of total excited state population. Singlet and triplet dynamics were fit to a mono-exponential (solid lines), and the sum of these fitted dynamics (dashed line) tracks the GSB dynamics, which is a probe of the total population of excited states.

at 5 ns (Figure 5.4B) show the SE region has been replaced by a broad negative PIA signature for all oligomers, which as discussed for **4T** is from triplet exciton absorption. This is clearly shown in the integrated kinetics of the SE region for each oligomer (Figure 5.4C), which shows in all cases a negative $\Delta T/T$ signal is resolved in the nanosecond timescales.

The dynamics of SE decay show a decreased rate for the longer oligomers compared to **4T** suggesting the relaxation processes may exhibit length dependent behaviour. Meanwhile, the progressive red-shifting of the triplet PIA means the transition from T_1 to higher triplet states is getting smaller as the conjugation length increases. It is interesting to note that unlike the structured PIA observed for **4T**, no vibronic

Figure 5.4 Transient absorption measurements of series of oligothiophenes showing spectral slices at 10 ps (A) and 5 ns (B) following 100 fs excitation at 400 nm. The spectral integration kinetics (C) are of the probe energy corresponding to the SE/PIA region for each oligomer. Kinetic traces are normalized to the average value between 10 and 15 ps.

structure is resolved in the PIA of longer oligomers (see Figure 5.4). This could be obscured by the PIA approaching the fundamental laser wavelength, or caused by differences in structural properties of the longer oligomers. Nevertheless, the similar spectral shapes/dynamics between **4T** and the longer oligomers are consistent with intersystem crossing occurring in all oligomers in this series.

5.3 Triplet exciton photophysics and molecular geometry

For each oligothiophene, it has been shown that the singlet state is initially populated upon photoexcitation, which forms triplet excitons *via* intersystem crossing (ISC) within 100's of picoseconds. With the extraction of singlet and triplet excited state dynamics it is possible to probe the photophysics of the excited state species. The singlet and triplet excited state TA dynamics for **4T** as a function of temperature are presented in Figure 5.1, which have been obtained using the SVD processes described above. The spectra of singlet excitons (Figure 5.5A) are normalized by the GSB intensity and show the same spectral signatures at all temperatures. Similarly, the spectra of triplet excitons normalised by the 0-0 PIA vibronic peak (Figure 5.5B) show the replacement of SE signatures with PIA signatures consistent with triplet absorption as already discussed. However, the vibronic peak progression in the triplet PIA changes to be dominated by the 0-0 peak (2.11 eV) over the 0-1 peak (2.24 eV). The vibronic ratio (0-1/0-0) is over twice as large at 77 K (1.8) compared to 295K (0.8). The redistribution of vibronic intensity (dominant 0-0) is indicative of reduced structural distortion (*i.e.*, more ordered) in the triplet state absorption.^{187,214}

Figure 5.5C shows the fractional population of excited states, calculated as previously discussed. Solid lines represent the summation of exponential fits of both singlet and triplet excited dynamics, overlaid with the integrated intensity of the GSB region (points). This shows that decay to the ground state is suppressed at lower temperature, with ~75% of excited state population remaining at 5.5 ns for 77 K measurements, compared to 50% for 295 K measurements. This indicates that a relaxation pathway to the ground state is suppressed as the temperature is lowered.

The singlet decay and triplet growth dynamics at all temperatures are well fitted to mono-exponential functions, and the extracted parameters as a function of temperature are presented in Figure 5.6. The lifetime parameter for both singlet decay and triplet growth are extracted from the exponential fits and presented as a mean

Figure 5.5 Transient absorption measurements of series of **4T** at different temperatures showing spectral slices of singlet (A) and triplet (B) excitons extracted from the fitting procedure described in the text. The population dynamic (C) are of the integrated GSB intensity (points) overlaid with the sum of the optimized exponential singlet and triplet fits (solid line). Only every second data point is plotted for the GSB for clarity.

lifetime (τ), which is related to the exponential decay constant (λ) by an inverse relationship ($\lambda = 1/\tau$). Error bars represent the 95% confidence interval calculated from the standard error of residuals from the exponential fitting. The dashed line denotes the glass transition temperature for methyl-tetrahydrofuran (MeTHF) which is 137 K.^{215,216} The singlet decay and triplet growth lifetimes (Figure 5.6A) are of similar magnitude; consistent with depopulation of the singlet state to directly populate the triplet manifold *via* intersystem crossing (ISC). Estimating the triplet yield as the horizontal asymptote of the exponential fit of triplet formation dynamics (Figure 5.6B) shows an increased triplet yield as the temperature is decreased. This suggests that the rate of ISC must dominate the relaxation from the excited state as the temperature is lowered. Furthermore, the lifetime parameters of the singlet growth and triplet decay (Figure 5.6A) appear to show different (opposing) dynamics upon decreasing temperature either side of the glass transition temperature (T_g) of MeTHF. Upon decreasing the temperature above T_g (295 K to 151 K), there is an increased lifetime of singlet decay, accompanied by an increased time for triplet formation (*i.e.*, slower rate). In contrast, when the temperature is decreased below T_g the singlet decay and triplet growth trend to shorter lifetimes, *i.e.*, faster rate for the corresponding process.

The changes in rates demonstrate that the relaxation pathways from the excited state are affected by temperature. In oligothiophenes, singlet decay occurs through the combination of internal conversion, photoluminescence, and ISC. The rate of ISC is significantly affected by structural dynamics, or by the presence/absence of heavy atoms. In this instance the structural relaxation dynamics are altered with decreasing temperature, which become more restricted upon the formation of a glass. Sun *et al.* recently proposed that the mechanism of quaterthiophene relaxation involved ISC occurring from the structurally relaxed S_1 state into the T_2 state.²¹¹ As noted in Chapter 3, the the lowest energy excited state geometry in π -conjugated systems tends toward planarity. However, Siegert *et al.* calculated that in a planar S_1 geometry the spin-orbit coupling is zero between S_1 and T_2 due to point-group symmetry of the excited state orbitals.²¹² From this the authors concluded that some out-of-plane or torsional vibrational activity is required for ISC processes to occur.

To probe the link between molecular geometry and singlet decay/triplet formation, the rates of the relaxation processes were calculated. The definition of triplet quantum yield is shown in equation (5.1); where Q_{ISC} is triplet quantum yield, k_{ISC} is the rate of ISC, k_{nr} is the rate of non-radiative relaxation in the singlet manifold (*e.g.*, internal conversion), and k_f is the rate of fluorescence from S_1 to S_0 . Triplet and singlet formation rates are the same, owing to a singlet-to-triplet bilinear decompo-

Figure 5.6 Singlet and triplet exciton dynamics of **4T** showing the lifetime of singlet decay and triplet growth (A), and the triplet yield (B) obtained from exponential fits of extracted TA dynamics. Error bars are the 95% confidence intervals calculated from the standard error of the exponential fit for the singlet and triplet dynamics.

sition model. The average of both rates (to take into account error) will give the denominator in equation (5.1). Since the yield is known, it is possible to derive the rate constant for ISC (k_{ISC}) and subsequently the rate of other relaxation pathways [$k_{\text{nr}} + k_{\text{f}}$]. The sum of the internal conversion and photoluminescence processes account for the S_1 to S_0 transition.

$$Q_{\text{ISC}} = \frac{k_{\text{ISC}}}{[k_{\text{nr}} + k_{\text{f}}] + k_{\text{ISC}}} \quad (5.1)$$

Figure 5.7 shows the comparison of these parameters for all oligomers calculated in this manner, as well as a comparison of the triplet yields. Attention will for the moment remain on the parameters obtained for **4T** (blue lines/symbols). As temperature is decreased, there is an increased lifetime of the S_1 to S_0 relaxation pathways (Figure 5.7A), demonstrating that at lower temperature the internal conversion and fluorescence rates are slowed. In contrast, the lifetime of ISC (Figure 5.7B) for **4T** shows a kink near the T_g temperature, and then a decreasing ISC lifetime as a function of cooling. As the temperature is lowered the distribution of ground state molecular geometries is narrowed. At the T_g temperature, the solvent will form a frozen glass which could constrain the molecular geometry of the excited state closer to the ground state geometry. In other words, after photoexcitation the excited state is constrained closer to the Franck-Condon state, which could be considered a ‘vibrationally hot’ state. Since this geometry will be non-planar, favourable spin-orbit coupling between S_1 and T_2 will be maintained, promoting ISC to occur. Although it is not just the presence of a twist that enables ISC, but motion along this coordinate, *i.e.* twisting, it could be possible to miss the opportunity to couple to the triplet manifold if this planarisation occurs too fast. These results are consistent with the increased triplet yield observed at low temperatures.

Focus now turns to the comparison of the dynamics for the longer oligomers (**6T**, **8T**, and **10T**). Figure 5.7A shows that the lifetime of relaxation to the ground state following photoexcitation appears to lack a clear trend; the value is approximately unchanged for **6T**, has a positive kink near the T_g temperature for **8T**, and decreased lifetime for **10T** until 77 K. It is known that the fluorescence quantum yield decreases with increasing conjugation length in oligothiophenes.²⁰⁴ Therefore, the dynamics may need further investigation by extracting the individual rates of internal conversion and photoluminescence as a function of temperature. This could elucidate if one of the decay pathways is being promoted significantly over the other and affecting the dynamics observed. Regardless of this, a comparison of the triplet formation lifetime (Figure 5.7B) shows all oligomers exhibit the same trend toward shorter lifetimes (faster rate) as temperature is decreased. The triplet formation

Figure 5.7 Comparison of relaxation dynamics for all oligomers showing lifetime parameters of non-radiative and fluorescence (S_1 to S_0) processes (A), lifetime of triplet exciton formation *via* ISC (B), and triplet yield (C) as a function of temperature.

lifetimes follow the trend of slower ISC as the length is increases, consistent with reports from Grebner *et al.* which showed the same trend with oligomers of 2–6 repeat units.²⁰⁶ Comparison of the triplet yield (Figure 5.7C) shows a lower yield for the longer oligomers. Additionally, the triplet yields of longer oligomers all show ~10% increase at 77 K compared to 295 K, in contrast to the 30% increased observed for 4T.

As predicted in theoretical calculations in the literature, the role of multiple triplet states below the excited state cannot be overlooked.²¹¹ Since the orbital coupling between the planar S_1 excited state and the T_2 state is zero, excited state theory states that ISC will not occur from a completely planar excited state geometry.²¹² This suggests that ISC to the triplet manifold must occur from conformations that have some torsional disorder. The results presented here provide experimental evidence linking the rate of ISC and molecular geometry. A model is proposed in Figure 5.8A whereby vibrational ‘hot states’ promote the formation of triplet excitons through ISC, and structural cooling is responsible for the lower triplet yields in more flexible geometries. Since the ground state conformation distribution is projected onto the excited state immediately after photoexcitation (*i.e.*, the Franck-Condon state), this is a vibrational ‘hot state’ since it is above the structurally relaxed S_1 excited state geometry. Subsequent structural relaxation results in excited state ‘cooling’ as the geometry is driven to planarity. This occurs on the order of 5 ps (see Chapter 4) which is much faster than the timescale for ISC (100’s of picoseconds). This means the competing processes for depopulation of the S_1 excited state is *via* IC/PL and ISC and occurs from the thermally equilibrated excited (thexi) state, represented by green arrows in Figure 5.8A.

Temperature dependent TA measurements probe the effect of structural relaxation of the oligomer backbone and ISC rates. As the temperature is lowered towards the T_g , the solvent viscosity increases which will govern the extent of structural relaxation able to occur.¹⁹⁷ Temperatures below T_g result in the formation of a glass, which narrows the distribution of ground state geometries and also restricts some torsional freedom of the oligomer backbone. It is proposed that this constrains the amount of structural relaxation occurring on fast timescales, effectively trapping the thexi state state geometry closer to the Franck-Condon geometry. In other words, the restricted movement prevents some structural cooling and maintains a relatively hot state at longer timescales (*i.e.*, >5 ps). These hot states will have a stronger orbital coupling with the triplet manifold (T_2 state) so more facile ISC can occur resulting in increased triplet yield. Temperatures > T_g provides less structural relaxation restriction due to the lower apparent viscosity of the environment, and the geometry relaxes deeper in the excited state potential. This explains the lower

Figure 5.8 Proposed model for triplet formation in oligothiophenes whereby ISC is driven by favourable coupling between high energy vibrational states in S_1 and the triplet manifold. (A) The Franck-Condon state formed immediately after photoexcitation is a non-planar conformation and considered a vibrational ‘hot state’. Structural relaxation (‘cooling’) decreases orbital overlap between the S_1 and T_2 states. Increased triplet yield is achieved by restricting the amount of structural cooling to trap the molecular in a less-planar geometry. (B) Increasing the conjugation length increases the planarity of the ground state resulting in a Franck-Condon geometry which is closer in energy to the structurally relaxed S_1 state, thereby decreasing the rate of ISC.

triplet yield at warmer temperatures observed for all oligomers.

With regard to conjugation length dependence, Siegert *et al.* reported theoretical calculations showing the ground state increases in planarity as the oligomer conjugation length is increased.²¹² This means the Franck-Condon state will have greater planarity, which is closer in energy to the structurally relaxed S_1 geometry, depicted in Figure 5.8B. It is proposed that as the oligomer length increases, the rate of ISC is decreased due to more planar (vibrationally cooler) conformation immediately after photoexcitation compared to shorter oligomers. This could also account for the minimal temperature dependence in triplet yield for oligomers >4 monomer units. Decreasing the amount of cooling through the formation of a glass has less of an effect on promoting ISC since a cooler state is initially formed. This is consistent with the highest triplet yield being observed for the shortest oligomer.

In order to test this proposed model, several avenues of investigation would be beneficial. Additional temperature dependent TA measurements would assist in defining the trend and reducing the error in the extracted parameters. In particular, the glass transition temperature appears to be of significance, and more data around this region could allow for a more conclusive discussion. Similar to this, the rate of internal conversion for **4T** seem to exhibit a clear temperature dependence, yet longer oligomers appear to have more complex behaviour and this needs to be accounted for. Indeed, a direct measure of the structural relaxation would be of great value. This could be achieved through time-resolved Raman spectroscopy, or through temperature dependent photoluminescence measurements to estimate Huang-Rhys parameters as a function of temperature. Unfortunately, time-resolved Raman spectroscopy was not available during the course of this work. Furthermore, the optical setup for the transient-grating photoluminescence spectroscopy was not able to facilitate the measurements of photoluminescence from within the temperature cryostat.

Aside from extrapolating the data series of the oligomers in MeTHF, there are several experiments that would test the validity of the proposed model. In particular, the proposed model highlights that it is not temperature that is the dominant driver of increased ISC, but rather restricted torsional freedom through solvent freezing. This could be probed by performing measurements in a series of solvents with different viscosity, whilst maintaining the same temperature. Another approach is to perform a temperature dependent study, but alter the T_g through solvent choice. If this model is correct, then the same trend should be observed centred around the new solvent T_g . It should be noted that changing the solvent will affect more than just viscosity, for example polarity. The solubility of the oligomers should be high in

non-polar solvents, possibly allowing minimal polarity change between solvent selection. Alternatively, solvent mixtures with solvents of similar polarity but different viscosities/freezing temperatures could be used. These would all require control experiments, and could form complicated solvent mix systems. Therefore, selection of an alternative solvent is not a trivial task, and in the interest of this work the focus was shifted to examine how the triplet dynamics in solution are altered by casting the chromophore to a thin film.

5.4 Triplet formation in thin films

To further probe the link between ISC and molecular geometry, the relaxation photophysics, in particular triplet formation, of an oligothiophene in the solid state was investigated. A thin film increases the apparent viscosity of the local environment and has been shown to restrict the extent of torsional relaxation.¹⁹⁷ Importantly, this approach provides a means to decouple the role of temperature and viscosity of the solvating environment. **4T** was chosen as the oligomer to study due to the triplet PIA signature being within the probe spectral window of TA measurements. In order to avoid aggregation effects **4T** was cast in a film of polystyrene (PS) in low weight percent (1:20, **4T**:polystyrene). This created a film whereby **4T** is suspended in polystyrene which acts as an electronically inert matrix.²¹⁷ This yielded solid state conditions which avoided electronic interactions between **4T** chromophores. The steady state optical absorption spectrum of **4T**:polystyrene at 295 K is shown in Figure 5.9, overlaid with spectrum of **4T** in solution (dilute MeTHF), normalised by the absorption maximum. The spectra have similar broadness with only a small spectral shift, confirming polystyrene is able to effectively prevent intermolecular interactions in the solid state between chromophores.

To investigate triplet formation in this film, transient absorption measurements, and the subsequent SVD fitting procedure previously discussed, were performed using 400 nm excitation at room temperature (~295 K). The overall dynamics were similar to **4T** in solution, and the entire TA surface for **4T**:polystyrene could be described by 2-components (species). The spectral shapes of each of these components are presented in Figure 5.10A. These show a clear similarity to the components obtained for **4T** in solution and confirm the formation of triplet excitons in the solid state. The relative weightings of these components over time is shown in Figure 5.10B, converted to a normalized population as described earlier. Immediately evident is almost no excited state population decay during the 5 ns time resolution of the experiment. This is similar to what was observed in the temperature dependent mea-

Figure 5.9 Normalized steady-state absorption spectrum of 4T:polystyrene (1:20) thin film at 295 K, overlaid with the spectrum of 4T in MeTHF solution. Overlapping features confirm isolated chromophores are present in the dilute polystyrene film.

measurements whereby a decreasing temperature suppressed relaxation to the ground state.

Both singlet decay and triplet formation dynamics are well fit to mono-exponential functions providing the lifetime of singlet decay and triplet formation. From this the lifetime of S_1 to S_0 relaxation and the lifetime of ISC were derived and summarised in Table 5.1, along with triplet yield measurements. The same parameters obtained for 4T in solution at 295 K and at 77 K are included for reference. The S_1 to S_0 lifetime represents the lifetime of both structural relaxation and photoluminescence. The long lifetime is consistent with restricted torsional motion in the solid film decreasing the rate of these relaxation pathways. The lifetime of ISC is on the order of 100's of picoseconds, an order of magnitude shorter than the S_1 to S_0 lifetime. Such a fast rate of ISC means conversion to the triplet manifold is the dominant pathway of S_1 depopulation. This is reflected in a triplet yield which is >90%.

4T:PS blend has the longest S_0 to S_1 lifetime when compared to 4T at 295 K or 77 K. Furthermore, 4T:polystyrene has almost twice the triplet exciton yield than obtained for 4T at 295 K, and in fact has a higher yield than 4T at 77 K. This suggests that dispersion in the solid support provides the most favourable conditions

Figure 5.10 SVD components for 4T dispersed in a polystyrene matrix (4T:polystyrene) following rotation using the TA spectrum at 5 ns as a physical constraint showing the spectra basis set (A) and the component weightings (B). The component weightings have been normalized based on the integrated intensity of ground state bleach (GSB) which is a measure of total excited state population. Singlet and triplet dynamics were fit to a mono-exponential function (solid lines), and the sum of these fitted dynamics (dashed line) tracks the total population dynamics, which is a probe of the total population of excited states.

Table 5.1 Summary of lifetime parameters derived from SVD fitting of TA data for 4T:polystyrene. Error bounds represent the 95% confidence interval resulting from the mono-exponential fitting.

Sample	S ₁ to S ₀ Lifetime (ps)	ISC Lifetime (ps)	Triplet Yield (%)
4T:polystyrene at 295 K	4171	240	92±3
4T at 77 K	1528	232	85±3
4T at 295 K	680	308	55±2

for ISC. The polystyrene matrix provides the most torsional relaxation restriction, supporting the proposed model whereby trapping the oligomer backbone in a conformational hot state maintains strong coupling between S₁ and the triplet manifold. The implications of the proposed model suggests that triplet formation not only occurs in thin films of oligothiophenes, but that ISC can be significantly enhanced in environments with highly restricted torsion mode. Although torsional motion could aid in triplet formation, locking the geometry in a twisted geometry would retain strong spin-orbit coupling into the triplet manifold and thereby accelerate triplet formation.

This dependence of triplet exciton formation on molecular geometry disorder has impacts on polymer thin films whereby different morphologies result in amorphous or crystalline films. Guo et al. studied poly-3-hexylthiophene (P3HT) of different regioregularities using transient absorption spectroscopy.²¹⁸ Results in solution showed both regioregular-P3HT (RR-P3HT) and regiorandom-P3HT (RRa-P3HT) formed triplet excitons form in solution. However, when cast into a pristine polymer thin film, triplet exciton formation could only be observed in RRa-P3HT. The regioregularity results in different film morphologies between the materials, with RR-P3HT forming a highly ordered/crystalline morphology, whereas RRa-P3HT has a more disordered morphology. The differing triplet dynamics were attributed to exciton-exciton annihilation being more prevalent in the disordered morphology.²¹⁸ However, the model proposed here using oligothiophenes could explain the poor triplet formation in ordered RR-P3HT films. With a crystalline morphology the highly ordered polymer chains could reduce spin-orbit coupling to triplet states, thus reducing ISC. Whereas in a disordered film (*e.g.*, RRa-P3HT) or in solution the molecular geometry can facilitate the transfer of hot excitons into the triplet manifold. Therefore, the mechanism explaining these results may not solely rely on exciton-exciton annihilation.

In OPV device applications the photoactive material is cast into a thin film. Since the formation of triplet states does not contribute to photocurrent in these devices, understanding the dynamics of formation can impact the design rules governing device performance optimization. Indeed, sub-nanosecond triplet formation has recently been reported to occur in polymer:fullerene blend films,^{103,105,112} yet the

mechanism responsible has not been fully resolved. One theory is that bimolecular recombination between spin-uncorrelated charge carriers could lead to triplet charge-transfer states.^{104,105} Etzold **et al.** have shown that this sub-ns triplet formation in polymer thin films is intensity dependent, which suggests that triplet formation depends on the concentration of charges which invokes the bimolecular recombination mechanism.¹⁰⁵ However, bimolecular recombination is generally expected to occur on nano- to microsecond timescales.^{11,111} Additionally, Etzold *et al.* found that the polymer triplet yield decreases when processed with ODT additive to induce a higher crystallinity of the polymer, which suggests molecular conformation could play a role in triplet exciton formation.¹⁰⁵

Based on the model of triplet exciton formation proposed here, triplet formation can occur *via* an intramolecular process, *i.e.*, in the absence of aggregation, energy transfer, or excitation annihilation processes. Since the oligothiophenes are valid models of conformational sub-units in a polythiophene backbone, it is reasonable to suggest that the same processes could occur in polythiophene. Upon photoexcitation of the polymer in a polymer:fullerene blend, an exciton that does not undergo charge separation will geminantly recombine and relax to the ground state. However, if this exciton was trapped in a state with torsional disorder (hot state) there could be favourable coupling of the singlet and triplet manifolds. This would provide a competing pathway to exciton relaxation but could also account for the formation of triplet states without the requirement for bimolecular recombination.

5.5 Summary

In this chapter, triplet exciton formation in π -conjugated materials was investigated using oligothiophenes as molecular models of polythiophene sub-units. Using transient absorption (TA) spectroscopy, spectroscopic signatures of singlet and triplet excitons were identified. Fitting the component kinetics to mono-exponential functions showed the rate (lifetime) of singlet exciton decay and triplet exciton formation were similar, consistent with the direct conversion of singlet states into the triplet manifold, *i.e.*, no intermediate state. This showed triplet excitons were formed on the order of 100's of picoseconds.

The link between molecular geometry and triplet exciton generation was probed by altering the amount of torsional freedom of the oligomer backbone, and hence the structural relaxation, following photoexcitation. A model was proposed whereby hot vibrational states with structural disorder are responsible for triplet exciton

formation. By constraining the amount of structural cooling from an initially hot (Frank-Condon) geometry, the molecule was trapped higher in the energy potential of the S_1 state after structural relaxation. The increased conformational disorder decreased the rate of IC and PL from S_1 , and increased the rate of ISC resulting in a greater triplet yield. The strong torsional restriction in a polystyrene matrix showed a 40% greater triplet yield compared to solution at 295 K. Thus, vibrationally hot singlet excitons could provide the driving force for spin mixing to generate triplet excitons. The proposed model is consistent with previous theoretical studies showing less planar molecular geometries have stronger spin-orbit coupling between singlet and triplet manifolds. These results suggest high vibrational states of the singlet excited state are important to consider in polymer relaxation dynamics, which could help guide the design of π -conjugated molecules through better understanding of triplet exciton formation.

Chapter 6

Charge separation in three-phase polymer:fullerene blends

6.1 Introduction

The morphology of polymer:fullerene blends used in organic photovoltaic (OPV) cells has long been recognized as a dominant contributor to device power conversion efficiency.^{80–83} In part, this is reflected by charge separation at a heterojunction not necessarily generating useful photocurrent, that is, extractable charges. Early studies on polymer:fullerene systems have highlighted the importance of balancing exciton diffusion with the percolation of free charge carriers through the nanoscale morphology.^{34,84} The early view was that a 2-phase bulk heterojunction network would provide an optimal balance of these factors. A 2-phase morphology consists of interpenetrating pure polymer phases and pure fullerene crystalline through the active layer. Additionally, charge generation photophysics was shown to be sensitive to blend morphology in a range of polymer:fullerene systems.^{6,85–87} However, in spite of this knowledge the question of how charge pairs overcome their mutual Coulomb attraction to separate was not completely resolved.^{11,65,88,89}

With the improvement of structural characterisation techniques, the complexity of polymer and fullerene component morphology in a BHJ has been revealed.⁴⁸ Not only can polymer and fullerene form either phase-pure amorphous or crystalline domains but recent investigations have identified an intermixed phase in a wide range of polymer:fullerene blends.^{54–63} The first report of intermixed polymer:fullerene phases was identified in a pBTTT:PC₆₁BM blends, whereby the polymer/fullerene components were found to form ordered intercalated co-crystals.⁵⁴ Subsequently, this

co-crystal 3-phase morphology was shown to be sensitive to structural modifications and processing conditions whose formation can be manipulated via structural modifications on the polymer backbone,⁵⁸ and also processing conditions during film preparation.⁹⁰

The potential role this phase has on the charge separation process is reflected by the highest device performance in polymer:fullerene blends often having a nanomorphology with both neat domains as well as intermixed regions. Indeed, the formation of this 3-phase morphology is now proposed to improve yields of charge separation and collection, and could actually present as a solution to the problem regarding what drives charge pair separation.^{56,62,63,92,93} Scarongella *et al.* recently investigated charge photogeneration channels in the pBTTT:PCBM system using ultrafast transient absorption (TA) spectroscopy.⁹⁴ In the presence of a 3-phase morphology, they resolved an electro-absorption signal that arises in the specific electrostatic environment of the co-crystal. The decay of this electro-absorption signature occurred on the sub-picosecond timescale, and is indicative of hole transfer from co-crystal domains into pure pBTTT crystals. Importantly, transfer of charges out of the intermixed region was found to suppress geminate charge recombination. Charge pairs are also found to be more localized and short-lived in co-crystals compared with pure phases.⁹⁸

In other higher efficiency polymer:fullerene blends, the intermixed phase is generally found to be amorphous rather than crystalline.^{55,57,59–63} Coexisting pure and intermixed amorphous phases creates an energetic landscape which could drive charge separation in 3-phase morphology systems. Pure fullerene regions show >100 meV higher electron affinity than that observed in dispersed fullerene,⁹⁶ which is coupled with holes being stabilized by >300 meV in pure polymer phases compared with amorphous intermixed phases.⁹⁹ Thus, charge pairs which are generated in intermixed regions may be driven into pure phases *via* this energetic bias as well as diffusion. This proposed model of an energetic landscape favouring charge separation is consistent with improved device efficiencies in these blends.^{54,56,96} It is also consistent with a spectroscopic investigation showing long-lived free charges.⁹⁶ However, the morphologically driven charge separation process invoked must occur on earlier timescales.

Work presented in this chapter aims to directly resolve whether charge migration occurs due to the energetics of coexisting amorphous intermixed and pure phases. If the energetics are important, the timescale of morphological charge separation will be correlated with free charge yields. TA spectroscopy was performed on a series closely related alternating thiophene-benzothiadiazole copolymers which have small

variations in polymer backbone structure. Polymer backbone curvature can be used as a ‘control handle’ to alter the component mixing in polymer:fullerene blends by altering the miscibility of fullerene. This yields the controlled formation of either 2- or 3-phase morphology over the series of polymer materials. The broadband TA probe covered visible to near-infrared wavelengths from femto- to microsecond timescales. Through identifying spectroscopic signatures related to holes (polarons), it was possible to spectroscopically track charge mobility in intermixed compared to pure polymer phases. In 3-phase blends, this process occurred over tens to hundreds of picoseconds, as reflected by a relaxation in polaron spectral features. In contrast, 2-phase blends lacked the dynamic spectral evolution attributed to interphase charge migration. This is consistent with 3-phase blends having suppressed geminate charge recombination, compared to 2-phase morphologies. These findings provide experimental evidence supporting the proposed model of 3-phase morphologies being an efficient pathway to charge photogeneration in OPV blends.

6.2 Materials

Figure 6.1 shows the molecular structures (and IUPAC names) of closely related donor-acceptor low band-gap polymers; PTTBT, PDTBT, and PTBT. The different polymer backbone curvature of these polymers has been found to significantly affect fullerene miscibility and interchain stacking, and ultimately charge mobility and photovoltaic device efficiency,²¹⁹ in line with recent work from other groups.^{220,221} The synthesis of these materials was performed by collaborators in the laboratory of Prof. H. Y. Woo at Pusan National University, South Korea. The experimental procedures, along with density functional theory calculations have been reported elsewhere for PTTBT and PTBT,²¹⁹ and PDTBT.²²² All polymer:fullerene blends studied in this chapter used phenyl-C[61]-butyric acid methyl ester (PCBM) as the fullerene acceptor.

Changing the structure of the thiophene-based linkage between benzothiadiazole units, whilst retaining the same C₁₄ side chains, transforms the polymer backbone from a linear shape in PTTBT to a curved shape in PTBT, while retaining a similar band gap.²¹⁹ In the case of PTTBT, the thienothiophene has a 1,4-substitution angle of 180° yields a polymer backbone with minimal curvature. In contrast, PTBT has a single thiophene ring as linker unit, whereby the 1,4-substitution angle ~160° results in a curved backbone, shown schematically in Figure 6.1. PDTBT adds an intermediate member to this series through an increased spacer length, resulting in a decreased curvature amplitude compared to PTBT. For PTBT and PDTBT

Figure 6.1 Molecular structures of polymers, and schematic showing the increasing backbone curvature. IUPAC names are also shown for each polymer.

the backbone curvature is within the plane of the backbone. Optimized molecular geometries have shown that intrachain torsion is minimized in each of the three polymers through in-plane attractive $\text{S} \cdots \text{O}$ interactions. Neighbouring thiopheneBT units allow for non-covalent Coulomb interactions between the partially positively charged sulfur of the linkage unit, and the negatively charged oxygen on the solubilising alkoxy-side chains causing a 'conformational lock'.^{221,223}

6.3 Thin film morphology

Optical absorption spectroscopy and 2D grazing incidence X-ray diffraction (2D-GIXRD) measurements were used to probe how the polymers' backbone curvature influences their ordering and miscibility with PCBM. 2D-GIXRD measurements were performed by collaborators at Pusan National University, South Korea,²²² and details can be found in the Experimental chapter. For this library of polymers, identifying the presence of 3-phase morphologies was of particular interest. A 3-phase morphology contains a strongly intermixed polymer:fullerene phase coexisting with pure polymer and pure fullerene phases. The absorption spectra shown in Figure 6.2 confirm that each of the neat polymers have a similar optical band gap of ~ 1.7 eV, however differences in their spectral shape are indicative of their ordering. Understanding the link between optical signatures and morphology provides valuable reference signatures for transient absorption studies. These differences arise due to

amorphous polymer phases having shorter conjugation lengths and differing exciton coupling compared with extended semi-crystalline phases.

Figure 6.2 Normalized steady-state optical absorption spectra of polymer and polymer:fullerene thin films cast from chlorobenzene. (A) PTTBT, (B) PDTBT, and (C) PTBT. Inset schematics depict the effect of structural distortion to create a blue shifted absorption when PCBM infiltrates the polymer stacking through the formation of shorter conjugation length polymer sub-units.

Figure 6.2A shows that neat PTTBT has visible absorption peaks at 660 nm and 610 nm, assigned to 0–0 and 0–1 vibronic transitions, respectively. The dominant 0–0 vibronic peak is indicative of extended J-aggregate-like polymer chains that pack in ordered lamellae.^{173,187} J-aggregates are a co-facially stacked aggregate with a offset in the plane of the transition dipole. The polymer absorption spectrum is largely unchanged when blended with PCBM, either with or without the octanedithiol (ODT) additive, noting that the additional absorption at $\lambda < 500$ nm is attributed to PCBM. The blend ratio of polymer:PCBM was chosen to be 1:1 by weight percent, which was shown to be the optimum ratio in OPV devices.²¹⁹ The lack of polymer

spectral perturbation from the addition of PCBM shows that highly ordered polymer stacking is retained in the blend, as shown in the inset of Figure 6.2A. In agreement, a previous 2D-GIXRD investigation of this system showed that PTTBT films are highly crystalline, and the strongly ordered interchain interactions are retained in fullerene blends.²¹⁹

This 2-phase picture was confirmed through additional 2D-GIXRD data whereby the blend ratio is varied.⁹¹ Varying the blend ratio from 1:0.2 to 1:4 (polymer:PCBM) showed that the polymer-based scattering peaks did not change, whilst the isotropic peak due to fullerene aggregates at $q = 1.4 \text{ \AA}^{-1}$ simply grows as the PCBM content was increased.²²² The observation of a fullerene aggregate peak with only 20% PCBM confirms the strong exclusion of PCBM of the ordered polymer aggregates. The structural and spectroscopic results demonstrate PTTBT and PCBM have poor miscibility leading to the formation of a 2-phase morphology comprised of largely pure ordered polymer and pure PCBM crystalline phases. The possibility of an intermixed ordered phase, for example a co-crystal as seen in pBTTT:PCBM blends,^{54,90,98,224} was ruled out for PTTBT because the X-ray scattering peaks do not show an expanded unit cell of a PTTBT:PCBM co-crystal.²²²

The intermediate curvature of PDTBT is reflected in the relative suppression of 0-0 vibronic peak (at 660 nm), which is comparable to the 0-1 peak at 620 nm for neat PDTBT thin films (see Figure 6.2B). Weakening of the 0-0 peak results from more H- rather than J-aggregate like exciton coupling.^{173,187} Both these aggregate types are co-facial (with respect to the polymer backbone), but an H-aggregate contains an angular displacement (twist), whilst a J-aggregate contains a translational offset.²²⁵ The lower crystallinity implied from absorption spectra of PDTBT compared with PTTBT agrees with 2D-GIXRD structural data.²²² Neat PDTBT exhibits a moderately ordered structure with out-of-plane lamellar spacing (30.6 Å), much larger than the highly crystalline PTTBT (23.0 Å). Unlike PTTBT, blending PDTBT with PCBM slightly increases the interlamellae stacking distance to 33.1 Å, and slightly suppresses the 0-0 vibronic intensity (Figure 6.2B). Processing with the ODT additive leads to recovery of the same interlamellae spacing as in neat PDTBT, but has little effect on the absorption spectrum. Importantly, the π - π stacking parameter determined from 2D-GIXRD is the same for the PDTBT:PCBM blends (with or without the ODT additive) and for the neat polymer (4.0).²²² This shows that PCBM does not strongly infiltrate the polymer network. Thus, the PDTBT:PCBM is described as having a predominantly 2-phase morphology composed of relatively pure polymer regions, and pure PCBM clusters.

Figure 6.2C shows that in the case of PTBT, the most curved polymer, addition of

PCBM strongly disrupts the polymer ordering. The infiltration of PCBM into the polymer domain is indicated by the suppressed 0-0 vibronic peak. This spectroscopic observation is also consistent with the 2D-GIXRD studies reported.^{219,222} Briefly, infiltration of PCBM causes loss of the polymer π - π stacking peak, along with growth of a diffraction peak from PCBM aggregates. This is consistent with a study by Reish *et al.* which showed a disruption of polymer order results in a blue-shifted absorption due to the formation of shorter polymer sub-units,²¹⁴ schematically shown in the inset of Figure 6.2C. The addition of the ODT co-solvent causes a recovery in the neat polymer's vibronic progression and 2D-GIXRD scattering peaks of neat PTBT. Therefore, ODT addition causes the recovery of polymer crystallinity due to partial demixing of the polymer and fullerene components. Based on the spectroscopic and scattering measurements it can be concluded that the PTBT:PCBM system (with an optimized 1:2 ratio) exhibits 3-phase behaviour; excellent miscibility results in a highly intermixed phase that can coexist with pure polymer and pure PCBM phases, which can be tuned by the use of co-solvent additives. This molecular level miscibility means that even a predominantly phase separated blend is likely to be intermixed at the important interface region. This morphology has been invoked in other polymer:fullerene blends,^{59,226,227} however the intermixed region was not often recognized because it is not directly detectable via scattering measurements, except for the case of co-crystals.^{58,90} Since poor fullerene miscibility excludes the existence of an intermixed phase in PTTBT, and to a lesser extent PDTBT, this series of polymers is ideally suited to directly probing charge generation processes in the 3-phase versus 2-phase morphologies of closely related polymers.

6.4 Photocurrent generation pathways

Table 6.1 summarises the optimised polymer photovoltaic device characteristics for each polymer:PCBM blend.^{219,222} The PTBT:PCBM blends are superior to the other polymers in every respect. This leads to a power conversion efficiency (PCE) of 5.56% when processed with ODT which is more than twice the efficiency of the most efficient PTTBT blend.²¹⁹ Polymer crystallinity promotes charge carrier mobility, but does not have a direct correlation with device efficiency. The poorest devices were obtained from PDTBT blends (least ordered/crystalline), yet PTTBT blends have the highest polymer crystallinity but do not yield the highest PCE. The two most efficient devices were obtained using PTBT:PCBM blends, with the addition of ODT causing an increase in PCE by a factor of 1.5 compared to without ODT. The increased crystalline domain in the donor phase in PTBT:PCBM + ODT also improves hole carrier transport, improving J_{sc} . Device performance

metrics only provide information of charges that have contributed to photocurrent, but provides little insight into the overall generation pathways of charges, which is a critical step in improving device efficiency. Since these device parameters are shown to be uncorrelated with charge carrier mobilities, we undertook TA spectroscopy to investigate charge photogeneration pathways in these blends. This is possible due to the 2- and 3-phase systems exhibiting distinct optical signatures, providing a method of comparing dynamics in these systems. TA spectroscopy enabled us to establish the link between phase morphology and photocurrent generation by probing signatures of photoexcitations moving from disordered to ordered polymer regions and correlating with free charge generation.

Table 6.1 Summary of optimized photovoltaic device characteristics, short-circuit current (J_{sc}), open-circuit voltage (V_{oc}), device fill-factor (FF), and power conversion efficiency (PCE). Reproduced from Gallaher *et al.*²²²

Active layer	Additive (2%)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	PCE (%)
PTTBT:PCBM (1:1)	None	5.49	0.77	0.57	2.40
	ODT	7.00	0.74	0.51	2.62
PDTBT:PCBM (1:1)	None	4.18	0.66	0.46	1.27
	ODT	4.72	0.68	0.33	1.06
PTBT:PCBM (1:2)	None	8.05	0.92	0.50	3.67
	ODT	9.37	0.88	0.68	5.56

6.4.1 Charge generation dynamics

The first stage of analysis was to examine the spectra and dynamics of excitons and charges in each of the blends on early (femtosecond to nanosecond) timescales. The TA data presented in this section were all conducted at sufficiently low fluence to avoid annihilation and bimolecular effects.¹¹¹ This requires pumping (exciting) the materials at a excitation density whereby the dynamics are independent of fluence. Overlaid dynamics which confirm this are presented in Appendix I.

PTTBT

The TA measurements of neat PTTBT and PTTBT:PCBM blend are presented in Figure 6.3. TA measurements in the absence of PCBM (Figure 6.3A) allows to first identify spectroscopic signatures associated with excitons in films of each polymer. This information is then able to guide the interpretation of spectra (Figure 6.3B) and kinetics (Figure 6.3C) of PTTBT:PCBM blends.

Figure 6.3 Transient absorption measurements of PTTBT showing spectral slices at indicated time delays for a neat PTTBT film (A), and PTTBT:fullerene blend (B), following 100 fs excitation at 532 nm. The spectral regions labelled GSB, PIA-1, and PIA-2 refer to the wavelength integration regions shown in the kinetic traces (C), with dashed traces corresponding to the neat polymer film, and solid traces corresponding to the polymer:fullerene film.

For the neat PTTBT film (Figure 6.3A), the TA spectra are dominated by two features; a positive ground state bleach (GSB) feature in the visible, which is dominated by the 0-0 vibronic peak at ~660 nm, and a negative photoinduced absorption (PIA) peak at ~1300 nm. The equal decay rates of all features (Figure 6.3C) confirms the presence of a single excitonic species with a half-life ($\tau_{1/2}$) of 14 ps, which is significantly shorter than the lifetime of other conjugated polymer films.²²⁸ The dominance of the 0-0 vibronic peak in the GSB is even more pronounced than the absorption spectrum (Figure 6.2A) and shows that excitons rapidly localize onto the lowest energy extended polymer chains within the 100 fs time-resolution of the measurement.^{12,18,68,229}

Having identified the spectrum and lifetime of excitons, the PTTBT:PCBM blend is studied and the TA spectra and kinetics presented in Figure 6.3B and C, respectively. Charge transfer is evident in the blend through the emergence of a new absorption peak at ~1050 nm (labelled PIA-2), which is distinct from the broad exciton band (PIA-1). PIA-2 appears as a shoulder even at the earliest delay time (200 fs), and persists beyond the 3 ns timescale of this measurement. The new PIA-band is accompanied by a long-lived GSB signature which has a dominant 0-0 peak. Consistent with numerous previous studies, this pattern of visible and near-IR TA signatures indicates charge transfer to PCBM, leaving hole polarons on the polymer.^{11,65,86,128,218}

This new sub-band-gap PIA (PIA-2) and extended lifetime of polymer excitations are indicative of an additional species being formed. It has recently been shown that polymer triplet exciton formation can occur on sub-ns timescales, and often produces near-IR PIA features similar to charges in blends of other low band gap polymer systems.^{103,105} To investigate this, a study of polymer triplet sensitization was performed using platinum(II) 2,3,7,8,12,13,17,18-(octaethyl)porphyrin (PtOEP) as triplet sensitizer. The TA spectra of PTTBT:PtOEP film is presented in Figure 6.4 and shows that the near-IR TA spectrum of polymer triplet excitons in PTTBT is distinctly different from the PIA signature present in the PTTBT:PCBM blend. This confirms that the PIA-2 signature is caused by hole polarons remaining on the polymer following electron transfer to PCBM.

Having identified that charges are generated in PTTBT:PCBM, discussion turns briefly to a comparison of the exciton kinetics (PIA-1) of the PTTBT:PCBM blend with the neat polymer in Figure 6.3C which confirms a reduced exciton lifetime due to charge photogeneration in the polymer:fullerene blend. However, partial GSB decay within the first 10 ps shows that some excitons decay before generating charge pairs. Since the exciton band (PIA-1) has nearly the same initial intensity in the

Figure 6.4 Polymer triplet sensitized (polymer:PtOEP) TA spectra showing sensitized spectral shapes at 25 ns compared to the photoinduced absorption at the time indicated for PTTBT:PCBM. Excitation wavelength was 532 nm.

blend as the neat polymer (relative to the GSB), it is evident that most polymer excitons are not generated in immediate proximity to PCBM acceptors, which would deplete the exciton population within our time resolution. These TA dynamics are consistent with charge photogeneration in a 2-phase morphology; the small fraction of excitons generated near polymer:fullerene interfaces generate charges on an ultrafast timescale, while other excitons are formed in polymer phases too far from fullerene acceptors to generate charges.

Casting a PTTBT:PCBM film with the co-solvent additive octanedithiol (ODT) showed little enhancement of device efficiency (Table 6.1). To investigate this the TA spectra (Figure 6.5A) and kinetics (Figure 6.5B) of PTTBT:PCBM + ODT thin film were investigated. The dynamics appear very similar to the PTTBT:PCBM film without ODT, showing that the additive has little effect on the TA dynamics. This is consistent with the steady-state optical absorption spectroscopy and the 2D-GIXRD discussed earlier, which showed no observable change in morphology upon processing with ODT. The TA dynamics for PTTBT:PCBM blend will be discussed in further detail in the subsequent sections when comparing charge spectral dynamics and charge recombination between the different polymer systems.

PDTBT

TA spectra for PDTBT, which has an intermediate curvature in the series, are shown in Figure 6.6 with neat polymer film spectra in Figure 6.6A, polymer:fullerene blend

Figure 6.5 TA spectra (A) and kinetics (B) of PTTBT:PCBM + ODT. Excitation wavelength was 532 nm.

in Figure 6.6B, and the associated kinetics in Figure 6.6C. The analysis is broadly similar to PTTBT above with a vibronically structured GSB (~550-700 nm) and a broad PIA at ~1400 nm. Once more the equal decay rates of both signatures confirms the presence of one excitonic species. Notable differences are a longer lived exciton spectrum ($\tau_{1/2}$ ~160 ps), and greater 0-1 vibronic intensity in the GSB compared with PTTBT. The vibronic progression of the GSB in neat PDTBT films has a more intense 0-0 peak than the 0-1, compared to near equal intensities observed in the steady-state spectra (see Figure 6.2). Like PTTBT, this enhancement of the 0-0 vibronic peak in the GSB compared to steady-state shows that excitons rapidly collapse onto more extended polymer segments.

TA spectra and kinetics for the PDTBT:PCBM blend are shown in Figure 6.6B and C, respectively. Similar to PTTBT:PCBM, the GSB at time delays >10 ps is accompanied by a PIA peak at ~1100 nm (PIA-2) extending into the visible region. The PIA bands associated with excitons (PIA-1) and charges in the PCBM blend (PIA-2) are slightly red-shifted compared with the PTTBT system, however the kinetics are similar, with excitations in the blend outliving the pristine polymer. These dynamics are consistent with charge transfer taking place between the polymer and fullerene components. Once more it is important to consider the formation of triplet excitons in this system. The polymer triplet sensitization TA spectrum is presented in Figure 6.7 again using PtOEP as sensitizer. For PDTBT, the PIA-2 peak at approximately 1100 nm is similar to the sensitized triplet exciton spectrum of PDTBT:PtOEP, which on its own prevents a definitive assignment as to whether PIA-2 is caused from polarons after charge transfer processes, or caused by triplet exciton formation. However, charge photogeneration is confirmed by the growth of a sharp electro-absorption peak at ~730 nm that resembles the derivative of the ground-state absorption spectrum. This spectral signature can be seen when the electric field created by separated charge pairs perturbs the energy levels of the surrounding polymer via the Stark effect.^{88,94} Due to triplet excitons being neutrally charged it is unlikely they could cause such an effect, allowing us to assign PIA-2 to the formation of polarons. The strength of electro-absorption is sensitive to the geometric configuration of chromophores relative to the electric field, as well as the sharpness of the ground-state absorption edge.

Since the 0-0 peak is likely affected by the overlapping electro-absorption, the inversion of 0-0 and 0-1 vibronic intensities in the PDTBT blend versus the neat polymer cannot be attributed to charges occupying more disordered polymer chains. Recall PDTBT polymer ordering has minimal disruption when blended with PCBM resulting in a 2-phase morphology. The kinetics of the PDTBT:PCBM blend (see Figure 6.6) are similar to those observed for the PTTBT system above. A high

Figure 6.6 Transient absorption measurements of PDTBT showing spectral slices at indicated time delays for a neat PDTBT film (A), and PDTBT:fullerene blend (B), following 100 fs excitation at 532 nm. The spectral regions labelled GSB, PIA-1, and PIA-2 refer to the wavelength integration regions shown in the kinetic traces (C), with dashed traces corresponding to the neat polymer film, and solid traces corresponding to the polymer:fullerene film.

Figure 6.7 Polymer triplet sensitized (polymer:PtOEP) TA spectra showing sensitized spectral shapes at 25 ns compared to the photoinduced absorption at 2 nanoseconds for PDTBT:PCBM. Excitation wavelength was 532 nm.

initial exciton population (PIA-1) is indicative of a low fraction of prompt charge generation, together with the loss of some excitons is consistent with a morphology with domain sizes slightly exceeding the exciton diffusion length.

The use of ODT additive for the PDTBT:fullerene blend has little effect on the OPV device performance (Table 6.1), similar to that observed for PTTBT. This is consistent with the TA measurements of PDTBT:PCBM + ODT presented in Figure 6.8 that show similar dynamics as the PDTBT:fullerene blend without ODT. Furthermore, this is consistent with steady-state optical absorption and 2D-GIXRD showing minimal change in morphology induced by ODT additive. Charge dynamics and recombination in the PDTBT:PCBM blend will be discussed later.

PTBT

The TA measurements of neat PTBT and PTBT:PCBM blend are presented in Figure 6.9, which follow a similar pattern as with the previous two polymer systems discussed. TA spectral features for neat PTBT (Figure 6.9A) show two main features; a GSB in the visible region which resembles that of the steady state absorption spectrum, and a broad PIA at ~1440 nm. In this case, a stimulated emission (SE) signature is also evident around 775 nm. Once more, the equal decay rates of all spectroscopic features confirm the presence of a single species with $\tau_{1/2} \sim 18$ ps. This is consistent with the interpretation for the other neat polymer systems already discussed. However, several important differences are immediately noticeable

Figure 6.8 TA spectra (A) and kinetics (B) of PDTBT:PCBM + ODT. Excitation wavelength was 532 nm.

in spectra and kinetics of the PTBT:PCBM blend (Figure 6.9B and C) compared with the other polymer blends.

First, the low initial intensity of the exciton band (PIA-1) shows that nearly all excitons are quenched within the 200 fs time resolution of the experiment. Loss of the exciton PIA is complemented by the ultrafast appearance of a PIA band between 1000 and 1200 nm within 200 fs, which is too fast to be explained by triplet exciton formation, which has been shown to occur on the hundreds of picosecond timescales.¹⁰⁵ Together with the retention of GSB intensity, this dramatic reduction from the 18 ps exciton lifetime suggests extremely efficient charge transfer processes (approaching unity). This is expected for a finely intermixed blend morphology that does not require excitons to diffuse to reach an interface. Secondly, the TA spectrum undergoes pronounced changes beyond the charge generation timescale; the charge-based PIA-2 band dynamically shifts to lower energy, and the relative intensity of the 0-0 band in the GSB increases. The shifting PIA and dynamic GSB have previously been attributed to the migration of excitations from disordered polymer segments to those with larger delocalisation through chain extension (*i.e.*, ordered chains) in a closely related PTBT polymer that only differed by its shorter (C_8) side chains.²¹⁴

Unlike the previous polymer blends, the processing additive ODT induces changes to TA dynamics which are shown in Figure 6.10. This is consistent with the ODT additive inducing partial demixing of the intermixed phase, as discussed earlier from steady-state optical absorption and 2D-GIXRD scattering data. First, recovery of intensity in the 0-0 vibronic band of the GSB indicates that the excited species resides within pure polymer domains. Second, the exciton-based PIA-1 band is now clearly resolved with a longer lifetime when ODT is used. However, ODT does not induce the strongly separated 2-phase morphology of the other polymer systems. This is evident through the majority of the GSB intensity being retained when the excitons decay, which is indicative of a high charge transfer yield. Furthermore, significant prompt charge generation indicated by the ultrafast appearance of the polaron-based PIA-2 is consistent with the higher interfacial area in the intermixed region of a 3-phase system. The polaron PIA peak undergoes a dynamic red-shift comparable to the blend lacking ODT, however in the blend with ODT, the PIA-2 peak also intensifies. This growth could result from hole transfer from PCBM to PTBT, as observed in other polymer:fullerene blends.^{230,231} However, hole transfer from PCBM would increase the polymer GSB intensity, in contrast to the constant GSB intensity observed during the timescale of PIA-2 dynamics here. In fact, the PIA-2 peak intensities are comparable (within 15%) at 1 ns when integrating the entire bands on an energy scale. This indicates that the apparent PIA-2 growth is due to dynamic spectral narrowing rather than population transfer.

Figure 6.9 Transient absorption measurements of PTBT showing spectral slices at indicated time delays for a neat PTBT film (A), and PTBT:fullerene blend (B), following 100 fs excitation at 532 nm. The spectral regions labelled GSB, PIA-1, and PIA-2 refer to the wavelength integration regions shown in the kinetic traces (C), with dashed traces corresponding to the neat polymer film, and solid traces corresponding to the polymer:fullerene film.

Figure 6.10 Transient absorption measurements of PTBT:PCBM + ODT showing spectral slices at indicated time delays (A) following 100 fs excitation at 532 nm. The spectral regions labelled GSB, PIA-1, and PIA-2 refer to the wavelength integration regions shown in the kinetic traces (B).

As discussed above, triplet excitons accounting for PIA-2 in the PTBT:PCBM system with and without ODT is unlikely due to the timescale of formation of the species responsible. However, in the previous study of the (C_8) side chain PTBT polymer, sensitization with PtOEP was performed and triplet formation could not be ruled out due to overlapping spectral signatures of both species.²¹⁴ To this end, triplet sensitization was performed for the (C_{14}) side chain PTBT polymer studied here with data presented in Figure 6.11. This shows that the PIA-2 band in the PCBM blends is significantly broader than the sensitized triplet spectrum, and its peak shifts from higher energy than the triplet peak at early times to substantially lower energy than the relaxed triplet by 2 ns. This is consistent for both PTBT:PCBM with and without ODT additive. Thus, the PIA-2 band in PTBT:PCBM can be attributed to hole polarons, and the significance of the spectral dynamics will be explored in the subsequent sections below.

Figure 6.11 Polymer triplet sensitized (polymer:PtOEP) TA spectra showing sensitized spectral shapes at 25 ns compared to the photoinduced absorption at the times indicated for PTBT:PCBM with and without ODT additive. Excitation wavelength was 532 nm.

6.4.2 Charge recombination dynamics

For each polymer:fullerene sample, it has been shown that charge transfer is occurring between polymer and PCBM. However, charge transfer at a heterojunction does not necessarily mean charge carriers are sufficiently separated to contribute to extractable photocurrent. Since the sub-gap PIA-2 peak in each of the polymer:fullerene blends is attributed to hole polarons, its integrated intensity can be used to track charge dynamics. Charge recombination kinetics are examined in order to compare the long-lived extractable charge populations for each of the blends. The

combination of mechanical and electronic pump–probe delay configurations allows TA dynamics to be captured from femtosecond to microsecond timescales. At the low excitation fluences used, recombination on early- or sub-nanosecond timescales is attributed to recombination of bound (geminate) charge pairs that would not be extractable in a device.^{6,11,37} As shown in Figure 6.12, longer lived charges exhibit strongly intensity–dependant decay through bimolecular recombination of free charges that would be extractable in a device.^{6,11,232}

Figure 6.12 Intensity dependent recombination for polymer:fullerene blends without ODT additive at the fluences indicated in the legend entries (units are $\mu\text{J cm}^{-2}$). Excitation wavelength was 532 nm. (A) PTTBT:PCBM, (B) PDTBT:PCBM, and (C) PTBT:PCBM.

To probe the quality of charges formed we examine the recombination dynamics to probe the effects of phase morphology on extractable photocurrent, which governs device performance. In all polymer systems, excitons have fully decayed within 10 ps, so spectral overlap of exciton and polaron signatures is avoided by excluding the earliest times from the analysis. Figure 6.13 shows the charge recombination kinetics from pico- to microsecond timescales for PTTBT:PCBM with and without ODT.

Traces are obtained by integrating over the near-IR probe region (900–1400 nm). The subsequent integrated intensity is then normalised by the maximum intensity of each sample. Measurements were performed with an excitation fluence of $\sim 5 \mu\text{J cm}^{-2}$ which allows comparison of intensity dependent decay dynamics.

Figure 6.13 Transient absorption recombination kinetics integrated over the 0.9–1.4 eV wavelength region for PTTBT:PCBM processed with and without ODT additive. Kinetic traces are normalised by the maximum intensity and were collected with an excitation fluence of approximately $5 \mu\text{J cm}^{-2}$ allowing comparison of intensity dependent decay dynamics. Spectral overlap of polarons with excitons is avoided by excluding the dynamics before 10 ps, at which time excitons have decayed.

For the 2-phase PTTBT blend without ODT, approximately half of the charge population has decayed within just three nanoseconds. This is significantly faster than efficient blends previously characterised, which points to severe geminate recombination losses.¹¹ The sub-nanosecond recombination phase is suppressed when the ODT additive is used, yet a comparably small fraction ($\sim 10\text{--}20\%$) of charges survive beyond 100 ns. Differences in the sub-nanosecond geminate recombination dynamics show that the molecular level interfaces of PTTBT and PCBM are affected by processing with ODT. It is likely that a very low fraction of PCBM is trapped in PTTBT phases when ODT is not used. Based on 2D-GIXRD studies, it is not enough PCBM to disrupt the crystallinity or form a truly intermixed phase, but enough to form a significant fraction of trapped charge pairs. Nevertheless, neither of the PTTBT blends produces appreciable yields of long-lived free charges, consistent with the poor device characteristics in Table 6.1.

Charge recombination dynamics for the disordered 2-phase PDTBT:PCBM blends are presented in Figure 6.14. Regardless of whether or not ODT is used, these blends also suffer significant geminate charge recombination within a few nanoseconds, and

only ~30% of charges remain beyond 100 ns. Unlike the 3-phase pBTTT:PCBM system where rapid decay of electro-absorption signal reflected separation of geminate charge pairs, here the electro-absorption feature remains for the charge lifetime (see TA spectral traces in Figure 6.6). The slightly higher long-lived charge yields compared with the PTTBT blends is at odds with the PDTBT blends having the lowest PV device efficiencies (Table 6.1), which may be caused by the high charge mobility for PTTBT. Nevertheless, it is apparent from this analysis that the 2-phase PTTBT:PCBM and PDTBT:PCBM blends with and without ODT all have poor PV efficiencies and suffer from rapid geminate charge recombination.

Figure 6.14 Transient absorption recombination kinetics integrated over the 0.9–1.4 eV wavelength region for PDTBT:PCBM processed with and without ODT additive. Kinetic traces are normalised by the maximum intensity and were collected with an excitation fluence of approximately $5 \mu\text{J cm}^{-2}$ which allows comparison of intensity dependent decay dynamics. Spectral overlap of polarons with excitons is avoided by excluding the dynamics before 10 ps, at which time excitons have decayed.

Next, the quality of charge separation in the PTBT:PCBM blend with and without ODT, through the charge recombination kinetics in Figure 6.15. Recall that the high miscibility of the polymer and PCBM components allows for a 3-phase morphology. Whereas the PTTBT and PDTBT blends suffer substantial geminate recombination within the first 3 ns, the PTBT blends have maximal charge populations retained at this time. The apparent PIA growth for the ODT processed blend relates to the spectral narrowing process identified in the discussion of charge generation kinetics. The charge kinetics show a suppression of rapid geminate recombination, and higher yields of long-lived charges, especially in the PTBT blend processed with ODT which has >50% charges remaining at 100 ns. These results are in line with the superior device characteristics in Table 6.1 for PTBT based devices compare to PTTBT or PDTBT devices. The recombination kinetics for the optimized PTBT blend is also

comparable to other efficient polymer:fullerene blends where well-separated charge pairs are created.¹¹

Figure 6.15 Transient absorption recombination kinetics integrated over the 0.9–1.4 eV wavelength region for PTBT:PCBM processed with and without ODT additive. Kinetic traces are normalised by the maximum intensity and were collected with an excitation fluence of approximately $5 \mu\text{J cm}^{-2}$ allowing comparison of intensity dependent decay dynamics. Spectral overlap of polarons with excitons is avoided by excluding the dynamics before 10 ps, at which time excitons have decayed.

6.4.3 Spectroscopically tracking charge migration

To account for the superior charge generation observed for the PTBT:PCBM blends attention turns to the mechanism of charge separation which has previously been proposed, whereby charge pairs are separated via energetically biased transfer from intermixed to pure phases.^{56,62,93} Just as the steady-state optical absorption spectra of PTBT revealed disordered regions induced by PCBM intermixing coexisting with more phase pure regions (when processed with ODT), TA spectra can be used to probe the dynamic link between excitations occupying each of these regions. PTBT was the only polymer whose UV-visible absorption spectrum was significantly shifted upon PCBM blending and processing with ODT (see Figure 6.2). This is matched by the PTBT blends being the only data to exhibit TA spectral dynamics beyond simple exciton-to-charge conversion.

Figure 6.16A compares the position of polaron peak (PIA-2) position as a function of time for the 2-phase (PTBT:PCBM and PDTBT:PCBM) and 3-phase (PTBT:PCBM) blends. In the 2-phase blends, the polaron PIA-2 peak remains at a constant position throughout the entire sub-picosecond to microsecond timescales.

In contrast the polaron PIA-2 peak in the 3-phase PTBT:PCBM blends (with and without ODT) dynamically red-shifts over the first hundreds of picoseconds, and then remains at a constant position during recombination (nano- to microseconds). The decreased signal-to-noise ratio at long time delay is caused by extracting the peak intensity from a decaying signal. The PIA-2 spectral shift is unlikely to be due to triplet formation, as the final spectra is inconsistent with measured triplet spectra (discussed above).

Figure 6.16 Analysis of GSB and PIA dynamics in TA spectra for polymer:fullerene blends. (A) Polaron peak position as a function of time for PT-TBT:PCBM, PDTBT:PCBM, and PTBT:PCBM with and without ODT. (B) Vibronic ratio (0-0/0-1) of the GSB region.

To gain further insight into the local environment polarons occupy in each of these polymer:fullerene systems, analysis of the vibronic progression intensity in the GSB TA spectral signatures are shown in Figure 6.16B. The shape of the GSB band

remains constant for the PTTBT blends consistent with no observed PIA shift. It is noteworthy that the GSB for the PDTBT blend is obscured by the electro-absorption feature and is omitted from this analysis. In contrast, for the highly mixed PTBT:PCBM blend without ODT, the PIA dynamics are also coupled with relative growth of the 0-0 vibronic peak in the GSB (Figure 6.16B). The GSB vibronic ratio remains constant in the PTBT:PCBM blend with ODT, and is coupled with a lower amplitude of PIA-2 peak shifting dynamics. Since the ratio of 0-0/0-1 vibronic peaks is indicative of polymer order, this suggests that the polarons occupy ordered regions of polymer domains. This is consistent with the lower conformational disorder in the polymer regions confirmed by UV-visible absorption and X-ray scattering. This implies that after a few hundred picoseconds, polarons occupy more ordered segments of polymer which is reflected in the GSB vibronic progression and also a lowering in polaron PIA energy.

It is worth noting that these ordered domains could exist in the mixed phase of a 3-phase morphology, through the formation of trap states comprised of smaller crystalline phases embedded within the intermixed domains. Recall, the electron affinity of the PCBM and the ionisation potential of the polymer is greatest in the respective crystalline domains.^{96,99} The presence of isolated trap states in the intermixed region was probed directly in the analysis of PTBT:PCBM blends with and without ODT additive (see Section 6.4.2), and showed better charge extraction in the 3-phase blend processed with ODT. The increased polymer crystallinity promoted with ODT processing is proposed to reduce trap states within the mixed domain, and lead to the majority of polarons occupying the bulk-neat polymer phase, which provides the most stabilisation energy of polarons.

Global fitting of polaron dynamics in a 2-phase morphology

Based on the lack of TA shifting dynamics in PTTBT:PCBM and PDTBT:PCBM blends, the entire TA surface, covering sub-picosecond to microsecond timescales, can be accounted for using just two spectral components in a linear least-squares fit; excitons and a single polaron spectrum. Spectral fitting was achieved using a combination of two algorithms. Firstly, for fitting of the near-IR probe region >10 ps (after exciton decay) soft-modelling global analysis was used, namely, evolving factor analysis and model-free multivariate curve resolution alternating least-squares (MCR-ALS) algorithm.^{233,234} The number of components required was guided by performing singular value decomposition and the constraint of non-negative concentration profiles was enforced. By cropping the data set after exciton decay, the polaron dynamics could be isolated. The result of this is shown for PTTBT:PCBM

in Figure 6.17 as an example, with Figure 6.17A showing the kinetics resulting from globally fitting the IR probe region, with the inset showing the spectral shape, and Figure 6.17B presenting the residuals from this fitting procedure. The residuals are unstructured along the temporal axes confirming that the polaron TA dynamics in this system can be accounted for by a single spectral shape, that of polaron PIA.

Figure 6.17 MCR-ALS global fitting of PTTBT:PCBM TA surface (>10 ps, IR probe only) showing this region can be accounted for by a single polaron signature. (A) Kinetics obtained using the spectral shape (shown as inset), and (B) residuals from the optimized fit showing no time-correlated signatures.

Secondly, fitting was performed for the time involving exciton decay (-1 ps to 1 ns) by expanding the spectral basis set obtained using MCR-ALS, to include a spectral component representing the exciton contribution. Due to the short lifetime of the exciton (decaying on sub-picosecond timescales), the weighting of this component in MCR-ALS was often lower than noise. To circumvent this, the exciton spectral shape was obtained by taking a spectral slice from the TA surface obtained for neat polymer films. This is a valid selection of the exciton component due to the excitation in neat polymer films being solely excitonic in nature, *i.e.*, no polaron formation. The polymer:fullerene blend data from sub-picosecond to nanosecond was fit with every combination of neat polymer spectra using linear non-negative least-squares

(NNLSQ) and the minimum residual, using the residual sum of square method, was chosen as the optimum spectral basis set. Figure 6.18 shows the result of this procedure on the PTTBT:PCBM blend (following on from the example above), where the globally fit kinetics in Figure 6.18A now reflect exciton and polaron dynamics. Figure 6.18B confirms that these dynamics fully account for the spectral signatures for the PTTBT:PCBM system.

Figure 6.18 MCR-ALS global fitting of PTTBT:PCBM TA surface (>10 ps, IR probe only) showing this region can be accounted for by a single polaron signature. (A) Kinetics obtained using the spectral shape (shown as inset), and (B) residuals from the optimized fit showing no time-correlated signatures.

Global fitting of polaron dynamics in a 3-phase morphology

In the PTBT:PCBM blend systems, the dynamic PIA shift requires an additional component in a linear least-squares fit of the entire TA surfaces to account for two spectrally distinct charge populations: those occupying disordered and ordered polymer chains. The dynamics of these two charge populations in the 3-phase PTBT:PCBM blends are shown in the MCR-ALS fitting results in Figure 6.18B. The figure highlights the NIR region where the two charge populations are dis-

tinguished, and excludes the first 10 ps so that an additional exciton spectrum is not required. It is noted that the same two charge components emerged from a 3-component fit that includes the earlier exciton timescale through non-negative least-squares fitting, but this is excluded here for clarity. Figure 6.19A shows the time-dependent weightings of these two charge-based spectral components peaked at ~ 1.15 eV and ~ 1.05 eV, which are shown in Figure 6.19B.

Figure 6.19 Analysis of the polaron dynamics for PTBT:PCBM with and without ODT. (A) Kinetics resulting from globally fitting the polaron spectral shift in PTBT:PCBM using MCR-ALS (described in the text), showing the migration of charges from disordered to ordered polymer domains, and (B) the two spectral shapes used for the MCR-ALS global fit.

In both PTBT:PCBM blends, the lower energy peak grows at the expense of the higher energy peak. The nature of the spectral dynamics, and the correlation with GSB shape dynamics for the blend with the most pronounced PIA shift (the blend lacking ODT) suggests that we are observing holes migrating from disordered regions to ordered and extended polymer chains. Given that the disorder is induced by mixing with PCBM and relieved in pure polymer domains, it is possible to further attribute these spectral dynamics to the previously invoked hole migration from intermixed to phase-pure regions of the 3-phase blends.^{56,62,93} This spectral assignment is supported by the observation that the amplitude of population transfer is lower for the PTBT:PCBM blend processed with ODT. In this system, a lower

fraction of charges occupy disordered polymer regions (1.15 eV PIA peak) initially (at 10 ps) due to the lower volume fraction of the intermixed region when ODT is used. Additionally, the data sets with- and without ODT were fit using the same pair of basis spectra, confirming that their differences relate only to the extent of population transfer.

Probing the mobility of charge carriers in a 3-phase morphology

To confirm that the spectral dynamics reflect migration of charges, polarization-resolved TA spectroscopy was performed (Figure 6.20) using a dual line visible camera to simultaneously resolve parallel and perpendicular components of the GSB signal. Anisotropy is retained near the theoretical maximum of 0.4 in the 2-phase PTTBT:PCBM blend within the 2 ns range probed. This shows that either most charges are immobile on this timescale in the 2-phase blends, or that charge motion does not depolarize the signal, which could be achieved with a film containing highly aligned chromophores. The immobility of charges in the 2-phase morphology is consistent with the geminate recombination of charges seen in these blends, as discussed above.

In contrast, the polarization anisotropy decay observed in the 3-phase PTBT:PCBM blends confirms that charges are mobile and lose memory of their polarization through hopping to differently oriented sites. The polarization anisotropy value for the more disordered blend is initially only ~ 0.2 . This loss of anisotropy within the time resolution of the experiment is attributed to the ultrafast localization of excitations generated in orientationally disordered regions.^{68,69,184} The anisotropy dynamics for the 3-phase blends occur throughout the same timescale as the spectral dynamics from hole migration (PIA red-shifting), as well as on earlier timescales when exciton dynamics are occurring.

Due to the disordered polymer chains being most likely to exist in intermixed regions, and ordered chains in polymer-pure domains, the comparison of 2-phase and 3-phase system shows that polarons are generated in intermixed domains and migrate to pure regions in the film. Therefore, it is proposed that the higher PV efficiency of the 3-phase blends, together with the higher yields of long lived charges, are linked to the dynamics of charge migration on the sub-nanosecond timescale. This process is likely driven by the ‘downhill’ energy gradient present in 3-phase blends between intermixed and phase-pure domains, shown in Figure 6.21, and previously proposed.^{56,62,92,93} This model is confirmed in the present system due to clear spectroscopic signatures allowing for the discrimination of different charge populations.

Figure 6.20 TA polarisation anisotropy showing charges are immobile in the 2-phase PTTBT:PCBM blend, and mobile in the 3-phase PTBT:PCBM.

Although the data presented here only provides information on polarons, and does not directly probe electron dynamics, the same argument could apply to electron migration from intermixed to pure PCBM regions.^{63,98,99}

Similar dynamic polaron-PIA dynamics have been reported in the literature, for example by Szarko *et al.* on a PTB7:PCBM blend,²³⁵ whereby the spectral shifting dynamics were attributed to the dissociation of charge transfer states. The authors considered this as an inherent property of charge separation, rather than the transfer of hole from intermixed regions. In another study, Howard *et al.* found that TA spectral shifts were able to track the relaxation dynamics of charges in PCDTBT:PCBM blends.²³⁶ This was used to invoke that high charge mobility at short time delays could account for efficient charge separation, although the phase separation morphology was not explicitly addressed in that study.

There have been two recently published observations regarding photocurrent generation in OPV device. Vandewal *et al.* have reported that excess energy in a donor:acceptor material cannot be used to improve device efficiency, and relaxed charge-transfer states efficiently generate photocurrent.⁸⁹ Whereas on the other hand, Barker *et al.* have shown that charges can separate at low temperature, implying that charges separate during the energetic relaxation after initial charge transfer.¹¹ The morphologically driven separation of charges generated in intermixed regions in the present work allows reconciliation of these observations. Due to the energetic differences of phase-pure and intermixed regions, if the pure phases are in close proximity to intermixed regions then charges can efficiently dissociate. This is aided by the energetic driving force shown in Figure 6.21 between phases.

Figure 6.21 Schematic of energy levels and charge behaviour in 2-phase, and 3-phase polymer:fullerene blend morphologies. (A) Charge generation in 2-phase blend yields immobile holes resulting in rapid geminate recombination and poor free charge generation. (B) The energetic disorder present in 3-phase blends yields mobile holes which are longer-lived. The energy gradient between intermixed domains and phase-pure polymer domains may be sufficient to efficiently separate charge pairs, resulting in more effective photocurrent generation.

This pathway to charge generation also explains the differences observed in device photocurrent and recombination dynamics for PTBT:PCBM with and without ODT.²²² Without ODT, the blend has a highly intermixed morphology, as shown in the steady-state optical spectroscopy and the initial shape of the GSB and PIA bands in the TA spectrum. This morphology is also consistent with the ultrafast quenching of all excitons within just 200 fs. Given the lack of pure-phase domains generated in such a intimately mixed system, it is unlikely that there are percolation pathways to enable charge extraction. Thus, while charge pairs may be initially well separated via energetically driven transport to a nearby phase pure region, they may become trapped there due to all other pathways being of higher energy. The formation of such morphological traps would suppress the current and fill-factor of the device. This requirement for phase pure percolation pathways has previously been highlighted for other 3-phase blends.^{62,94} In the PTBT:PCBM processed with ODT, the resulting 3-phase morphology exhibits a better balance of intermixed regions to phase pure regions. This is reflected by the spectral signatures of ordered polymer being dominant, and also the lower fraction of prompt (ultrafast) charge generation, which is accompanied by longer lived excitons than the blend without ODT. Although this morphology sacrifices some prompt charge generation, due to the intermixed domains no longer causing widespread disruption, there is a network of phase-pure domains which act as percolation pathways for more effective charge extraction. An additional benefit of more interfaces between intermixed and pure phase domains is that there could be an energetic barrier toward charge recombination across an interface due to charges being more stable in the phase pure regions.

In contrast to these dynamics, the 2-phase donor/acceptor blends are characterized by a lack of spectral dynamics that would suggest energetically biased charge migration, and concomitantly poor yields of free charges and low PV efficiencies, matching the observed device characteristics.

6.5 Summary

In this chapter, the pathways of charge photogeneration in polymer:fullerene blends was investigated using a series of closely related co-polymers with differing backbone curvature. This allowed control over the miscibility of fullerene, which governed phase behaviour in the blended thin films. The PTTBT and PDTBT polymers have linear or weakly curved backbones and formed a 2-phase morphology when each polymer was blended with PCBM. In contrast, the curved polymer PTBT yielded highly miscible PCBM which lead to the coexistence of intermixed and phase pure regions. The volume fraction of these phase domains could be altered through the use of the solvent processing additive ODT. Owing to distinct spectroscopic signatures of the differing electronic environments of polymer segments in either intermixed or pure polymer phases, it was possible to track the motion of hole polarons between disordered and ordered regions and link these dynamics to long-lived charge yield and overall PV efficiencies.

A summary of the findings is presented in Figure 6.22. For the polymers whose rigid backbones lead to 2-phase blends lacking an intermixed region, the observation of minimal spectral dynamics, along with polarization anisotropy retention, shows that holes are immobile. Rapid geminate charge recombination and poor photovoltaic performance are observed in such blends. In contrast, the 3-phase morphology supported by the polymer with a curved backbone exhibits highly mobile holes that are observed to migrate from the intermixed domains to phase-pure polymer domains. Such blends feature longer-lived populations of extractable charges and concomitantly better device performance. The energy gradient between the intermixed and phase-pure regions may be sufficient to drive efficient separation of charge pairs initially generated in intermixed regions, with free charges subsequently percolating through these phase-pure domains. These results provide valuable spectroscopic insight into the pathway of efficient charge separation and its link to blend morphology and polymer structure.

Figure 6.22 Summary of charge behaviour in 2-phase, and 3-phase polymer:fullerene blend morphologies. Spectroscopic signatures show holes (polarons) are immobile in 2-phase blends, whereas a 3-phase morphology results in highly mobile charges which undergo morphologically driven charge separation due to the resulting energy cascade.

Chapter 7

Charge generation in low band-gap polymer:polymer blends

7.1 Introduction

The highest efficiency organic photovoltaic (OPV) devices have active layers consisting of a low band-gap polymer donor paired with a fullerene derivative (acceptor), generally PC₆₁BM or PC₇₁BM. Indeed, the polymer:fullerene system has been extensively studied in order to improve the design principles governing polymer donor components,^{221,237–241} and to enhance the active layer morphology for better photocurrent generation.^{43,54,94,242,243} This interest has resulted in a significant increase in power conversion efficiencies (PCE) for polymer:fullerene blends,²⁴⁴ with 10% PCE now achievable using tandem structure devices.^{245,246}

Polymer:polymer (or all-polymer) OPVs, whereby both electron donor and electron acceptor components are conjugated polymers have attracted considerable attention in the literature.²⁴⁷ Whilst polymer:polymer OPVs generally exhibit poorer device efficiencies than the polymer:fullerene counterparts to date, the use of a polymer as an acceptor presents multiple potential advantages over a small molecule acceptor, such as stronger light absorption by the acceptor phase, lower cost of processing, easier structural modification, and improved morphological control.^{47,247,248} Several research groups have reported polymer:polymer device efficiencies of over 4%.^{249–251} *Gao et al.* recently reported an all-polymer OPV with a PCE of 8.27%, which is the most efficient polymer:polymer blend to date.²⁵²

Common to these high efficiency polymer:polymer solar cells is the use of low

band-gap acceptor polymers, which are paired with low band-gap donor polymers used in high performance polymer:fullerene blends. Low band-gap acceptor polymers have commonly utilized naphthalenediimide or perylenediimide moieties, with the naphthalenediimide-based polymer P(NDI2OD-T2), available commercially as N2200, being particularly well studied.^{251,253–256} In fact, the current record efficiency of 8.27% has P(NDI2OD-T2) as the acceptor polymer component in the active layer of the polymer:polymer blend.

Similar to the research focus on polymer:fullerene blends, continual improvement of device efficiencies for polymer:polymer blends is heavily reliant on an understanding of optimal blend morphology and charge generation photophysics. In particular, it is common for polymer:polymer OPVs to suffer from geminate recombination, indicating that charge separation is not as efficient as in polymer:fullerene solar cells due to sub-optimal morphology in all-polymer blends.^{37,248,253} In this chapter, the photophysics of a novel polymer:polymer blend is studied, which achieves optimised device PCE of >4%. Additionally, the electronic matching of the polymer components allows for a high open-circuit voltage of >0.9 V which is the highest achieved for P(NDI2OD-T2) based OPVs to date. Time-resolved and steady-state optical spectroscopy reveals incomplete exciton dissociation and rapid geminate recombination in the blends. Together with morphology studies performed by collaborators, it is shown that this is caused by a phase-separated morphology with domains greater than the exciton diffusion length. This work shows that even in polymer:polymer blends with promising efficiencies and well-matched electronic properties of polymer components, device performance is still severely hampered by blend morphologies. This highlights that the most pressing problem in realizing efficient polymer-based OPVs lies on optimizing blend morphology to realise facile charge separation.

7.2 Materials

Figure 7.1 shows the chemical structures of the two low band-gap polymers, BFS4 and P(NDI2OD-T2). These polymers were synthesized by collaborators in the laboratory of Prof. C. McNeill, at Monash University, Melbourne, Australia. The details of the synthesis has been reported elsewhere.²⁵⁷ BFS4 is composed of dithienylbenzo[1,2-b:4,5-b']dithiophene (DT-BDT) and 5-fluoro-2,1,3-benzothiadiazole (FBT) sub-units. Noteworthy are the solubilising side-chains on the DT-DBT in the repeating monomer unit, along with the substitution position of the fluorine atom on the FBT sub-units with respect to the DT-DBT units. Due to a non-symmetrical arrangement of both these substituents, the BFS4 contains an intrachain configu-

ration of A-D1-A-D2, where A denotes an acceptor moiety, and D represents the two differing donor motifs. Co-polymers with two differing donor sub-units tethered to an acceptor have shown improved supramolecular interactions compared to the corresponding A-D co-polymers, resulting in enhanced photovoltaic device performance.²⁵⁸ With regards to electronics in this pairing, BFS4 acts as the donor components and P(NDI2OD-T2) acts as the acceptor component.

Figure 7.1 Chemical structures of polymers BFS4 and P(NDI2OD-T2).

7.2.1 Optical properties

Steady-state optical absorption spectra of neat BFS4 and P(NDI2OD-T2) films, as well as polymer:polymer blends of varying ratios, are shown in Figure 7.2. Before discussion of polymer:polymer blends, attention remains with the electronic properties of the neat polymer components. P(NDI2OD-T2) has a broad absorption band from 550–850 nm and also a higher energy feature at ~400 nm, which is attributed to a π - π^* transition. The absorption spectrum of neat BFS4 exhibits clear vibronic features in the visible band, which is peaked at ~675 nm and ~615 nm, along with an additional peak in the visible at ~490 nm. The π - π^* absorption features appear in the ultraviolet region. This confirms the optical band gap of ~1.56 eV for BFS4, which is higher than the ~1.45 eV band gap of P(NDI2OD-T2).

The band gap of BFS4 is lower than other common polymers based on the DBT sub-unit, such as PTB7,²³⁷ and PBDTTT-EF-T.²⁵¹ Although the highest occupied molecular orbital (HOMO) levels of these polymers are all similar, the electron withdrawing character of the FBT moiety results in a deeper-lying lowest unoccupied molecular orbital (LUMO) in BFS4. Therefore, the BFS4:P(NDI2OD-T2) combination yields a HOMO/HOMO offset of 0.3 eV, LUMO/LUMO offset of 0.4 eV, and a theoretical maximum open-circuit voltage in a device of 1.15 V.²⁵⁷ Addition-

Figure 7.2 Normalized steady-state optical absorption spectra of neat BFS4 and P(NDI2OD-T2) and polymer:polymer thin films cast from chlorobenzene. Blend ratios correspond to BFS4:P(NDI2OD-T2) by weight percent.

ally, the pairing of the two polymer components provide good coverage of the entire UV-visible spectrum. P(NDI2OD-T2) has low optical absorption in the range of 450–600 nm, whilst there is moderate optical absorption in this region from BFS4.

Figure 7.2 shows the normalized optical absorption spectra of BFS4:P(NDI2OD-T2) thin films of different weight percentage ratios. In all blends the near-IR absorption tail (~800 nm) and the feature ~400 nm both increase as the content of P(NDI2OD-T2) is increased with respect to the BFS4. This is consistent with the combination of the absorption spectrum of P(NDI2OD-T2) and BFS4. To this end, Figure 7.3 shows the absorption spectra of each blend film fitted by the sum of neat polymer spectra for (A) 3:1, (B) 2:1, (C) 1:1, and (D) 1:2 (BFS4:P(NDI2OD-T2)). This was achieved through least-squares fitting using the neat BFS4 and neat P(NDI2OD-T2) as components. This shows the absorption spectra of blends track the relative contribution of the two components. However, it highlights that the extinction coefficient of each polymer is not the same. This is most clearly observed with the 1:2 blend (Figure 7.3D) fitting an almost 1 to 1 weighting of the neat polymer component spectra, *i.e.*, BFS4 is more strongly absorbing than the P(NDI2OD-T2). The same result comes from normalizing the absorption by film thickness, and may be related to the side chains on the P(NDI2OD-T2) being longer than BFS4, thereby diluting the active chromophore in a weight ratio dilution.²⁵⁷

Figure 7.3 Normalized steady-state optical absorption spectra of polymer:polymer blends fitted to a linear combination of neat polymer absorption spectra. (A) 3:1, (B) 2:1, (C) 1:1, and (D) 1:2. Blend ratios correspond to BFS4:P(NDI2OD-T2) by weight percent.

7.2.2 Morphology

The microstructure and device performance of BFS4:P(NDI2OD-T2) blends were studied by several collaborators based in Australia. In this section, a brief summary of the findings will be presented with full details being published elsewhere.²⁵⁷ Thin films of neat BFS4 and P(NDI2OD-T2) both adopted a fibrillar morphology. These fibres were smaller for the neat P(NDI2OD-T2) compared to BFS4, consistent with previous reports on P(NDI2OD-T2) showing a high degree of ordering between polymer chains.²⁵⁹ Both BFS4 and P(NDI2OD-T2) were shown to form a semi-crystalline morphology when cast into a film through the use of two-dimensional grazing incidence wide-angle X-ray scattering (GIWAXS), which is consistent with other reports in the literature.^{258,260} Blending of the two polymers maintained a fibrillar network

but with a coarse phase-separated morphology. This yielded isolated domains of BFS4 and P(NDI2OD-T2) which are tens of nanometres in width. The fibril domains become longer with increasing BFS4 content, suggesting a more connected morphology in these systems. The use of the solvent additive 1,8-diiodooctane (DIO) increased the length of the domains to create a bi-continuous network of fibres. However, the width of the domains remained ~20-100 nm, which is significantly longer than the exciton diffusion length of ~10 nm. The GIWAXS data of the blends showed scattering peaks of the individual components, confirming the polymer crystallisation in the blend is similar to the neat films.

7.3 Polymer:polymer blend photophysics

Table 7.1 summarises the photovoltaic device characteristics of BFS4:P(NDI2OD-T2) blends.²⁵⁷ The 2:1 blend processed with DIO is the superior device in all aspects, culminating in a PCE of 4.3%. The lowest efficiency devices were obtained from blend with low BFS4 content, consistent with the morphology study showing a more interconnected morphology with high BFS4 fractions. The 4.3% PCE of the BFS4:P(NDI2OD-T2) is one of the highest reported to date and also achieves the highest open-circuit voltage using P(NDI2OD-T2) as an acceptor. However, the large phase separated morphology suggests exciton dissociation may hinder device performance. To this end, the photophysics of BFS4:P(NDI2OD-T2) was probed with steady state photoluminescence (PL) and transient absorption (TA) spectroscopy.

Table 7.1 Summary of BFS4:P(NDI2OD-T2) photovoltaic device characteristics, short-circuit current (J_{sc}), open-circuit voltage (V_{oc}), device fill-factor (FF), and power conversion efficiency (PCE). Reproduced from Deshmukh *et al.*²⁵⁷

Active layer	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	PCE (%)
3:1	8.1	0.90	0.46	3.4
2:1	8.8	0.92	0.48	3.9
2:1 (with 1% DIO)	9.2	0.90	0.52	4.3
1:1	8.3	0.90	0.41	3.1
1:2	6.0	0.88	0.34	1.8

7.3.1 Exciton dissociation dynamics

Figure 7.4 presents the photoluminescence (PL) spectra of BFS4:P(NDI2OD-T2) blends compared to that of neat BFS4 and neat P(NDI2OD-T2) films. The excitation wavelength was 620 nm, which is near the absorption maximum for both

polymers. PL intensity has been corrected by differences in the number of absorbed photons resulting from differing optical density at the excitation wavelength for each sample. Neat BFS4 has emission covering 700 nm to beyond 850 nm, with clear vibronic peaks at ~730 nm and ~800 nm. The PL of P(NDI2OD-T2) extends from ~800 to beyond 850 nm, which is the cut-off due to the detector response being highly non-linear at wavelengths >850 nm. P(NDI2OD-T2) shows a weaker PL compared to BFS4. Extending the wavelength range was attempted using detectors sensitive in the IR region, however the signal-to-noise ratio was 1000 times worse than the visible detector, and no PL signal could be obtained. However, the PL obtained here is consistent with that reported by Zhou *et al.*, which showed P(NDI2OD-T2) emission is peaked at ~1000 nm, and extends out to 1300 nm.²⁶¹

Figure 7.4 Normalized photoluminescence spectra of neat BFS4 and P(NDI2OD-T2) and polymer:polymer thin films cast from chlorobenzene. Blend ratios correspond to BFS4:P(NDI2OD-T2) by weight percent. Excitation wavelength was 620 nm for all samples. Intensity has been corrected by absorbed photons, and then normalized with respect to the BFS4 emission.

BFS4:P(NDI2OD-T2) blends exhibit quenching of both BFS4 and P(NDI2OD-T2) emission (Figure 7.4), which is consistent with exciton dissociation due to both electron transfer and hole transfer. However quenching is not complete and the amount of quenching can be estimated by comparing the amount of BFS4 emission in each sample, for example at 720 nm where there is no spectral overlap of P(NDI2OD-T2) emission. For the 2:1 blend, ~25% emission remains which means only 75% of excitons dissociate and the rest are lost to radiative recombination. Processing the 2:1 blend with DIO additive (the most efficient device) only shows a slight increase of PL quenching, with ~23% emission intensity remaining. Blends with a higher fraction of P(NDI2OD-T2) show an apparent increase in quenching of BFS4 emission, however this is likely due to the reduced BFS4 content since both BFS4 and P(NDI2OD-T2) are excited at the pump wavelength. This is consistent with

the increased emission at 850 nm as the P(NDI2OD-T2) content is increased. The residual emission from the blends indicates that a significant fraction of excitons (of the order of 25% or higher) are not being dissociated at interfaces. Such incomplete exciton dissociation is consistent with the observed morphological characterization showing domains which are 20-100 nm in width, which is larger than the exciton diffusion length.

7.3.2 Charge recombination dynamics

To gain further insight into charge generation and recombination, transient absorption (TA) spectroscopy was performed using an excitation wavelength of 532 nm. TA measurements of individual polymers (Figure 7.5) allows to first identify spectroscopic signatures associated with excitons in films of each polymer. This information is then able to guide the interpretation of TA measurements of the polymer:polymer blends. Measurements were conducted at sufficiently low fluence in order avoid non-linear recombination effects, such as exciton-exciton annihilation.¹¹¹ This was confirmed by performing intensity dependent measurements showing overlapping decay dynamics at higher fluences than presented here. Figure 7.5A shows the TA spectral slices for neat BFS4, which contain two features; a ground-state bleach (GSB) feature which has the same vibronic progression as observed in the steady-state absorption spectrum at ~690 nm and ~615 nm, and a photo-induced absorption (PIA) peak which is peaked at ~1300 nm. Additionally, a weak stimulated emission feature is observable at 790 nm confirming the presence of excitons. Integrating these spectral features provides the kinetic traces for neat BFS4 shown in Figure 7.5C. The equal decay rates of all features confirms the presence of a single excitonic species with a half-life ($\tau_{1/2}$) of ~80 ps.

In the case of P(NDI2OD-T2), TA spectral traces (Figure 7.5B) show a broad GSB feature peaked at ~700 nm, which matches the steady-state optical absorption spectra. This feature is accompanied by two PIA features at ~840 nm and ~1100nm. The broadband probe used in this work resolves the lower energy PIA peak, labelled PIA-1, which was not observed in a previous study on P(NDI2OD-T2) due to a narrower probe spectral range used in that study.²⁵³ The presence of two PIA peaks and the fact no stimulated emission is observed in P(NDI2OD-T2) could imply that the exciton exhibits some charge-separated character. All features decay with the same time scale (Figure 7.5D), which suggests the presence of a single excitonic species with a half-life ($\tau_{1/2}$) of ~80 ps.

Figure 7.5 Transient absorption measurements of neat polymer films showing spectral slices at indicated time delays for BFS4 (A), and P(NDI2OD-T2) (B), following 100 fs excitation at 532 nm. The spectral regions labelled GSB, PIA-1, and PIA-2 refer to the wavelength integration regions shown in the kinetic traces for BFS4 (C) and P(NDI2OD-T2) (D). Kinetics are normalized by the average value within the first picosecond.

With the exciton spectra and lifetimes for both polymers elucidated, the dynamics of the blends in the low fluence regime can be considered, presented in Figure 7.6 for the 2:1 blend. As shown above, the optical absorption of the blend films is a linear combination of the individual polymer components. For the 2:1 blend this results in 89% of the 532 nm excitation pump pulse being absorbed by the BFS4 component. This results in the initial (200 fs) TA spectral slice (Figure 7.6A) resembling that of neat BFS4, *i.e.*, the BFS4 exciton. However, the ratio of the exciton PIA at 1300 nm to the GSB peak at 690 nm in the blend (31%) is less than half of that observed in the neat polymer (84%). Since free charge carriers would retain the GSB peak, it suggests that over 50% of excitons are converted to charges within the first 200 fs. Consistent with this interpretation is the absence of net stimulated emission on the ultrafast timescale due to overlapping PIA from promptly generated charges. At longer time delays, the exciton PIA decays to yield a PIA feature from ~720 into the near IR, with a peak at 1000 nm. These TA dynamics are consistent with charge photogeneration via charge transfer to yield polarons on BFS4 and electrons on P(NDI2OD-T2).³⁷ The appearance of these PIA features could be accounted for by energy transfer from BFS4 to the lower band-gap polymer P(NDI2OD-T2) instead of charge separation. However, this was ruled out due to the GSB spectral shape of

BFS4 being retained after exciton decay. It is noteworthy that the TA spectra of the blend are lacking any obvious contribution from P(NDI2OD-T2), this is proposed to be due to the lower oscillator strength of these features compared to BFS4, since the majority of excitation is absorbed by the latter component.

Figure 7.6 Transient absorption measurements of the 2:1 blend (BFS4:P(NDI2OD-T2)) thin film. (A) Spectral slices at indicated times, (B) kinetics of the regions specified normalized by the average value within the first picosecond.

Figure 7.6B shows the kinetics of the integrated wavelength regions specified for the 2:1 blend. In addition to the prompt (<200 fs) reduction in the BFS4 exciton PIA peak (PIA-1), exciton decay is only slightly faster than what was resolved for neat BFS4, with a half-life of ~20 ps. The similar lifetime suggests that a large fraction of excitons are formed too far from interfaces to undergo dissociation and contribute to photocurrent. This is consistent with the residual photoluminescence for the blend, discussed above. The integrated intensity of PIA-2 tracks the charge population. This reveals that charges do not substantially outlive excitons, and begin recombining after only 10 ps. This results in only 30% of the initial charge yield

remaining into the nanosecond timescale. The integrated intensity of the GSB region matches the decay dynamics of charges (PIA-2). Since the GSB is proportional to the total population of excitations, this confirms that the decay observed for charges (>10 ps) is through rapid geminate recombination to the ground state.

These dynamics were the same for higher pump fluence, as shown for the 2:1 blend in Figure 7.7A. This confirms that measurements were performed in the linear regime with minimal exciton-charge annihilation effects.¹¹¹ Using the GSB as probe of the charge population, measurements were performed from the nano- to microsecond timescale regime using an electronic delay configuration. The integrated intensity of the GSB region is shown in Figure 7.7B, and charges which have survived to this timescale are able to contribute to extractable photocurrent. The presence of free charge carriers is confirmed by the presence of intensity dependent recombination, whereby decay is accelerated *via* bimolecular recombination at higher fluences. However, even at the lowest fluence used here, most charges recombine within just tens of nanoseconds and very few survive beyond 1 μ s. This recombination rate is substantially faster than what is typically observed in polymer:fullerene blends.¹¹ The dynamics of the other BFS4:P(NDI2OD-T2) blend ratios are shown in Figure 7.7C, and clearly show similar recombination kinetics as the 2:1 ratio. Ensuring each sample was measured with the same excitation fluence (*i.e.*, 1.1 1.1 μ Jcm⁻²) allowed for a direct comparison between these blend ratios. These recombination dynamics were also found to be similar for the 2:1 blend processed with 1,8-diiodooctane (DIO), as shown in Appendix I.

Analysis of the photophysics of charge generation in BFS4:P(NDI2OD-T2) blends has revealed these blends suffer severe geminate recombination, indicating inefficient charge separation. Based on morphology information (see Section 7.2.2) the main cause of this is likely the coarse phase-separated film morphology which is composed of domains that are larger than the exciton diffusion length. However, TA measurements show evidence of rapid charge generation which suggests significant intermixing occurs within the large domains. This means the residual photoluminescence in the blends is likely to occur from relatively phase-pure isolated semi-crystalline domains which are present in the microstructure. Additionally, the low population of long-lived charges, which can contribute to extractable photocurrent, limits device performance. The short lifetime of free charge carriers suggests there is a lack of percolation pathways to aid charge separation, resulting in geminate recombination, and causing severe loss of charges available to be extracted as photocurrent.

Figure 7.7 Intensity dependent charge recombination kinetics integrated over the GSB region for the 2:1 blend sample covering the femto-nanosecond (A), and the nano- to microsecond (B) timescales, and for BSF4:P(NDI2OD-T2) blends of various ratios (C) measured at 1.1 $\mu\text{J cm}^{-2}$ excitation fluence.

7.4 Summary

In this chapter, the photophysics of a polymer:polymer OPV system was studied. This novel combination of BFS4 (donor) and P(NDI2OD-T2) (acceptor) showed a promising PCE of 4.3% and has the highest open-circuit voltage for a blend utilising P(NDI2OD-T2) of 0.92 V. However, morphology measurements revealed the presence of coarse phase-separated domains between donor and acceptor polymer components. Steady-state photoluminescence was used to probe the efficiency of exciton dissociation, and revealed only a 70% quenching ratio in the blend compared to neat polymer emission. This ratio of exciton quenching is lower than is observed in polymer:fullerene blends and highlights the inefficient exciton dissociation common in other polymer:polymer blends. This is consistent with the domain sizes being greater than the exciton diffusion length, resulting in a significant portion of excitons being generated too far away from an interface. Additionally, transient absorption spectroscopy revealed the BFS4:P(NDI2OD-T2) blend suffers from severe rapid geminate recombination; only 30% of initial charge yield remains at 1 ns to contribute to extractable photocurrent, limiting device efficiency. Such results are similar to other polymer:polymer blends reported in the literature and suggests that further work is required to realise long-lived charge separated states and efficient exciton dissociation in order to improved device efficiencies, and surpass those observed in polymer:fullerene blends. Central to this is an improved understanding of the factors governing polymer:polymer blend morphology to reduce domain size and promote the presence of charge percolation pathways.

Chapter 8

Conclusions and Future Work

Organic photovoltaic (OPV) cells show significant promise as a renewable energy resource with the potential of providing a low cost source of solar energy. Despite the significant progress made over the past decade, further improvements regarding device efficiency is required in order to achieve an economically viable option for widespread applications. Many of the outstanding questions regarding photogeneration processes in OPV cells relate to the mechanism by which excitons (electron-hole pairs) escape their Coulombic attraction and generate photocurrent. Although this process has been the focus of research for some time, traditional theories fail to explain the rate and efficiency of charge separation that is observed to take place in many of these materials.

Due to the formation of excitonic states upon photoexcitation of π -conjugated polymers, photocurrent generation in OPVs relies on overcoming the binding energy of the exciton to generate free charge carriers. This needs to occur before relaxation to the ground state and is a critical component of efficient OPV cell operation. A breakthrough in device performance was realised through the measurement of photoinduced electron transfer from a conjugated polymer to fullerene in the mid 1990's.^{33,42} This led to the view that the operating mechanism must rely on an interface between an electron-donor material and an electron-acceptor material with optimised HOMO and LUMO offsets in order to drive charge separation.

However, numerous experimental studies have subsequently shown that the true mechanism must be more complex. For example: The formation of charges has been shown to occur within 100 fs, with CT states forming in 45 fs.⁴⁻⁸ Applying point-like excited state diffusion and measured exciton diffusion coefficients, the majority of excitons would not be able to reach an interface in the bulk heterojunction architec-

ture within this timescale.^{9,46} Additionally, photocurrent can be generated in neat polymer films casting a question as to the precise role of donor:acceptor interfaces and phase separation morphology. An emerging set of theories invoke the nature of primary excitations, in particular their delocalisation, as providing the driving force for sufficient spatial separation of charge pairs to overcome the Coulombic binding energy. To add to this, the complex nature of the donor:acceptor phase morphology has been revealed and its role in charge generation cannot be over-looked.

Charge pairs overcoming their mutual Coulomb attraction, to yield free charge carriers, has been shown to occur on sub-picosecond timescales. Since Conformational disorder present in a polymer backbone breaks the chain into sub-units of varying size, the relaxation dynamics of conjugated polymers contains structural relaxation and energy transfer processes. This raises the question of how do the complex conformational dynamics of a conjugated polymer chain affect this process, and what is the kinetic competition with charge separation? Understanding the relaxation photophysics occurring in polymer system requires isolating and studying well-defined systems. To date, separating the inherent relaxation dynamics of chromophore sub-units from the energy transfer processes has not been realised.

In Chapter 3, oligothiophenes with the same repeat unit as the polymer P3HT were synthesised to act as molecular models for chromophore sub-units of a polymer backbone. The oligomers synthesised in this work were chosen to model conformational sub-units of P3HT for 2 reasons; Firstly, understanding the excited state photophysics in P3HT has direct relevance to the research field of optoelectronic devices, owing to P3HT being extensively studied in OPV applications, and secondly, the relatively simple nature of the polymer backbone compared to low band-gap donor-acceptor co-polymers. Through structural design, regiochemistry was controlled in order to prevent steric interactions between alkyl-substituents on thiophene rings, which would significantly impact torsional disorder.

The library of oligomers were synthesised using the Suzuki-Miyaura metal-catalysed cross-coupling reaction. This allowed selective coupling of two monomeric building blocks to yield a well defined extension of oligomer chain length. The conjugation lengths contained 4, 6, 8, and 10-thiophene units. The length dependent band gap was well described through the particle-in-a-box quantum mechanics model. Reports in the literature have shown that the effective conjugation length of P3HT is between 11 and 20 thiophene units, which is longer than the library obtained in this work. To further this work, the synthesis of oligomers with conjugation length closer to the effective conjugation length of P3HT would be beneficial. The synthesis of longer oligomers was attempted using the same step-wise synthetic strategy for

the others but purification complications prevented the successful synthesis. The difficulty surrounding the synthesis of long oligothiophenes is highlighted by the majority of oligomer synthesis in the literature yielding oligomers of 2–8 thiophene units in length.^{138,139,154–156} This could be accounted for by competitive reactivity between α - and β -positions of thiophene rings as the conjugation length increases.¹⁵² A 24-mer oligothiophene with only alkyl-substituted thiophene rings was recently reported by Zhang *et al.* using Stille coupling in a similar step-wise chain growth reaction protocol used here.¹⁵⁹ Stille cross-coupling is similar to the Suzuki-Miyaura reaction used here, but the successful synthesis of long oligomers by those authors suggests that the installation of the organotin functional group (*i.e.*, stannylation reaction) required for a Stille cross coupling could have better site selective reactivity compared to the borylation reaction used for Suzuki-Miyaura precursors on longer oligomer substrates. Based on this, the synthesis of oligomers longer than 10-thiophene rings should be attempted through a Stille cross-coupling reaction, and would be a strong emphasis in future work from this thesis.

The conformational disorder in polymer systems allows sub-units to interact with each other through overlap of orbitals resulting in intermolecular coupling of chromophores. This interaction is highly sensitive to the relative orientation of the π -conjugated chromophoric units. The contributions of intermolecular aggregates on the dynamics of conjugated polymer relaxation following photoexcitation could be an important process, but to date is not well understood. To probe this, it is useful to impart structural constraints to control both the distance and orientation between chromophores. The synthesis of a oligothiophene-dimer was reported in Chapter 3, whereby two quaterthiophenes were attached to a xanthene scaffold to control their proximity to one another. The dimer scaffold was designed to have flexible spacers between xanthene and the 4T oligomer in order to provide freedom for the chromophores to assembly co-facially in a energetically favourable manner, as opposed to forcing them through rigid linkers to adopt a particular geometry. This was designed in order to provide a molecular model with well-defined electronic coupling (π - π interactions) between chromophores.

Steady-state optical spectroscopy was used to probe the local electronic environment of the chromophores, but revealed no intramolecular interaction between oligomers in a variety of organic solvents. Solvent titration studies were performed to induce assembly whereby the addition of a poor solvent (water) increasing the energy of solvating the oligothiophene dimer. However, this also failed to induce intramolecular interactions between dimers. This idea was pursued further through the supervision of undergraduate research projects performed by students working in the Hodgkiss group. First, Kimberly Savill investigated other solvent mixtures to obtain isolated

dimers in solution. Unfortunately, these ended in the same manner as outlined above. Subsequently, the use of the dimer as a molecular tweezer whereby a electron acceptor motif is contained between the oligomer donors was explored.²⁶² The idea was motivated by the potential of obtaining well-defined, isolated donor:acceptor interactions which could act as a molecular model for a heterojunction. This did not provide a positive result as no intercalation observed for a range of electron-accepting chromophores. Following on, Joe Bracegirdle investigated the covalent attachment of C₆₀-fullerene to the 4T-dimer to investigate intramolecular charge transfer, utilising a similar approach to that observed in the literature for linear oligothiophenes.^{263,264} However, complications during the synthesis and purification of a product meant this molecular model was not realised.

Future work should involve synthesising a dimer using longer oligothiophenes, as this would likely increase the favourability of π - π interactions between the chromophores. Also the linker scaffold could be selected such that the space between chromophores was reduced in order to force less spatial displacement, an example could be using a 1,8-disubstituted naphthalene derivative instead of the xanthene motif. Another avenue of future work would be to directly substitute the oligomer onto the xanthene scaffold, without the flexible linking unit used in this work. Although the studies with the 4T-dimer in this study did not yield a positive result, the synthesis of the 4T-dimer lays a platform for which to perform future studies towards a isolated molecular model of aggregates in order to determine what role electronic coupling has on polymer relaxation dynamics. Furthermore, a significant focus should be on adapting the synthesis presented here to obtain a molecular model of a donor:acceptor interface to probe the charge transfer dynamics in detail, which is of significant relevance to research surrounding increasing OPV device efficiency.

Results presented in Chapter 4 used the library of oligothiophenes synthesised to investigate the evolution of the non-mirror image absorption-emission spectra as a function of oligomer length. Broad absorption and sharp, vibronically structured fluorescence spectra in conjugated polymers is widely considered a signature of excitation energy funnelling from a broad distribution of absorbing chromophores to a narrow distribution of emitters. However, recent literature reports have proposed that intrinsic conformational relaxation dynamics mix with energy transfer in producing fluorescence decay on tens of picoseconds on the high-energy side of conjugated polymer fluorescence spectra. Explicitly separating conformational dynamics in such systems is important because structural relaxation may profoundly change the outcome of competing charge- and energy transfer processes in OPVs.

Conjugated oligomers comprised of a single chromophore are ideally suited to iso-

lating these intrinsic conformational dynamics because they cannot support inter- or intramolecular energy transfer in dilute solution. Steady-state absorption and emission spectroscopy of the library of oligomers synthesised in Chapter 3 in dilute solution confirm the non-mirror image relationship is an inherent property of the chromophores. By assuming that the vibronic structure arises from an electronic transition coupled to a single vibrational mode (*e.g.*, C=C stretch) the fluorescence spectra are modelled by a Franck-Condon progression of Gaussians. In the model the fitted parameters are: 1) the full-width half-maximum of the Gaussian lineshapes, which is proportional to the distribution of conformation states, 2) the energy of the 0-0 transition, and 3) the Huang-Rhys pre-exponential factor, which is proportional to the displacement between ground- and excited state equilibrium coordinates, which is largely torsional for oligothiophenes.

In order to probe length dependent relaxation dynamics, transient-grating photoluminescence spectroscopy was used to provide time-resolved, broadband emission spectra of each oligomer in the library. This revealed the emergence of vibronic structure in emission signatures, in addition to a dynamic Stokes shift. Applying the Franck-Condon model to each spectral slice showed that the Huang-Rhys factor for all oligomers rapidly increased to their steady-state values near 1. The Huang-Rhys factor cannot explain the dynamic loss of fluorescence intensity on the high-energy side. Further, the energy of the 0-0 transition was found to vary little beyond 0.5 ps, suggesting dynamic stabilization of 0-0 transition energies through solvation does not play a major role. Rather, the Gaussian full-width half-maximum (FWHM) values decreased for all oligomers within a few picoseconds. This accounts for the decreased intensity on the high energy side of the fluorescence spectra, where there are no overlapping peaks to conceal changes in peak widths. This dynamic narrowing was attributed to structural relaxation funnelling the molecular geometry to a narrow distribution of conformations. The dynamics of the planarisation revealed the majority of the torsional relaxation occurred within a few picoseconds. Furthermore, the insensitivity to oligomer length suggests localised relaxation of the torsional angle between neighbouring thiophene rings in the backbone is the main conformational relaxation process on these timescales.

Transient absorption spectroscopy was also performed on the oligomers in dilute solution, owing to its higher data density and signal sensitivity. The spectral dynamics of the stimulated emission (SE) region (2.6-2.1 eV) were reminiscent of those observed in the ultrafast fluorescence measurements; at 200 fs, SE is broad and unstructured, and vibronic structure develops over a few picoseconds. Although overlapping TA features prevented fitting the SE region to a full Franck-Condon progression, the Gaussian peak width dynamics were obtained from the high-energy

edge of SE. This was achieved by taking advantage of the high energy side of the SE region having minimal contribution from the 0-1 transition Gaussian, and only spectral overlap with the ground state bleach (GSB). Fitting the GSB region in each TA spectral slice with the steady-state absorption spectrum allowed the Gaussian FWHM to be modelled, which was found to be consistent with those obtained in TRPL measurements. A slower structural relaxation (>10 ps) was attributed to a large scale conformational relaxation of the backbone.

Subsequently, Chapter 4 then progressed to probe the role of torsional dynamics in thin films, whereby 6T dispersed in polystyrene at a 1:20 (6T:polystyrene) weight ratio was used to ensure that the oligomers are isolated in an inert matrix. Ultra-fast fluorescence and TA measurements confirmed that, although vibronic structure is not clearly resolved, the main spectral narrowing dynamics are maintained in the solid state on the sub- and early picosecond timescale. Thus, it was concluded that torsional relaxation still takes place in the more restrictive environment of a thin film. Additionally, it was found that the magnitude of the slow phase of peak narrowing is slightly lower in the solid film, consistent with the expectation that longer range chain arching dynamics will be restricted in a thin film. Beyond the insights into intrinsic torsional dynamics, these results also impact the interpretation of fluorescence spectra and dynamics in conjugated polymer films. Conformational dynamics, particularly the sub-picosecond phase, are expected to make a strong contribution to the observed non-mirror image fluorescence spectra in such films. The results of Chapter 4 highlight that future models of energy funnelling in conjugated polymer films must go beyond static energetic distributions of chromophores to include intrinsic relaxation dynamics.

A possible extension to this work would be to use the fluorescence spectral dynamics of the oligomers to quantify the transient enhancement of resonant energy transfer before conformational dynamics occur. Energy transfer from an excited oligomer donor to another oligomer of the same type is representative of iso-energetic energy transfer in conjugated polymer thin films.²⁶⁵ The rate of this homo- energy transfer process is proportional to the spectral overlap integral,¹⁹ which can be evaluated from time-resolved fluorescence spectra and the steady state absorption spectra of the same material. Comparing those relaxation dynamics to the photophysics of a polymer thin film may allow the role of non-relaxed geometries on the energy transfer process to be elucidated. For example, the broad emission spectra immediately following following excitation could provide strong overlap with other chromophores, which would increase the mobility of excitons on early time scales through Förster resonance energy transfer (FRET) processes and contribute to the large diffusion lengths of excitons in OPV blends on the sub-picosecond timescale.

In the quest for improved device efficiency, conjugated polymer design has led to the synthesis of low-band gap polymers which absorb lower energy photons of the solar spectrum. In high-band gap polymers, such as poly-3-hexylthiophene (P3HT), the lowest lying polymer triplet (T_1) state is higher in energy than the CT state. In contrast, low-band gap polymers have the T_1 state lower in energy than the CT state. This energy landscape, coupled with the possible formation of triplet CT states through bimolecular recombination of spin uncorrelated charges, has been proposed to allow a relaxation pathway into the triplet manifold. The formation of triplet excitons has emerged as a potential limit of OPV device efficiency. However, the mechanism of triplet exciton formation is still up for debate. In Chapter 5, triplet exciton formation through intersystem crossing (ISC) was investigated using oligothiophenes as molecular models of polythiophene sub-units. Using TA spectroscopy, spectroscopic signatures of singlet and triplet excitons were identified through global analysis of the data matrix. The singlet and triplet exciton populations in oligothiophenes were tracked to probe the mechanism of triplet exciton formation and investigate any length dependent behaviour. The rate of singlet exciton decay and triplet exciton formation were similar, which confirmed the direct conversion of singlets to triplets *via* ISC.

In oligothiophenes, singlet decay occurs through the combination of internal conversion, photoluminescence, and ISC. Meanwhile, the rate of ISC is significantly affected by structural dynamics, with theoretical studies showing the spin-orbit coupling is zero between the singlet and triplet manifolds for a planar geometry. Chapter 5 probed the link between molecular geometry and triplet yield for the series of oligothiophenes. Results showed a length dependent triplet formation, with longer oligomers exhibiting lower triplet yields owing to their more planar thermally equilibrated excited state geometries. The role of structural relaxation following photoexcitation was also investigated by altering the amount of torsional freedom of the oligomer backbone. This was achieved by controlling the conformational relaxation through temperature dependent studies, whereby the solvating environment becomes more restricted upon the formation of a frozen glass. At low temperatures, the oligomer backbone is restricted in a more Franck-Condon geometry, and thereby maintains high torsional disorder. This was evidenced by an increased triplet yield as the temperature was decreased below the glass transition temperature of the solvent.

To decouple the role of temperature and viscosity of the solvating environment, the triplet dynamics were investigated in the solid state by dispersing an oligomer in polystyrene at a 1:20 (6T:polystyrene) weight ratio. Results confirmed the increased triplet yield in the restrictive environment of an inert polymer matrix, which was free from interchromophore energy transfer processes. Based on these results, a model

was proposed hot vibrational states, characterised by high structural disorder, are able to drive triplet exciton formation through ISC. Thermal equilibration (cooling) from the Franck-Condon geometry following photoexcitation decreases the rate of ISC, due to a decreased spin-orbit coupling between S_1 and T_2 (the lowest triplet state in oligothiophenes) excited states. These results suggest that triplet formation in polymer based OPV blends could occur *via* an intramolecular process; without aggregation, energy transfer, or excitation annihilation processes. Upon photoexcitation of the polymer in a polymer:fullerene blend, an exciton that does not undergo charge separation will geminantly recombine and relax to the ground state. However, if this exciton was trapped in a state with torsional disorder (hot state) there could be favourable coupling of the singlet and triplet manifolds. This would provide a competing pathway to exciton relaxation but could also account for the formation of triplet states without the requirement for bimolecular recombination. The impact of these results mean future models on the mechanism of triplet exciton traps in OPV blends need to account for the inherent energy relaxation landscape of the chromophore sub-units of the polymer backbone.

In order to test the model proposed in Chapter 5, several avenues of investigation would be beneficial. For instance, a direct measure of the structural relaxation would be of great value and could be achieved through time-resolved Raman spectroscopy, or through temperature dependent photoluminescence measurements to estimate Huang-Rhys parameters as a function of temperature. Unfortunately, time-resolved Raman spectroscopy was not available during the course of this work. Furthermore, the optical setup for the transient-grating photoluminescence spectroscopy was not able to facilitate the measurements of photoluminescence from within the temperature cryostat. Additional temperature dependent TA measurements would assist in defining the trend in ISC rates. In particular, the glass transition temperature appears to be of significance, and more data around this region could allow for a more conclusive discussion.

Since it is not temperature that is the dominant driver of increased ISC but rather restricted torsional freedom through solvent freezing, future work could entail performing measurements in a series of solvents with different viscosity, whilst maintaining the same temperature. Alternatively, it would be interesting to perform a temperature dependent study with solvents of differing glass transition temperatures. This should yield the same trend reported here, centred around the solvent glass transition temperature. It should be noted that changing the solvent will affect more than just viscosity, for example polarity, solubility, and hydrophobic/hydrophilic energetics. The solubility of the oligomers should be high in non-polar solvents, possibly allowing minimal polarity change between solvent selection. Alternatively,

solvent mixtures with solvents of similar polarity but different viscosities/freezing temperatures could be used to minimise the polarity changes. These would all require control experiments, and could form complicated solvent mix systems. This research serves as a base for future studies and further studies which take these variables into account would be valuable.

Efficient OPV devices are formed using both an electron-donor acceptor, and the mixing morphology has been shown to significantly effect device performance. The advancement of characterisation techniques has resolved the heterojunction structure is more complex than the 2-phase morphology initially proposed. Numerous reports in the literature have identified polymer and fullerene blends form an intermixed phase of the components, in addition to phase-pure amorphous or crystalline domains. Furthermore, it cannot be overlooked that the most efficient OPV devices are obtained in systems that adopt such a three-phase microstructure, whereby neat domains are interfaced by intermixed regions. These devices are characterised by the increased yield of long-lived free charges, as these are the only charges which are able to contribute to extractable photocurrent. However, the morphologically driven charge separation must be occurring on much earlier timescales.

Chapter 6 investigated charge photogeneration pathways in polymer:fullerene blends in a series of three closely related copolymers, where differences in the backbone connectivity induces varying degrees of curvature. These structural differences result in differing phase behaviour in PCBM blends; the linear and weakly curved polymers PTTBT and PDTBT form 2-phase morphologies with PCBM, whereas PCBM is more miscible with the curved polymer PTBT, which leads to the coexistence of intermixed and phase pure regions that can be balanced through cosolvent processing. This was achieved through altering the linker unit between benzothiadiazole monomer components to maintain the electronic properties of each polymer and therefore provide model systems to investigate the link between morphology and charge generation processes. Since these phases present spectroscopic signatures, it was possible to track the motion of hole polarons between disordered and ordered regions and link these dynamics to yields of long-lived charges and overall PV efficiencies.

Using transient absorption spectroscopy, it was shown that free charge generation is most efficient in a 3-phase morphology that features intimately mixed polymer:fullerene regions amongst neat polymer and neat fullerene phases. Results showed a dynamic peak shift of polaron PIA peaks coupled with a loss of polarisation anisotropy, and shows highly mobile holes. This allowed the migration of holes to be tracked as they moved from intermixed domains to phase-pure polymer

fomains. This accounted for the longer-lived populations of charge carriers and concomitantly better device performance present in the 3-phase morphology. For the polymers whose rigid backbones lead to 2-phase blends lacking an intermixed region, the lack of spectral dynamics and polarization anisotropy retention reflects immobile holes in phase-pure domains. The result is rapid geminate charge recombination and poor photovoltaic performance in such blends.

The results in Chapter 6 are the first reported experimental results to visually track the migration of holes through a polymer based OPV active layer. This work shows that the energy gradient between the intermixed and phase-pure regions may be sufficient to drive efficient separation of charge pairs initially generated in intermixed regions, with free charges subsequently percolating through these phase-pure domains. Additionally it was shown that for 3-phase blends, isolated trap islands of crystalline polymer domains contained within an extensive intermixed morphology could be reduced through the processing using solvent additives. This decreased the rate of charge recombination and resulted in a greater population of charges at long time which were able to contribute to photocurrent. These results provide a valuable contribution to understanding morphologically driven charge separation in OPV cells.

Future work probing the morphologically driven charge separation would be worthwhile investigating the energetic cascade present between intermixed regions with less crystalline neat polymer domains. This could be achieved by altering the polymer molecular weight to disfavour the entropic factors of crystallisation resulting in more amorphous domains, or through altering the solubilising substituents on the polymer backbone. Likewise, using PCBM derivatives which form more amorphous solid state microstructures would also be of interest. Since the crystallinity of the phase-pure domains is a governing factor in stabilisation energies of charge carriers, altering this landscape could provide valuable guidance into future design principles of novel donor and acceptor components for OPV devices.

Finally, Chapter 7 presented the photophysics of a high performance all polymer blend to investigate how these blends can rival their polymer:fullerene counterparts. Whilst polymer:polymer OPVs generally exhibit poorer device efficiencies than the polymer:fullerene counterparts, the use of a polymer as an acceptor presents multiple potential advantages over a small molecule acceptor, such as stronger light absorption by the acceptor phase, lower cost of processing, easier structural modification, and improved morphological control. The photophysics of a novel BSF4:P(NDI2OD-T2) blend, which achieves optimised device PCE of >4%, was studied using time-resolved and steady-state optical spectroscopy. Optical absorption spectroscopy

confirmed that various blend ratios were well described by a linear combination of the neat polymer absorption spectra. The efficiency of exciton separation was probed using steady-state photoluminescence, which is a direct measure of the exciton quenching yield due to charge transfer between polymer components. This revealed 70% of neat BSF4 (donor component) emission was quenched in the most efficient device blend ratio. This quenching ratio is much poorer than what is commonly observed in polymer:fullerene blends, and suggests a major gain in all-polymer OPV devices could be achieved by increasing the exciton dissociation in these blends.

The morphology of the BSF4:P(NDI2OD-T2) blend was studied using X-ray scattering techniques and revealed fibrillar microstructure. However, the phase separation was 20-100 nm in size, which is significantly larger than excitons can migrate within their lifetime. This is consistent with the relatively poor exciton dissociation in the blends whereby a significant portion of excitons are generated too far away from an interface to undergo charge transfer. The polaron dynamics were investigated using TA spectroscopy and showed that the PIA from polarons started to decrease in amplitude after only 10 ps. Using the integrated GSB kinetics as a measure of the total population of excited states revealed the blends suffer severe geminate recombination with only 30% of initial charge yield remaining on the nanosecond timescale to contribute to extractable photocurrent. Such a significant loss of charge carriers highlights that optimising polymer:polymer blend morphology to realise long-lived charge separated states and efficient exciton dissociation is required in order to improve device efficiencies.

In the field of OPVs, continual attention by the research community has made steady progress towards increasing OPV device performance. However, a holistic mechanism of charge photocurrent generation has not been established. The results presented in this thesis highlight that a future model of the efficient pathway towards charge separation must be expanded on to consider account for the complexity of the process. The kinetic competition of structural relaxation and charge separation invoked by the dynamic energetic landscape as the polymer backbone geometry relaxes after photoexcitation cannot be overlooked. Particular focus on continual improvement of OPV efficiencies should be focussed on understanding the limit of efficiency, and if improved V_{oc} values comes at the cost of the formation of triplet excitons. Understanding the formation of these triplet trap states is a significant hurdle facing the field of OPVs as this has the potential to put a significant limit on maximum efficiency. This has the potential to impact design principles of donor and acceptor components as the field moves forward. For example, triplet formation via ISC could possibly be limited by restricting torsional freedom of the polymer backbone. Additionally, the role of mixing morphology and triplet yield is yet

to be revealed and the energetic cascade promoting morphologically driven charge separation could reduce the occurrence of recombination of spin-uncorrelated charge pairs.

In spite of these challenges, the continual increase in device efficiency has been a positive motivator for OPV technologies moving forward. The rising interest of the research community in all-polymer OPVs promises a bright future for the field. The use of a polymer as the acceptor component is attractive as it can increase absorption in the active layer which increases the fraction of the solar spectrum that can be used for photocurrent generation. Fundamental problems plaguing all-polymer systems surround the miscibility of active layer components in order to yield long-lived charge-separated states similar to polymer:fullerene blends. Improved understanding of the factors governing donor-acceptor miscibility in all-polymer blends will go a long way in advancing this technology.

Appendix I: Additional Figures

Chapter 6

Fluence dependence

The following figures present TA dynamics of neat PTBT and PTBT:PCBM blend at different excitation densities. The overlapping kinetics confirm no bimolecular effects are occurring at the fluence used in these measurements. These data are representative of the equivalent measurements performed for all samples.

Figure 8.1 Decay kinetics of neat PTBT at 2 different fluence, this is reminiscent of the data collected for all samples.

Figure 8.2 Decay kinetics of neat PTBT:PCBM at 2 different fluence, this is reminiscent of the data collected for all samples.

Global Fitting

The methods used for global fitting of TA data were discussed in detail in the text. The following section contains the spectral and kinetic basis sets, along with the residuals of each fit. This is presented for each sample discussed in Chapter 6.

Figure 8.3 Results from global fitting of PTTBT:PCBM (-1ps to 1 ns timescales) showing spectral (A) and weightings (B) basis sets used in the fit, along with the residual surface (C).

Figure 8.4 Results from global fitting of PDTBT:PCBM (-1ps to 1 ns timescales) showing spectral (A) and weightings (B) basis sets used in the fit, along with the residual surface (C).

Figure 8.5 Results from global fitting of PTBT:PCBM (-1ps to 1 ns timescales) showing spectral (A) and weightings (B) basis sets used in the fit, along with the residual surface (C).

Figure 8.6 Results from global fitting of PTBT:PCBM + ODT (-1ps to 1 ns timescales) showing spectral (A) and weightings (B) basis sets used in the fit, along with the residual surface (C).

Chapter 7

The following section contains additional charge dynamics, and steady-state optical spectroscopy for BSF4:P(NDI2OD-T2) blend ratios discussed in Chapter 7.

Figure 8.7 Intensity dependent charge recombination kinetics from transient absorption integrated over the GSB region for the BSF4:P(NDI2OD-T2) blends of varying blend ratios covering the femto-nanosecond timescales.

Figure 8.8 Intensity dependent charge recombination kinetics from transient absorption integrated over the GSB region for the BSF4:P(NDI2OD-T2) blends with different processing conditions covering the femto-nanosecond timescales.

Figure 8.9 Normalized steady-state optical absorption (A) and photoluminescence (B) of 2:1 BSF4:P(NDI2OD-T2) blend subjected to thermal annealing, addition of DIO, or both.

Appendix II: Experimental

General methods

All chemicals were purchased from Sigma-Aldrich (St. Louis, MO) and used as received, unless otherwise stated. Full 1D and 2D NMR data were obtained on a Varian spectrometer operating at 500 MHz for ^1H or a Varian Direct-Drive spectrometer operating at 600 MHz for ^1H and equipped with a HCN coldprobe. All NMR spectra were referenced internally to residual solvent peaks. Mass spectrometry data were collected on a Agilent 6530 Series Q-TOF mass spectrometer. Time-resolved transient absorption was performed on a home-build system. The system is driven by a Ti-sapphire amplifier (Spitfire, Spectra-physics) with a pulse duration of 100 fs, fundamental wavelength of 800 nm operating at 3kHz. Absorption spectroscopy (UV-Vis) was performed with an Agilent 8453 UV-Visible spectrophotometer over the range 220-1100 nm using a quartz cuvette with 1 cm path length. Steady state fluorescence spectroscopy was performed with a Horiba Jobin Yvon Fluorolog 3 spectrofluorometer using a quartz cuvette with 10 mm path length and four polished sides, or on Spectrosil Quartz substrates. Quantum yield measurements were performed on dilute solutions (absorbance 0.05) in anhydrous THF using a quartz cuvette with pathlength of 10 mm. Excitation wavelength was at the absorption maximum of each sample. An absolute method of determination was employed using a Quanta-phi F-3029 Integrating Sphere (Horiba Scientific) and the photoluminescence was collected on a Horiba Jobin Yvon Fluorolog 3 spectrofluorometer.

Synthetic procedures

The synthesis of PTTBT, PDTBT, and PTBT, along with GIXRD and device characterisation were performed by collaborators based at Pusan National University, South Korea, and have been reported in a previous papers (Chapter 6).^{219,222}

The synthesis of BFS4 and N2200 (Chapter 7) were performed by collaborators at Monash University, Melbourne, Australia, and have been reported in previous papers.²⁵⁷ The following section details the synthesis of the oligothiophenes conducted as part of this work (Chapter 3).

2-bromo-3-hexylthiophene

To a 50 mL round bottom flask 3-hexylthiophene (2.6197 g, 0.0156 mol) was placed under N₂ and anhydrous THF (15 mL) was added and stirred in a salt-ice bath for 15 minutes. At this time, N-bromosuccinimide (2.7745, 0.0156 mol) was added and the solution was stirred for 1 hour at 0 °C. Subsequently, the reaction was quenched with H₂O (10 mL) and extracted with Et₂O (2 x 15 mL). The organic layer was washed with 10% aqueous Na₂S₂O₄ (15 mL), 10% aqueous KOH (15 mL), and distilled H₂O (15 mL). The pale yellow organic layer was dried over anhydrous Na₂SO₄ and solvent removed. Pure title compound was obtained by vacuum distillation (74 °C at 0.5 mm/Hg). Yield: 2.7453 g (71%). ¹H-NMR: (500 MHz, CDCl₃) δ_H 7.18 (d, *J*_{HH} = 5.6 Hz, 1H), 6.79 (d, *J*_{HH} = 5.6 Hz, 1H), 2.62 – 2.49 (m, 2H), 1.60 – 1.54 (m, 2H), 1.36 – 1.26 (m, 6H), 0.91 – 0.86 (m, 3H); ¹³C-NMR: (126 MHz, CDCl₃) δ_C 142.1, 128.4, 125.3, 108.9, 77.4, 77.2, 76.9, 31.8, 29.9, 29.5, 29.0, 22.8, 14.2.

5,5'-dibromo-2,2'-bithiophene

This procedure followed those already published in the literature: A 50 mL round bottom flask was 'flame-dried' by placing the flask under vacuum and heated with a head-gun, then cooled under N₂. To this, 2,2'-bithiophene (1.0042 g, 6.01 mmol) and anhydrous DMF (15 mL) was added and stirred in a salt-ice bath for 15 minutes. Subsequently, N-bromosuccinimide (2.1567, 12.1 mmol) was added and allowed to come to room temperature and stirred overnight. The pale yellow solution was poured over ice (100 g) and a beige solid was collected and recrystallised (hexane) to afford title compounds as white crystals. Yield: 1.5933 g (82%). ¹H-NMR: (500 MHz, CDCl₃) δ_H 6.96 (d, *J*_{HH} = 3.8 Hz, 1H), 6.85 (d, *J*_{HH} = 3.8 Hz, 1H).

5-bromo-3,3''-dihexylquaterthiophene (4T-Br)

A 50 mL round bottom flask was 'flame-dried' by placing the flask under vacuum and heated with a head-gun, then cooled under N₂. To this, **9** (0.5377 g, 1.08 mmol) and anhydrous DMF (15 mL) was added and stirred in a salt-ice bath for

15 minutes. Subsequently, N-bromosuccinimide (0.1729, 0.97 mmol) was added and allowed to come to room temperature and stirred overnight. To the reaction was added distilled H₂O (25 mL) and extracted with chloroform (3 x 15 mL). The combined organic layers were washed with 10% aqueous Na₂S₂O₃ (15 mL), 10% aqueous KOH (15 mL), and distilled H₂O (15 mL). The organic layer was dried over anhydrous Na₂SO₄, and solvent removed. DMF was extracted by redissolving the residue in chloroform (20 mL) and washing with saturated aqueous CuSO₄ (4 x 50 mL) and then distilled water (2 x 30 mL), dried over anhydrous Na₂SO₄ to give a yellow oil. Pure title compound was obtained from a silica column (eluent: hexane) as a yellow oil. Yield: 0.2753 g (44%). ¹H-NMR: (500 MHz, CDCl₃) δ_H 7.18 (d, *J*_{HH} = 5.2 Hz, 1H), 7.12 (d, *J*_{HH} = 3.7 Hz, 2H), 7.02 (d, *J*_{HH} = 3.7 Hz, 1H), 6.95 (d, *J*_{HH} = 4.5 Hz, 2H), 6.90 (s, 1H), 2.84 – 2.75 (m, 2H), 2.74 – 2.68 (m, 2H), 1.62 (m, 6H), 1.46 – 1.24 (m, 14H), 0.89 (m, 3H); ¹³C-NMR: (126 MHz, CDCl₃) δ_C 140.6, 140.1, 137.5, 136.6, 135.7, 133.9, 132.8, 131.9, 130.3, 130.3, 127.1, 126.7, 124.2, 124.1, 123.9, 110.7, 31.8, 31.8, 30.8, 30.7, 29.4, 29.4, 29.3, 22.8, 22.7, 14.3; HR-ESI-MS: *m/z* C₂₈H₃₃S₄Br [M+H]⁺ calcd 576.0648, found 576.0652.

5,5''-dibromo-3,3''-dihexylquaterthiophene (4T-Br₂)

Title compound was obtained in the same reaction as **10**, and obtained as a yellow solid. Isolated yield (0.0148 g). ¹H-NMR: (500 MHz, CDCl₃) δ_H 7.11 (d, *J*_{HH} = 3.8 Hz, 1H), 6.97 (d, *J*_{HH} = 3.8 Hz, 1H), 6.90 (s, 1H), 2.76 – 2.66 (m, 2H), 1.66 – 1.07 (m, 8H), 0.94 – 0.75 (m, 3H).

2,2'-[2, 2'-bithiophene]-5, 5'-diylbis- 4,4,5,5-tetramethyl-1,3,2-dioxaborolane

In a 100 mL Schlenk flask 2,2'-bithiophene (1.0670 g, 6.42 mmol) was placed under N₂ and anhydrous THF (20 mL) and stirred in a dry-ice/acetone bath (-78 °C) for 1.5 hours. To this *n*-BuLi ((2 M cyclohexane solution) 7.0 mL, 14 mmol) was added drop wise. Reaction is stirred at -78 °C for 15 minutes, then allowed to warm to room temperature for 2 hours. After which, the flask is cooled to -78 °C for 1.5 hours and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.4 mL, 17 mmol) was added quickly. Orange solution was allowed to warm to room temperature and stirred overnight. To this, distilled H₂O (20 mL) was added and solution extracted with Et₂O (2 x 20 mL). The organic layer was then washed with brine (2 x 20 mL) and distilled water (2 x 20 mL) and dried over anhydrous Na₂SO₄. Solvent was removed to yield title compound as a pale green/grey solid, which can be used

without further purification. Yield: 0.5109 g (19%). $^1\text{H-NMR}$: (500 MHz, CDCl_3) δ_{H} 7.52 (d, $J_{\text{HH}} = 3.6$ Hz, 1H), 7.29 (d, $J_{\text{HH}} = 3.6$ Hz, 1H), 1.35 (s, 12H); HR-ESI-MS: m/z $\text{C}_{20}\text{H}_{29}\text{B}_2\text{O}_4\text{S}_2$ $[\text{M}+\text{H}]^+$ calcd 419.1693, found 419.1697.

3,3''-dihexylquaterthiophene-5,5'-diylbis-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

The procedure followed was similar to that described in the synthesis of **1**. Whereby **10** (0.0506 g, 0.09 mmol), $n\text{-BuLi}$ (0.05 mL, 0.10 mmol), and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.02 mL, 0.11 mmol) were used. Title compound was purified using a silica column (eluent Chloroform:Hexane (7:3)). Yield: 0.0043 g (6%). $^1\text{H-NMR}$: (500 MHz, CDCl_3) δ_{H} 7.46 (s, 1H), 7.13 (d, $J_{\text{HH}} = 2.5$ Hz, 1H), 7.08 (d, $J_{\text{HH}} = 3.7$ Hz, 1H), 2.82 – 2.73 (m, 2H), 1.71 – 1.61 (m, 2H), 1.44 – 1.21 (m, 6H), 0.87 (d, $J = 14.6$ Hz, 3H).

3,3''-dihexylquaterthiophene (4T)

A 100 mL (2-neck) round bottom flask is 'flame-dried' (as above) and placed under N_2 , to which magnesium turnings (0.2577 g, 10.1 mmol) are added and dry-stirred overnight under N_2 . To this, anhydrous Et_2O (20 mL) is added and stirred for 10 minutes. At this point, the stirring was paused and 1,2-dibromoethane (0.15 mL) was added to the centre of the magnesium, and heated until small bubbles were observed, left for 3 minutes. Subsequently, **2** (2.5138 g, 10.1 mmol) was added drop-wise and refluxed for 2 hours. In a 250 mL round bottom flask, **3** (1.3152 g, 4.0 mmol) and Ni(dppp)Cl_2 (0.0326 g) were placed under N_2 and anhydrous Et_2O (20 mL) and anhydrous toluene (30 mL) were added. Subsequently, the Grignard reagent prepared from thiophene-**2** was added drop-wise to the red suspension and refluxed overnight. To the resulting orange solution, saturated ammonium chloride (100 mL) was added and stirred vigorously for 5 minutes. Extracted with chloroform (2 x 30 mL), and the combined organic fractions were washed with saturated aqueous NaHCO_3 (2 x 100 mL), saturated aqueous NaCl (2 x 100 mL), and distilled H_2O (2 x 100 mL). Organic layer was dried over anhydrous Na_2SO_4 and solvent removed. Purification using a silica column eluted with hexane affords pure title compound as a yellow oil. Yield: 1.8464 g (91%). $^1\text{H-NMR}$: (500 MHz, CDCl_3) δ_{H} 7.18 (d, $J_{\text{HH}} = 5.2$ Hz, 1H), 7.13 (d, $J_{\text{HH}} = 3.7$ Hz, 1H), 7.02 (d, $J_{\text{HH}} = 3.7$ Hz, 1H), 6.94 (d, $J_{\text{HH}} = 5.2$ Hz, 1H), 2.84 – 2.72 (m, 2H), 1.71 – 1.59 (m, 2H), 1.44 – 1.24 (m, 6H), 0.89 (m, 3H); $^{13}\text{C-NMR}$: (126 MHz, CDCl_3) δ_{C} 140.0, 137.0, 135.5, 130.5, 130.2, 126.7, 124.0, 124.0, 31.8, 30.8, 29.4, 29.4, 22.8, 14.2; HR-ESI-MS: m/z $\text{C}_{28}\text{H}_{34}\text{S}_4$ $[\text{M}+\text{H}]^+$

calcd 498.1538, found 498.1538.

3,3''-dihexylsexithiophene (6T)

In a 100 mL round bottom flask **1** (0.0650 g, 0.151 mmol), **10** (0.1828 g, 0.316 mmol), Pd(dppf)Cl₂ (0.0092 g, 7 mol%), degassed toluene (6 mL), degassed aqueous K₂CO₃ (2 M, 6 mL), and Aliquat 336 (1 drop) were added under the protection of N₂. The solution was heated to 80 °C overnight, at which point a second amount of Pd(dppf)Cl₂ (0.0055 g) was added using degassed ethanol (3 mL) as solvent and stirred at 80 °C overnight. The solution was then allowed to cool to room temperature and 2M HCl (6 mL) was added and stirred for 20 minutes. The crude product was then extracted with chloroform (2 x 50 mL) and the combined organic fractions were washed with saturated NaCl (2 x 40 mL), and distilled H₂O (2 x 40 mL). The organic layer was dried over anhydrous Na₂SO₄ and the solvent removed to yield a red solid. Title compound was obtained after a silica column (eluent: hexane). Yield: 0.0350 g. ¹H-NMR: (500 MHz, CDCl₃) δ_H 7.23 (d, *J*_{HH} = 4.6 Hz, 1H), 7.20 - 7.17 (m, 2H), 7.14 (d, *J*_{HH} = 3.7 Hz, 2H), 7.09 (d, *J*_{HH} = 3.7 Hz, 1H), 7.07 (d, *J*_{HH} = 3.7 Hz, 1H), 7.06–7.01 (m, 4H), 6.95 (d, *J*_{HH} = 5.2 Hz, 1H), 2.80–2.75 (m, 4H), 1.77–1.11 (m, 16H), 0.98–0.79 (m, 6H); HR-ESI-MS: *m/z* C₃₆H₃₈S₆ [M+H]⁺ calcd 662.1298, found 662.1301.

3,3'',3''',4'''-tetrahexyloctithiophene (8T)

Title compound was obtained from the same reaction as **6T** using a silica column (eluent: 5% dichloromethane:hexane). Yield: 0.0394 g. ¹H-NMR: (500 MHz, CDCl₃) δ_H 7.19 (d, *J*_{HH} = 5.2 Hz, 1H), 7.14 (d, *J*_{HH} = 3.7 Hz, 2H), 7.06–6.99 (m, 3H), 6.95 (d, *J*_{HH} = 5.2 Hz, 1H), 2.81–2.74 (m, 4H), 1.72–1.63 (m, 4H), 1.46–1.22 (m, 12H), 0.94–0.84 (m, 6H); HR-ESI-MS: *m/z* C₅₆H₆₆S₈ [M+H]⁺ calcd 994.2930, found 994.2936.

3'',3''',4,4'''-tetrahexyldecithiophene (10T)

Title compound was obtained from the same reaction as **6T** using a silica column (eluent: 10% dichloromethane:hexane). Yield: 0.1897 g. ¹H-NMR: (500 MHz, CDCl₃) δ_H 7.23 (dd, *J*_{HH} = 5.1, 1.2 Hz, 2H), 7.20–7.17 (m, 2H), 7.14 (d, *J*_{HH} = 3.7, 2H), 7.10–7.00 (m, 10H), 6.95 (d, *J*_{HH} = 5.2 Hz, 2H), 2.78 (q, *J*_{HH} = 7.5 Hz,

8H), 1.79–1.60 (m, 8H), 1.50–1.19 (m, 24H), 0.97–0.80 (m, 12H); HR-ESI-MS: m/z $C_{64}H_{70}S_{10}$ $[M+H]^+$ calcd 1158.2685, found 1158.2688.

4-(3,3''-dihexylquaterthiophen-5-yl)phenol (4T-PhOH)

In a 250 mL three-neck round bottom flask 4-hydroxyphenylboronic acid pinacol ester (0.2798 g, 1.22 mmol) and anhydrous K_2CO_3 (20.7706 g) were added and placed under N_2 . To this was added 4T-Br (0.6387 g, 1.11 mmol) dissolved in degassed toluene (75 mL), $Pd(dppf)Cl_2$ (0.0649 g, 7 mol%) which was dissolved in dichloromethane (0.7 mL), and 0.5 mL of degassed water and stirred at 80 °C overnight. The solution was then allowed to cool to room temperature and 2M HCl (6 mL) was added and stirred for 20 minutes. The crude product was then extracted with chloroform (2 x 100 mL) and the combined organic fractions were washed with saturated $NaHCO_3$ (150 mL), brine (150 mL), and distilled H_2O (150 mL). The organic layer was dried over anhydrous Na_2SO_4 , filtered, and the solvent removed to yield a brown solid. Title compound was obtained after a silica column (eluent: dichloromethane). Yield: 0.21 g (15%). 1H -NMR: (600 MHz, $CDCl_3$) δ_H 7.48 (d, $J_{HH} = 8.6$ Hz, 2H), 7.18 (d, $J_{HH} = 5.2$ Hz, 1H), 7.13 (dd, $J_{HH} = 3.7, 0.9$ Hz, 2H), 7.06–7.00 (m, 3H), 6.94 (d, $J_{HH} = 5.2$ Hz, 1H), 6.85 (d, $J_{HH} = 8.5$ Hz, 2H), 4.94 (br-s, 1H, OH), 2.78 (t, $J_{HH} = 8.3$ Hz, 4H), 1.82–1.06 (m, 16H), 0.89 (m, 6H); ^{13}C -NMR: (151 MHz, $CDCl_3$) δ_C 155.2, 141.9, 140.7, 139.8, 136.8, 136.5, 135.4, 135.3, 130.3, 130.1, 128.9, 127.1, 127.1, 126.5, 126.1, 125.2, 123.9, 123.8, 123.8, 115.8, 31.7, 31.7, 30.6, 30.5, 29.7, 29.6, 29.3, 29.3, 29.2, 22.6, 14.1, 14.1.

2,7-di-tert-butyl-4,5-bis(chloromethyl)-9,9-dimethyl-9H-xanthene (8)

Title compound was synthesised according to the literature.¹⁷² A mixture of 2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene (0.5038 g, 1.55 mmol), paraformaldehyde (0.2079 g), orthophosphoric acid (0.14 mL, 2.07 mmol), acetic acid (8.2 mL, 0.143 mol), and hydrochloric acid (0.6 mL, 7.26 mmol) were heated in a pressure tube at 85 °C overnight. The resulting white solution was allowed to cool and chloroform (20 mL) was added and the white precipitate dissolved into a colourless solution. Crude product was washed with saturated $NaHCO_3$ (300 mL) and distilled water (300 mL), and the organic layer was dried over anhydrous Na_2SO_4 , filtered, solvent removed, and subsequently dried under vacuum (10^5 mbar) for 3 hours to yield a white solid. Yield 0.6256 g (96.2%). 1H -NMR: (500 MHz, $CDCl_3$) δ_H 7.41 (d, $J_{HH} = 2.4$ Hz, 2H), 7.28 (d, $J_{HH} = 2.3$ Hz, 2H), 4.87 (s, 4H), 1.65 (s, 6H), 1.34 (s, 18H); ^{13}C -NMR: (126 MHz, $CDCl_3$) δ_C 145.9, 145.6, 129.6, 125.5, 124.0, 123.5, 42.1, 34.6,

34.5, 32.4, 32.3, 32.0, 31.5, 31.5, 31.4.

2,7-di-tert-butyl-4,5-bis((4-(3,3''-dihexylquaterthiophen-5-yl)phenoxy)-methyl)-9,9-dimethyl-9H-xanthene (4T-Dimer)

In a 50 mL round bottom flask 4T-PhOH (0.1945 g, 0.338 mmol), **8** (0.0705 g, 0.169 mmol), K₂CO₃ (0.2406 g, 1.69 mmol), and acetonitrile (15 mL) were refluxed for 3 days. The yellow solution was allowed to cool and the crude product was extracted with dichloromethane (2×50 mL washes). The combined organic fractions were washed with brine (100 mL) and then distilled water (200 mL), and then dried over anhydrous Na₂SO₄ and the solvent removed to yield a yellow waxy oil. Title compound was obtained after a silica column (eluent: 20% dichloromethane:hexane). Yield: 0.1028 g (40%). ¹H-NMR: (500 MHz, CDCl₃) δ_H 7.47 (d, *J*_{HH} = 2.3 Hz, 1H), 7.43 (d, *J*_{HH} = 8.8 Hz, 2H), 7.39 (d, *J*_{HH} = 2.3 Hz, 1H), 7.16 (d, *J*_{HH} = 5.2 Hz, 1H), 7.05 (d, *J*_{HH} = 3.7 Hz, 1H), 7.01 (d, *J*_{HH} = 3.7 Hz, 1H), 6.99–6.96 (m, 2H), 6.93 (dd, *J*_{HH} = 4.5, 2.7 Hz, 2H), 6.78 (d, *J*_{HH} = 8.8 Hz, 2H), 5.05 (s, 2H), 2.80–2.73 (m, 2H), 2.72–2.66 (m, 2H), 1.71 (s, 3H), 1.64 (s, 3H), 1.37 (s, 14H), 1.31 (s, 7H), 0.89 (s, 6H). ¹³C-NMR: (126 MHz, CDCl₃) δ_C 158.9, 146.4, 145.6, 142.0, 140.7, 139.8, 137.0, 136.3, 135.7, 135.2, 130.6, 130.2, 129.6, 129.2, 127.1, 127.0, 126.6, 126.0, 125.3, 125.0, 123.9, 123.8, 123.8, 123.1, 123.0, 114.9, 110.1, 66.1, 34.8, 34.7, 32.5, 31.9, 31.8, 31.7, 30.8, 30.7, 29.9, 29.5, 29.5, 29.4, 22.8, 22.8, 14.3, 14.3; HR-ESI-MS: *m/z* C₉₃H₁₀₆O₃S₈ [M+H]⁺ calcd 1549.5805, found 1549.5828.

Transient absorption spectroscopy

All thin film samples were measured under dynamic vacuum (10⁵ mbar) using a homebuilt sample chamber. In general, solution measurements were performed in a quartz cuvette with 1 mm pathlength. Temperature dependent measurements were performed using a custom designed cuvette of optical glass which was adapted with a teflon stopcock. This allowed the measurement of samples in solution under vacuum, which were then fitting into a cryostat. Pump/probe spot sizes sampled 100's of micrometers, which is at least an order of magnitude greater than the phase separation morphology in polymer blends. For PTBT:PCBM different sample locations were probed in order to confirm the polaron PIA dynamics. Similarly, TA-polarisation anisotropy was performed on different film locations, which all showed the same TA features.

Transient absorption (TA) spectroscopy was carried out using an amplified Ti:sapphire laser (Spectra Physics, 100 fs pulse duration, 800 nm, 3 kHz). The broadband probe pulses were generated via two different methods. Visible wavelengths (550–850 nm) were generated using a homebuilt non-collinear optical parametric amplifier (NOPA),²⁶⁶ pumped by a fraction of output from the amplifier. Infrared wavelengths (830–1700 nm) were generated by focusing a small portion of output from the amplifier in a 3 mm YAG window.

After transmission through the sample, visible probe pulses were coupled into a spectrograph (Acton SP2150, Princeton Instruments, 150 lines per millimetre grating) using optical fibres, and referenced to a probe pulse that was not transmitted through the sample. Near-IR probe pulses were transmitted through an 830 nm long pass filter before reaching the sample chamber and then spectrally dispersed using a homebuilt prism based polychromator after transmission through the sample. Probe shots were read out at 3 kHz using a camera controller (Stresing) equipped with a dual channel linear Si photodiode array (visible) and a single channel linear InGaAs photodiode array (near-IR). The differential transmission signal ($\Delta T/T$) is calculated using sequential probe shots corresponding to pump on vs off, where the excitation repetition rate is $\omega/2$. In a typical measurement, 2000 shots were averaged per time point and a time series were repeated 5 times.

For ultrafast (<3 ns) measurements, an optical parametric amplifier (TOPAS) provided 100 fs excitation pulses at 532 nm, which were chopped at 1.5 kHz. The excitation beam was attenuated to achieve an excitation intensity which was low enough to avoid non-linear artefacts (typically $5 \mu\text{J cm}^2$). The observation of comparable dynamics at higher fluence confirmed bimolecular effects were insignificant on sub-nanosecond timescales. The relative delay between pump and probe pulses was varied using an automated delay stage (Newport). For charge recombination measurements (ns–ms), excitation pulses were obtained using the 2nd harmonic (532 nm) of a Q-switched Nd:YVO₄ laser (AOT-YVO-25QSP, 700 ps) which was synchronized with the amplifier output. Excitation intensities were varied and each measurement were averaged 1000 shots per time point, with the number of repeat scans to achieve sufficient signal:noise and account for signal strength at different intensities. The delay between pump and probe pulses was varied using an electronic delay generator (Stanford Research Systems DG535).

All transient absorption data was processed using MATLAB, starting with chirp correction for ultrafast measurements and combining visible and near-IR components. In the cases where excitation densities were not identical for visible and near-IR measurements of the same sample, near-IR spectra were re-scaled by the

ratio of excitation fluences used. Observing a smooth transition between data in the visible and near-IR wavelength ranges after correction verified the validity of this procedure.

Sample Preparation

Photophysical measurements conducted on thin film samples involved casting the material on Spectrosil quartz substrates. For polymer samples, films were spun cast from chlorobenzene at 1500 rpm for 60 seconds, with the concentration of stock solutions given below. The polymer:fullerene blend ratios for spectroscopic measurements were chosen based on the optimised device results. For polymer:PCBM blends processed with additive, ODT (2 vol%) was added to each stock solution of PCBM before combining with polymer stock solutions, and then mixed for 2 hours before casting (Table 8.1).

Table 8.1 Thin film casting solutions of polymer:fullerene blends

Sample	Total component concentrations (mg mL ⁻¹)
Neat PTBO	10.0
PTBO:PC[71]BM	10.0
Neat PTTBT	7.5
PTTBT:PCBM (1:1)	22.2
Neat PDTBT	16.7
PDTBT:PCBM (1:1)	22.2
Neat PTBT	11.1
PTBT:PCBM (1:2)	22.2

For triplet sensitized measurements, thin film samples were prepared from a stock solution of polymer (matching the concentration used for each neat sample) doped with 40 wt% PtOEP (with respect to the polymer) in chlorobenzene. For oligothio-phenes cast in polystyrene thin films 20:1 wt%, polystyrene:oligomer in CHCl₃ was used. This involved making a stock solution of polystyrene at 57.3 mg/mL.

Appendix III: Structural Characterisation Spectra

Figure 8.10 ^1H NMR spectra for the series of oligomers, quaterthiophene (4T), sexithiophene (6T), octithiophene (8T), and decithiophene (10T). ^1H NMR spectra were collected in CDCl_3 and are cropped to show the spectral region containing aromatic protons (6.90–7.25 ppm) and α -CH₂ protons (2.65–2.85 ppm).

Figure 8.11 ^1H NMR spectrum of **1**.

Figure 8.12 ^1H NMR spectrum of 3,3''-dihexylquaterthiophene (4T).

Figure 8.13 ^1H NMR spectrum of 5,5''-dibromo-3,3''-diethylquaterthiophene (4T-Br₂).

Figure 8.14 ^1H NMR spectrum of 5-bromo-3,3''-dihexylquaterthiophene (4T-Br).

Figure 8.15 ^1H NMR spectrum of 3,3''-dihexylsexithiophene (6T).

Figure 8.16 ^1H NMR spectrum of 3,3'',3''''',4''''-tetrahexyloctithiophene (8T).

Figure 8.17 ^1H NMR spectrum of 3'',3''''',4,4''''-tetrahexyldecithiophene (10T).

Figure 8.18 ^1H NMR spectrum of 4-(3,3''-dihexylquaterthiophen-5-yl)phenol (4T-PhOH).

Figure 8.19 ^1H NMR spectrum of 4T-Dimer.

Appendix IV: MATLAB Scripts

Franck-Condon Gaussian progression fitting

```
%% FC Fitting PL
%Perform Franck-Condon fits on TRPL slices

%Set up initial values
Huang_Rhys_Factor = 1; %Initial value of S
E_00 = 2.26; %Energy of 0-0 peak in emission (in eV)
FWHM = 0.05; %FWHM of vibronic peaks
E_phonon = 0.17;
% Loading data into MATLAB workspace omitted for clarity

%% Fitting
for n=1:size(TRPL, 2) %fit one spectral slice at a time
    current_PL_spectrum = [energy_array, TRPL(:, n)];
    current_time = num2strEng(TRPL_headers(n).*10^-15);
    varname = current_time;
    varname(ismember(varname, '-/, ')) = [];
    current_time = matlab.lang.makeValidName(varname);
    gauss_name = matlab.lang.makeValidName([num2str(num_Gauss), '
    Gaussians']);

    X = [Huang_Rhys_Factor ; E_00 ; FWHM]; % Paramters of fitting
    [FC_solution,resnorm,residual,exitflag,output,lambda,jacobian] =
        lsqcurvefit(@f_Franck-Condon.PL_fit, X , current_PL_spectrum
        (:,1), current_PL_spectrum(:,2), -inf(length(X),1), inf(length(
        X),1),...
        optimset('MaxFunEvals', 3000000000000000, 'MaxIter',
        30000000000, 'TolFun', 1E-6),...
        current_PL_spectrum , E_phonon , num_Gauss);

    % Degrees of freedom
    dof = size(current_PL_spectrum(:,1),1) - length(FC_solution);
    % Standard deviation of the residuals
```



```

sdr = sqrt(sum((residual.^2)/dof));
% Standard error
Sigma = sdr^2*inv(jacobian'*jacobian);
se = sqrt(diag(Sigma))';
% Determine confidence values
abupper = FC_solution' + 2*se;
ablower = FC_solution' - 2*se;

[fitted_spectrum , scalar , gauss, ~, FC_solution] =
    f_Franck-Condon_PL_fit( FC_solution , current_PL_spectrum(:,1),
        current_PL_spectrum(:,2), E_phonon, num_Gauss );
[fitted_spectrum_upper , scalar_upper , gauss_upper, ~,
    FC_solution_upper] = f_Franck-Condon_PL_fit( abupper' ,
        current_PL_spectrum(:,1), current_PL_spectrum(:,2), E_phonon,
        num_Gauss );
[fitted_spectrum_lower , scalar_lower , gauss_lower, ~,
    FC_solution_lower] = f_Franck-Condon_PL_fit( ablower' ,
        current_PL_spectrum(:,1), current_PL_spectrum(:,2), E_phonon,
        num_Gauss );

% Organise output
FC_Progression_Results.(temp).(gauss_name)(n).time = {num2str(
    TRPL_headers(n).*10^-15)};
FC_Progression_Results.(temp).(gauss_name)(n).time_label = {
    num2strEng(TRPL_headers(n).*10^-15)};
FC_Progression_Results.(temp).(gauss_name)(n).energy_array =
    current_PL_spectrum(:,1);
FC_Progression_Results.(temp).(gauss_name)(n).PL_spectrum =
    current_PL_spectrum(:,2);
FC_Progression_Results.(temp).(gauss_name)(n).fitted_spectrum =
    fitted_spectrum;
FC_Progression_Results.(temp).(gauss_name)(n).gaussians = gauss;
residual = current_PL_spectrum(:,2) - fitted_spectrum;
FC_Progression_Results.(temp).(gauss_name)(n).residual = residual;
FC_Progression_Results.(temp).(gauss_name)(n).huang_rhys_factor =
    FC_solution(1);
FC_Progression_Results.(temp).(gauss_name)(n).E_00 = FC_solution(2)
;
FC_Progression_Results.(temp).(gauss_name)(n).gauss_FWHM =
    FC_solution(3);
FC_Progression_Results.(temp).(gauss_name)(n).E_phonon = E_phonon;
se_output = full(se);
FC_Progression_Parameters.(temp)(n+1,:) = [{TRPL_headers(n)
    .*10^-15},...
    FC_solution(1),2*se_output(1)...
    FC_solution(2),2*se_output(2)...
    FC_solution(3),2*se_output(3)...
    num_Gauss ];
end

```

```

function [ FC_Gauss_Fit, const, Gauss, res , Soln_X] =
    f_Franck-Condon_PL_fit( X, PLinEnergy, Y, E_phonon, num_Gauss )
% Function called to perform fitting of TRPL spectral slice
%   X = [Huang-Rhys-Factor ; E_00 ; FWHM];
if size(Y, 2) ==2
    PLinEnergy = Y;
else
    PLinEnergy = [PLinEnergy,Y]; %data set together (x,y data) for
        lsqcurvefit alogorithm
end

X(3) = X(3)/2.35; %Gaussian FWHM definition

if nargin <= 2 ,
    E_phonon = 0.17;
    num_Gauss = 1;
end
if nargin <= 3 ,
    num_Gauss = 1;
end

Gauss = zeros(length(PLinEnergy(:, 1)),num_Gauss);
FC_Gauss = zeros(length(PLinEnergy(:, 1)),num_Gauss);
for n= (1:num_Gauss)
    factor = n-1;
    Gauss(:,n) = ((X(1).^factor)/factorial(factor)) * ((exp( -( (
        PLinEnergy(:, 1)) - X(2) + factor*E_phonon).^2) / (2* (X(3))
        ^2) ) ) );
end
for k =1:size(PLinEnergy(:, 1),1)
    Gauss(k,:) = power((6.582119514*power(10,-16))*PLinEnergy(k , 1),3)
        *(1.50219).*Gauss(k,:);
end
FC_Gauss_Fit = sum(Gauss,2);
const = (FC_Gauss_Fit)\PLinEnergy(:, 2);
FC_Gauss_Fit = const*FC_Gauss_Fit;
Gauss = const.*Gauss;
Soln_X = [X(1) ; X(2) ; X(3)*2.35];
FC_GaussResidual = PLinEnergy(:,2) - FC_Gauss_Fit;
res = sum(FC_GaussResidual .^2);
end

```

Rotational transformation of SVD results

```
%% SVD Rotation fitting
%Performs SVD, does spectral rotation and/or kinetics rotation based on
%a mask input

%% Configuration
num_components = 2;
normalize = 1;
smooth_masks = 1;
flip_SVD_result = [-1,-1];
spectral_rotation = 1;
flip_spectra_rotation_result = [1,1];
kinetics_rotation = 0;
flip_kinetics_rotation_result = [-1,-1];

%Data loading omitted for clarity

%% Perform SVD on data matrix (TA)
[U,S,V] = svd(data);
SVD_spectra = V(:,1:num_components);
SVD_kinetics = U(:,1:num_components);

if ~isempty(flip_SVD_result)
    SVD_spectra = bsxfun(@times,SVD_spectra,flip_SVD_result);
    SVD_kinetics = bsxfun(@times,SVD_kinetics,flip_SVD_result);
end

if normalize
    %Normalize kinetics
    UMax = max(max(abs(SVD_kinetics)));
    SVD_kinetics_scaled = SVD_kinetics./UMax;
    %Normalize spectra
    VMax = max(abs(SVD_spectra));
    SVD_spectra_scaled = bsxfun(@rdivide,SVD_spectra,VMax);
else
    SVD_kinetics_scaled = SVD_kinetics;
    SVD_spectra_scaled = SVD_spectra;
end

SVD_predicted = U(:,1:2)*S(1:2,1:2)*V(:,1:2)';
SVD_residual = data - SVD_predicted;

%% Spectral rotation
if spectral_rotation
    SVD_spectra = S(1:num_components,1:num_components)*V(:,1:
        num_components)';
    SVD_kinetics = U(:,1:num_components);
```

```

w = SVD_spectra' \ spectral_mask; %calculate rotation based on
    input spectral shape
inv_spectra_rot_mat = [w';-1*w(2),w(1)];%calculate rotation matrix
spectra_rot_mat = inv(inv_spectra_rot_mat);
spectra_rotated_kinetics = SVD_kinetics*spectra_rot_mat; %apply
    rotation to kinetics
spectra_rotated_spectra = inv_spectra_rot_mat*SVD_spectra; %apply
    rotation to spectra

if ~isempty(flip_spectra_rotation_result)
    spectra_rotated_spectra = bsxfun(@times,spectra_rotated_spectra
        ,flip_spectra_rotation_result');
    spectra_rotated_kinetics = bsxfun(@times,
        spectra_rotated_kinetics,flip_spectra_rotation_result);
end

if normalize
    UMax = max(max(abs(spectra_rotated_kinetics')));
    VMax = max(max(abs(spectra_rotated_spectra')));
    spectra_rotated_kinetics_scaled = spectra_rotated_kinetics./
        UMax;
    spectra_rotated_spectra_scaled = bsxfun(@rdivide,
        spectra_rotated_spectra',VMax);
else
    spectra_rotated_kinetics_scaled = spectra_rotated_kinetics;
    spectra_rotated_spectra_scaled = spectra_rotated_spectra;
end
spectra_rotated_predicted = spectra_rotated_kinetics*
    spectra_rotated_spectra;
spectra_rotated_residual = data - spectra_rotated_predicted;
end

%% Kinetics rotation
if kinetics_rotation
    SVD_kinetics = U(:,1:num_components)*S(1:num_components,1:
        num_components);
    SVD_spectra = V(:,1:num_components)';

    w = SVD_kinetics \ kinetics_mask; %calculate rotation based on
        input kinetic decay
    kinetics_rot_mat = [w';-1*w(2),w(1)]; %calculate rotation matrix
    inv_kinetics_rot_mat = inv(kinetics_rot_mat);
    kinetics_rotated_kinetics = SVD_kinetics*kinetics_rot_mat; %apply
        rotation to kinetics
    kinetics_rotated_spectra = inv_kinetics_rot_mat*SVD_spectra; %apply
        rotation to spectra
    if ~isempty(flip_kinetics_rotation_result)
        kinetics_rotated_spectra = bsxfun(@times,

```

```

        kinetics_rotated_spectra, flip_kinetics_rotation_result');
    kinetics_rotated_kinetics = bsxfun(@times,
        kinetics_rotated_kinetics, flip_kinetics_rotation_result);
end
if normalize
    UMax = max(max(abs(kinetics_rotated_kinetics)));
    VMax = max(abs(kinetics_rotated_spectra'));
    kinetics_rotated_kinetics_scaled = kinetics_rotated_kinetics./
        UMax;
    kinetics_rotated_spectra_scaled = bsxfun(@rdivide,
        kinetics_rotated_spectra', VMax);
else
    kinetics_rotated_kinetics_scaled = kinetics_rotated_kinetics;
    kinetics_rotated_spectra_scaled = kinetics_rotated_spectra;
end
kinetics_rotated_predicted = kinetics_rotated_kinetics*
    kinetics_rotated_spectra;
kinetics_rotated_residual = data - kinetics_rotated_predicted;
end

```

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