Photo-induced Charge Generation and Recombination in Conjugated Polymer - Methanofullerene Blend Films

by

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Steffan Cook

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Abstract

Polymer-fullerene blend films are of increasing interest in the field of organic solar cells. This thesis describes the use of transient absorption spectroscopy (TAS) as a means to study charge generation and recombination in these blend films.

In blend films of P3HT and PCBM, the absorption spectrum associated with the positive and negative charges have been identified and the transient decay kinetics analysed to reveal the mechanisms leading to charge recombination losses in the films. The effects of annealing treatment, along with the effects of decreasing polymer regioregularity or different polymer chain terminating end-groups on the blend film properties and morphology are also discussed.

For films with a low concentration of PCBM in polystyrene, absorption and emission from the individual PCBM molecules are observed. As the PCBM concentration is increased, aggregation related changes causes the absorption in the visible region to increase disproportionately, an additional emission peak at higher energies to appear and a decrease in the lifetime of the PCBM triplet excited state. These changes are linked to electronic interactions between fullerenes in a molecular crystal form of PCBM.

Blends of F8BT polymer with PCBM show poor photovoltaic device performance. This is explained by the quick deactivation of the F8BT excited state by Förster energy transfer to the PCBM. As the PCBM excited state is stable compared to the charge separated state, the PCBM triplet is formed via inter-system crossing from the singlet to be the final product of photoexcitation. The high energy of the charge separated state is interpreted as a result of the high F8BT HOMO energy.
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Comparison of the transient decays in the blends of increasing weight fraction of PCBM. Higher excitation powers were used for the higher PCBM concentration films in order to have all the decays begin at comparable initial amplitudes (excitation used 5-20 µj/cm²). Decays were probed at 830nm following excitation at 470nm. The pristine PCBM film gave no detectable signal.

Transient decay kinetics for the 50% blend film following excitation at 470nm at different intensities. Probe wavelength was 830nm and excitation is marked in the key in units of µj per cm² per pulse. Inset plots the maximum signal amplitude against used excitation intensity (~30ns).

Excitation spectra for the yield of triplet against the wavelength of excitation in the 5% blend film (black squares). The absorption for the film is also shown (black line). Triplet yield was monitored at the triplet absorption maxima at 720nm.

Proposed kinetic scheme following photoexcitation of F8BT in a F8BT:PCBM blend. There are two possible mechanisms to energy transfer from F8BT* to PCBM, either by (1) direct Förster dipole-dipole energy transfer or (2) via the formation of an intermediate charge separated state (CSS) that undergoes recombination to form the PCBM singlet or triplet.

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## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BRP</td>
<td>Bound radical pair</td>
</tr>
<tr>
<td>CP</td>
<td>Conjugated polymer</td>
</tr>
<tr>
<td>CSS</td>
<td>Charge separated state</td>
</tr>
<tr>
<td>cw</td>
<td>Continuous wave</td>
</tr>
<tr>
<td>$\Delta G^+$</td>
<td>Transition state activation energy <em>(electron transfer theory)</em></td>
</tr>
<tr>
<td>$\Delta G^0$</td>
<td>Gibbs free energy difference</td>
</tr>
<tr>
<td>$\Delta OD$</td>
<td>Change in optical density</td>
</tr>
<tr>
<td>e$^-$</td>
<td>Electron</td>
</tr>
<tr>
<td>E.Q.E</td>
<td>External Quantum Efficiencies <em>(incident light to collected electron)</em></td>
</tr>
<tr>
<td>Ea</td>
<td>Electron affinity</td>
</tr>
<tr>
<td>$E_f$</td>
<td>Fermi level</td>
</tr>
<tr>
<td>Eg</td>
<td>Bandgap</td>
</tr>
<tr>
<td>eV</td>
<td>Electron Volt</td>
</tr>
<tr>
<td>FET</td>
<td>Field Effect Transistor</td>
</tr>
<tr>
<td>FF</td>
<td>Fill factor</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Overall solar cell efficiency or Refractive index</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>IP</td>
<td>Ionisation potential</td>
</tr>
<tr>
<td>$J_{sc}$</td>
<td>Short circuit current</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Re-organisation energy or Wavelength</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>$\mu J, mJ$</td>
<td>Microjoule, millijoule</td>
</tr>
<tr>
<td>nm, $\mu$m</td>
<td>nanometre, micrometre</td>
</tr>
<tr>
<td>ns, $\mu$s, ms</td>
<td>Nanosecond, microsecond, millisecond.</td>
</tr>
<tr>
<td>OLED</td>
<td>Organic Light Emitting Diode</td>
</tr>
<tr>
<td>PHT or PT</td>
<td>Polythiophene</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>----------------------------</td>
</tr>
<tr>
<td>PPV</td>
<td>Poly-phenylenevinylene</td>
</tr>
<tr>
<td>RR</td>
<td>Regioregular</td>
</tr>
<tr>
<td>RT</td>
<td>Room temperature</td>
</tr>
<tr>
<td>t</td>
<td>time</td>
</tr>
<tr>
<td>τ</td>
<td>lifetime</td>
</tr>
<tr>
<td>$V_{oc}$</td>
<td>Open-circuit voltage</td>
</tr>
</tbody>
</table>
1 Introduction

1.1 Energy issues.

In the first few years of 21st Century, climate change brought about by the increasing emission of carbon dioxide and other greenhouse gases has been headline news on almost a daily basis\(^1,2\). Of the world energy consumption of 13TW, 85% comes from burning fossil fuels, all of which adds CO\(_2\), the primary greenhouse gas, into the atmosphere\(^3\). Despite stark warnings from scientists, few of the governments in the developed world (who are the main polluters) have the political will to tackle climate change perhaps as the long-term nature of the problem is outside the remit of short-lived individual governments.

![Figure 1-1. Britain’s total greenhouse gas emissions over the last twenty five years and breakdown of the source of CO\(_2\) emission by sector. From Ref. 5.](image)

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1. BBC Ten O Clock News 13th April 2006 ‘Climate Warming’. Information on the BBC website can be found at www.bbc.co.uk/sn/hottopics/climatechange/
2. The Independent Saturday 3rd December 2005 Front Page’ Climate Change: Time For Action’ www.independant.co.uk/environment
A good example of the lack of political will to tackle climate change can be seen in the failure of the Kyoto Protocol of 1997, where ‘Western Countries’ pledged to reduce CO\(_2\) emission on average by 5\% on 1990 levels by 2008-2012\(^4\). Of these countries only Britain and Germany will seemingly meet these targets, however even Britain will fail to meet its own self-imposed target of a 20\% reduction in CO\(_2\) by 2010\(^5\) (Figure 1-1).

The problems of greenhouse gas emissions will only be compounded if we choose to meet the projected energy needs of the future, a projected additional 30TW by 2050\(^3\), by traditional fossil fuel sources. In addition to the climate change issues however, are further perhaps more pressing issues, on meeting the demand for more energy and the security of that supply. Already the ‘squeeze’ on fuel sources has sent the price of oil and gas, the two most commoditable fossil fuel sources, sky-rocketing with a barrel of oil now priced at over $70\(^6\) a barrel compared to a base rate of $20 a barrel throughout the 1990’s. (see Figure 1-2).

![Figure 1-2.](image)

\(^4\) Oh no, Kyoto. The Economist April 5th 2001 or www.economist.com
\(^5\) Hot under the Collar. The Economist March 30th 2006 or www.economist.com
\(^6\) as of April 18th 2006.
Furthermore with the demand for energy ever increasing and the majority of that energy coming from imported oil and gas, there are serious issues on an individual country level about the security of energy supply. With oil and gas production centred very much in only a handful of countries an over-reliance on forms of imported fuels leaves countries vulnerable to terrorist or even political strikes on the supply of energy. This point was clearly illustrated earlier this year, when Russia shut off the supply of natural gas to the Ukraine for a day over political disputes on distribution revenues, which while doing also affected gas supply to parts of Europe. While that dispute was quickly resolved, the uncertainty of the future supply of energy remains and the concern is not more apparent than here in Britain, where the Government recently called for a new review on the U.K. energy policy only 3 years since the last. It is perhaps unlikely that the new review will repeat the call that 70% of the U.K’s energy needs be met by natural gas.

The desire for countries to be more energy self-sufficient and therefore less at risk to disruption in energy supply, alongside concern over global warming, are having a synergistic effect in encouraging the development of alternative energy away from fossil fuels. Of these alternative energy sources, photovoltaics the conversion of sunlight into electricity is an attractive prospect. Everyday 170,000 TW of energy from the sun strike the earth at any moment, more than enough energy in an hour to meet global demand for a year. This energy can be harvested to produce electricity directly or used to convert the energy into hydrogen gas, the much promised fuel of the future. While Solar power therefore definitely has the potential to supply the world’s power needs, its high production and associated costs means however it is not yet economical for development in mainstream electricity production. This means that while the Solar industry is worth $7.5 billion dollars and growing rapidly (40% a year) this industry is largely limited to niche markets such as off grid energy production and space applications.

The price of solar electricity is between 20-50 cents per kilowatt hour, higher than that from other renewable sources (see Figure 1-2) and much higher than energy production costs from coal 1-4 cents per kWh or gas 3-5 cents per kWh. For solar energy to be practical on a massive scale there is a need for solar cells of modest efficiencies but cheaper production costs. A whole range of different solar cells types have been developed to address that need, such as dye-sensitised solar cells, organic material solar cells, organic-inorganic hybrid devices, nanocrystal inorganic-organic devices and all nanocrystal inorganic devices. All these solar cells have generated much interest as they offer the possibility of being easily processable and potentially flexible solar cells\textsuperscript{10} which above all will be cheap and easy to make. Of these new technologies, the polymer-fullerene solar cell is one of the most advanced and commercially viable designs. A key barrier to the commercial success of this device is its relatively low device efficiency\textsuperscript{11} but there are hopes that if a better understanding of the science behind these devices could be gained then higher efficiencies could be achieved. One of the most important parameters governing device efficiency in solar cells are charge generation and recombination and so these topics are the main focus of this doctoral work.

1.2 History and photovoltaic principles.

In principle solar cells act as current generators, providing a fixed amount of current over a range of working voltages depending on the level of illumination. The electrochemical potential of the device is created by the ejection of high energy electrons at one end of a device which are replaced with low energy electrons at the other end. In order to achieve current flow in only one direction, the electrodes must be selective to either the high energy electrons or the low in energy ‘holes’ and as such the solar cell must be a diode.


The photovoltaic effect was first noted by Edmund Bequerel in 1839 at age 19 while working in his father’s laboratory. He noted that light incident on a silver coated platinum electrode in electrolyte produced electric current. The ancestors of modern day inorganic solar cells however was not discovered until 1939 by Russel Ohl, while testing the resistivity of silicon ingots at Bell laboratories in the U.S. He noted that a crack in the silicon ingot (a natural P-N junction) gave rise to different types of resistivity in the silicon while under illumination. Over a decade later improvements lead by the revolution in the semiconductor electronics industry allowed the first truly ‘efficient’ silicon solar cell to be reported by Chaplin, Fuller and Pearson in 1954 with a sunlight to electrical power conversion efficiency of 6%. These silicon solar cells worked on the same principles as all of today’s conventional inorganic solar cells, whereby absorption of light leads to the formation of an electron and ‘hole’, which due to the low coulombic attraction in the high dielectric crystalline material, are freely mobile charges. The separation of charges is achieved by a p-n junction whereby an electric field generated at the interface between negatively doped (n-type) and positively doped (p-type) materials drives the electrons in the conduction band across to the n-type layer and the holes in the valence band to the p-type layer.

![Figure 1-3. Pictorial representation of how holes and electrons separate across a p-n junction.](image-url)
From 1954 onwards, photovoltaic device efficiencies were to rise significantly however their high production costs, the Achilles heel of solar cells, meant that solar cells would not become commercially viable for applications outside such niche markets as remote location power generation and space applications.

The oil crisis of the 1970’s created an intense interest in photovoltaics as a means of power generation and lead to the development of many new lower cost solar cells such as polycrystalline or amorphous silicon and more efficient device architectures such as tandem and multiple band gap designs. Unfortunately, the return of cheap oil in the 1980’s and disappointment in the lack of a viable solar cell for power generation dampened interest in solar cells until recently, when interest in solar cells rose again due to increasing concern over the environment and the growing need for alternative energy supplies. In the continuing search for cheaper photovoltaics breakthroughs in efficiency have come from a new generation of low cost ‘excitonic’ solar cells, such as the dye sensitised solar cell in 1991 and the organic bulk heterojunction solar cell in 1995.

1.3 Excitonic Solar Cells.

Organic solar cells behave very differently from their inorganic counterparts. Organic semiconducting materials tend to be single molecules or polymers and do not show extensive regular 3-D lattices. As such charge transport in these materials is usually several orders of magnitude slower and characterised by ‘hopping’ from molecule to molecule rather than a flowing band-like conduction. Furthermore unlike in solar cells made from inorganic materials, the absorption of light in organic materials forms a stable excited state

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(excitons) that do not thermally dissociate into free electrical charges at room temperature. The formation of charged states directly following photon absorption in organic materials therefore is rare, with charges typically only being formed when the exciton is quenched by an impurity or by a metal contact\textsuperscript{15}. Single layer organic devices therefore tend to show low efficiencies \textless;1\% PCE\textsuperscript{16} due to poor current generation.

In 1986 Tang \textit{et al}\textsuperscript{17} made a breakthrough innovation in the creation of donor-acceptor junction (D-A junction) formed at the interface between a bilayer of two organic materials of different electronegativity. The difference in electron affinity creates a driving force for electron transfer in the excited state, ‘splitting’ the excitons formed during light absorption into electrical charges. In the ‘Tang’ cell the donor-acceptor junction was formed between electron donating CuPC and an electron accepting perylene derivative. A representation of the workings of a D-A junction is shown below.

\textbf{Figure 1-4.} Picture of a donor acceptor junction. The offset in electron affinity between the materials insures charge transfer at the interface between the donor excited state and the acceptor, forming charges which percolate through the materials for collection at the electrodes.

Another leap in efficiency came with the design of a bulk heterojunction device, where the donor and acceptor materials are blended together to form a giant bulk donor - acceptor heterojunction\(^{14,18}\). This solved the problem of the short diffusion distance for the exciton (typically \(<10\text{nm}\)) by mixing the donor and acceptor on a nanometre scale and ensuring charge generation before the exciton could decay. The importance of the initial exciton and its separation across a donor-acceptor (D-A) interface is the reason these devices are typically called ‘excitonic solar cells’\(^{12}\).

### 1.4 Existing types of excitonic solar cells

What will follow are short descriptions of the different types of excitonic solar cells being developed with recent reported efficiencies under laboratory conditions given in Table 1-1.

<table>
<thead>
<tr>
<th>Material</th>
<th>Jsc (mA)</th>
<th>FF</th>
<th>Voc (V)</th>
<th>PCE (%)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSSC: TiO(_2/dye/I-\text{I}_2)</td>
<td>19.4</td>
<td>0.71</td>
<td>0.795</td>
<td>11.0</td>
<td>19</td>
</tr>
<tr>
<td>Nanocrystal-Polymer: CdSe-MDMOPPV</td>
<td>6.4</td>
<td>0.44</td>
<td>0.76</td>
<td>2.4(^a)</td>
<td>27</td>
</tr>
<tr>
<td>All Nanocrystal: CdTe-CdSe</td>
<td>13.2</td>
<td>0.49</td>
<td>0.45</td>
<td>2.9</td>
<td>30</td>
</tr>
<tr>
<td>Inorganic - Organic hybrid: ZnO-MDMOPPV</td>
<td>2.40</td>
<td>0.59</td>
<td>0.81</td>
<td>1.6(^b)</td>
<td>25</td>
</tr>
<tr>
<td>Small molecule: CuPC:C(_{60})</td>
<td>15.0</td>
<td>0.61</td>
<td>0.54</td>
<td>5.0(^c)</td>
<td>33</td>
</tr>
<tr>
<td>Polymer-Polymer: M3EH-PPV-CN-ether-PPV</td>
<td>3.57</td>
<td>0.35</td>
<td>1.36</td>
<td>1.7</td>
<td>37</td>
</tr>
<tr>
<td>Polymer-Fullerene: P3HT:PCBM</td>
<td>11.1</td>
<td>0.54</td>
<td>0.6</td>
<td>4.9(^d)</td>
<td>18</td>
</tr>
</tbody>
</table>

\(^a\) (89.9\text{mW/cm}^2 \text{ light intensity})

\(^b\) (71\text{mW/cm}^2 \text{ light intensity})

\(^c\) (active surface area 0.8mm\(^2\))

\(^d\) (80\text{mW/cm}^2 \text{ light intensity})

Table 1-1. Reported device efficiencies for several types of ‘excitonic’ solar cells.

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1.4.1 Dye Sensitised Solar Cell

Dye sensitised solar cells (DSSC) were invented more than ten years ago by Michael Gratzel and co-workers and have since then reached calibrated efficiencies of $\sim 11\%^{19}$. In DSSC’s an inorganic nanoporous membrane (usually TiO$_2$) is coated with a light absorbing dye which upon illumination injects an electron into the surface of the inorganic. Complete pathways to the electrode then allow for facile electron collection while the hole charge is carried to the anode by an electrolyte usually based on a I$_2$/I$_3^-$ redox couple. Recent developments have tried to avoid the use of a liquid electrolyte by using a quasi or solid state hole transporter. Unfortunately cells using these new hole transporters have reduced efficiencies [up to 4%]$^{20,21}$.

1.4.2 Inorganic-Organic hybrid solar cells

Inorganic-organic hybrid solar cells utilise the known good electron transport properties of inorganic materials with the light absorbance and hole transport of organic semiconducting polymers. Typical examples are ZnO or TiO$_2$ particles with polyphenyl vinylenes (PPV) or polythiophene (PHT) as polymers$^{22,23,24}$. Ultimately, the use of a carefully nano-structured inorganic semiconductor may allow control over the desired film morphology, however to date the highest efficiencies have been reached with random blending of the conjugated polymer and inorganic nanoparticles [1.5% efficiency]$^{25}$. If finer mixing of the inorganic and organic components in film or solution can be achieved then improvements in efficiency are expected.

1.4.3 Nanocrystal (Quantum Dot) -Polymer solar cells

A variation on the inorganic-organic solar cell but using nanometre size quantum dots as the electron transporter (usually CdSe or CdTe). Nanorods have been found to give better performance over dots\textsuperscript{26} due to their improved charge transport properties but best efficiencies are gained with tetrapod nanocrystals\textsuperscript{27}. The main problem for nanocrystal-polymer solar cells is the aggregation and separation of the nanocrystal and polymer in solution and in the film, which requires surfactants to help bring the two components together\textsuperscript{28}. It is thought that the presence of these surfactants are detrimental to the device and efficiencies can be improved with thermally removable surfactants\textsuperscript{29}. Efficiencies of up to 2.4% have been reported\textsuperscript{27}.

![Figure 1-5. TEM images of CdSe nanorods in polythiophene. From Ref 26.](image)

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1.4.4 All inorganic nano-dot solar cells

All inorganic nano-dot solar cells are the blend mixture of two nanocrystal types e.g. CdS and CdTe. Using an all inorganic phase potentially creates higher charge transport properties and because there are no organic materials present, less degradation with use and a greater working lifetime. These types of cell have only recently emerged but already show efficiencies of 2.9%\textsuperscript{30}. Of all known solar cells this is the only type of solar cell which breaks the Shockley-Queisser efficiency limit for photovoltaics\textsuperscript{31}, a limit imposed as the energy of a photon greater than the band gap is lost as heat. Due to carrier multiplication, a reverse Auger recombination effect, absorbed light of more than two times the band gap energy can be used to create two excitons instead of one. While carrier multiplication has not yet been seen in a working photovoltaic device, in principle the effect raises the maximum theoretical device efficiency to 70%\textsuperscript{32}.

1.4.5 Small molecule solar cells

Using molecular beam deposition thin layers or blends of small molecule organic material can be deposited onto a substrate by sublimation. The very first two component donor-acceptor solar cell (the so called Tang Cell) was made this way using copper pthalocyanine and a perylene derivative. Beam deposition has advantages in having fine control over the growth of the materials on the substrate and that both the photoactive blend and electrode can be deposited in sequence using the same equipment under high vacuum. Device architectures can be either bulk-heterojunction or bilayer or as employed for the most efficient small molecule blend film (CuPc and C\textsubscript{60} \textasciitilde 5\%\textsuperscript{33} PCE) a mixture of both\textsuperscript{34}.


1.4.6 Polymer-Polymer solar cells

Polymer-Polymer solar cells are made from a mixture of two conjugated polymer materials, one more electronegative than the other, with ideally complementary absorption spectra so both components can harvest light throughout the solar spectrum. In addition to the efficient light harvesting, the ease of customisability and solution processability of polymers are attractive properties favouring their commercialisation. However to date polymer-polymer solar cells have shown disappointing efficiencies. Despite polymer-polymer devices typically showing high open circuit voltages (>1V), the highest of all the excitonic solar cells, the low fill factors and poor current collection badly limit their efficiencies\textsuperscript{35,36,37}. That the highest reported polymer-polymer device efficiency to date of 1.9% (POPT and MEH-CN-PPV\textsuperscript{38}) is still that from a bi-layer device of two materials rather than a bulk heterojunction exemplifies these problems.


1.4.7 Polymer - Fullerene solar cells

Figure 1-7. Schematic drawing of organic photovoltaic devices based on the blend of MDMO-PPV and PCBM.

Since the report of a 2.5% efficient solar cell\(^\text{39}\) in 2001, polymer-fullerene solar cells have been of increasing interest. Despite the high efficiencies, there is only limited information about how these devices work and what parameters limit their performance. For MDMOPPV:PCBM devices, the reported near 90% absorbed photon to collected electron efficiencies suggests that both charge formation and charge recombination processes are near the optimal, being very high and very low respectively\(^\text{39}\). Such high internal efficiencies are only possible however as the photoactive blend layer is thin where typically more than 40% of the incident light in the absorbing region of the polymer is transmitted through the sample. Thicker blend films can absorb more or even all of the incident light however these devices tend to show much lower efficiencies overall despite the higher light absorption due to heavier bimolecular recombination losses in these low mobility materials\(^\text{40}\).


Studies of charge recombination losses therefore are necessary if greater efficiencies are to be made by having thicker blend layers.

Recent optical studies on MDMOPPV:PCBM films have highlighted the presence of charge trap sites in the photoactive blend where these sites prolong the lifetime of the hole charges in the device by preventing their recombination\textsuperscript{41,42}. The prolonged lifetime of charges in trap sites offer potentially one avenue for decreasing bimolecular losses in polymer:fullerene devices, however their origin and nature are not yet understood.

For blends films of PPV derivatives and PCBM, the electronegativity of the fullerene molecule leads to ultra-fast and therefore near unity charge formation in the blend films, maximising charge generation\textsuperscript{43,44,45}. Not all material combinations however display as complete charge generation, for instance blend films of two polymer materials, F8BT and PFB, show much promise as polymer:polymer devices, however photoluminescence quenching of the donor PFB, often used as a measure of charge formation, is only 70\% in a 1:1 PFB:F8BT film\textsuperscript{46}. This represents up to a 30\% loss in device efficiency from the initial charge generation step alone, even before any recombination losses. The mechanism leading to, and the efficiency of charge generation therefore are crucial parameters to device efficiency and deserve careful study.


1.5 Aims of this thesis

Initially polyphenyl vinylene (PPV) derivatives were used in conjunction with PCBM to create the most efficient solar cells\textsuperscript{39,47}. However in 2003 a report by Padinger et al\textsuperscript{48} showed that polythiophene with its smaller band gap (~1.9eV) and higher hole mobilities could give higher efficiencies. This report highlights the potential of new polymer materials in combination with PCBM, however nothing is known on the nature of charge recombination in this new material combination or how it compares to MDMOPPV:PCBM devices. The third chapter in this thesis will focus on studies characterising charge recombination in P3HT:PCBM blend films with the aim of establishing a fundamental understanding of the charge recombination processes and by doing so provide a basis for comparing recombination in many different polymer:PCBM material combinations. In the report by Padinger et al the importance of thermal annealing processes on improving the device efficiency were also established\textsuperscript{48}. The effect of annealing on the charge recombination in P3HT:PCBM blend films therefore will also be studied in order to establish if reduction in recombination losses maybe responsible for the improvements in device efficiency.

In the fourth chapter in this thesis the effect of decreasing P3HT polymer regioregularity and the effects of P3HT polymer chain end-functionalisation with either bromine or methyl groups will be studied. The high mobility of holes in P3HT is known to be associated with its high level of packing which may be disrupted in the lower regioregularity or functionalised chain end P3HT\textsuperscript{49}. The efficiency of polymer:fullerene devices however

depends on many factors other than charge mobilities and this chapter aims to study which polymer qualities are most pertinent to device efficiency.

PCBM, just as C₆₀, is a relatively new material and its material properties are yet to be fully characterised. The lack of information on the character and properties of PCBM however is particularly far-reaching as the PCBM component in polymer:fullerene devices typically constitutes more than 50% of the photoactive layer. Already there is some confusion in the literature over the behaviour of polymer:fullerene blends, for instance in the unexpected increases in hole mobilities in MDMOPPV:PCBM blend devices and the presence of a photocurrent edge leading down to low energies. This unexpected behaviour may be related to the properties of PCBM and therefore the fifth chapter in this thesis will concentrate on the characterisation of PCBM.

Polyfluorenes are polymer materials more commonly used in organic light emitting diodes than photovoltaics. These materials however are attractive for use in solar cells due to their high HOMO energy (high ionisation potentials) as using high HOMO energy materials could potentially lead to larger device working voltages and overall higher efficiencies. Device results from blends of one such polyfluorene based polymer, F8BT, with PCBM however have shown very poor device efficiencies. The final data chapter in this thesis aims to establish and explain in terms of charge generation why this particular polymer:fullerene blend shows such poor device performance. Guidelines are given indica-

ing the appropriate electronic properties needed in any particular donor-acceptor material combination in order to obtain efficient charge generation.

## 1.6 Scientific concepts

### 1.6.1 Transmittance & Absorbance

The transmittance of a sample is given as the ratio in intensity of the light passed through the sample over the light incident upon it.

\[
T(\lambda) = \frac{I_{\text{out}}(\lambda)}{I_{\text{in}}(\lambda)}
\]

**Equation 1-1.** Transmittance as a function of light in and light out.

Experimentally analytical data generally shows a relationship with the log value of transmittance and so for convenience transmittance is often written in terms of absorbance where:

\[
dI(x) = -\alpha I(x)dx
\]

\[
I = I_0e^{-\alpha x}
\]

\[
\alpha = n\sigma \quad \text{absorption coefficient}
\]

\[
n \quad \text{density of absorbing centers}
\]

\[
\sigma \quad \text{absorption cross section}
\]

\[
T = e^{-\alpha l}
\]

**Equation 1-2.** Transmittance as a function of the path length and absorption co-efficient.

Experimentally analytical data generally shows a relationship with the log value of transmittance and so for convenience transmittance is often written in terms of absorbance where:
Equation 1-3. Absorption as a function of transmittance.

\[ A(\lambda) = \log \frac{I_{\text{in}}(\lambda)}{I_{\text{out}}(\lambda)} = -\log T(\lambda) \]

Equation 1-4. The Beer-Lambert Law

The most famous example of which is the Beer-Lambert law which states the relationship between the measured absorbance with the path length of the light and the concentration of a material. \( \varepsilon(\lambda) \) is the molar absorption co-efficient \([\text{l mol}^{-1} \text{ cm}^{-1}]\) or \([\text{M}^{-1} \text{ cm}^{-1}]\), \( c \) is the concentration \([\text{mol l}^{-1}]\) or \([\text{M}]\) and \( l \) is the thickness of the absorbing medium \([\text{cm}]\).

\[
\sigma = \frac{2.303 \varepsilon}{N_A} = 3.825 \times 10^{-19} \varepsilon
\]

Equation 1-5. Relation between molar absorption and cross section (cm²).

For reference the relationship between the absorption cross section of a molecule often used by physicists and the molar absorption co-efficient used by chemists is given in Equation 1-5.

1.6.2 Rehm-Weller equation.

\[ D^* + A \rightarrow D^+ + A^- \]

Electron (charge) transfer from the excited state of the donor to the acceptor leads to the formation of a charge separated state (CSS). The CSS can also be described as a bound radical pair (BRP) as the coulombic attraction of the opposite charges \( (E_c) \) provides a bar-
rier to the dissociation of the charges. The energy of the formed charge separated state \((E_{CT})\) can be expressed as the sum of terms;

\[
E_{CT} = E_{D^+/D} - E_{A^-/A^-} - \Delta H_{solv} - E_c
\]

where \(E_{D^+/D}\) \((E_D^{ox})\) is the oxidation potential of the donor, \(E_{A^-/A^-}\) \((E_A^{red})\) is the reduction potential of the acceptor, \(\Delta H_{solv}\) is the solvent re-organisation parameter and \(E_c\) is the coulombic energy of the separated charges. These terms were evaluated in the equation by Weller\(^{54}\) to give;

\[
-\Delta G_{CR} \approx (IP - EA) - \frac{e^2}{4\pi \varepsilon_0} \left\{ \frac{1}{\varepsilon_s r_{DA}} + \frac{1}{2} \left( \frac{1}{r_D} + \frac{1}{r_A} \right) \left( \frac{1}{37.5} - \frac{1}{\varepsilon_s} \right) \right\}
\]

**Equation 1-6.** Weller Equation.

where \(-\Delta G_{CR}\) represents the energy of the charge separated state above the ground state, IP and Ea are assumed to be \(-E_D^{ox} - E_A^{red}\) respectively in acetonitrile, \(e\) is the elementary charge, \(\varepsilon_0\) the vacuum permittivity, \(\varepsilon_s\) dielectric constant of the matrix, \(r_{DA}\) separation distance between donor and acceptor, \(r_D\) and \(r_A\) spherical radii of donor and acceptor moieties respectively.

From this the free energy of any photoinduced electron transfer reaction can be calculated by subtracting the energy of the donor excited state from the energy of the charge transfer state (Rehm-Weller equation\(^{55}\)).

\[
\Delta G^0_{et} = E_{CT} - E_D^{

**Equation 1-7.** Rehm-Weller Equation.

\[\text{Equation 1-7. Rehm-Weller Equation.}\]

\[\text{Equation 1-6. Weller Equation.}\]

\[\text{Equation 1-7. Rehm-Weller Equation.}\]

---


1.6.3 Marcus electron transfer theory

During photoinduced electron transfer the change from reactant to product can be discussed in terms of formation of a transition state with an activation energy for formation of $\Delta G^+$. The rate of electron transfer is then given by;

Equation 1-8. Classical expression for the rate of electron transfer in terms of an energy barrier $\Delta G^+$.

where $\kappa_{el}$ is the electronic transition co-efficient and $\nu_n$ is the frequency of passage through the transition (nuclear vibrational frequency). While the free energy change for the reaction can be measured ($\Delta G^0$) the activation energy ($\Delta G^+$) is not easily known. In Marcus theory the activation barrier to electron transfer ($\Delta G^+$) is calculated in terms of the measurable free energy change ($\Delta G^0$) and another parameter known as the re-organisation energy($\lambda$). The re-organisation energy is the energy required for all structural adjustments (in the reactants and in the surroundings) which are needed in order that A and D assume the configuration required for the transfer of the electron. From this the activation energy can be expressed in terms of;

$$k_{et} = \kappa_{el} \nu_n \exp\left(-\frac{\Delta G^+}{kT}\right)$$
\[ \Delta G^+ = \frac{(\lambda + \Delta G^\circ)^2}{4\lambda} \]

**Equation 1-9.** Relationship between the activation energy for electron transfer and the free energy of the electron transfer reaction and the re-organisation energy in Marcus theory.

Yielding an electron transfer rate equation where;

\[ k_{et} = \kappa_{el} \upsilon_n \exp\left(\frac{(\lambda + \Delta G^\circ)^2}{4\lambda kT}\right) \]

**Equation 1-10.** Rate equation for electron transfer in Marcus theory.

Plotted on a graph of \( k_{et} \) versus \( -\Delta G^0 \) (eV) this gives rise to a region where the rate of reaction increases with increasing \( -\Delta G^0 \) (the normal region), but then beyond a point further increases lead to decreases in the rate of electron transfer (the Marcus inverted region).

**Figure 1-8.** Marcus normal and inverted regions for electron transfer.
The figure above shows the normal and inverted regions to Marcus’s electron transfer theory. In the figure above the rate of electron transfer has been plotted using the following parameters, $\kappa_{el} = 1$ (typical in classic electron transfer), $\nu_n = 10^{14}$ Hz, $\lambda = 1$ eV, $T = 300K$. Electron transfer in MDMOPPV:PCBM solar cells has been measured by transient absorption studies to be on the timescale of $\sim 45$fs\textsuperscript{56} on similar timescales to the maximum rate of electron transfer in the example above.

### 1.6.4 Förster energy transfer

Coulombic (dipole-dipole) excitation transfer between molecules at distances greater than their combined Van Der Waal radii. For dipole-dipole induced energy transfer the rate of energy transfer is proportional to the overlap in the transition dipoles of donor and acceptor, the oscillator strength and the distance between donor and acceptor to the sixth power.

$$k_{EnT} \propto \frac{\kappa^2 \kappa_f}{R_{DA}^6} J(\varepsilon_A)$$

**Equation 1-11.** Rate of energy transfer.

where $k_f$ is the rate of radiative decay, $\kappa$ denotes a dimensionless geometric factor determined by the orientations in space for the transition dipole moments of $D^*$ and $A$. Its average is 0.816 for fast brownian rotation of both molecules (Förster 1948) and 0.690 for random but rigid orientations (Maksimov and Rozman 1962, Steinberg 1968). $R_{(DA)}$ is the distance between donor and acceptor and $J(\varepsilon_A)$ is the spectral overlap integral.

Equation 1-11 can be expressed as:

\[ k_{\text{EnT}} = k f\left(\frac{R_0}{R_{DA}}\right)^6 = \frac{1}{\tau_f} f\left(\frac{R_0}{R_{DA}}\right)^6 \]

**Equation 1-12.** Relation between the Förster radius and the rate of energy transfer.

where \( R_0 \) is:

\[
(R_0)^6 = \frac{9000(\ln 10)\kappa^2}{128\pi^5\eta^4 N_A} \int_0^\infty f_D(\tilde{\nu})e_A(\tilde{\nu}) \tilde{\nu}^4 \, d\tilde{\nu}
\]

**Equation 1-13.** Förster equation.

In Equation 1-13, \( \eta_D^0 \) represents the quantum yield of fluorescence of the donor in the absence of the acceptor; \( \eta \) is the refractive index; \( N_A \) is Avogadro’s number; \( E_A(\nu) \) is the molar decadic extinction co-efficient of the acceptor and \( f_D(\nu) \) the spectrum of the donor fluorescence measured in quanta per wavenumber interval and normalised to unity on the same scale.

### 1.6.5 Einstein Relation

The diffusion distance of charges \( \langle L \rangle \) can be calculated from the average lifetime of charges \( \langle t \rangle \) using the Einstein Relation.

\[
\langle L \rangle = \sqrt{2D(\tau)}
\]

**Equation 1-14.** Einstein Relation for charge diffusion distances in non-dispersive systems.

In Equation 1-14, \( D \) is the diffusion constant which in non-dispersive systems is given by:

\[
D = \frac{\mu kT}{e}
\]

where \( \mu \) is the mobility, \( k \) is Boltzmann’s constant, \( T \) is temperature and \( e \) is the charge on an electron. Note that \( kT/e \) is \(-0.026\)V at room temperature. If the charge
mobility is extracted from dispersive measurements then the value of $\bar{L}$ obtained will be an overestimate depending on the degree of dispersity.

1.7 Bibliography


2 Experimental Method

2.1 Materials

All the materials in this thesis were used as received and underwent no further purification. Poly(3-hexylthiophene) (P3HT) polymer and all derivatives were obtained from Merck PLC, poly(9,9-dioctylfluorene-co-benzothiadiazole) (F8BT) polymer was from the Dow Chemical Company (now a subsidy of Sumitomo Corporation) while 1-(3-methoxy carbonyl)-propyl-1-phenyl-(6,6)C_{61} (PCBM) was purchased from Nano-C Inc.. The characterisation of the polymer materials (e.g Mw, DPI) used in this thesis are given in the methodology section of the individual chapters.

2.2 Sample preparation

2.2.1 Blend film fabrication

Polymer and fullerene of the desired weight ratio, were dissolved in a common chlorobenzene or dichlorobenzene solution from which thin films were spun-cast. Spin-casting conditions and polymer concentration in solution were adapted to achieve homogeneous looking films of suitable optical thickness f of between 0.1-0.3 in absorbance. Typically, films were spun-cast at 2000RPM for 60 seconds and the polymer concentration in solution was between 10-20mg per ml. Films were deposited onto spectrosil (quartz) or slide glass which had been previously cleaned by sonication for 15 minutes successively in acetone, water and then isopropanol before drying under a stream of gaseous nitrogen. To avoid degradation to the samples by exposure to light and air, after spin coating films were immediately sealed in an Argon filled quartz-window cuvette with for testing, (see picture below) or if longer term storage was necessary kept in a nitrogen glovebox. In Chapter 3
of this thesis the samples were annealed at 140°C for 15 minutes using a hot-plate open to the air but in the dark to avoid exposure of the film to light during the annealing process. In Chapter 4, annealed samples were heated on a hot-plate for 2 hours at 140°C in a nitrogen glove-box (oxygen and moisture level <1ppm).

![Figure 2-1. Picture of the quartz-window cuvette used to contain the sample under inert atmospheres.](image)

2.2.2 Device fabrication

All device fabrication and measurements referred to in this thesis were completed by Y.Kim in the Department of Physics at Imperial College. A schematic drawing of the organic solar cells and their fabrication method is given here only for completeness.
Figure 2-2. Cross-sectional view of a typical polymer fullerene organic solar cell. Although not used in the devices mentioned here an additional lithium fluoride (LiF) layer is sometimes deposited in between the active layer and the top aluminium electrode.

For polymer-fullerene solar cell fabrication, on top of acetone and isopropyl alcohol cleaned indium-tin oxide (ITO) covered glass (25Ω/cm²), a layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Baytron P standard Grade; HC Stark) was spin-coated and then subsequently annealed at 230°C in air for 15 minutes. The active layer i.e. a P3HT:PCBM blend, was then spincoated on top of the annealed PEDOT layer using various spin conditions to achieve the desired thickness. Finally a 1500Å thick Al electrode was deposited on the blend film by thermal evaporation at base pressures of ~3x10⁻⁶ Torr or lower, defining an active area of 4.5mm². The photovoltaic characteristics of devices under monochromatic light exposure were measured using a system equipped with an electrometer (Keithley 237), a monochromator (Oriel CVI CM110), and a Xe lamp (150 W). The device performance under white light illumination (AM1.5) was measured using a home-built solar simulator based on a filtered Xe lamp with output intensity of 100 mW/cm² (Costronics Electronics).

2.3 Transient absorption spectroscopy

2.3.1 Principle

Transient absorption spectroscopy was developed by Lord Porter around the 1950’s for which he was awarded the Nobel Prize for Chemistry in 1967. The apparatus is best described as an elaborate spectrometer that allows the optical characterisation of short lived transient species. The technique involves irradiation of a sample with a short intense pulse of light (the excitation pulse) and observing the consequent change in the samples optical density. The change in optical density is determined by monitoring the transmission of a second, less intense beam of light that passes through the sample known as the ‘probe’. This technique yields information from a single excitation wavelength at a single probe wavelength but over a broad range of timescales to provide kinetic data on the decay of transients.

2.3.2 Calculating $\Delta OD$

The relationship between $\Delta OD$ and $-\Delta T/T$ can be derived in two parts as follows:

Equ. (2-1) \hspace{1cm} \Delta OD(t) = - \log T_1 - (-\log T_2)

Equ. (2-2) \hspace{1cm} \Delta OD(t) = - \log e^{-\alpha_1 \cdot l} - (-\log e^{-\alpha_2 \cdot l})

Equ. (2-3) \hspace{1cm} \Delta OD(t) = \log e^{(\alpha_1 \cdot l - \alpha_2 \cdot l)}

Equation 2-4. \hspace{1cm} \Delta OD(t) = \frac{1}{2.303} (\alpha_1 \cdot l - \alpha_2 \cdot l)

The change in absorption co-efficient ($\alpha_1 \cdot l - \alpha_2 \cdot l$) in Equation 2-4 can then be related to the change in transmission over transmission by;
Equ. (2-5) \[
\frac{-\Delta T}{T} = \frac{e^{-\alpha_1 \cdot l} - e^{-\alpha_2 \cdot l}}{e^{-\alpha_1 \cdot l}}
\]

Equ. (2-6) \[
\frac{-\Delta T}{T} = (e^{(\alpha_1 \cdot l - \alpha_2 \cdot l)} - 1)
\]

using the Maclaurin series expansion for \(e^x\) (\(e^x = 1 + \frac{x}{1!} + \ldots\)) where all terms higher than \(x^2\) become negligible due to the very low value \(x\), Equation 2-6 becomes approximately:

Equation 2-7. \[
\frac{-\Delta T}{T} \cong \alpha_1 \cdot l - \alpha_2 \cdot l
\]

Putting Equation 2-7 into Equation 2-4 gives the relationship between the change in optical density and the negative change in transmission over transmission.

\[
\Delta OD(t) = \frac{1}{2.303} \int \frac{\Delta T}{T} \]

Equation 2-8. Relationship between \(\Delta OD\) and \(-\Delta T/T\).

2.3.3 Apparatus

Two different transient absorption set-ups were used in this work in order to benefit from their specific advantages. The primary transient absorption set-up allowed the sample to be probed at a range of wavelengths (400-1050nm) however the set-up showed a limited time resolution due to scatter and emission noise from the sample. The second set-up used a \(cw\) (continuous wave) laser diode as a probe source allowing the use of a photodiode with a quicker time response however the probe wavelength choices were limited. Under the correct conditions (matching probe wavelengths and excitation pulse intensities) data from both set-ups can be joined together to give a single transient decay covering a ns-ms timescale.
2.3.3.1 Microsecond system

The microsecond transient absorption system is capable of monitoring kinetics from $\sim 10^{-7}$ s to greater than milliseconds in timescale. Due to scatter and emission noise from the pump excitation source however the system resolution is typically from a microsecond onwards. The PTI GL-3300 Nitrogen Laser produced 600ps laser pulses at a wavelength of 337nm with a pulse energy of $\sim 1\text{mJ}$ at a variable repetition rate chosen using a frequency generator. A GL-301 PTI dye laser module was used in conjunction with the nitrogen laser to provide a variable wavelength source of excitation (400-750nm). The energy of the pulse at the different wavelengths depended on the type of dye employed in the dye laser. A part of the light from the dye module was used as a trigger signal to start the oscilloscope but the majority was focused into a light guide pipe and then onto the sample. A series of neutral density filters were used to modify the power of the laser beam.

![Diagram of the microsecond transient absorption system](image)

**Figure 2-3.** The layout of the microsecond transient absorption system.

A 100W tungsten lamp was used as the probe-light source. An advantage of having a tungsten lamp is that transient signals over a whole wavelength range can be observed (400-
1050 nm). The monitoring wavelength from the lamp was selected by using monochromator one. Appropriate filters were placed in front of the monochromator aperture in order to block the ‘second harmonic’ of the selected wavelength from leaving the monochromator. A second monochromator was used after the sample to check any emission or pump scatter from the sample from reaching the photodiode. The detection system comprised of a silicon photodetector and a Tektroniks TDS 220 oscilloscope. Costronics software was used for data acquisition and averaging. Typically in this thesis each trace is the average of between 400-1200 individual traces. Time equals zero was calibrated from the peak response of the photodiode to a scatter pulse. The layout of the ‘microsecond’ transient absorption system is shown in Figure 2-3.

When required a cold temperature cryostat with quartz windows (Oxford Instruments, Optistat DN-V) with a temperature control unit (Oxford Instruments, ITC502) was used so that transients at different temperatures could be measured.

2.3.4 Nanosecond system

A second transient absorption system with a quicker response photodiode was used in order to obtain earlier time resolution transient decays (~20ns). The use of a quicker photodiode was made possible by having less electronic signal amplification and by increasing the distance between the sample and photodiode so that scatter and emission noise were reduced. This required the use of a probe beam that was cohesive over long distances and so a laser diode was used. Initially only a 830nm (~40mW) laser diode was available however later work used a 980nm (~100mW) laser diode. A series of neutral density filters were used to modify the power of the laser diode so that the photodiode was not over-
loaded. The system response was typically 20ns and the photodiode was responsive until 10 microseconds.

![Diagram of nanosecond transient absorption system](image)

**Figure 2-4.** The layout of the nanosecond transient absorption system.

The same nitrogen laser excitation source and data acquisition software was used as that for the microsecond system. The layout of the ‘nanosecond’ transient absorption system is shown in Figure 2-4.

### 2.4 Other data collection methods:

#### 2.4.1 Steady state UV/visible absorption spectroscopy

All steady state absorption spectra of films or solutions were obtained using a Shimadzu UV-1601 spectrometer. Spectra were recorded at the fast scan rate mode with a bandwidth of 1nm.
2.4.2 Steady state fluorescence emission and excitation spectroscopy

All Steady state fluorescence emission and excitation spectra were obtained using a Jobin-Yvon Fluoromax or Fluorolog spectrofluorometer. Steady state emission spectra were gathered following excitation of the sample at the absorption maxima unless otherwise stated. The excitation spectra followed the change in emission yield at the emission maxima while varying the excitation wavelength.

2.4.3 Emissive state lifetime measurements

All time-correlated single photon counting (TC-SPC) measurements were obtained on home made equipment as described in detail in the PhD thesis of Dr Andrew Ferguson at Imperial College London\(^2\) (2006). The only change from the set-up as described in Ref 2 was the use of a PicoQuant GmbH (Germany) laser diode excitation source with a lasing wavelength of 440nm and typical pulse widths of ~30ps FWHM and energies of ~20pJ per pulse (~0.7mW equivalent). In short, the TC-SPC was run in reverse mode using a micro-channel plate photomultiplier tube (Hamamatsu R3809U) with an overall system response ~200ps while the emission wavelength was selected by interference filters (fwhm ~15nm).

2.4.4 Optical camera pictures

All camera pictures were taken by a Kodak digital camera attached to a microscope.

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3 P3HT:PCBM
Charge Recombination Dynamics

3.1 Abstract

The charge recombination dynamics in P3HT:PCBM blend films have been monitored by transient absorption spectroscopy over 5 orders of magnitude in time, from $\sim 10^{-8}$ to $10^{-3}$ s. The results reveal the presence of three distinct phases of recombination during this time, occurring on a ns, ns-$\mu$s, and $\mu$s-ms timescales. The three phases are distinguished by their differing responses to laser power intensity and by changes to the recombination dynamics following annealing on the blend film. The recombination on a ns timescale is tentatively
assigned to the recombination of geminate bound radical pairs generated across the interface by electron transfer. The subsequent phase (ns-µs) is assigned to the bimolecular recombination of mobile charges, while the final and slowest (µs-ms) phase of recombination occurs due to the presence of charge traps in the film which inhibit the recombination of charges.

3.2 Introduction

To date solar cells made from P3HT:PCBM are the most efficient of the conjugated polymer - PCBM (CP:PCBM) devices with reported efficiencies of 3.5%\textsuperscript{1}. For commercialisation however a higher power conversion efficiency (P.C.E.) than this is desired and so research is needed on understanding the parameters that limit the efficiencies of these devices. As mentioned in the introduction to this thesis, the recombination of photogenerated charges is a major device parameter that potentially limits not only the collectable current but the device fill factor and open circuit voltage in solar cells\textsuperscript{2}. The study of the charge recombination dynamics in P3HT:PCBM blend films therefore is needed in order to quantify recombination losses and to gain a better understanding of the parameters that control recombination in devices.

The charge recombination dynamics in CP:PCBM blend films and devices have received limited study to date with some conflicting reports in the literature. Transient absorption spectroscopy (TAS) is an optical characterisation technique where the decay of transient species created in the blend film is probed by their light absorption over time. TAS studies on P3HT:PCBM blend films on pico to millisecond timescales have revealed two time regimes for the recombination of charges. Following excitation at high laser powers (~2mJ/cm\textsuperscript{2} per pulse) a large percentage (~80%) of the charges created recombine within


the first 30ns, with the remainder of the decay recombining more slowly following a
power law expression \( (t^{-\alpha}) \) where \( \alpha=0.21 \), on much slower timescales. A similar nano-
second or quicker recombination was observed by time-resolved microwave conductivity
measurements on MDMOPPV:PCBM blend films where analysis of the signal magnitude
and decay suggest that approximately 30% of the initially formed charge carriers are lost
on a timescale before the resolution of the equipment (<18 ns). In both these reports the
recombination is proposed to be from the geminate recombination of charges before dis-
sociation of the charges at the interface.

Transient absorption studies on MDMOPPV:PCBM blend films on a nano to millisecond
timescale have also proposed two time regimes to the recombination decay. Similar to the
TAS studies on P3HT:PCBM, the recombination on a microsecond timescale onwards
was observed to follow a power law expression. The long-lived power law decay was
reported to be consistent with the slow recombination of charges caught in charge ‘traps’
where trap sites in the conjugated polymer inhibit the recombination process by
providing an unusually large stabilisation energy to the hole charge. The charges that
move into a trap have to wait a significant ‘de-trapping’ time before they are released and
can undergo recombination, thereby creating a long slow tail of recombination. Continu-
os-time random walk Monte-Carlo simulations based on the assumption of a small frac-
tion of trap sites added to an otherwise iso-energetic or gaussian distribution of MDMO-
PPV sites successfully recreated the behaviour of power-law decays.

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81(16): 3001-3003.

in Conjugated Polymer/Fullerene Blended Films Studied by Transient Absorption Spectroscopy." Journal of Physical Chemistry B
107(7): 1567-1573.

The transient studies on MDMOPPV:PCBM blend films also identified an additional quick recombination dynamic on a 40 nanosecond or quicker timescale which at high laser powers (>20µJ per cm² per pulse) accounted for the large majority of the signal decay. In contrast to the two previous reports on recombination on this timescale, the recombination was not assigned to geminate recombination but to the bimolecular recombination of charges as the amplitude of the recombination signal was found to be dependant on the pump fluence.

Besides optical characterisation, limited electrical characterisation of P3HT:PCBM solar cells has also been employed to study the recombination of charges. In the study, the high reported E.Q.E’s for these devices suggested an internal electron collection efficiency of near unity and that the charge losses due to bimolecular recombination in these devices were small\(^9\). A value for the rate of bimolecular recombination however was not reported.

In this Chapter the charge recombination dynamics in P3HT:PCBM blend films is studied by transient absorption spectroscopy on a ns-ms timescale in order to clarify the mechanics governing charge recombination losses in the blend films. P3HT:PCBM blend films fabricated in a similar fashion and made into devices have been shown to give good efficiencies\(^10\). As annealing of P3HT:PCBM devices is observed to be an important parameter to device efficiency\(^1,10\), changes to the recombination dynamics of the P3HT:PCBM blend film with annealing will also be studied.

---

3.3 Methodology

P3HT polymer was synthesised by Merck Ltd. following their own synthetic method\textsuperscript{11}. The polythiophene was bromine terminated with a molecular number average (Mn) and molecular weight average (Mw) of 2.8x10\textsuperscript{4} & 4.4x10\textsuperscript{4} respectively. The polydispersity index was 1.6. Polymer showed greater than 96% regioregularity as judged by nuclear magnetic resonance measurements and Ni and Mg impurities were both <10\textmu g/g each. PCBM was used as received from Nano-C Inc.. The samples were prepared as described in the Experimental methods chapter of this thesis. The data in Figure 3-2 was collected using a separate transient absorption system to those reported in the Experimental Methods and consisted of a nanosecond response silicon photodiode, a Nd-YAG laser (Ultra Nd:YAG BigSkyLaser Company) as the excitation source (532nm FWHM <6ns) and a 75W Xenon arc lamp as the probe source coupled to a single PTI model 101 monochromator after the sample. This system showed much less sensitivity than the ‘microsecond’ system (only \textasciitilde10\textsuperscript{-4} \Delta OD cf. \textasciitilde10\textsuperscript{-6} \Delta OD for the ‘microsecond’ set-up) but the typical system response was quicker being around a few tens of nanoseconds. Neutral density filters were used to modify the energy of the excitation source.

3.4 Results

3.4.1 Pristine P3HT transient absorption data film.

Pristine P3HT film transient data are given for later comparison with P3HT:PCBM blend films.

Figure 3-2. Pristine P3HT film recombination dynamics probed at 975nm at RT following excitation at 532nm (80µJ/cm²). Inset: RR P3HT transient absorption spectra taken at 77K, 10µs after excitation at 525nm with an energy 15µJ/cm² per pulse.

Figure 3-2 shows the time-resolved transient decay dynamics of a pristine RR-P3HT film taken at room temperature following excitation at 532nm and at a probe wavelength of 975nm. The decay is short lived and appears crudely first order with a half life of approximately 30ns. The inset shows the transient absorption (TA) spectra for a pristine RR-P3HT film taken at 77K, 10 microseconds after excitation. The transient absorption spectra is broad and shows a single peak at around 975nm (1.27eV).

The signal decay in the film of pristine P3HT is most likely to originate from the charged species P3HT⁺:P3HT⁻. Charged species formed following excitation have been reported previously for films of regioregular P3HT¹², while the absorption peak at 975nm is similar to that reported for delocalised positive charges in gate doped P3HT F.E.T’s¹³. The

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assignment of the spectra and decay to the charged species however over that of other potential transient such as the P3HT triplet, cannot be confirmed. Regardless of the assignment to the transient species, it is clear that optical excitation of pristine films at RT results in a short lived transient on a sub microsecond timescale.

### 3.4.2 Blend film transient absorption spectra

![Figure 3-3](image-url)

**Figure 3-3.** RR P3HT:PCBM (1:1 w/w) blend film transient absorption spectra taken at 77K, 10µs after excitation at 525nm (15µJ/cm² beam intensity). Inset shows the reported absorption spectra of the anion radical of a malonic ester methanofullerene \([\text{C}_{60}-\text{C}({\text{COOEt}})_{2}]\) obtained by pulse radiolysis; Ref.16.

In contrast to the short lived signal seen in the pristine P3HT film, P3HT:PCBM blend films show a much longer lived signal (see following figures) and a very different transient absorption spectrum. Figure 3-3 shows the transient absorption spectra for a P3HT:PCBM blend film taken at 77K, 10 microseconds after flash excitation. The absorption spectrum is broad and shows a single sharp peak at ~1020nm with a less well defined peak at 700nm. A broad absorption with a sharp absorption peak at ~1020nm is typical of fuller-

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ene anion moieties\textsuperscript{14,15}. For comparison the inset to Figure 3-3 shows the reported anion spectra of another methanofullerene which has a similar shape and peak absorption maxima\textsuperscript{16} to the P3HT:PCBM film. Oligothiophene cations have been reported to show absorption peaks at $\sim$700nm\textsuperscript{17}, however given the close similarity between this absorption spectra and those in the literature for fullerene anions\textsuperscript{14,15,18}, a contribution from the cation absorption to the spectra cannot be confirmed. The lack of any visible contribution in this case may be due to a smaller extinction co-efficient for the P3HT cation, than for the PCBM anion.


3.4.3 Blend transient absorption decay kinetics

Figure 3-4. Transient decay kinetics of a P3HT:PCBM (1:2 w/w) non-annealed blend film probed at 830nm following high (20µJ/cm² per pulse) and low (1µJ/cm² per pulse) intensity excitation at 560nm.

Figure 3-4 shows a normalised transient absorption decay typical for P3HT:PCBM blend films. Excitation was at 560nm at high (20µJ per cm² per pulse) and low (1µJ per cm² per pulse) excitation intensities while the absorption at the probe wavelength of 830nm is assigned to the PCBM anion. The signal decay in Figure 3-4 continues over 5 orders of magnitude in time, up to 10 milliseconds and beyond, in contrast to the very short lived decay seen in the pristine film. The decay signal can be divided into two time regimes based on the response of the signal to the employed excitation intensity. At early times (<2µs) the rate of signal decay shows a dependence on the excitation intensity, being much quicker following excitation at a high laser energy than at a low excitation energy. After a few microseconds in time there is a change in signal behaviour where the rate of decay becomes independent of the laser intensity used. This rate of decay follows a power law expression (t^{-\alpha}) which appears linear on a log-log plot. The contrasting rates of decay with respect to excitation intensity distinguish the recombination dynamics in the two time regimes and suggest two different recombination mechanisms. While precisely pinpoint-
ing the end of one recombination dynamic and the beginning of the other is difficult, typically the divide occurs around 2-3µs in time as shown by the dotted line.

**Figure 3-5.** Transient absorption decay for a P3HT:PCBM blend film (1:2 w/w non-annealed), probing the PCBM anion at 980nm. Excitation was at 450nm at different intensities. The decays at the highest and lowest excitation intensity are only partially resolved. Incident laser energy is in units of µJ per cm² per pulse.

Figure 3-5 shows a more detailed transient absorption decay from a similar P3HT:PCBM blend film. The decays were monitored at 980nm following excitation at 450nm using a range of laser energies covering two-orders of magnitude in difference. As explained previously, the decay in Figure 3-5 can be divided into two regimes. At early times (<<3µs), both the rate and amplitude of signal decay shows a clear dependence on the excitation intensity. After a few microseconds however the rate of decay become fixed, regardless of the employed laser intensity, and the amplitude of the signal saturates at excitation intensities of ~11µJ/cm² per pulse or above.
Figure 3-6. Transient absorption decay kinetics from Figure 3-5 on a nanoseconds to microsecond timescale. Excitation intensities are marked in the graph key and in units of microjoules per square cm per pulse. Decay data was fit to a bimolecular rate equation, with a rate constant $\kappa_{bi} = 4.5 \times 10^{10} \Delta \text{OD s}^{-1}$. Special boundary conditions had to be applied to get a confident fitting to the decays, where the top of the subsequent power law phase of recombination was used as the zero baseline for the bimolecular fit.

Figure 3-6 highlights the recombination data from Figure 3-5 on the earlier timescale of tens of nanoseconds to a few microseconds. As stated previously, on this timescale both the rate of the decay and amplitude of the absorption signal are excitation intensity dependant. For example, at the highest excitation intensity, where many charges are generated, the recombination on this timescale represents up to 70% of the overall signal size, while at the lowest excitation intensity, the recombination on this timescale is less than 10% of the signal size. A correlation between the rate of recombination and the concentration of charges is usually interpreted as relating to a second order or bimolecular rate of reaction;
Equation 3-1. Second order or bimolecular rate equation with respect to the signal amplitude ∆OD.

\[
-\frac{d}{dt}(\Delta OD) = k_{bi}[e][h]
\]

In Equation 3-1 [e] & [h] are the concentration of electrons and holes respectively (which are considered equal in this case), and \( k_{bi} \) is the calculated bimolecular rate constant. When fitting the signal decay to a kinetic equation, it would have been preferable to fit the decay data over the entire timescale of the experiment (ns-ms) to a single equation. In this case however, a better fit to the data was achieved by modelling both the early (ns-μs) and latter parts (~μs-ms) of the decay separately than by using a single equation for the entire timescale of the data. A reason why the two timescales give better fits when modelled independently and a justification for this method will be given in the discussion. In order to model the recombination at early times independently, the contribution to the signal amplitude from the latter stage of recombination had to be removed. This was achieved by adjusting the baseline for the decays to the amplitude of the signal belonging to the following recombination phase. After adjustment the recombination decays at early times show a good fit to a bimolecular rate equation (see Figure 3-6) with a bimolecular rate constant of \( k_{bi} = 4.5 \times 10^{10} \text{ OD s}^{-1} \). As the decays can be successfully fit to a bimolecular rate equation, the recombination on this timescale shall be labelled the bimolecular recombination phase. Later on in the discussion these rate values will be converted into standard units.
Figure 3-7. Transient absorption decay kinetics from Figure 3-5 on a microsecond timescale onwards. Excitation intensities are marked in the graph key and in units of microjoules per square cm per pulse. The decay for the highest excitation intensity (black line) is incomplete but the decay is expected to be analogous to that of the orange or green line while the decay at the lowest excitation (red line) is incomplete due to noise on earlier time scales.

Figure 3-7 shows the latter stage of the transient absorption decay kinetics from Figure 3-5 on a few microseconds to longer than milliseconds time scale. The decay is linear on a log-log plot which can be represented with a power law equation $\Delta \text{OD} \propto t^{-\alpha}$, with a power law exponent of -0.28. Note on a log-log plot the exponent represents the slope of the decay. Similar power law recombination decays on this timescale has been seen previously for MDMOPPV:PCBM blend films$^5,6$. In those reports the origin of the long-lived power law decay is explained as arising from the ‘trapping’ of the hole charges in the polymer material which inhibits the bimolecular recombination of charges. In the previous reports the assignment of the power law decays to the presence of traps was established by experiments on MDMOPPV:PCBM blend films. For MDMOPPV:PCBM, the power-law recombination was found to be insensitive to PCBM concentration, was inhibited at lower temperatures and accelerated in the presence of a bias white light$^6$. For white-light
illumination, a steady state population of charges permanently occupy the deepest traps in the blend film, and so the additional ‘flash’ created charges can only occupy shallower trap sites and the observed power law decay is accelerated. A similar experiment was carried out on P3HT:PCBM films and a similar effect observed as shown in Figure 3-8.

![Figure 3-8](image.png)

Figure 3-8. Effect of steady state white light (130µW/cm²) on the power law charge recombination dynamics for a P3HT:PCBM (1:2w/w) annealed film. Probe wavelength was 980nm and excitation was at 450nm. Excitation intensity is in units of µj per cm² per pulse.

Potentially other recombination processes are known to follow a power law, such as the geminate recombination of charges in blends of organic chromophores and inert polymers which causes delayed fluorescence¹⁹. However in this case delayed geminate recombination could not be the cause of the power law, as that recombination mechanism would not show signal saturation at higher excitation intensities nor show a dependence on the presence of white light bias as is seen for the power law decay in these blends.

Figure 3-9 is a density of states picture and portrays the energy distribution of hole polaron sites in the polymer phase. The gaussian distribution represents the energy of the majority of polaron sites close to or above the transport level in the polymer while an exponential distribution of deep in energy sites below the normal gaussian distribution of states\textsuperscript{20}, represent the trap states that give rise to the observed power law decay. The observed saturation at higher laser powers in the amplitude of the power-law signal occurs when the number of generated polarons fills all the traps present in the film and any excess charge carriers are lost to a quicker phase of recombination.

As an aside, it is worthy of note that while the energy of the trap sites follows overall an exponential distribution (hence giving a power-law decay), the appearance of an exponential distribution can be simulated by two or more gaussians distributions of different energies (see right side of Figure 3-9). In this manner the traps in the film can be considered to consist of more than just one type of trap (e.g. chemical defect) and can be represented

by two or more different types of traps (e.g. chemical and structural) of different energies and with gaussian distributions. Such a method is employed successfully by Nelson in simulation of charge movement through trap sites in TiO$_2^{21}$.

![Graph showing signal amplitude versus incident laser intensity.](image)

**Figure 3-10.** Plot of the signal amplitude versus incident laser intensity for the data in Figure 3-7 taken at 1 millisecond after excitation.

Figure 3-10 plots the signal amplitude at 1 millisecond against the excitation intensity employed. While at high laser excitation intensities, as mentioned previously, the amplitude of the power-law decay saturates due to trap filling, at lower laser excitation intensities before the onset of saturation, it is also clear that the signal amplitude scales sub-linearly with respect to the laser excitation intensity. For instance, comparing the decays for the 0.4 and 4µJ/cm$^2$ pulse energies, the increase in signal amplitude at a millisecond is only a factor of two and a half, despite using an order of magnitude greater laser intensity. The bimolecular loss of charges cannot account for this missing signal amplitude, as at the very low flash intensities used (<4µJ/cm$^2$ per pulse), bimolecular recombination losses are small (<10%; see Figure 3-6). Neutral excited state annihilation could explain the sublinear dependence on laser intensity however given the very low light intensity this is unlikely. The sublinear dependence on excitation intensity therefore may be the result

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of another recombination dynamic that precedes both the power law and bimolecular recombination regimes.

3.4.4 Effects of annealing

As was highlighted in the introduction, annealing treatment to P3HT:PCBM devices plays a critical role in achieving higher efficiencies\(^1\). In this section the changes to the transient absorption decays with annealing of the blend film will be investigated.

![Figure 3-11](image-url)  
**Figure 3-11.** UV-Vis absorption spectra and PL spectra for a non-annealed and annealed (1:2 w/w) P3HT:PCBM blend films. Excitation wavelength for the PL spectra was at the film absorption maximum.

Figure 3-11 shows the absorption and photoluminescence (PL) spectra for non-annealed and annealed (140\(^0\)c for 15 minutes) P3HT:PCBM blend films. The UV absorption spectra in the non-annealed (as-spun) film is broad and centred at 450nm with only a weak shoulder at ~602nm. With annealing there is a red-shift in the P3HT absorption maxima to ~510nm, the formation of a shoulder at ~550nm and a strengthening of the shoulder at 602nm. The PL from conjugated polymers is efficiently quenched in the presence of PCBM due to ultrafast electron transfer to the fullerene\(^{22,23,24}\). Despite a large concentra-
tion of PCBM in these blends, some P3HT photoluminescence remains unquenched in the as-spun (non-annealed) film due to the radiative decay before migration of the exciton to an interface with PCBM. Following annealing of the blend film an increase in PL yield is observed which suggests that more excitons are radiatively decaying and subsequently less charge splitting of excitons. The observed changes to the absorption and PL spectra will be explained in greater detail in the following chapter of this thesis but are respectively a result of greater packing of the P3HT backbones and an increase in the phase segregation of the polymer and fullerene.


Figure 3-12. Transient absorption decay for a (1:2w/w) P3HT:PCBM film which has been given annealing treatment at 140°C for 15 minutes. Probe wavelength was 980nm and excitation was 450nm at various laser intensities. Key units are in incident photons per cm² per pulse. (a) Transient decay from ns-ms. (b) Transient decay on a tens of ns to microseconds timescale fitted with bimolecular decay kinetics. The calculated bimolecular rate constant is $k_{bi}$ of $1.4 \times 10^{10} \Delta OD s^{-1}$. 
Figure 3-12 (a) shows the decays (ns-ms) for a P3HT:PCBM blend film following annealing at 140°C for 15 minutes. The decay kinetics for the annealed film look qualitatively similar to the non-annealed film (as-spun). As before for the non-annealed film, the decay on a timescale of tens of ns to microseconds can be fit to bimolecular decay kinetics, yielding a confident fit with a rate constant \(k_{bi}\) of \(1.4 \times 10^{10} \Delta \text{OD} \text{s}^{-1}\) (see Figure 3-12 b). For the power-law decay there are small changes to the exponent of the power law, which becomes larger (from -0.28 to -0.30) and to the signal amplitude at the onset of the power law which also increases by ~10%. (Note that larger changes are observed for films in the following chapter in this thesis and these observations are given here only for completeness). The most significant effect of annealing on the film however, is the near two-fold increase in the signal amplitude at near the system resolution.

![Figure 3-13](image)

**Figure 3-13.** Decay of the transient absorption signal at 980 nm in the as-spun (non-annealed) and annealed condition films following excitation at 450 nm with an intensity of \(~11 \mu \text{J/cm}^2\) pulse.

Figure 3-13 highlights the increase in signal amplitude after annealing of the blend film. The rise of the polaron absorption signal is system limited as would be expected when the photogeneration of charges in these blends is thought to occur on an ultrafast timescale (<200ps)\(^3\). This increase in signal amplitude cannot be explained by an increase in absorp-
tion of the flash energy as after annealing the film absorbs fewer photons at the excitation wavelength (see Figure 3-11). Neither is the increase in signal amplitude consistent with an increase in the extinction co-efficient as firstly; the increase in signal amplitude with annealing is not consistent over the range of laser powers used and at higher laser intensities a smaller increase in signal size is observed than at lower laser powers (40% cf. 100%). This would not be the case if the increase in signal amplitude was due to a simple increase in extinction co-efficient. Secondly, the rate of signal decay for the annealed film is faster than that for the non-annealed film, which is inconsistent with an increase in extinction co-efficient but is consistent with an increase in the number of polarons.

The increase in signal amplitude with annealing therefore represents a real increase in the number of polarons observed at the system resolution. As charge generation is already thought to be very efficient this change can only be explained by a reduction in recombination losses with annealing. A recombination dynamic therefore must precede the bimolecular recombination phase in time and annealing treatment must have a large effect on reducing the yield of this recombination. Previously the presence of such a recombination dynamic was predicted from the sub-linear increase in the amplitude of the power-law signal with excitation intensity.
Figure 3-14. Transient decay kinetics for a P3HT:PCBM (1:2 w/w) non-annealed blend film made from a chlorobenzene solution, probed at 830nm following excitation at 520nm. The number of incident photons are in units of microjoules per cm\(^2\) per pulse. Film absorbance at the excitation wavelength was 0.15.

Figure 3-14 shows a transient decay from a P3HT:PCBM blend film (1:2 w/w non-annealed) where the presence of an additional recombination dynamic (<40ns) is visible at higher laser powers. At the lowest laser intensity the additional recombination cannot be seen but increases in amplitude with increasing excitation intensity. Note that the rate of signal decay before 40ns is instrument limited and appears symmetrical to the signal rise. While the rate of decay is instrument limited the amplitude of the signal at the system time response is unaffected.
Figure 3-15. Normalised transient decay for a P3HT:PCBM (1:2w/w) blend film made from dichlorobenzene solution before annealing and following cumulative annealing treatment at 75°C and then 140°C for 6 minutes each. Incident excitation intensity was 19 µJ per cm² per pulse at 550nm and the probe wavelength was at 830nm. Film absorption at the excitation wavelength was ~0.15.

The effect of film annealing on the amplitude of the sub 40ns decay phase is shown in Figure 3-15. The transient dynamics were measured on a single film before annealing (red), after annealing for 6 minutes at 75°C (black) and then after further annealing for 6 minutes at 140°C (green). The decays seen in Figure 3-15 are similar to those in Figure 3-14 seen at high laser powers. Following annealing treatment on the film, relatively less of the signal amplitude is lost to the sub 40ns recombination, increasing the signal associated with the subsequent recombination phase.
3.5 Discussions

3.5.1 Recombination dynamics in P3HT:PCBM blend films.

From the above data, evidence for three different recombination phases in P3HT:PCBM blend films from a nanosecond to millisecond timescale have been observed. Each of the three recombination dynamics will be approached in turn and their relevance to the working of solar cell devices discussed. The effects of annealing on the recombination dynamics will also be discussed.

To begin at the end, the latter phase of recombination seen from microseconds onwards in the transient absorption decays is consistent with a trap-limited recombination process. When a hole in the polymer phase occupies a trap site, the further movement of the charge is inhibited by an energy barrier and so the recombination becomes dominated (limited) by the de-trapping step of charges. The assignment of the decay to a trap-limited process is consistent with the effect of white light bias on accelerating the recombination kinetics, the saturation of the trap signal amplitude at high laser powers and with previous reports in the literature on MDMOPPV:PCBM\textsuperscript{5} and reports published since this work on CuPC:PTCDA\textsuperscript{25} blend films. The number of charges that undergo recombination following de-trapping, and hence the number of trap sites, can be determined from the amplitude of the saturated trap limited signal. This can then be correlated to an absolute number of trap sites by the Beer-Lambert law using the molar absorption extinction co-efficient for the PCBM anion at that wavelength.

An estimate for the absorption co-efficient for the PCBM anion at 980nm can be obtained from the data in Figure 3-13 on page 76 for the annealed film. Assuming all absorbed photons generate polarons and that any recombination before the system resolution is negligible, then the maximum amplitude of the signal is related to the number of absorbed photons by the film. The full calculations are given in the appendix however in short, an absorption signal of $4 \times 10^{-4} \Delta O D$ equates to $1.2 \times 10^{13}$ polarons per cm$^2$ which yields an extinction co-efficient at 980nm for the PCBM anion of 20,000 L M$^{-1}$ cm$^{-1}$. The value of 20,000 L M$^{-1}$ cm$^{-1}$ for the PCBM anion at 980nm is comparable to reported values in the literature, for a similar methanofullerene anion $\sim 10,000$ L M$^{-1}$ cm$^{-1}$ 26 and the C$_{60}$ anion $\sim 12,000$ L M$^{-1}$ cm$^{-1}$ 18. The difference between the calculated value and those in the literature may be explained by a possible contribution from the polymer cation to the signal amplitude which leads to an overestimate for the PCBM extinction co-efficient.

Returning to the initial calculation of the number of traps in the blend film, using this extinction co-efficient, and a signal amplitude maximum of $\sim 9 \times 10^{-5} \Delta O D$ for the trap limited decay (non-annealed film), the number of traps is calculated to be $\sim 3 \times 10^{12}$ for a blend film approximately 100nm thick or $\sim 3 \times 10^{17}$ per cm$^3$. This value is similar to the previously reported number of charge traps in a MDMOPPV:PCBM blend films of $\sim 10^{17}$ per cm$^3$ measured also by TAS 5. This value may seem large however the total number of P3HT monomers is $10^{21}$ per cm$^3$ and traps therefore are only 0.03% of the sites in the film 27 and represent a very small minority of the potentially occupiable sites. Assuming a homogeneous distribution for traps throughout the film, then on average each trap is $\sim 30$nm apart.

27. Assuming a density of 1gcm$^{-3}$ for P3HT (mol.weight 164g mol$^{-1}$)
The recombination on a tens of nanoseconds to microsecond timescale precedes the trap limited recombination phase. The rate of decay on this timescale was found to be excitation intensity dependant and could be well fitted to a second order bimolecular rate equation. On this evidence the recombination on this timescale is assigned to the recombination of free-moving (mobile) charges within the blend. Previously, for the fitting of the decay kinetics the recombination on this timescale was deemed to be independent of the following power law phase. The justification for such an analysis is now clear, as the power law recombination represents immobile trapped charges, the number of trapped charges would naturally play no part in the recombination of freely mobile charges.

This is the first report to date where the bimolecular rate constant for the recombination of charges has been calculated from direct measurements and not inferred from secondary measurements. The calculated rate constant $k_{bi}$ for the non-annealed P3HT:PCBM film is $9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ ($1.5 \times 10^{-11} \text{cm}^3 \text{s}^{-1}$) where after annealing the recombination rate constant decreases slightly to $3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ ($5 \times 10^{-12} \text{cm}^3 \text{s}^{-1}$). The bimolecular recombination constant for the annealed P3HT:PCBM film reported here is in reasonable agreement with a report subsequently published in the literature of $2 \times 10^{-13} \text{cm}^3 \text{s}^{-1}$ as measured by the photocell technique\textsuperscript{28}. The slight difference between the photocell and transient absorption values, as well as the difference between the rate constants for the non-annealed and annealed films as measured by TAS is explained as due to possible differences in blend film morphology as will be argued below.

Bimolecular recombination in solar cells is often associated with the equation by Langevin. For pristine single materials of a low di-electric constant Langevin predicted that the bimolecular recombination co-efficient would be related to the sum of the hole and electron mobilities;

\[ \beta_L = \frac{q}{\varepsilon} (\mu_e + \mu_h) \]

Equation 3-2. Relation between the Langevin recombination co-efficient and charge mobilities.

where \( q \) is the elemental charge, \( \varepsilon \) is the material di-electric constant and \( \mu_e \) (\( \mu_h \)) are the electron (hole) mobility. From second order fits to the TAS data reported here the bimolecular recombination rate constant decreases slightly following annealing treatment, \( k_{bi} \approx 5 \times 10^{-12} \text{cm}^3 \text{s}^{-1} \) compared to \( k_{bi} \approx 1.5 \times 10^{-11} \text{cm}^3 \text{s}^{-1} \) for the non-annealed film. This is in contrast to the increase predicted following Langevin recombination, as annealing improves carrier mobilities by orders of magnitude in both the P3HT\(^{29}\) and PCBM\(^{4}\).

The apparent breakdown of the Langevin relation seen here, is in agreement with reports in the literature published subsequent to this work where deviation from Langevin recombination has been seen in the results of device modelling\(^{30}\) and in recent studies using the electrical photo-CELIV technique\(^ {28}\). A possible answer to why the recombination in these organic bulk heterojunction solar cells does not follow Langevin behaviour may come from the unique blending of two components. Instead of free movement in these blend films, the charges are confined to their own polymer or PCBM phases, with recombination only possible across an interface. The presence of the interface therefore may be more dominant in controlling the bimolecular rate constant than the mobility of charges. This emphasises the opportunity that control over the blend morphology could offer for device efficiencies.


The last recombination dynamic to be discussed precedes in time both the recombination of free mobile charges and the recombination of trapped charges. As this recombination precedes the trapping of charges physically, the recombination process must occur before separation of the charges at the interface. The geminate recombination of charges, where charges are lost before the radical pair can separate at the interface, is an ideal candidate for this kind of recombination.

This is not the first report to suggest the geminate recombination of charges in CP:fullerene films. From ps-ms transient absorption studies of P3HT:PCBM blend films, Meskers suggested that a nanosecond timescale geminate pair recombination accounted for up to 80% losses to charges in the film. Geminate recombination of charges on a <20ns timescale has also been inferred from time resolved microwave conductivity studies as the cause of substantial photoconductivity losses in both MDMOPPV:PCBM and subsequent to this work, P3HT:PCBM blend films also. The presence of a geminate pair is also a crucial element in the model of charge generation at polymer:polymer D-A interfaces proposed by Morteani et al at Cambridge University.

Monte-Carlo simulations have suggested that the low mobility of charges in polymer:fullerene blends is the prime reason for geminate recombination. The simulations suggest that the separation of the bound pair is limited by the mobility of the charge slowest away from the interface, typically the hole mobility, and the yield of geminate recombination at the interface therefore can be minimised in materials of high charge mobilities and of balanced hole and electron mobility. From the simulation results a change in hole

mobility therefore could explain the inferred decrease in geminate recombination in P3HT:PCBM blend films following annealing (see Figure 3-13). As annealing is known to improve the P3HT hole mobility in P3HT:PCBM blends by several orders of magnitude, the increase should lead to a reduction in geminate recombination losses.

The model proposed by Offermans and later developed by Koster also suggests that the separation of geminate pairs at the interface can be hindered by their environment, whereby following some initial charge separation, space-charge effects would then oppose further formation of separated charges. For transient experiments this suggests that the stronger the initial flash excitation, the lower will be the efficiency of successful geminate separation and a greater proportion of the signal amplitude that will undergo geminate recombination. This prediction describes very well the behaviour of the sub 40ns recombination dynamic seen in Figure 3-14, where little recombination is seen at low laser powers but a large proportion of the signal amplitude is lost at higher laser intensities. The <40ns very fast recombination dynamic seen at higher laser powers in Figure 3-14 therefore is potentially also assigned to geminate recombination. The assignment of the <40ns recombination dynamic at higher laser powers to geminate recombination is also consistent with the reduction in signal losses seen with annealing of the blend film in Figure 3-15.
To gain a potential estimate for the rate of geminate recombination, the transient signal decays from Figure 3-14 have been fit to a geminate and then a subsequent bimolecular recombination decay (Equation 3-3).

\[-\frac{d}{dt}(\Delta OD) = k_{bi}[e][h] + k_{mono}[e]\]

**Equation 3-3.** Simultaneous second order and first order equation with respect to the signal amplitude \(\Delta OD\).

Note that for the fitting, geminate recombination was estimated to be a first order decay process with a fixed rate of recombination and that the first and second order processes should have individual initial values. The results of the fitting were successful (see Figure 3-16) giving the results of \(k_{bi} \sim 3.3 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}\) & \(k_{GR} \sim 3 \times 10^{8} \text{s}^{-1}\). The value for \(k_{bi}\) is similar to that seen for the other P3HT:PCBM blend films in this chapter while the rate of geminate recombination is in good agreement with that proposed by Offermans of \(k_{GR} \sim \text{ns}^{-1} (1 \times 10^{9} \text{s}^{-1})\).
3.5.2 Implications of recombination on device efficiency

As devices working at maximum power output will ideally be near $V_{oc}$, the recombination dynamics in devices can be expected to behave similarly to those reported here for blend films without the presence of electrodes.

Analysis of the TAS data provides a direct measure of the bimolecular rate constant ($k_{bi}$) in solar cell devices. A quantitative comparison of the bimolecular recombination in films of different morphologies, component composition or even of different donor polymer are therefore possible. This will allow different blend morphologies or polymer materials to be screened effectively for possible high bimolecular recombination losses without the need for device fabrication. Using the bimolecular rate constant reported in this chapter ($\sim 3 \times 10^{9} \text{M}^{-1}\text{s}^{-1}$) and assuming an approximate steady state density of $10^{16}$ charges in the device working under one sun, then the average charge lifetime can be roughly estimated to be 0.1s. An upper limit for the diffusion distance of charges with this lifetime can then be calculated by using the Einstein relation, which assuming a hole mobility of $10^{-4} \text{cm}^{2}/\text{Vs}$ gives a diffusion distance for the charges of $7 \times 10^{-6} \text{m}$. The long diffusion distance for the charges therefore suggests that bimolecular recombination losses in devices will be small, in agreement with the high E.Q.E values reported for P3HT:PCBM devices.

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35. The diffusion distance may be overestimated by orders of magnitude when using the Einstein relation if the charge mobility shows dispersive behaviour.
The geminate recombination of charges on the other hand, may be a significant recombination mechanism. In this study the geminate recombination of charges has been inferred to occur even at low excitation intensities representative of solar illumination levels. For instance geminate recombination accounted for at least 50\% of the charge recombination losses in the non-annealed P3HT:PCBM film following excitation at only 4\(\mu\)j/cm\(^2\) per pulse. From the results in this chapter however it is hard to quantify how efficient geminate recombination would be in a working device and further experiments are needed.

While for the TAS studies, the presence of traps dominates the recombination response at low excitation intensities, it is unclear if the long lifetime of trapped charges has much bearing on the rate of recombination in working devices under steady state white light illumination. Slow recombination kinetics are desirable so that charges can reach the electrode and provide useful current before a recombination event can occur. The long lifetime of a charge in a trap therefore is not beneficial as although the charge may live longer, the charges effective mobility is zero. The charge therefore makes no progress towards an electrode while in the trap and in order to continue on its journey to the electrode must occupy sites closer to the transport level in the polymer where bimolecular recombination is dominant.

While not likely to affect the rate of recombination, the long lifetime of charges in traps mean that under steady state illumination trap sites will effectively be permanently occupied. As polymer-fullerene devices are regarded as being space-charge limited\(^39\), where the collection/injection at the electrodes is faster than the mobility of the charges, the increasing space-charge build up may slow-down the mobility of charges, affecting the device fill factor and may also have a negative impact on the charge separation rate of

geminate pairs. In the following chapter in this thesis, the effect (if any) of charge trap sites on device characteristics will be discussed further.

### 3.6 Conclusions

Transient absorption spectroscopy has proved to be an exemplary technique in the observation of charge recombination in P3HT:PCBM blend films. TAS allows the determination of three distinct charge recombination mechanisms, monomolecular recombination of geminate pairs, the bimolecular recombination of free charges and finally the drawn-out recombination of charges that occupy trap sites in the blend film.

For non-annealed P3HT:PCBM films geminate recombination accounts for at least 50% of the charge recombination losses (at 4µJ per cm² per pulse or greater). With annealing of the blend film the efficiency of geminate recombination is reduced, possibly due to the increased hole mobility in P3HT. The rate of geminate recombination in P3HT:PCBM films is estimated to be \( \sim 10^{9} \text{s}^{-1} \).

The bimolecular recombination rate constant for P3HT:PCBM 1:2w/w blend film is found to be \( \sim 10^{9} \text{M}^{-1}\text{s}^{-1} \), but differs slightly between the non-annealed \( (9.0 \times 10^{9} \text{M}^{-1}\text{s}^{-1}) \) and the annealed blend films \( (2.8.0 \times 10^{9} \text{M}^{-1}\text{s}^{-1}) \).

The density of traps in P3HT:PCBM blend films is estimated to be \( \sim 10^{17} \text{cm}^{-3} \). It is speculated that charge traps in the polymer only present a hindrance to the mobility of holes through the blend and do not regulate the recombination in the device.
The PCBM anion extinction co-efficient is calculated to be a ~20,000 LM\(^{-1}\)cm\(^{-1}\) at 980nm.

### 3.7 Appendix

#### 3.7.1 Calculations for the absorption co-efficient of PCBM anion at 980nm.

For identification of the absorption at 980nm to the PCBM anion see Figure 3-3 on page 63. Assuming no recombination before the timescale of the equipment then an absorption of 4\(\times\)10\(^{-4}\) ΔOD is equivalent to 1.2\(\times\)10\(^{13}\) polarons (assuming quantum yield for exciton splitting is 1);

\[
A = \varepsilon_{980} \times C \times L
\]

**Equation 3-4.** Beer Lambert Law.

where \(\varepsilon_{980}\) is the extinction co-efficient at 980nm, L is the beam path length and thickness of the film, approximately 100nm, and C is the concentration of polarons in units of ML\(^{-1}\). 1.2\(\times\)10\(^{13}\) polarons in a 100nm thick film of 1cm\(^{2}\) surface area is equivalent to 1.2\(\times\)10\(^{18}\) polarons per cm\(^{3}\) and 1.2\(\times\)10\(^{21}\) polarons per L. Sharing this value with the Avogadro’s number gives us the moles of polarons per litre 2.0\(\times\)10\(^{-3}\) ML\(^{-1}\). With an absorption value of 4\(\times\)10\(^{-4}\) ΔOD the resulting extinction co-efficient value becomes 20,000 L M\(^{-1}\)cm\(^{-1}\).
The Effect of Regioregularity and Chain-end Functionalisation on the Properties of P3HT:PCBM Blend Films

4.1 Abstract

The effects of the degree of polymer regioregularity or the presence of bromine or methyl functionalised ends (cf. hydrogen ends) to the polymer chains on the properties of P3HT:PCBM blends in the spun cast state and following annealing treatment (140°C, 2 hours) has been studied. Decreasing regioregularity was found to have negative effects on the packing and crystallinity of P3HT, along with increasing the density of traps and their average depths. The addition of a bromine or methyl chain end group showed only a
minor effect on packing structure and crystallinity compared with regioregularity, however the presence of functionalised chain ends caused a substantial increase in trap densities.

4.2 Introduction

Studies have revealed that the morphology of CP:PCBM blend films plays a significant role in device efficiencies. To date, the effects of solvent\textsuperscript{1,2}, PCBM weight composition\textsuperscript{2} and the effect of annealing treatment on device efficiency\textsuperscript{2,3} have been related to differences in the blend film morphology. Despite the crucial role of film morphology, no reports in the literature have explored the potential for optimisation of the blend morphology by modification of the polymer component. Of potential modifications, the polymer regioregularity or chain terminating end-group are parameters most easily changed as part of the synthesis.

Highly regioregular (RR)-P3HT is commonly used in F.E.T’s due to its relative high hole mobility for a conjugated polymer, up to 0.1cm\textsuperscript{2}/V s \textsuperscript{4,5}. The mobility values have been shown to vary by orders of magnitude however, depending on the morphology of the P3HT\textsuperscript{6,7,8}. It is clear that for the highest mobilities, a high P3HT regioregularity is desirable, as this favours the formation of highly ordered packing domains and crystalline P3HT. For instance, Sirringhaus et al reported that a low degree of regioregularity (~81%), has large detrimental effects on the FET mobility compared to a 96% RR film\textsuperscript{6}.

\begin{thebibliography}{9}
  
  
  
  
  
  
\end{thebibliography}
The high mobility of regioregular P3HT is attributed to the effective alignment and close stacking of the conjugated polymer backbones which leads to the effective delocalisation of the polaron charge over neighbouring chains. Unlike in more disordered conjugated polymers where the cation is solely localised on a single chain (intramolecular), the delocalisation of the charge in P3HT increases both the polarons effective radius and reduces its relaxation energy. These factors improve the phonon-assisted hopping of charges from site to site by circumventing obstacles that might stop movement along a single chain and by reducing the energy barrier to movement\(^9\). Conversely, too high a degree of crystallinity can also be detrimental to mobility, as the formation of grain boundaries between crystallites are thought to provide an obstacle to charge transport\(^7,10\). Instead a P3HT with a high degree of long range order but without sharp distinctions between crystalline boundaries is the most favourable for transport\(^7,11\).

Highly regioregular P3HT may bring about further improvements in device performance besides improving charge collection. As reported in a previous chapter, the increasing regioregularity of P3HT also leads to lower geminate recombination losses by improving the mobility of the positive polaron away from the interface\(^12\). This potentially may be a crucial factor on device performance, as reports in the literature have suggested that the geminate recombination of charges is a limiting factor to solar cell device efficiency\(^13\).

The presence of end-groups on polymer chains can also lead to steric or electronic effects on material properties. For instance, the addition of hexyl-alkyl and styryl chain ends to oligothiophene in F.E.T’s has been reported to be beneficial to stability and the hole

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\(^7\) Kline, R. J., M. D. McGehee, E. N. Kadnikova, J. S. Liu and J. M. J. Frechet (2003). "Controlling the field-effect mobility of regio-


\(^10\) Horowitz, G., M. E. Hajlaoui and R. Hajlaoui (2000). "Temperature and gate voltage dependence of hole mobility in polycrystal-


mobility by adapting the orientation of the oligothiophene backbone\textsuperscript{14,15}. The use of bulky end-caps at the ends of polyfluorene chains has been used to prevent chain stacking in polyfluorenes\textsuperscript{16,17} and excimer emission in OLED’s while the addition of an amine end-group to polythiophene leads to improvements in polythiophene - Cadmium Selenide (CdSe) device efficiencies by enhancing the fine scale mixing of components\textsuperscript{18,19}. While the above examples illustrate the potential effects of end-groups, a previous report found only negligible effects of methyl or bromine end groups on the hole mobilities\textsuperscript{7} of pure P3HT FET’s. The presence of methyl or bromine polymer end-groups however may effect other blend properties such as light-absorption, PL quenching or the density of charge traps present in the film.

In this chapter three different regioregularity P3HT polymers (90.7\%, 93\%, 95.2\%RR) with standard hydrogen end caps and P3HT polymers of high RR (~95\%) but with different polymer chains end-groups, namely bromine or methyl, will be studied in blend films with PCBM. The effect of P3HT regioregularity and end-group on the changes with annealing of the blend films will also be studied. Finally correlations between blend film properties and device properties will be drawn. The high overall regioregularity of the polymers (>90\%) used for this study is appropriate as a high hole mobility is required for efficient solar cell devices. As the change in regioregularity corresponds to a decrease in irregular couplings from 1 in every 11 monomers to 1 in 20 monomers along the chain, nearly a factor of two difference, large changes for the range of regioregularity under study are expected.

\begin{itemize}
\end{itemize}
4.3 Methodology

All polymers were synthesised by Merck following their own synthetic method\textsuperscript{20}. The level of impurities were Ni<2\(\mu\text{g/g}\) and Mg<50\(\mu\text{g/g}\). The 90.7\% regioregular P3HT polymer was hydrogen terminated with a weight average molecular weight (Mw) of 4.59\(\times\)10\(^4\) and a number average molecular weight (Mn) of 2.37\(\times\)10\(^4\). The polymer PDI was 1.9 with a melting transition temperature (Tm) found by differential scanning calorimetry (DSC) to be 203\(^\circ\text{C}\). The 93\% regioregular P3HT was hydrogen terminated with a Mw 3.19\(\times\)10\(^4\) and Mn 1.78\(\times\)10\(^4\), PDI of 1.8 and a Tm of 211\(^\circ\text{C}\). The 95.2\% regioregular P3HT was hydrogen terminated with a Mw 2.19\(\times\)10\(^4\) and Mn 1.42\(\times\)10\(^4\), PDI of 1.5 and a Tm of 212\(^\circ\text{C}\). The methyl end capped P3HT polymer was 94.9\% regioregular with a Mw 4.21\(\times\)10\(^4\) and Mn 2.39\(\times\)10\(^4\), PDI of 1.8. The bromine end capped P3HT polymer was 94.3\% regioregular with a Mw 4.49\(\times\)10\(^4\) and Mn 2.55\(\times\)10\(^4\), PDI of 1.8.

Blend solutions (P3HT:PCBM 1:1 by weight) were prepared using chlorobenzene with a solid concentration of 60mg/ml. These solutions were spin-coated at 1500rpm for 30seconds onto quartz substrates (Spectrosil B), followed by soft-baking at 50\(^\circ\text{C}\) for 15min. The thickness of as-coated blend films was ~200 nm. Polymer solar cell fabrication was as described in the methodology chapter of this thesis. Note the film and device annealing for the samples in this chapter was carried out at 140\(^\circ\text{C}\) for 2hr inside a nitrogen filled glove box. All measurements were carried out as described in the Experimental methods chapter of this thesis except for the device characterisation which was done by Y.Kim with the results published in his doctoral thesis\textsuperscript{21}.


4.4 Results

The results section is broken into two, such that the effects of P3HT regioregularity and chain end functionalisation to the blend film properties can be considered separately. Each of these sections contains both optical measurements (U.V. absorption & PL spectra), digital microscope pictures of the surface of the film and TAS data. Discussion of the data and implications on device performance will follow the results section.

4.4.1 Polymer regioregularity effects (90.7%, 93%, 95.2% RR)

4.4.1.1 Optical measurements and digital microscope pictures

![UV-Vis absorption spectra of a series of P3HT:PCBM blend films of decreasing P3HT regioregularity. The peak at 602nm is assigned to an interchain electronic transition where the exciton is intermolecular and is delocalised over neighbouring chains.](image)

Figure 4-2. UV-Vis absorption spectra of a series of P3HT:PCBM blend films of decreasing P3HT regioregularity. The peak at 602nm is assigned to an interchain electronic transition where the exciton is intermolecular and is delocalised over neighbouring chains.

Figure 4-2 shows the absorption spectra for the series of P3HT:PCBM blend films of decreasing P3HT regioregularity. In the highest regioregularity P3HT blend three features are clearly pronounced in the absorption spectra; a peak at ~500nm, with shoulders at ~550nm and ~602nm$^{22}$. With decreasing regioregularity the absorption spectra
becomes less structured and the absorption maximum becomes blue-shifted. The blue shifting of the absorption maxima in conjugated polymers is usually attributed to a disruption to the delocalisation length of the conjugation across the chain, raising the energy of the chromophore. Likewise the shoulders to the absorption spectra become less clear due to broadening of the absorption peaks as the chromophores adopt varying lengths. The lowest energy peak in the absorption spectra at ~602nm seen in all films is assigned not to the 0-0 intrachain transition in P3HT but to an interchain excitation transition where the exciton is delocalised between chains. As such this transition does not show a blue shift in energy with disorder but the intensity of the transition relates to the level of favourable chain on chain packing in the films. The lower regioregularity blend films show a less intense interchain excitation peak compared to the high regioregularity blend film which again is an indication of greater disorder in the P3HT and subsequently fewer possible interchain interactions. Note that the blend film with even the highest RR P3HT shows some signs of disorder in the blend film compared to that of a pristine P3HT film attributed to the addition of PCBM.


Table 4-1. P3HT regio-regularity effects on blend film properties.

Table 4-1 compares the important optical data (U.V. absorption & PL spectra) for all of the blend films of decreasing regioregularity, annealed and non annealed. The annealed films compared to their non annealed counterparts, show a large red-shift in the absorption maxima however the annealed films still follow the same trend with the lowest regioregularity P3HT showing the most blue-shifted absorption peak.

Another useful indication of the general level of order in the P3HT is to look at the photoluminescence (PL) maximum of the blend film. As P3HT excitons will favourably migrate to the lowest energy chromophore the PL can be used to measure the level of disruption to emitting chromophores. All films showed a similar shape to the PL spectra with only small differences in PL maxima. As expected the annealed films show a red-shifted PL compared to the non annealed films and that generally within a series the higher regioregularity P3HT shows the most red-shifted peak. This is in general agreement with the results found for the absorption spectra.

The PL quenching in polymer:fullerene blend films is typically used as a measure of the efficiency of charge separation. Efficient quenching is achieved by the fine scale mixing
of the donor and acceptor components on nanometre length scales such that polymer excitons can be quenched by the fullerene. If the scale of component mixing becomes more segregated or if the number of fullerenes present in the P3HT phases becomes less, then a rise in the yield of P3HT photoluminescence due to reduced quenching is expected. From Table 4-1 the relative yield of PL increases in the higher RR blend films and is higher for the annealed films rather than the non-annealed films. A larger PL yield suggests a greater degree of phase separation in the high regioregularity and annealed films, and correlates to a greater degree of P3HT order seen in these films by their absorption spectra. Potentially therefore, the formation of pure polymer domains with favourable chain on chain stacking is the driving force behind the phase segregation of components.

Figure 4-3. Microscope pictures of the 95.2% RR blend film (a) without and (b) with annealing treatment at 140°C for 2 hours. The ravine in the left hand side of the pictures are a reference mark estimated to be 400µm wide.

Figure 4-3 shows pictures of the surface of the 95.2% RR P3HT blend film, non-annealed (a) and annealed (b), taken through a digital camera fitted microscope. In the non-annealed (a) picture the film shows no features and at this magnification the film looks uniform and amorphous. The picture of the annealed blend film (b) however is starkly different with the appearance of micrometre size features on the surface of the film. Mainly the features are monoform and crystalline in appearance being tens of

micrometers long and only a few micrometres wide, however a few much longer crystalline rods and a single hundreds of micrometre large crystalline feature are also visible. Surrounding the crystalline features is a halo where the blend film is a different colour to the surrounding amorphous phase.

As for the 95% RR film, the non-annealed films for the 93% and 91% RR P3HT:PCBM blends also look uniform and amorphous under the microscope. Again, with annealing of these films micrometre size crystalline features with their distinctive ‘halos’ appear on the surface, however for the lower regioregularity films they appear fewer and no larger features are apparent. This suggests that growth of the crystalline features is facilitated by a high P3HT regioregularity.

The crystals which become visible under the microscope could be those of P3HT or PCBM. While crystalline P3HT has been reported, typical reported grain sizes are too small to make them visible under the microscope\textsuperscript{7,8,11,25}. On the other hand, micrometre size crystals of PCBM have been observed previously for CP:PCBM blend films, with their frequency and size dependant on the film fabrication and treatment conditions\textsuperscript{26,27,28}. The halo’s surrounding the crystallites have been suggested to be areas of the blend film which become deficient in PCBM due to the migration and aggregation of PCBM out of the polymer phase\textsuperscript{26}. The formation of visible PCBM crystals and their associated ‘halo’s’ therefore are signs of increasing phase segregation in the blend film, in agreement with the heightened PL yields for the annealed films. In the following chapter in this thesis, the formation of crystalline PCBM and the associated changes to its photophysics will be reported.


4.4.1.2 Transient spectroscopy data

Figure 4-4. Typical TAS data obtained from the P3HT:PCBM blend films under study. The markers [A], [B] and [C] represent different data values of interest. Data shown here belongs to the 95.2% RR P3HT:PCBM annealed blend film. Excitation wavelength was 525nm, probe wavelength was 980nm with an excitation intensity of 7µJ (blue) and 70µJ cm⁻² per pulse (green).

Figure 4-4 shows a transient absorption signal from the annealed 95.2% RR-P3HT:PCBM blend film which is typical of all the transient data collected in this study. The markers [A], [B] and [C] all represent relevant data that can be taken from the transient decay data. Marked in Figure 4-4 as [A] is the amplitude of the transient absorption signal at 300ns. The signal amplitude correlates with the number of charges that have survived geminate recombination to dissociate into mobile charge carriers and is therefore a measure of the potentially extractable charges formed in the blend. Marker [B] represents the signal amplitude at the onset of the trap limited decay and can be used to calculate the number of traps in the blend film. High laser powers were employed to generate sufficient charges to fill all the traps in the film, as demonstrated by the saturation of the trap limited recombination signal in Figure 4-4. As this value must be judged by eye, the noise on the transient signal creates an error margin of ±20%, however a variation in trap density of greater than 100% for the films under study is observed and therefore an error margin of ±20% is justifiable. Marker [C] represents the value of the power
law exponent when fitting the trap limited decay. As a power law appears linear on a log-log log plot the exponent is reflected in the slope of the decay. The exponent to the power law reflects the distribution of energies to the traps in the blend film and can be used to gauge the average energy (or ‘depth’) to the traps in the film. For instance, a larger power law exponent (and a steep slope to the decay) is consistent with relatively few ‘deep’ in energy trap sites and a small average trap energy, while a small power exponent (and a shallow slope to the decay) represents on average much deeper traps. These values [A], [B] and [C] for all the films of different regioregularity, both non annealed and annealed are shown in Table 4-2. A detailed discussion of the recombination dynamics in P3HT:PCBM blend films is given in Chapter 3 of this thesis.

Table 4-2 summarises the relevant data extracted from the transient decay spectra for all the blend films under study. The initial signal amplitude was taken after excitation with 7µj/cm² pulse of 525nm light. Table 4-2. P3HT regio-regularity effects on blend film properties. Values for column A are taken 300ns after excitation with 7µj/cm² pulse of 525nm light.

<table>
<thead>
<tr>
<th>Type</th>
<th>Initial Signal Amplitude (x10⁻⁴ ΔOD)</th>
<th>Trap Signal Amplitude (x10⁻⁴ ΔOD)</th>
<th>Recombination Power Law Exponent</th>
</tr>
</thead>
<tbody>
<tr>
<td>95.2% RR</td>
<td>3.9</td>
<td>1.1</td>
<td>-0.34</td>
</tr>
<tr>
<td>93.0% RR</td>
<td>3.6</td>
<td>1.5</td>
<td>-0.34</td>
</tr>
<tr>
<td>90.7% RR</td>
<td>2.7</td>
<td>1.6</td>
<td>-0.30</td>
</tr>
<tr>
<td>95.2% RR²</td>
<td>4.3</td>
<td>1.4</td>
<td>-0.46</td>
</tr>
<tr>
<td>93.0% RR²</td>
<td>3.8</td>
<td>2.0</td>
<td>-0.43</td>
</tr>
<tr>
<td>90.7% RR²</td>
<td>4.4</td>
<td>2.1</td>
<td>-0.42</td>
</tr>
</tbody>
</table>

a. annealed films (140°C for 2 hours).

Table 4-2 summarises the relevant data extracted from the transient decay spectra for all the blend films under study. The initial signal amplitude was taken after excitation with 7µj/cm² pulse light at 525nm and shows a marked increase in the annealed compared to the non-annealed films and typically is larger in the higher regioregularity polymers. The difference in signal size is explained by changes to the dissociation efficiency of geminate pairs in the various blends, which is most efficient in the annealed and highest regio-
regular P3HT and suggest a greater amount of extractable current is produced in these blends.

The amplitude of the trap signal shows a marked increase as the regioregularity of the P3HT decreases. This suggests that more traps are formed in the less-ordered lower RR P3HT. As well as a greater number of traps, the lower regioregularity P3HT films also have a smaller power law exponent, indicative of on average deeper traps. These correlations are consistent with the assignment of disorder in the polymer structure as a cause of trap formation.

![Figure 4-5](image)

**Figure 4-5.** Change in the exponent (slope) of the power law with annealing of the 95.2% RR blend film. Excitation wavelength was 525nm, probe wavelength was 980nm with an excitation intensity of 70µJ cm⁻² per pulse.

Following annealing, the exponents to the power law decays become much larger than their non-annealed equivalents. An example of the change in the decay is shown in Figure 4-5 where the 95.2% RR P3HT:PCBM blend film shows a steeper slope after annealing. The change in the slope of the power laws is consistent with a reduction in the average trap ‘depth’ and suggests that some traps have been removed by annealing of the blend film. For this to be the case these traps would have to be structural rather than
chemical in nature consistent with the assignment of traps to disorder in the polymer phase.

Surprisingly, and contradictory to the previous statement however, the annealed films typically show a higher number of traps present than their non-annealed equivalents. While this appears inconsistent with the picture of traps being related to structural disorder in the polymer, there is no contradiction if we consider that annealing may be creating another type of charge trap related to greater order in P3HT. Potential sources for these types of traps will be considered in the discussion.

Note the results of annealing on the blend film in Chapter 3 of this thesis are consistent with the above results. The slope to the power law decay in a (1:2 w/w) P3HT:PCBM film was calculated to be -0.28 for the non-annealed film and -0.30 for the annealed film (140°C, 15 min.). The smaller exponent to the power laws in the 1:2 w/w P3HT:PCBM films are ascribed to a more disordered film morphology caused perhaps by the greater amount of PCBM in the film while the smaller effect of annealing on the slope of the power law is ascribed to the shorter annealing time (15 minutes compared to 2 hours).
4.4.2 Effect of end group functionalisation (-H, -Br, -CH₃)

4.4.2.1 Optical measurements and digital microscope pictures

Figure 4-6. UV-Vis absorption spectra of a series of annealed P3HT:PCBM blend films with -H, -Br, -CH₃ chain end-groups. The peak at 602nm is assigned to an interchain electronic transition where the exciton is delocalised over neighbouring chains.

Figure 4-6 shows the absorption spectra of the annealed blend films with the different chain end-group P3HT, -H, -Br, -CH₃. All the spectra reveal the familiar three absorption peaks structure of P3HT however the -Br and -CH₃ end group blend films show some signs of disruption to the P3HT structure in the blue shifted absorption peak and the decrease in intensity of the interchain transition at 602nm. The amount of disruption to the absorption spectra however is less than that seen for the 93% and 90.7% RR blend films and suggests a weaker amount of disruption to the packing from the chain ends. Such an effect is to be expected as physically chain ends are present at a significantly lower volume than irregular P3HT couplings (roughly 1 irregular coupling in 10 compared to 1 in a 100 end-chain monomers).
Table 4-3 displays the optical properties of the blend films depending on the polymer chain end-group present and whether the film was non-annealed or annealed. While both the bromine and methyl end groups show different results to the standard hydrogen end-group, they are also slightly different to each other. The trends in the absorption maxima of both the non-annealed and annealed films suggest that the addition of a bromine end-group to the polymer disrupts the conjugation length and packing of the P3HT chains a little more than the methyl group. Furthermore, the higher PL yield in the bromine P3HT blend films (in fact higher than in the standard hydrogen end P3HT for the annealed films), suggests the presence of bromine also appears to encourage phase separation of the components. Conversely, for the methyl group the PL yield is the lowest in the series, for both the annealed and non-annealed films, suggesting that the presence of the methyl end-group encourages the fine scale mixing of the blend components even more than with the standard hydrogen P3HT.

Table 4-3. Blend film properties for P3HT with different chain end groups in as-spun and annealed films.

<table>
<thead>
<tr>
<th>Type</th>
<th>Abs. Peak</th>
<th>PL Yield$^d$ (a.u.)</th>
<th>PL maxima (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-H</td>
<td>500</td>
<td>0.98</td>
<td>667</td>
</tr>
<tr>
<td>-Br</td>
<td>487</td>
<td>0.88</td>
<td>668</td>
</tr>
<tr>
<td>-CH$_3$</td>
<td>490</td>
<td>0.78</td>
<td>667</td>
</tr>
<tr>
<td>-H$^a$</td>
<td>507</td>
<td>1.12</td>
<td>670</td>
</tr>
<tr>
<td>-Br$^a$</td>
<td>504</td>
<td>1.17</td>
<td>669</td>
</tr>
<tr>
<td>-CH$_3$$^a$</td>
<td>506</td>
<td>0.94</td>
<td>670</td>
</tr>
</tbody>
</table>

a. annealed films (140°C for 2 hours).

As for the different regioregularity P3HT polymers, annealing of the film has the largest effect on blend morphology, with all films showing red-shifts in the P3HT absorption maxima and increases in PL yield. The effect of annealing in enhancing phase segrega-
tion of the blend components is highlighted by the surface pictures of the blend films following annealing.

(a)  

(b)  

Figure 4-7. Microscope pictures of the blend films with -Br (left) and -CH₃ (right) P3HT chain end groups after annealing treatment at 140°C for 2 hours. The ravine in the left hand side of the pictures is a reference mark approximately 400µm wide. Inset to the left hand picture shows a magnification of the annealed Br end-group blend film where the black circle highlights an area of interest.

Figure 4-7 shows the digital camera microscope pictures for the annealed blend films with bromine (a) and methyl chain (b) end-group P3HT. The non-annealed films however appeared amorphous and showed no crystalline features on the surface of the films within the magnification of the microscope. The micrometre size ‘black dot’ features seen on the surface of the two annealed films are similar to those seen in the -H end group P3HT blend film except that larger crystalline features are not as common. The inset to picture (a) is a magnification of an area of the -Br end group blend film where a larger crystalline feature was found and shows that it is built up from the accumulation of several smaller crystalline features. The polycrystalline nature of the larger crystal may be detrimental to transport by the formation of crystalline grain boundaries¹⁰.
4.4.2.2 Transient spectroscopy data

Table 4-4 displays the chosen parameters taken from the transient absorption data of the different end group P3HT:PCBM films. The method behind this analysis was mentioned earlier in reviewing Figure 4-4 on page 101. In comparing the amplitude of the signal at the system resolution, surprisingly more mobile charge carriers are present following excitation of the methyl and bromine end-group than for the standard hydrogen end-group P3HT. With annealing the signal amplitude rises however, the trend remains of a greater number of long-lived mobile charges in the methyl and bromine than with the standard hydrogen P3HT. This results suggests that potentially the bromine and methyl end-group P3HT, but especially the methyl, may produce solar cells with a higher short circuit current than those created with the standard H-terminated P3HT.

Table 4-4. Initial transient absorption signal amplitudes near the system resolution, trap quantities and power law exponents for the recombination dynamics in the blend films with different P3HT chain end groups, before and after annealing. Values for the initial signal amplitude are taken 300ns after excitation with 7µJ/cm² pulse of 525nm light.

<table>
<thead>
<tr>
<th>Type</th>
<th>Initial Signal Amplitude (x10⁻⁴ ∆OD)</th>
<th>Trap Signal Amplitude (x10⁻⁴ ∆OD)</th>
<th>Recombination Power Law</th>
</tr>
</thead>
<tbody>
<tr>
<td>-H</td>
<td>3.9</td>
<td>1.1</td>
<td>-0.34</td>
</tr>
<tr>
<td>-Br</td>
<td>4.1</td>
<td>1.4</td>
<td>-0.36</td>
</tr>
<tr>
<td>-CH₃</td>
<td>4.4</td>
<td>1.8</td>
<td>-0.35</td>
</tr>
<tr>
<td>-Hₐ</td>
<td>4.3</td>
<td>1.4</td>
<td>-0.46</td>
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<tr>
<td>-Brₐ</td>
<td>5.0</td>
<td>1.9</td>
<td>-0.44</td>
</tr>
<tr>
<td>-CH₃ₐ</td>
<td>5.4</td>
<td>2.4</td>
<td>-0.41</td>
</tr>
</tbody>
</table>

a. annealed films (140ºC for 2 hours).

Looking at the trap densities in the blend films, the P3HT with the methyl chain end-group shows the largest amount of traps, with bromine there are fewer traps and the stan-
standard hydrogen end-capped P3HT shows the least number of traps. The same trend applies for the annealed as for the non-annealed films however as was seen for the low regioregularity P3HT data, the annealed films have a near two fold increase in the number of traps compared to the non-annealed films.

As introduced earlier the slope of the trap limited decay is a measure of the average depth of the traps in the blend film. In the as-spun (non annealed) films the power laws for all three end groups are similar suggesting the presence of the functionalised end-groups influences little on the trap depth in the spin-coated film. However, following annealing treatment a significant difference in trap depth between the standard -H cap and the substituted methyl end group is seen from the slope of the decays, as highlighted in Figure 4-8.

![Figure 4-8](image)

**Figure 4-8.** Recombination dynamics for annealed P3HT:PCBM blend films with methyl, bromine and hydrogen terminated P3HT. Excitation wavelength was 525nm, probe wavelength was 980nm with an excitation intensity of 70µj cm⁻² per pulse.

That a difference appears following annealing suggest that the methyl group maybe hindering the structural changes to the P3HT that occur with annealing. This resistance may
also inadvertently reduce the phase segregation of the film components, by reducing the driving force for separation. This is in accord with the photoluminescence results for the methyl polymer which showed the smallest PL yield. The bromine end-group P3HT shows a similar slope to the trap limited decay both with and without annealing to the standard hydrogen group and suggests that bromine does not play a similar role to methyl.

4.5 Discussion

4.5.1 Overview of the data

Both the polymer regioregularity and polymer chain end-group cause substantial changes to the properties of P3HT:PCBM blend films. This finding is significant as several reports in the literature have emphasised the importance of blend film morphology on device efficiency\textsuperscript{1,2,29} but to date this is the first report to suggest that small modifications to the polymer structure can exert control over the polymer and blend morphology.

The effects of P3HT regioregularity on the blend film properties are substantial even for the small variation in regioregularity seen here (90.7%-95.2%). In the non-annealed and annealed films the differences in absorption peak maxima vary by over 20nm from the highest to lowest regioregularity. For optimal solar light absorption, a blend with more absorption in the red of the spectrum is beneficial and so a lower RR P3HT with its blue shifted absorption is immediately detrimental. This variation in absorption maxima is consistent with a greater level of disorder in the polymer chains with decreasing polymer regioregularity, in agreement with reports in the literature of higher hole mobility in the higher RR P3HT films\textsuperscript{6,30}.

Another effect of using a high regioregularity P3HT (and also caused by annealing of blend films) is that alongside the greater organisation of P3HT comes an increase in phase segregation of the components. This effect is most clearly seen in the loss of polymer PL quenching in the higher RR blend films and digital photographs of the surfaces of the annealed films, where segregation of components on a micrometre scale is visible. Both the PL results and the microscope pictures agree that the degree of phase segregation is reduced by using a lower regioregularity P3HT, suggesting a lower driving force for the separation of components in a more disordered P3HT material. A correlation between greater order in the P3HT domains and the segregation of components can be seen in Figure 4-9 where the blend film absorption maxima is plotted against the yield of PL emitted from the films.

![Figure 4-9](image.png)

**Figure 4-9.** Absorption maxima versus PL yield for the blend films.

The phase segregation of components may be detrimental to device efficiency through the loss of charge generation in exciton splitting. These are potentially outweighed by positive changes to the films morphology such as increases in the hole mobility and light absorption, however if greater phase segregation were to occur, perhaps by using an even
higher RR P3HT then the segregation of components may become extensive and limit solar cell efficiency\textsuperscript{18,19}.

The impact of chain ends on P3HT structure and segregation are much smaller than with the changes in regioregularity. Evidence for this is seen in the absorption spectra maxima for the bromine and methyl chain end P3HT which, while they do show some blue shifting associated with greater disorder, the shift is not to the same extent as that seen for the lower regioregularity P3HT films. For the bromine and methyl terminated P3HT the PL yields also tend to be closer to the values seen in the standard P3HT than with the lower regioregularity films suggesting only small changes to the phase segregation in the blend film.

\textbf{Figure 4-10.} (left) Ball and chain ChemDraw 3D image of an oligothiophene with methyl and bromine end-caps (atoms are 25\% real size). This picture highlights the similar size of the two different end-groups. (right) Key to the atoms/molecules in the left picture and full size representation of their atomic/molecular sizes as represented by their Van der Waal radii. \textit{Left to right} atomic Hydrogen, Sulphur, Bromine and molecular CH$_3$.

Figure 4-10 highlights perhaps why the two end groups are so similar in their properties and not so different to the standard H-terminated P3HT. It shows a ball and chain molecular picture of an oligothiophene with a methyl and bromine substituted chain end-caps at either end. From this picture and from the key on the right of the figure, that while both the bromine and methyl are much larger than hydrogen and represent much larger groups
at the end of a chain, both groups are of a similar size in consideration of the extent of their electronic clouds. Furthermore neither of these are particularly larger than the sulphur atom already present on the thiophene and as such may not present that much additional steric hindrance.

Of the slight differences with end-group, there is some evidence to suggest that the methyl end group P3HT has some advantages over the standard H-termination. The higher amount of PL quenching in the methyl blend suggests a greater amount of charge generation compared to the bromine or hydrogen, while the presence of methyl does not affect the films chain packing to much of an extent. This is in accord with the literature where the presence of bromine or methyl were reported as having negligible effect on P3HT hole mobility\textsuperscript{7}. 

![Figure 4-11](attachment://figure4-11.png)

**Figure 4-11.** Number of traps present in the blend films of decreasing P3HT regioregularity or different end-group. Green triangles are for annealed films and red squares the as-spun (non-annealed) films. Note the 95.2%, 93.0% and 90.7% RR polymers are standard -H terminated P3HT.

An area where the presence of end-groups does have a large effect, is in increasing the charge trap density in the film. Previously it was stated that a lower regioregularity polymer catalysed trap formation in the blend films due to the increasing disorder in the
P3HT. Surprisingly however, it is clear that the bromine or methyl termination have an equally if not greater effect on increasing the number of traps in the blend than regioregularity (see Figure 4-11). The increase in trap density with the addition of -CH$_3$ and -Br end groups opens up the possibility that these substituted end groups could be acting as ‘chemical’ traps for passing charges by localising the density of charge onto themselves or an adjacent segment of chain. The increase in trap density however is too small to justify this hypothesis, as chain ends represent ~1 out of a 100 monomers where the trap density is nearly two orders of magnitude smaller than this at only ~1 in a 1000 monomers. While not traps in themselves therefore, they are however playing a part in increasing trap numbers in the film by being present at chain ends. This suggests that chain ends alongside structural disorder are potential sources of trap formation in the blends.

A final influential parameter on trap formation is annealing of the blend films. For all the P3HT types under study annealing of the blend films consistently causes increases to the trap density (see Figure 4-11). As stated in the results, the increase in trap numbers with annealing suggests the formation of traps associated with order in P3HT. A possible example of this kind of trap would be grain boundaries between P3HT crystallites formed during the annealing process$^{10}$. This is consistent with reports in the literature where grain boundaries have been reported to potentially slow the movement of charges in P3HT$^{8,10}$.

### 4.5.2 Correlation with device characteristics

A series of devices made in a similar way to the blend films were made and characterised by Youngkyoo Kim in the Physics Department at Imperial College. This section will discuss any correlations found between the properties of these devices and those of the corresponding blend film. Figure 4-12 plots the main device characteristics from the set of photovoltaic devices against the film absorption maxima. The absorption maxima was chosen as it is representative of the overall level of order/disorder in the P3HT phases.
Figure 4-12. Device (a) short circuit current, (b) fill factor and (c) open circuit voltage plotted against the blend film absorption maxima. The device and blend films were fabricated similarly and differ only in the presence of electrodes. The regioregularity or end-functionalisation of the P3HT is marked, for the as spun films (empty shapes) and annealed films (filled shapes). Device current-voltage curves were measured at an illumination of 100mW/cm² AM1.5.
As can be seen from (a) and (b) in Figure 4-12 both the short circuit current (Jsc) and Fill Factor (FF) show a clear positive correlation with the blend film absorption peak maxima. The correlation with Jsc is not only due to the increased light absorption with the red-shift of the absorption spectrum, but other factors such as increased hole mobilities and potentially a reduction in any geminate recombination which are also related to the P3HT chain packing. The correlation between the blend film absorption maxima and the FF is consistent with the reported increases in hole mobilities, which decreases series resistance and any recombination losses. The open circuit voltage of the device shows a negative correlation (an inverse relationship) with the P3HT absorption maxima. While the difference in open circuit from highest to lowest is only marginal (~0.1eV) such a drop in open circuit voltage is common in annealed P3HT:PCBM devices and as yet unexplained. A possible explanation is that as Voc of the device is governed by the difference in LUMO of the acceptor and HOMO of the donor, better alignment of the P3HT chains accords a slight shift in the energy of the P3HT HOMO. Such a shift in energy is plausible as the surrounding environment of the P3HT chains may disturb the energy of the chromophores. As the reduction in open circuit voltage is only small but the Jsc and FF show a large positive correlation, the device power conversion efficiencies (PCE’s) also naturally shows a positive correlation to the P3HT absorption maxima. That all three device parameters have a strong correlation with the absorption maxima of P3HT demonstrates how dependant device efficiency is on the morphology of the polymer and highlights the potential advantages that changing the polymer regioregularity or end-group may have in optimising device efficiencies.

Figure 4-13. Device short circuit current versus blend film ΔOD maxima at 300ns following 7 µJ cm⁻² pulse⁻¹ at 525nm. The regioregularity or end-functionalisation of the P3HT is marked, for the non-annealed films (empty shapes) and annealed films (filled shapes).

A more direct and reliable measurement than the absorption maxima to predict the short circuit current of a potential device would be the transient absorption signal amplitude at the system resolution of 300ns. As this measurement monitors the number of mobile charges generated in the blend film it is a direct measure of the blend films potential current generating capacity. Figure 4-13 highlights the correlation between the amplitude of the transient signal associated with the presence of free charges with the short circuit current of the corresponding device. In the scatter graph there is a clear correlation between a higher TAS signal and a higher device short circuit current. This correlation is potentially useful as a means to directly test materials for their potential current generation without the need and complication of device fabrication. Note that the methyl end-group polymer produces the highest current device as was previously predicted by the favourable morphology of the methyl P3HT blend films.

Reports in the literature have highlighted the negative impact of annealing P3HT: PCBM blend films for too long or at too high a temperature on device efficiency²,³,²⁹ however to
date there is no explanation for this negative downturn in efficiency with ‘over annealing’. Results from this study however point to increasing segregation of the P3HT and PCBM components as being potentially responsible. Extensive segregation of components may prove detrimental to device efficiency by destroying continuous pathways for charge carriers to the electrodes and by reducing the amount of donor-acceptor interface and exciton splitting. Examples of both these features can be seen for the annealed 95.2% RR blend film, which has a relatively low amount of PL quenching and the presence of micrometre size PCBM crystallites surrounded by their ‘halo’s’ as seen by surface photographs of the film. These halo’s especially potentially serve as a problem as they are deficient in PCBM and therefore may effectively cut-off the PCBM crystallite from the remainder of the film35, creating an inactive ‘dead’ region to the blend film.

Independent of the effect of overall blend morphology, would be the additional effect of the presence of charge traps on device efficiency. The influence of charge traps on the recombination lifetimes of charges, may potentially be a controlling factor in the open circuit voltage of devices. Similarly charge traps may also decrease the hole mobility through the device, potentially causing a decrease in device fill factor, by increasing series resistance. However no clear correlation was found in this study between the number of traps or the exponent to the power law that describes the trap-limited decay and any device properties. This is in accord with results of device modelling where the presence of traps could be safely neglected36 in calculations.

**4.6 Conclusions**

The changes in P3HT:PCBM blend film morphology using different regioregularity P3HT polymer (90.7%-95.2) and methyl or bromine chain end-groups were studied and correlated to device efficiency. A clear correlation between the morphology of the P3HT


and device efficiency was found. Regioregularity of the polymer was found to have substantial effects on the blend morphology and a higher regioregularity P3HT was found to be beneficial to device efficiency by increasing the level of order and chain packing in the P3HT. The presence of methyl or bromine terminating end groups on the polymer was found to have little effect on the blend film morphology and subsequently device efficiency, compared to the standard hydrogen end-group P3HT.

The origin of charge traps in the blend film are tentatively assigned to structural disorder in the polymer, the formation of grain boundaries between P3HT crystallites and the presence of polymer chain ends, due to the effect of decreasing RR, film annealing and the presence of methyl or bromine chain ends respectively on increasing the trap density. No correlation between the presence of charge traps and any device characteristics were found.
5 Optical Characterisation of Methanofullerene PCBM.

![Methanofullerene](image)

Figure 5-1. Methanofullerene \(6\)-1-[3-(methoxycarbonyl)propyl]-\(6\)-1-phenyl[6,6]-\(C_61\).

5.1 Abstract

A pristine film of PCBM and films of increasing PCBM concentration in a polystyrene (PS) host matrix were studied by absorption-emission and transient absorption spectroscopy. In the low PCBM concentration film, the isolated PCBM molecule shows weak absorption of light in the visible range and an emission at \(\sim720\)nm. In films with a high concentration, heightened absorption in the visible region and a new emission at \(\sim500\)nm associated with a charge transfer state in the aggregated PCBM molecular crystal is observed.

5.2 Introduction

In the development of organic electronics \(C_{60}\) fullerene and its derivatives have been widely studied as components in amongst others superconductors\(^1,2\), thin film transistors\(^3,4\)
and organic solar cells\textsuperscript{5,6,7}. Due to the poor solubility of C\textsubscript{60} in solution, many C\textsubscript{60} derivatives have been synthesised with the addition of solubilising side chain groups in order to increase their solution processability\textsuperscript{8,9}. One such methanofullerene derivative of C\textsubscript{60} is 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C\textsubscript{61} (PCBM), which is extensively used as the electron accepting component in conjugated-polymer organic solar cells\textsuperscript{5,6,7}.

Despite constituting the bulk of the photoactive material in organic solar cells, typically between 50-90\% by weight, only little characterisation of the PCBM material in its pure form or at different weight fractions has been reported in the literature\textsuperscript{10,11}. Furthermore there are many conflicting reports and debates in the literature on the properties of PCBM. Reports in the literature for the PCBM LUMO, which is a critical parameter for electron transfer, vary in range from as much as 3.7-4.3\textit{eV}\textsuperscript{12,13,14} versus vacuum, more than half an electron volt difference. The commonly reported energy for the PCBM HOMO of 6.1\textit{eV}\textsuperscript{15} versus vacuum is also ambiguous, given that there are no direct nor indirect data for this HOMO energy. In addition there are many contentious issues in the literature concerning the properties of PCBM, such as the observation that addition of PCBM to films of MDMO-PPV results in an increase in the hole mobility by over an order of magnitude over the pristine polymer film\textsuperscript{16,17}. Emission from PCBM has been reported at 1.7\textit{eV}\textsuperscript{10} and assigned to emission from the first singlet state (S\textsubscript{1}). Crystallisation of PCBM in blend films with conjugated polymers have been reported by TEM\textsuperscript{11}, and electron diffraction studies, consistent with the optical microscopy studies of PCBM/P3HT films shown in Chapter 4 of this thesis.

\begin{thebibliography}{99}
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Looking at the parent molecule, the optical and electrical character of C\textsubscript{60} has been well documented. The C\textsubscript{60} molecule HOMO-LUMO optical gap is reported to be \(-1.9\text{eV}\)\textsuperscript{20,21}, but due to the molecules high symmetry the electronic transition from the HOMO (h\textsubscript{u}), to the LUMO (t\textsubscript{1u}) is forbidden, with the first allowed transitions being in the U.V\textsuperscript{22}. In solution, the dispersed monomolecular C\textsubscript{60} typically lies in equilibrium with an aggregated state\textsuperscript{23,24,25} where interactions within aggregates help relax optical excitation rules for the highly symmetrical C\textsubscript{60} molecule, leading to greater absorption of light in the visible wavelength region\textsuperscript{26}. Furthermore, while optical excitation of monomeric C\textsubscript{60} in dilute solution, has been shown to give rise to the triplet state with almost unity quantum efficiency\textsuperscript{23}, quick deactivation of the singlet excited state in the aggregate leads to little if any triplet formation\textsuperscript{25}.

Films of solid C\textsubscript{60} (fullerite) are crystalline, held together by weak Van der Waal forces, where the interactions between fullerenes leads to relaxation of the optical transition rules relative to the single molecule and shrinking of the HOMO-LUMO gap\textsuperscript{27,28,29}. Electronically, solid C\textsubscript{60} is commonly described as being a direct gap semiconductor material with a thermal bandgap of \(-2.2\text{eV}\)\textsuperscript{30,31,32}, but a photoconduction edge of \(-1.7\text{eV}\)\textsuperscript{33} due to broad conduction and valence bands. Within the crystal, the close proximity of the molecules gives rise to additional charge transfer (CT) excited states as well as Frenkel excited states, the most significant of which are at 2.43eV and 3.5eV. It is the mixing of these many CT and Frenkel excited states which give rise to the crystals electronic properties\textsuperscript{29}. The electronic structure of fullerite is further complicated by the presence of electronic transitions of energy within the HOMO-LUMO band gap which give rise to a tail of absorption in the red part of the visible spectrum\textsuperscript{32,34}.

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To maximise the potential efficiency of conjugated polymer:PCBM devices, a thorough understanding of the individual material properties is required. In this chapter results of absorption-emission and transient absorption data from a pristine PCBM film and of PCBM at different concentrations in blends with inert polystyrene are reported and implications of these observations on solar cell performance are discussed.

5.3 Methodology

Chlorobenzene solutions of pure PCBM, and by weight 1:7 and 1:1 PCBM:Polystyrene (PS) were spin-coated onto cleaned spectrosil glass to create the 12% PCBM (1:7w/w), 50% PCBM (1:1w/w) and pristine (100%) PCBM films. Samples were stored and tested as described in the Experimental Methods chapter of this thesis.

5.4 Results

Figure 5-2. Normalised absorbance spectra from films with increasing loading of PCBM in polystyrene; 12% PCBM (blue), 50% PCBM (green) and 100% PCBM films (red).

Figure 5-2 shows the absorption spectra for the 12%, 50% and 100% PCBM films. All features are assigned to PCBM as polystyrene shows negligible absorption at this wavelength. At low PCBM concentrations there is absorption mainly in the near UV and above, with little absorption in the visible range. This is in agreement with reports in the literature for fullerenes, where the allowed optical transitions in fullerene are all in the UV region, with all transitions of lower energy being forbidden\(^2\). Some relaxation of the optical

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selection rules due to the presence of the symmetry breaking side chain group and aggregation of the fullerenes however does lead to some absorption in the visible range. With increasing concentration in the 1:1 and pristine film there is heightened absorption of light in the visible region with the largest increases in absorption seen around 400nm. The origin of the loss in absorption around 600nm in the 50% film is unclear but maybe related to the aggregation of PCBM.

![Figure 5-3. Emission spectra from the 12%, 50% and 100% PCBM films after excitation at 433, 436 and 433nm respectively (normalised to equal densities of absorbed photons).](image)

In Figure 5-3 the emission spectra of these films shows the presence of two luminescence peaks from PCBM. The low energy emission peak is seen from all the films but is most intense in the 12% PCBM film and centred at 712nm. As the PCBM concentration increases, the low energy emission peak becomes red-shifted and the intensity of the emission drops. An emission at ~720nm (1.7eV) has been reported previously for both solutions and films of C_{60}^{35} and is ascribed to emission from the lowest excited state (S_1). By comparison therefore, we assign the low energy emission to be from the lowest excitonic state in PCBM (S_1).

The high energy emission around 500nm observed for higher PCBM concentration films is similar to an emission partially observed in films of C_{60}^{35}, although its origin has not been clarified.

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Figure 5-4. Excitation spectra for the emission at ~720nm (squares) and at ~500nm (triangles) overlaid on top of the film absorbance spectra in the 12% (a), 50% (b) and 100% PCBM films (c). The inset to the bottom figure overlays the emission and the emission excitation spectra for the high energy emission normalised to peak values. The midpoint of the two lines is at 440nm (2.8eV) and is a good estimate for the energy of the emissive state.

Figure 5-4 shows the excitation spectra for the high and low energy emission bands in the 12% (a), 50% (b) and 100% PCBM film (c). In all cases the excitation spectra for the low-energy emission (open squares) follows closely the line of absorption. The excitation
spectra for the high energy peak however distinctly deviates from the overall film absorption, showing a new excitation maximum around 400nm. These excitation spectra clearly indicate that the high and low energy emission cannot originate from the same emissive species and therefore must be from two separate optical transitions in PCBM. That the high energy emission is only seen in films with a high concentration of PCBM, and is more intense in the pristine film than the 50% film, suggest that the emission is linked to aggregation and the formation of larger domains of PCBM. As calculated from the crossing point of the excitation and emission spectra (see inset bottom Figure 5-4) the energy of this new state is ~2.8ev above the ground state.

**Figure 5-5.** Transient Absorption (TA) Spectra for the 12% PCBM film taken at different times following excitation with ~200µJ/cm² pulse of 337nm light. Squares (5µs), circles (10µs), triangle (20µs), diamond (30µs), star (40µs). The inset shows a transient absorption spectra for a similar methanofullerene triplet taken from the literature. Ref. 36.

Figure 5-5 shows a transient absorption spectra from the 12% PCBM film from 5-40µs after excitation at 337nm. By comparison with previously published work on solution phase methanofullerenes, the transient in Figure 5-5 is identified as triplet PCBM. The

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spectra from the literature reference is shown in the inset. No changes to the shape of the spectra or the peak maxima can be discerned over time (5-40\( \mu \)s), suggesting that there is no contribution from other states to the transient absorption (TA) spectra other than the triplet. A similar absorption spectra was found for the 50\% PCBM film under the same conditions.

![Figure 5-6](image)

**Figure 5-6.** (a) Transient absorption decay at 720nm following excitation at 337nm for the 12\% PCBM film. Excitation energies are marked in the key and are in units of \( \mu \)J per cm\(^2\) per pulse. The delay with respect to the rise of the absorption signal is due to emission noise from PCBM at the same wavelength. (b) Plot of the peak signal amplitude (\(~2\mu s\)) against excitation energy.

Transient decay kinetics for the 12\% and 50\% film are shown in Figure 5-6 (a) & Figure 5-7 (a) respectively. The 100\% PCBM film gave no signal within the resolution of the equipment. For the 12\% PCBM film, the triplet decays are first-order with a fitted lifetime of \(~25\mu s\). The first order decays are consistent with the assignment of the transient to the PCBM triplet, and the observed lifetime of 25\( \mu \)s, is in good agreement with that published for triplet methanofullerenes in solution \(~30\mu s\)\(^{36}\). As seen in (b) in Figure 5-6, at higher laser powers the triplet signal amplitude shows deviation from linear dependence on excitation density.
Figure 5-7. Transient absorption decay at 720nm following excitation at 337nm for the 50% PCBM film. Excitation energies are marked in the key and are in units of µJ per cm² per pulse. The delay with respect to the rise of the absorption signal is due to emission noise from PCBM at the same wavelength. (b) Plot of the peak signal amplitude (~1µs) against excitation energy.

Compared to the 12% film, for the 50% film the lifetime to the decays are shorter ~17µs, again mostly first order in appearance but with a faster decays phase at earlier times. The 50% film also shows a four-fold reduction in signal amplitude (normalising over absorbed photon density) compared to the 12% film. As for the 12% film, the signal amplitude shows deviation from linearity at higher laser powers, as seen in (b) of Figure 5-7. The faster decay phase as well as the non-linear excitation density behaviour are assigned to triplet-triplet annihilation processes, as discussed in more detail in Chapter 6 of this thesis.

5.5 Discussion

The increasing level of aggregation and interaction between PCBM molecules is key to understanding the change in optical properties of these films. In the 12% PCBM film the low concentration of PCBM results in only a small degree of interaction between fullerene molecules. As absorption in the visible region is, as for C₆₀, symmetry forbidden this
masks the HOMO-LUMO transition in the absorption spectra, but transition due to light absorbed in the near UV are allowed, and represent transitions to higher Frenkel excited states. From the excitation spectra for the 12% PCBM film we see that light absorbed by these higher excited states decays to the S\textsubscript{1} state, from which low energy emission at 712nm is observed.

In the 50% (1:1 w/w) and pristine PCBM films, the greater level of interaction between fullerenes leads to increases in absorption in the visible region and the rise of an additional emission at 500nm. The increase in visible absorption at 400nm corresponds well with the excitation spectra (Figure 5-4) for the 500nm emission. The 500nm emission in PCBM is not ascribed to the formation of a Frenkel type exciton, as this would be expected to relax down to give emission from the lowest in energy S\textsubscript{1} state. Instead the 400nm absorption and 500nm emission are assigned to a charge transfer exciton (CTE), where the exciton is delocalised as an ion-pair over adjacent molecules. Such CTE states are common in organic materials which form molecular crystals (such as perylenes\textsuperscript{37,38} and C\textsubscript{60}\textsuperscript{29}) and are important precursors for charge generation in these materials. From the crossover point of the excitation and emission spectra the energy of this CT transition is estimated to be \(~2.8\text{eV}\), slightly larger than that reported for crystalline C\textsubscript{60} of \(~2.4\text{eV}\)\textsuperscript{29}.

The aggregation of PCBM into a molecular crystal form could explain many of the observed changes to the properties of the excited states of PCBM. In the high PCBM concentration films the red-shift of the emission peak can be ascribed to shrinking of the HOMO-LUMO gap, just as for C\textsubscript{60}, while the drop in emission yield from the S\textsubscript{1} state could be explained by an increase in the non-radiative decay rate. In addition to changes


in the absorption and emission data, aggregation of the PCBM appears to result in reductions in both the lifetime and yield of the PCBM triplet. This observation is in agreement with the literature, where for monomolecular C₆₀ in solution, the triplet is formed with near unity efficiency, however their formation in severely reduced in the crystal due to quick deactivation of the singlet.

Figure 5-8. Intramolecular (left) and intermolecular (right) transitions in PCBM. Light absorbed within a single fullerene molecule can lead to the population of the S₁ state either directly or following relaxation from a higher singlet state. The singlet state will then either undergo emissive decay or I.S.C to give the triplet. Alongside the intramolecular transitions shown on the left, inside the molecular crystal form of PCBM a further intermolecular transition, a charge transfer exciton (CTE), becomes available. The emissive CT exciton is decoupled from the singlet states of PCBM and therefore does not relax to the singlet state of PCBM despite being higher in energy.

Based on the above results an energy diagram for the transitions in PCBM are shown in Figure 5-8. The energy of the first singlet state (S₁) of PCBM is ~1.8eV above the ground state and from here can undergo emissive decay or intersystem crossing (I.S.C) to the triplet state (1.5eV). As seen from the excitation spectrum for the S₁ emission at ~720nm, light absorbed at energies greater than 1.8eV by the higher singlet states, relaxes...

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40. Calculated as the midpoint energy of the absorption peak and the emission peak in solution. Unlike in the film where the absorption peak is broadened and not clearly visible, an absorption peak in chlorobenzene solution is clearly visible at 697nm.
down to the S\textsubscript{1} state. The exception to this rule is when the light absorbed leads to the formation of the CTE in PCBM. The CTE state appears decoupled from the singlet states and does not relax to the S\textsubscript{1}. The origin of this de-coupling is unclear but maybe a result of the stringent group symmetry rules or the extensive delocalisation of the exciton.

Polymer:fullerene solar cells typically include a large concentration of PCBM, up to 80% by weight. At such high concentrations, there is significant phase segregation and aggregation of PCBM in the photoactive film\textsuperscript{11,18} has been observed. Furthermore, when films are annealed at high temperatures, as is commonly employed for P3HT:PCBM devices\textsuperscript{42}, this only heightens the segregation and crystallisation of the PCBM\textsuperscript{43}.

The PCBM in organic solar cells is therefore likely to be, at least in parts, crystalline. If the crystalline form of PCBM is likened to that of crystal C\textsubscript{60} as indicated by the data reported above, this would suggest that the crystalline regions of PCBM, as for C\textsubscript{60}, are best thought of in terms of a direct band gap semiconductor. This is a large departure from the current perception of PCBM as a purely excitonic molecular material but this notion may prove useful in answering some of the difficulties in characterising PCBM. For example, semiconductor behaviour could be the reason for the high electron mobility in PCBM and improvements in electron transport with annealing observed by both microwave conductivity\textsuperscript{44} and electrical measurements\textsuperscript{45} could be explained by purification of PCBM crystals in the device films (for C\textsubscript{60} annealing treatment is commonly used as a method to purify fullerite molecular crystals by removing defects\textsuperscript{46}). Potentially wide


conduction and valence bands (0.5-1eV in C$_{60}$\textsuperscript{30,47}) to PCBM crystals could offer an explanation to both the large disparity in cyclic voltammetry (CV) measurements of the first reduction potential and the improved hole mobility observed in MDMOPPV:PCBM devices. As fullerenes are known to aggregate in polar solutions\textsuperscript{25} such as those used for CV measurements, the mixing of aggregated and individual molecular states may broaden the obtained reduction peak, giving rise to the 0.6eV disparity between reported values for the PCBM reduction. Improved hole conduction in MDMO-PPV:PCBM blends could be explained by an energy overlap between the HOMO of the MDMO-PPV and the valence band of PCBM, giving rise to the reported increase in hole mobility with PCBM concentration\textsuperscript{16}. More fundamentally, as a direct gap semiconductor the absorption of light by PCBM could lead directly to the production of charges in the solar cell either by direct CTE formation or by creation of a Frenkel exciton which is then thermally excited to dissociation\textsuperscript{33}. Formed electrons and holes would then be separated at the interface between polymer and fullerene like charges at a p-n junction.

The origin of the long tail of absorption in PCBM films seen to stretch out further than 850nm (1.5eV) is also in need of clarification. In C$_{60}$ fullerite this red-tail of absorption is not thought to be an extension to the S$_1$ state of the fullerene but instead the formation of new weakly allowed transitions inside the band gap of C$_{60}$ with crystallisation. While the nature of these transitions is still currently under debate they are likely made up of a mixture of charge transfer and Frenkel exciton transitions\textsuperscript{32,34}. These weak inter band-gap transitions may become significant, as reports in the literature have confirmed that in polymer:PCBM solar cells light as low in energy as 830nm (1.5eV) can produce photocurrent\textsuperscript{48}. If future advances allow the creation of fullerene materials where these transitions have a greater intensity, analogous to C$_{70}$\textsuperscript{49,50} for instance, then these would help improve light absorption in the low energy region of the solar spectrum.

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5.6 Conclusions

With increasing concentration of PCBM in PCBM:PS films we see heightened absorption in the visible region and the rise of a new high energy emission at ~500nm. The origin of this heightened absorption and emission is assigned to the formation of a charge transfer exciton transition in crystalline PCBM where the exciton is delocalised over adjacent molecules as radical pairs. Following excitation, the triplet state of PCBM is formed by intersystem crossing from the singlet state, however both the lifetime and yield of the triplet are reduced by increasing PCBM crystallinity.


6 F8BT:PCBM
Photo-induced Formation of Triplet PCBM.

Figure 6-1. Chemical structures of PCBM and F8BT.

6.1 Abstract.

F8BT:PCBM blends show qualitatively different behaviour following photoexcitation compared to the free-charge producing blends of MDMOPPV or P3HT with PCBM. A series of F8BT:PCBM blend films with increasing weight concentration of PCBM have been studied by steady-state and time correlated photoluminescence measurements and by transient absorption spectroscopy (TAS). Upon photoexcitation the F8BT photoluminescence is quenched by two or more orders of magnitude in the presence of PCBM even at concentrations as low as 5%. Unlike in the previously mentioned charge producing blends
of polymer and PCBM, the steady state photoluminescence emission of PCBM is clearly visible in the blend films. TAS studies on the blend films show that the long-lived transient product produced following photoexcitation of the F8BT moiety is the PCBM triplet. The efficient quenching of F8BT photoluminescence but the lack of any free charge production, as monitored by TAS results, is attributed to efficient energy transfer (EnT) from $^1$F8BT* to the $^1$PCBM* which lies lower in energy than the charge separated state (CSS). The singlet PCBM can then decay emissively or undergo ISC (inter system crossing) to form the triplet.

6.2 Introduction

F8BT is a copolymer containing alternate fluorene and benzothiadiazole units. It is widely used in OLED’s due to its solution processability and high green luminescence yield$^{1,2,3}$. Recently it also has been incorporated in polymer:polymer solar cells with other polymers, showing moderate efficiencies$^{4,5,6}$ and studied as a photophysical standard$^{7,8}$. The high IP of F8BT (5.9eV)$^9$ makes it attractive for blending with PCBM in conjugated polymer:PCBM (CP:PCBM) solar cells as the high IP would potentially raise the open circuit voltage of devices$^{10}$ above those using other polymers such as P3HT ($\sim$4.9eV) or MDMO-PPV ($\sim$5.3eV). Despite the potentially high open circuit voltage, devices made from F8BT:PCBM have shown almost negligible power conversion efficiency (PCE $<$0.02%)$^{11}$ due mainly to the very low photocurrent collection. This is rather surprising considering a very similar polymer PFDTBT both structurally and electronically (IP 5.8 E\text{a} 3.5)$^{12}$, when blended with PCBM has made efficient solar cells with high photocurrent.

efficiencies and a high open circuit voltage ~1V\textsuperscript{13,14,15}. To understand why the F8BT:PCBM devices show such poor performance, blends of F8BT with PCBM will be studied by transient absorption spectroscopy in order to discover if the poor short circuit current can be explained by a high rate of charge recombination or by another factor such as the inefficient photogeneration of charges.

### 6.2.1 Photochemistry of donor-fullerene dyads in solution

The study of bound polymer-fullerene dyads in solution provide an ideal model for studying the photophysics of interfacial electron transfer in polymer:fullerene blend films. Charge generation in various donor-fullerene dyad combinations have been studied including perylenes\textsuperscript{16}, azulene\textsuperscript{17}, aniline\textsuperscript{18}, azoaromatic dyes\textsuperscript{19}, ferrocene\textsuperscript{20}, oligomers\textsuperscript{21} and porphyrins\textsuperscript{22} among others. Besides their use as model compounds for studying charge transfer reactions, these dyads are commonly investigated for their potential application as one material photovoltaic devices\textsuperscript{23}. However to date no devices made from films of these dyads have reached even moderate photogeneration efficiencies\textsuperscript{24}. Studies of donor-fullerene dyads in solution have revealed that the generation of charges can proceed via two different mechanisms, either by direct or indirect charge generation. While direct charge generation involves the splitting of the donor excited state to form charges, in some conditions energy transfer from the donor to fullerene molecule is quicker than the electron transfer step resulting in the excitation energy passing to the fullerene molecule. Charge generation may then occur ‘indirectly’ by electron transfer from the polymer to fullerene via the HOMO rather than LUMO orbitals. A competition exists therefore...

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11. Personal communication 2005 with Y.Kim, Department of Physics, Imperial College London
between direct and indirect charge transfer which depends on the rate of electron transfer versus energy transfer and critically the $\Delta G$ for the electron transfer step as governed by Marcus theory$^{25,26,27}$. Where energy transfer from donor to acceptor does occur the generation of charges becomes highly dependant on the choice of solvent as the energy of the charge separated state (CSS) relative to the energy of the fullerene $S_1$ depends on the solvent polarity. For instance in a series of oligophenylenevinylene (OPV)-fullerene dyads, charge generation is not observed following energy transfer in toluene, whereas in more polar solvents like ortho-dichloro benzene (ODCB) indirect charge generation occurs as the energy of the CSS is lowered below that of the fullerene excited state$^{28}$. The changing energy of the CSS may also inadvertently increase the rate of direct electron transfer due to a change in $\Delta G$ and shift the balance between direct and indirect charge generation$^{29}$. Competition between energy and electron transfer therefore can be sensitive to the energy of the CSS. Where energy transfer does occur, the energy of the CSS should be below that of the fullerene excited state or charge generation will not occur.

In certain cases, more complicated energy and electron transfer dynamics have been reported where the CSS is formed but is not the most stable state and only acts as an intermediate on the pathway to a lower energy state. In some cases the lowest in energy state is the triplet of the donor$^{30}$ or fullerene$^{31,32}$, formed via charge recombination of an intermediate CSS state rather than by ISC from the singlet state. In reports of porphyrin-fullerene dyads, the exciplex rather than an individual excited state or charge separated state is found to be the most stable state. This is due to the favourable orbital interactions between

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porphyrins and the fullerene however the conditions satisfying this formation are very narrow\textsuperscript{33,34}.

Detailed reports on the dynamics of charge generation in polymer-fullerene dyads are very limited to date. Reports on the charge generation dynamics in oligomer - fullerene dyads however are more numerous. For oligophenylene-vinylene (OPV)-fullerene dyads, energy transfer from oligomer to fullerene is reported to be ultrafast, occurring typically within a few hundred fs, and preceding electron transfer whatever the solvent or conditions\textsuperscript{27,28}. In a polar solvent subsequent charge transfer generates the charge separated state on a ps timescale with recombination on a ns timescale. In non-polar solvents charge generation doesn’t occur attributed to the charge separated state lying higher in energy than the fullerene singlet state. Following energy transfer to the fullerene, the triplet state is formed via ISC from the singlet\textsuperscript{24,28}. For oligothiophene based donor-fullerene dyads there is more competition between energy and electron transfer from donor to fullerene, depending on the conditions surrounding the dyad. In polar solutions, the formation of the CSS is reported on a ps timescale from both direct and indirect mechanisms, suggesting a competition between energy and electron transfer on this timescale\textsuperscript{26,30}. Recombination of the separated charges is reported on a ps-ns timescale. In non-polar solutions, charge formation occurs indirectly, if at all, due to the energetic de-stabilisation of the CSS state\textsuperscript{29,32}.

\begin{thebibliography}{99}


\end{thebibliography}
The charge generation dynamics in dyads in solution therefore show a great dependence on factors such as the energy of the charge separated state or a preceding energy transfer step. These may be potential reasons behind the poor charge generation seen in F8BT:PCBM devices as we address in detail below.

6.3 Methodology

F8BT was synthesised by Dow Chemicals and used as supplied. The F8BT had a $M_w 4.95 \times 10^4$ and $M_n 1.5 \times 10^4$. The PCBM was purchased from Nano-C Inc. and used without further purification. All F8BT and PCBM films were made from chlorobenzene solution typically at a concentration of $\sim 10$mg per ml. Films are labelled by their weight percentage of PCBM in solution, 5%, 10%, 25%, 50%, 66% or as pure F8BT and PCBM respectively. Films were fabricated and tested as described in Experimental methods chapter of this thesis.

6.4 Results

This chapter presents the results of absorption and photoluminescence spectra, emission lifetime and transient absorption data on the pristine F8BT, PCBM and blend films.

6.4.1 Absorption and Photoluminescence

Figure 6-2. UV-Visible absorption data for the F8BT and PCBM pristine films and a series of 5%, 25%, 50%, 66% F8BT:PCBM blends films (PCBM by weight).

Figure 6-2 shows the absorption spectra of the pristine and blend films. Pristine F8BT absorption shows two maxima at ~330nm and another at ~460nm, with an intensity ratio of 0.92:1 for the 330 and 460nm peaks respectively. The 460nm absorption peak has been assigned to a charge transfer (CT) transition with the electron residing mainly on the benzothiadiazole unit and the hole on the fluorene unit, while the blue absorption has been assigned to the direct $\pi - \pi^*$ transition delocalised over the whole chain and is a split transition\(^{14}\). With increasing PCBM concentration in the blend films, we see heightened...
absorption in the U.V. due to absorption by PCBM, which distorts the ratio of the two absorption maxima and eventually masks the split absorption of the F8BT blue peak. The long tail of absorption that persists out to 900nm in the pure PCBM film has been reported previously in this thesis. As the spectra of the blend films are a superimposition of the two component spectra this suggests that there is no noticable charge transfer interactions occurring between the two materials in the ground state.

**Figure 6-3.** Steady-state photoluminescence measurements (ss-PL) for the F8BT, blend and PCBM films adjusted for film absorption. Excitation was at 470nm around the peak F8BT absorption. Inset shows the magnification of the low intensity PL at 680nm-750nm. Note that the PL yield from the pristine F8BT film has been reduced in scale by a factor of a hundred.

Figure 6-3 shows the photoluminescence emission spectra for the pristine and blend films. F8BT is highly emissive and shows a single broad emission with a maximum at 536nm.

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With the addition of 5% by weight PCBM we see more than 2 orders of magnitude quenching of the F8BT emission and the quenching ratio continues to increase with increasing PCBM concentration in the blend films. Not present in the pure F8BT film but visible in the blend and pristine PCBM film is an emission peak at ~720nm. The inset to Figure 6-3 shows a magnification of this emission peak. The emission peak steadily red-shifts with increasing PCBM concentration but shows a maximum in emission intensity in the 25% film. From previous results in Chapter 5 of this thesis on PCBM films in polystyrene, this emission peak and its behaviour is recognised as coming from the $S_1$ state of PCBM. Previously it has been shown that with increasing aggregation of PCBM the $S_1$ transition shifts to lower energies and decreases in emission yield.

![Figure 6-4](image)

**Figure 6-4.** Excitation spectra for the emission around ~720nm for the 5% and pristine PCBM film compared to the normalised absorption spectra for those films.

The excitation spectra of the emission peak at ~720nm is shown in Figure 6-4 for the pristine PCBM film and the 5% PCBM blend film. As expected for the pristine PCBM film, the excitation spectrum of the 720nm emission follows closely the shape of the absorption spectrum. At the same wavelength the excitation spectrum of the 5% blend film however follows closely the absorption spectrum of both components in the film, the spectra fol-
following the absorption of the F8BT peak at ~470nm. This result suggests that excitation of F8BT leads to the population of the $S_1$ state of PCBM and therefore some mechanism of energy transfer from F8BT to PCBM.

**Figure 6-5.** Normalised PL emission from the blend and pristine films at a higher energy. The 100% PCBM film was excited at 443nm while the blend and F8BT films where excited at 337 nm.

Figure 6-5 shows a normalised emission spectra for the pure and blend films at higher energies around the F8BT emission maxima. The emission at 500nm seen in the pure PCBM films is attributed to luminescence from a charge transfer state in crystalline PCBM as discussed in Chapter 5. In the blend films with increasing PCBM concentration the observed emission maxima becomes increasingly blue shifted and broadened on the high energy side with respect to the original F8BT emission. The broadening of the emission is assigned to a rise in PCBM high energy emission associated to the crystallisation of PCBM, while the F8BT emission becomes increasingly quenched.
6.4.2 Time-resolved single photon counting

Figure 6-6. Single photon counting data for the emission ~720nm in the blend and pristine films. (a) and (b) display the same data however (b) has the emissive decays normalised at 1.3ns. Excitation wavelength was 440nm.

Figure 6-6 shows the Single Photon Counting data taken from pristine and blend films monitoring the emission at ~720nm. As the tail of F8BT emission extends further than 700nm into the red, these decays monitor both the F8BT emissive decay and the emissive decay belonging to the PCBM emission peak at 720nm. In (a) the decay from the pristine F8BT film (red line) is mono-exponential with a characteristic lifetime of ~1.1ns. In the 5% film (orange line) we observe a 2 component decay, the quenched lifetime of the F8BT emission and the lifetime of the new emission at 720nm. The fluorescence lifetime of F8BT in the 5% film is quenched close to the system response of ~200ps with the longer-lived component having a ~1.2ns lifetime. In blend films with a PCBM concentration of 25% upwards, the F8BT emission lifetime is no longer visible at all, attributable to the quenching of the emission lifetime to beyond the resolution of the system. In Figure 6-6, (b) shows the same data but normalised at 1.3ns, so any contribution from the quenched F8BT component can be negated and a fair comparisons of the lifetime of the remaining emissive state at different PCBM concentrations can be made. From (b), the lifetime of the PCBM emissive state in all the blend films is found to be similar to the lifetime of that from the pristine PCBM film with perhaps only a small decrease in lifetime with increas-
ing PCBM concentration from 5% to 100%. The calculated lifetime of ~1.2ns is close to the reported PCBM lifetime of ~1ns\textsuperscript{35} and further supports the assignment of this decay to PCBM emission. The small change in emissive lifetime with PCBM loading however does not reflect the large changes to the ss-PL for the emission at this wavelength (see Figure 6-3 on page 143). This suggests that it is not a quenching of the emissive state that lowers the PL yield at 720nm with increasing PCBM concentration, but a decrease in the initial yield of $^1$PCBM* states.

![Figure 6-7](image)

**Figure 6-7.** Single Photon Counting data on the pristine and blend films for the emission ~560nm. Graphs (a) and (b) display the same data however (b) has the emissive decays normalised at 2ns. Excitation wavelength was 440nm.

The emission lifetimes for the pristine and blend films monitored at 560nm are shown in Figure 6-7. The pure F8BT blend shows an emissive lifetime of ~0.5ns at 560nm in contrast to the ~1.1ns lifetime seen at 700nm. Such a distinction in lifetimes depending on emission wavelength is not unexpected in organic films, which have previously been reported to show slower dynamics at longer wavelengths. The pristine PCBM film shows a lifetime at 560nm of ~1ns. As with the emission at ~720nm, the 5% PCBM by weight film shows two components to its decay with the shorter lived component ascribed to the quenched F8BT emission, again close to the system response. At higher concentration

ratios, the F8BT emission is quenched beyond the resolution of the SPC system and cannot be observed. Graph (b) shows the emissive decays from the blend films normalised to a time of 2ns in order to negate any contribution to the blend decays from the quenched F8BT emission. The pristine F8BT lifetime (red line) is added for comparison. As the lifetimes for the emission coming from the blends is similar to that seen from the pristine PCBM film, the emission at this wavelength likely originates from the PCBM as was suggested earlier.
6.4.3 Transient absorption spectroscopy

6.4.3.1 Pristine F8BT films

Figure 6-8. Transient absorption spectra (a) and transient decay kinetics (b) for a pristine F8BT film following excitation at 470nm. Absorption spectra was taken at 800ns using 20µJ per cm² per pulse excitation at 470nm. Film absorption was 0.7 at 470nm. For the transient kinetics the probe wavelength was 830nm. Inset to the bottom graph shows a plot of the signal amplitude against excitation intensity. Lifetime of the decays are found to be ~1µs.

Figure 6-8 shows the transient absorption spectra and decay kinetics taken from a pristine F8BT film. The transient decays show approximate first order decay kinetics with a 1 µs lifetime. Reports in the literature suggest that the long lived transient in F8BT films is the F8BT triplet, in agreement with the observed first order decays. The transient absorption
spectra is broad and shows a single peak at 850nm (±30 nm) and is similar in shape to the reported triplet spectra of F8BT\textsuperscript{36}.

### 6.4.3.2 Blend films

![Figure 6-9](image)

**Figure 6-9.** Transient absorption spectra \((a)\) and transient decay kinetics \((b)\) for a 10% PCBM F8BT:PCBM blend film following excitation at 470nm. Absorption spectra was taken 12\(\mu\)s after excitation (20\(\mu\)J/cm\(^2\) per pulse) and the absorbance of the blend film was 0.37 at 470nm. For comparison an absorption spectrum of a methanofullerene triplet taken from the literature is also shown (grey line) taken from Ref 37. For the transient kinetics the probe wavelength was 830nm. Inset to \((b)\) graph shows a plot of the signal amplitude against excitation intensity. Lifetime to the decays are found to be \(\sim\)11\(\mu\)s (blue line).

Figure 6-9 (a) shows the transient absorption spectra for a 10% PCBM film following excitation at 470nm with 20µJ/cm² per pulse fluence. While the ground state absorption at 470nm is mainly due to the F8BT, the obtained transient spectra is not similar to that obtained from the pure F8BT film. Instead the spectra closely matches that reported for triplet methanofullerenes in solution, with a characteristic peak at 720nm and shoulder at 830nm\textsuperscript{19,37}. A reference absorption spectrum of a methanofullerene triplet is shown in Figure 6-9 as the grey line\textsuperscript{37} for comparison with the spectrum obtained from the blend film. Figure 6-9 (b) displays the transient absorption decay kinetics for the 10% PCBM blend film. In comparison with the decays from the pure F8BT film, the decay kinetics for the blend films are also first order in appearance but with an order of magnitude longer lifetime of \approx 11\mu s (cf. \approx 1\mu s). The comparison of the transient decay to the methanofullerene triplet is also in agreement with the observed lifetime of methanofullerenes in solution (\approx 30\mu s\textsuperscript{37}). Analogous experiments were done on a 5% PCBM film and a similar absorption spectra and first order kinetics were obtained, with a lifetime 19\mu s (see Appendix).

![Graph of transient decay kinetics for different F8BT:PCBM ratios](image)

**Figure 6-10.** Comparison of the transient decays in the blends of increasing weight fraction of PCBM. Higher excitation powers were used for the higher PCBM concentration films in order to have all the decays begin at comparable initial amplitudes (excitation used 5-20µJ/cm²). Decays were probed at 830nm following excitation at 470nm. The pristine PCBM film gave no detectable signal.

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Figure 6-10 shows the transient decays for the F8BT:PCBM blend films as a function of blend composition. The transient decays in both the 10% and 25% films are long lived and near first order, however further increases in PCBM concentration results in transients become faster and non-exponential. The decreasing halflife of the transient with increasing PCBM concentration is consistent with the analogous data for PCBM:PS films (Chapter 5) and in reports in the literature where triplet yield and lifetime are known to decrease with increasing aggregation of C$_{60}$. Table 6-1 shows approximate signal lifetimes for the transients in the pristine and blend films of increasing PCBM concentration.

<table>
<thead>
<tr>
<th>Film</th>
<th>Measured Lifetime ($\tau$ /$\mu$s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>95% F8BT: 5% PCBM</td>
<td>19</td>
</tr>
<tr>
<td>90% F8BT: 10% PCBM</td>
<td>11</td>
</tr>
<tr>
<td>75% F8BT: 25% PCBM</td>
<td>11</td>
</tr>
<tr>
<td>50% F8BT: 50% PCBM</td>
<td>0.7</td>
</tr>
<tr>
<td>34% F8BT: 66% PCBM</td>
<td>0.1</td>
</tr>
<tr>
<td>100% F8BT</td>
<td>1</td>
</tr>
<tr>
<td>100% PCBM</td>
<td>No signal</td>
</tr>
</tbody>
</table>

**Table 6-1.** Approximate measured lifetimes for the transient signal in the pristine F8BT & PCBM and blend films.
Figure 6-11. Transient decay kinetics for the 50% blend film following excitation at 470nm at different intensities. Probe wavelength was 830nm and excitation is marked in the key in units of µJ per cm² per pulse. Inset plots the maximum signal amplitude against used excitation intensity (~30ns).

Figure 6-11 shows the behaviour of the transient decay kinetics in the 50% PCBM film at various excitation intensities. In the figure the signal decay in the 50% film at the lowest excitation intensity of ~1.3µJ per cm² per pulse is roughly first order in appearance (τ ~0.7µs), however with higher excitation intensities the decays become more multi-exponential. The inset to Figure 6-11 shows a plot of the signal amplitude against the excitation intensity used as shows that the rise in signal amplitude is sublinear against excitation intensity. The deviation from single exponential kinetics and the sublinear increase in signal size at higher laser powers in the film suggests the presence of a bimolecular quenching mechanism such as triplet-triplet annihilation is occurring at earlier times. The proposed triplet-triplet quenching is in addition to the quenching of the triplet lifetime with increasing PCBM aggregation, which we assign to increasing non-radiative decay channels in the PCBM aggregate.
Figure 6-12. Excitation spectra for the yield of triplet against the wavelength of excitation in the 5% blend film (black squares). The absorption for the film is also shown (black line). Triplet yield was monitored at the triplet absorption maxima at 720nm.

Figure 6-12 shows the excitation wavelength dependence of the yield of triplet PCBM formation in the 5% film. The excitation spectra follows closely the absorption spectra of the film even at the F8BT absorption maximum at 470nm. This indicates that the triplets formed in the blend films are not only generated following PCBM light absorption but after F8BT absorption as well.

6.5 Discussion

The data in the results section can be broadly be described as belonging into two categories. The first category describes the de-activation of the F8BT singlet excited state to give rise to the PCBM singlet excited state through a mechanism of energy transfer. For the second category, the data reported for F8BT/PCBM blend films show close analogy with the results for PS/PCBM films reported in Chapter 5 of this thesis. As the behaviour of PCBM excited states has been discussed at depth in the previous chapter it will not be
repeated here and this discussion will focus on the mechanism of energy transfer from F8BT* to PCBM.

The quenching of the F8BT polymer emission in these blends with PCBM is correlated with a rise in another luminescence peak at 720nm. Analogy with literature results and the work on PCBM:PS films in this thesis the emission peak at 720nm is assigned to emission from the PCBM singlet state. Seen most clearly in the excitation spectrum in Figure 6-4, we observe that light absorbed by the F8BT leads to emission by the PCBM and as such the energy of the F8BT excited state is somehow transferred to the PCBM.

6.5.1 Energy diagram for the F8BT:PCBM blend film

![Energy Diagram](image)

**Figure 6-13.** Proposed kinetic scheme following photoexcitation of F8BT in a F8BT:PCBM blend. There are two possible mechanisms to energy transfer from F8BT* to PCBM, either by (1) direct Förster dipole-dipole energy transfer or (2) via the formation of an intermediate charge separated state (CSS) that undergoes recombination to form the PCBM singlet or triplet.
Figure 6-13 proposes a kinetic scheme for the F8BT:PCBM blend film. The energies of the important chromophore S₁ and T₁ states marked are from the literature (F8BT38, 3F8BT39, 1,3PCBM18). If electron transfer occurred from donor to acceptor in the blend, this would create a radical ion pair on the two components. Typically in papers on solution phase dyads this radical pair is named the charge separated state (CSS) as no concern need be given to the potential movement of charges. In films however, the dissociation and transport of charges may also be important and therefore this CSS is better described as a bound radical pair, held together by their mutual electrostatic attraction. For the sake of precedence we will continue to describe the bound radical pairs as the CSS and use the term ‘mobile’ charges to describe polarons which have overcome their own attraction. Typically in solution dyads and in films, the energy of the charge separated state (CSS) of F8BT⁺ & PCBM⁻ created by electron transfer across the interface between donor and acceptor can be calculated using the Weller equation40. Whilst there is ambiguity over the exact electron affinity of PCBM (reported in the literature between 3.7-4.3eV), boundaries for the energy of the CSS can be established. As the PCBM singlet state is stable with respect to the CSS then the energy of the CSS must be higher than 1.8eV. In the literature a similar polymer both structurally and electronically to F8BT, PFDTBT (IP 5.8 Ea 3.5)12, when mixed with PCBM shows efficient charge generation and collection12,13,15. If in PFDTBT:PCBM blends the energy of the CSS (as governed by Weller’s Equation) lies below that of the polymer singlet than by proxy so must the energy of the CSS in F8BT:PCBM blends. This being the case the energy of the F8BT singlet state (2.4eV) places an upper boundary to the energy of the CSS and so the CSS lies in between the energy of the two component singlet states as shown in Figure 6-13.

The kinetic scheme shown in Figure 6-13 presents two different mechanisms for the observed F8BT singlet excited state quenching and formation of the triplet methanofullerene as the final product of photoexcitation. The first mechanism under discussion is

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simply long range Förster energy transfer from F8BT* to PCBM. The second mechanism involves the quenching of the F8BT exciton at the interface with PCBM, creating a CSS intermediate which then decays into the PCBM singlet or triplet state.

6.5.1.1 Förster energy transfer efficiency

The efficiency of energy transfer between the F8BT and PCBM can be calculated using a modified form of the equation first proposed by Förster (Kawski et al 1973) which gives the rate of energy transfer ($k_{EnT}$) at any given distance from donor to acceptor ($R_{DA}$).

$$k_{EnT} = \frac{9000(\ln10)\eta_D^2\kappa^2}{128\pi^5N_A\tau_f(R_{DA})} \int_0^\infty \frac{f_D(\tilde{\nu})\epsilon_A(\tilde{\nu})}{\tilde{\nu}^4} d\tilde{\nu}$$

**Equation 6-1.** Modified Förster equation used by Kawski et al

In Equation 6-1, $\eta_D^0$ represents the quantum yield of fluorescence of the donor in the absence of the acceptor; $\eta$ is the refractive index; $N_A$ is Avogadro’s number; $E_A(\nu)$ is the molar decadic extinction co-efficient of the acceptor and $f_D(\nu)$ the spectrum of the donor fluorescence measured in quanta per wavenumber interval and normalised to unity on the same scale. $\kappa$ denotes a dimensionless geometric factor determined by the orientations in space for the transition dipole moments of D* and A. Its average is 0.816 for fast brownian rotation of both molecules (Förster 1948) and 0.690 for random but rigid orientations (Maksimov and Rozman 1962, Steinberg 1968). There is some argument to the proposition that $\kappa$ should equal 1 when using C$_{60}$ due to the fast rotation (<ps) and symmetrical nature of the molecule$^{41}$, however this does not hold for derivatised fullerenes where the adduct hinders rotation of the fullerene$^{42}$. In the case with PCBM therefore the value of $\kappa$...

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0.690 for \( \kappa \) proposed by Maksimov and Rozman for random but rigid molecules will be used.

Calculation of the spectral overlap integral between donor and acceptor used in Equation 6-1 requires knowledge of the absorption spectrum of the acceptor PCBM. The absorption spectra of the pristine PCBM film as seen in Figure 6-2 is not an accurate representation of the absorption spectra of PCBM at a low loading seen in the 5\% PCBM blend film, as the PCBM spectrum is reported to broaden significantly with PCBM loading in the visible region of the spectrum (see chapter 5). The absorption spectrum of PCBM is not easily extracted from the absorption spectrum of the 5\% film itself as the PCBM absorption is small and masked by the absorption of F8BT. In order to approximate the absorption spectrum of PCBM therefore, the absorption spectrum of a 1:7 w/w PCBM:PS film was used (from Chapter 5 of this thesis).

**Figure 6-14.** Normalised absorption spectrum of a 1:7 w/w PCBM:PS film overlaid with the emission spectrum of F8BT. The good overlap between F8BT emission and PCBM absorption leads to efficient energy transfer from F8BT to PCBM.
Figure 6-14 illustrates the spectral overlap between the F8BT emission and the PCBM absorption. For calculation of $k_{\text{EnT}}$ the absorption spectrum of F8BT in solution was used as this differs only little from that in the film. The extinction co-efficient for F8BT and PCBM were taken from the literature or estimated by using the film absorption and knowing the film thickness; $\varepsilon_{456}(\text{F8BT})=22,600 \text{ M}^{-1}\text{cm}^{-1}$ $\varepsilon_{333}(\text{PCBM})=45100 \text{ M}^{-1}\text{cm}^{-1}$ respectively$^{43,44}$. The refractive index of a pure F8BT film is reported to be $1.8^{45}$ with a quantum yield of fluorescence of $0.51^{38}$ and an emissive lifetime of 0.5ns is used.

Figure 6-15 shows a plot of the rate of Förster energy transfer versus the separation distance between the F8BT and PCBM (PCBM at approximately 5% weight concentration). A dotted line has been added representing the expected rate of energy transfer as calculated from the quenching of ss-PL spectra.

Figure 6-15. Rate of energy transfer against distance between F8BT and PCBM (PCBM at approximately 5% weight concentration). A dotted line has been added representing the expected rate of energy transfer as calculated from the quenching of ss-PL spectra.


44. Calculated from PCBM film thickness and ground state absorption spectra.

based on Förster energy transfer and shown in Figure 6-15 (red line). The calculated $R_0$ distance for F8BT:F8BT energy transfer was 2.1nm and F8BT:PCBM 2.8nm. Figure 6-15 shows how that the rate of energy transfer from F8BT to PCBM is effective at separation distances of greater than 2 nm and is faster than the equivalent energy transfer from F8BT to F8BT at similar distances.

To account for the >99% quenching of the F8BT emission seen in the 5% PCBM film, this requires the rate of quenching ($k_q$) introduced by addition of PCBM to be $\sim 2 \times 10^{11} \text{ s}^{-1}$. On Figure 6-15 this energy transfer rate is marked by a dotted line and we can see that to support such a rate of quenching the separation distance of F8BT from a PCBM should not exceed 1.3nm.

To check the feasibility of this physically if we consider a homogeneous distribution of PCBM inside the F8BT film we can calculate the average separation distance between PCBM's. While the weight contribution of PCBM in the film is 5%, due to the disparity in molecular weights of F8BT (522.79g/mol) and PCBM (910.88g/mol) the ratio of chromophores is actually closer to 30 to 1. Assuming that the blend film has an overall density of 1g cm$^{-3}$ then a single PCBM molecule would occupy the centre of roughly a 3.0nm$^3$ volume of F8BT. Assuming a uniform distribution to PCBM within the film, this would place only 32% of the volume of F8BT within a point to point distance of 1.3nm from the centre of a PCBM. A point to point estimation however may underestimate the amount of energy transfer as the distance between donor and acceptor are on the same length scale as the delocalisation or size of the molecules themselves. This can be accounted for by subtracting the dimensions of the donor and acceptor from their separation distances [F8BT radius = dimensions (1.5nm x 0.4nm x 0.5nm)$^{1/3}$ and PCBM has a radius 0.7nm]$^{7,46}$ or equivalently, adding these to $r$. Including the radii of the molecules/

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chromophores themselves \((r_D + r_A = 1.1\text{nm})\) the fraction of the F8BT volume that would undergo energy transfer to PCBM at a rate greater or equal to \(2\times10^{11}\text{s}^{-1}\) becomes \(\sim 1\) (c.a. 0.98).

The separation distance between F8BT and PCBM therefore maybe sufficiently small to facilitate the fast energy transfer and explain the observed two order of magnitude quenching. Furthermore the proposed quick rate of energy transfer \(\sim 10^{11}\text{s}^{-1}\) conforms with the time resolved emission data where the rise of the PCBM emission signal was found to be faster than the 200ps resolution of the equipment.

**6.5.2 Exciton migration**

The second mechanism is the most commonly proposed method of polymer emission quenching in polymer:fullerene blend films, namely the charge splitting of the polymer exciton by the fullerene following migration to the interface. The migration of the exciton through polymer films is also commonly described using the Förster mechanism of energy transfer\(^{47}\). In Figure 6-15 the rate of energy transfer from F8BT\(^*\) to F8BT calculated by the Förster mechanism is shown as the red line. Assuming a fixed distance between chromophores of \(\sim 1\text{nm}\)\(^{48}\), the exciton migration rate via energy transfer is calculated to be sufficiently fast \((>10^{-11}\text{s}^{-1})\) that >99% quenching of the excitons at the interface is feasible.

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48. Assuming a film density of \(1\text{gcm}^{-3}\), F8BT Mw (522.79g mol\(^{-1}\)) then the separation distance between neighbouring F8BT units is given by,

\[
R_{DD} = \left( \frac{M_w}{N_a \times d} \right)^{\frac{1}{3}}
\]
While exciton migration is sufficiently fast, in this particular material combination of F8BT and PCBM there is no evidence to suggest that this mechanism is actually active. If the CSS is formed as a stable intermediate then under certain conditions the charges should be directly observable. TAS studies of the recombination behaviour of charges have been explained in depth in a previous chapter, however no sign of charge formation were observed by TAS studies of F8BT:PCBM blends. Furthermore, in devices the electric field would be expected to split the CSS apart and drive the charges to the electrode for collection. The poor photovoltaic performance of F8BT:PCBM devices however with their negligible current collection even at short circuit, suggest that the CSS is never formed. This is in contrast to PFDTBT:PCBM devices\(^{13}\) that despite having an energy scheme similar to F8BT:PCBM, showed high current collection in devices.

Given the lack of evidence for the formation of a CSS it is prudent to assume that nearly all F8BT excitons in F8BT:PCBM blends are quenched via Förster energy transfer. The appreciation of the efficiency of Forster energy transfer is remarkable, as many publications to date regarding bulk heterojunction CP:PCBM films do not consider energy transfer to the fullerene to be a means of exciton quenching in blend films. Typically the level of polymer luminescence quenching is used directly as proof of charge generation but as can be seen here for F8BT:PCBM, this is a misconception and polymer quenching is not equivalent to charge generation. This may have lead some reports in the literature to overestimate the yield of charge generation based on photoluminescence quenching results. The demonstration of energy transfer in a bulk heterojunction polymer-fullerene blend also resolves the disparity between the charge-generation mechanisms reported in donor-fullerene dyads and those in bulk heterojunctions films.

The recognition of Forster energy transfer from polymer to fullerene may encourage research into making beneficial use of this effect. Beneficially for solar cell design, the presence of energy transfer from donor to fullerene would decrease the need for large exci-
ton migration distances. With less constraints over the scale of component mixing more phase segregated blend films would become just as efficient charge producers as finely mixed blends while retaining the beneficial properties of larger phases. Furthermore compounds which have good material properties for use in solar cells but are limited by their poor phase mixing in blend films such as many porphyrins or perylenes, could become viable materials for organic solar cells by maximising the potential for long range energy transfer.

There is also another more pragmatic implication of the work in this chapter. In the choice of polymer materials for polymer-fullerene solar cells there is a balance between using a polymer with a high ionisation potential, linked to a device with a larger open circuit voltage, against the potential loss in charge production as the fullerene singlet state will no longer undergo charge transfer. If energy transfer from the donor excited state to PCBM is a major path for quenching of the donor excited state, substantial losses to charge generation will occur, as is the case here for F8BT:PCBM, where energy transfer from F8BT* to PCBM, effectively impedes any charge generation. If a fullerene component with larger light absorption such as C₇₀ were to become commonly used or if a light harvesting replacement to the fullerene was used (such as another polymer,) the loss in charge generation would be critical in undermining the device efficiency. To minimise this constraint a donor polymer with a low quantum yield for fluorescence, and poor absorption-emission overlap with the fullerene is essential.

6.6 Conclusions

Following photoexcitation of F8BT, we see quenching of the F8BT excited state through fast Förster singlet-singlet energy transfer to the PCBM which then decays via ISC to yield the triplet. The CSS of F8BT⁺ and PCBM⁻ is not thought to be formed even as an intermediate. Unlike in many other CP:PCBM blend films the PCBM singlet is stable with

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regard to the energy of the free charges and does not undergo charge separation. This leads to negligible charge generation in F8BT:PCBM blends. The cause for the high energy of the charge separated state is the high ionisation potential of the F8BT of 5.9eV.

6.7 Appendix

6.7.1 Further discussions

6.7.1.1 Calculations for energy transfer from P3HT to PCBM

![Diagram](image)

**Figure 6-16.** Calculated rate of energy transfer in P3HT:PCBM 60% and F8BT:PCBM 60% blends for any given separation distance between polymer and fullerene.

While energy transfer rather than electron transfer from donor to fullerene acceptor is common in dyads\textsuperscript{16-22} the situation in polymer:fullerene blend films is less clear. As a brief illustration Figure 6-16 shows a plot of the rate of Förster energy transfer versus distance for F8BT:PCBM and P3HT:PCBM blends at a high (>60%) loading of PCBM. The values for P3HT fluorescence lifetime used was 200ps\textsuperscript{38}, with a refractive index 2\textsuperscript{50}.
It is clear that for the P3HT:PCBM blend films that the efficiency of Förster energy transfer is much reduced compared to F8BT:PCBM. This is primarily due to a weaker overlap between the P3HT luminescence and PCBM absorption spectrum (P3HT has a red-shifted luminescence compared to F8BT) and the low polymer fluorescence quantum yield (0.04$^{38}$). Given the low rate of Förster energy transfer P3HT exciton migration to the interface may be the dominant form of P3HT excited state quenching. For polymers with fluorescence quantum yields in between P3HT and F8BT we may expect some competitive behaviour between direct and indirect charge generation.

6.7.2 Supplementary data

6.7.2.1 Transient absorption spectra and decay kinetics of the 5% PCBM film

Figure 6-17. Transient Absorption Spectra of the transient present in the 5% film, 12µs following excitation at 470nm. The decay kinetics (inset) at the peak of absorption (720nm) have a lifetime of 19µs.

The TAS spectra of the transient in the 5% film looks similar to that shown in more detail in the 10% film. The decay in the 5% film however is slightly longer lived than in the 10% film, 19µs against 11µs respectively.
6.7.2.2 Solution spectra of F8BT

![Graph](image_url)

**Figure 6-18.** Absorption and emission spectra of F8BT in chlorobenzene solution. The absorption spectra was taken at a concentration of $5 \times 10^{-5}$ mol L$^{-1}$ and the emission spectra at a concentration of $2.5 \times 10^{-6}$ mol L$^{-1}$ using an excitation wavelength of 460nm.

The solution spectra of F8BT was used in the Förster energy transfer equations as the pure film tends to show non-corrected absorption due to scatter at low energy wavelengths. The absorption in solution shows slight blue shifting of the lowest energy absorption peak compared to the film (abs max. $\sim 470$nm) which will have some effect on the energy transfer calculations for the solid state. The emission spectra remains the same for the solution as in the film.
6.7.2.3 PCBM solution spectra

Figure 6-19. Absorption spectra of PCBM at different concentrations in chlorobenzene solution: (green line) $2.7 \times 10^{-5}$ mol L$^{-1}$, (blue line) $7.4 \times 10^{-6}$ mol L$^{-1}$, (purple line) $2.7 \times 10^{-6}$ mol L$^{-1}$, (dark yellow) $9.3 \times 10^{-7}$ mol L$^{-1}$. Inset overlays the absorbance and emission spectra for PCBM at a concentration of $7.4 \times 10^{-6}$ mol L$^{-1}$.

The solution spectra of PCBM. With increased solution concentration the absorption of light in the visible region increases disproportionately. Note that the PCBM S$_1$ absorption peak is visible in the chlorobenzene solution at ~700nm. The inset shows the overlaid solution absorption and photoluminescence spectra. There is some broadening to the PCBM photoluminescence however the emission peak is at 697nm in agreement with the absorption peak at the same wavelength. This absorption and emission is thought to come from the first singlet excited state in PCBM and therefore the energy of the S1 state is ~1.8eV.
General Conclusions

7.1 Photogeneration and recombination of charges in polymer-fullerene solar cells.

Through the combined work of all the chapters in this thesis a basic outline of the mechanisms leading to charge photogeneration and recombination in polymer-fullerene films can be drawn.

Figure 7-1. Charge photogeneration and recombination processes in polymer-fullerene films. The blue arrows are all excitation processes, green arrows are internal energy changes, and the red arrows represent charge recombination loss mechanisms.
7.1.1 Charge photogeneration

The left part of Figure 7-1 concerns the photogeneration of charges in polymer-fullerene films. As was inferred from the results in Chapter 3 ‘Recombination in P3HT:PCBM’ a bound radical ion pair is formed after charge transfer from the polymer to the fullerene and this is assumed to be the primary product formed at the interface. The rates of charge transfer to form the radical ion pair, $k_{CT(I)}$ and $k_{CT(II)}$, depend on the driving force for the forward electron transfer reaction ($\Delta G^0_{CT}$) which in turn depends on the energy of the radical ion pair with respect to the energy of the excited polymer or fullerene states, as given by the Rehm-Weller equation. As in most cases the energy of the polymer and fullerene excited states differ, the different Gibbs free energy for the forward electron transfer should give rise to a different rate for radical pair formation at the interface depending on which component is excited. Ultrafast (<ps) charge transfer between polymer and fullerene has been reported following excitation of the polymer ($k_{CT(I)}$)$^{1,2}$, however to date there had been no report on the rate of charge transfer following excitation of PCBM ($k_{CT(II)}$).

Figure 7-2. The initial formation of a ‘hot’ radical ion pair at the interface may explain the efficient dissociation of charges (ref.4). Besides recombination to the ground state, the bound radical pair may also recombine to form a low-lying triplet state (ref 6).

There is much debate in the literature over the mechanism by which bound ion pairs at the interface overcome their strong electrostatic attraction ($E_c$ in Figure 7-1) to become free charges. In Figure 7-1, free charge formation (i.e mobile charge carriers) is described as being an energetically ‘uphill’ process however reports in the literature suggest that the mechanism for charge formation at donor-acceptor interfaces maybe more complicated. Morteani et al have suggested that following charge transfer at the interface that a ‘hot’ radical pair is initially formed (see Figure 7-2). This hot state has a similar energy to that of the free charges and therefore the dissociation of charges is facilitated. If the hot state relaxes before dissociation, then a cold ‘bound’ radical pair is formed which is less likely to dissociate into free charges. In the report by Morteani et al, the formation of a cold bound radical pair was described as being a precursor to reformation of the singlet excited state, however in other reports the recombination of the bound radical pair is an intermediate step in the formation of the lower lying triplet state. For instance, reports on the

recombination of the geminate pair \((K_{\text{CR(III)}})\) formed at the donor-acceptor interface in PFB:F8BT, leads to greater yields of the F8BT triplet than by \textit{inter system crossing} from the F8BT singlet state \((k_{\text{ISC}})\) alone\(^6\,^7\).

Another important consideration in the charge generation process is the competing rate of energy transfer from the polymer to fullerene. If there is sufficient overlap between the donor emission and the acceptor absorption (or vice versa), then energy transfer from the donor excited state to the acceptor may compete with charge transfer to deactivate the donor excited state\(^8\,^9\). As was discussed in Chapter 6 for F8BT:PCBM films, a quick rate of energy transfer from the polymer excited state to PCBM \((k_{\text{EnT}}>k_{\text{CT(I)}})\) results in the PCBM singlet state being formed following excitation of F8BT, rather than yielding charges. If the radical pair energy lies below that of the excited state created by energy transfer then charge transfer will occur indirectly, otherwise as for the case of F8BT:PCBM blend films, charges will not be formed and the material combination will show poor photovoltaic ability.

A tentative additional charge generation process is shown near the top of Figure 7-1 and represents the direct formation of free charges within semiconductor-like PCBM. At high PCBM concentrations the aggregated PCBM forms a molecular crystal which has access to charge transfer excited states\(^10\). These charge transfer excitons can either thermally or


under the influence of an electric field dissociate to form free hole and electron charges in PCBM. While this charge generation process has not directly been observed in this thesis, studies on the behaviour of the parent molecule C$_{60}$, suggest that this process is possible$^{11}$.

7.1.2 Charge recombination

As shown in Figure 7-1, the bound radical pair formed after charge transfer can decay to ground state. Transient recombination decays in Chapter 3 of this thesis in accord with values suggested elsewhere in the literature$^{3}$ suggest that geminate recombination of charges in P3HT:PCBM films is around the ns timescale, however this is only a tentative assignment and further confirmation is necessary ($k_{CR(I)}$ ~ns$^{-1}$).

The rate of charge separation ($k_{diss}$) must be competitive with the rate of geminate recombination ($k_{CR(I)}$) otherwise polymer-fullerene blends would not show as high external quantum efficiencies (incident light to collected electron) as they do$^{12,13}$. By definition therefore the rate of charge dissociation must be on the same order or quicker than the proposed rate of geminate recombination ($k_{diss} > k_{CR(I)}$~ns$^{-1}$). In Chapter 3, the transient decays on a tens of ns to µs timescale were found to follow second order rate kinetics and were therefore assigned to bimolecular recombination of free charges. From fitting results to the kinetics the rate of bimolecular recombination ($k_{CR(II)}$) was found to be ~10$^{-12}$cm$^3$ s$^{-1}$ for P3HT:PCBM blend films in good agreement with literature values$^{14}$, however the actual rate varied on the fabrication conditions of the P3HT:PCBM blend film.

For the mobile hole charges in the polymer phase the presence of hole ‘traps’ causes the bimolecular recombination of charges to become distorted. Hole charge trap sites offer greater stabilisation to the polaron thereby localising the charge and providing a barrier to its further movement and bimolecular recombination. Studies of the trap limited recombination in P3HT:PCBM films by transient absorption spectroscopy place the number of trap sites to be $\sim 10^{17} \text{cm}^{-3}$. The large range in energy of the trap sites means that the rate of detrapping $k_{tr}^{-1}$ varies from microseconds to longer than a millisecond. At a low number of generated charges the recombination decay is completely dominated by the trap limited decay and the bimolecular recombination of charges only becomes visible near or above the limit where all the trap states become filled.

### 7.2 Future work

Both the geminate and bimolecular recombination of charges are mechanisms which place limits on polymer-fullerene device efficiency\(^{15}\). The geminate recombination of charges was inferred from results on P3HT:PCBM blends in Chapter 3, however observations of the geminate recombination directly were hampered by the time resolution of the equipment. Further studies using a quicker response transient absorption system may allow the geminate recombination of charges to be studied with the aim of understanding the crucial parameters governing that recombination. Also in Chapter 3, a link between the surface area of interface between donor and acceptor and the rate of bimolecular recombination was proposed. Further study in needed to establish if a reduction in bimolecular recombination, and therefore the use of thicker photoactive blend films that absorb more light, is possible by limiting the D-A interface. In Chapter 6 on studies of F8BT:PCBM blend films, the high IP of F8BT (5.9eV) meant that the PCBM excited state was lower in energy than the charge separated state and would not undergo charge splitting. A high IP however is desired as this is linked to a higher device open circuit voltage\(^{16}\), and so further work

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could focus on identifying the highest IP a polymer can have without hindering charge
generation from splitting of the PCBM excited state. In chapter 5, the presence of interac-
tions between PCBM molecules was observed leading to different properties over those
of the single isolated molecule. Further experiments to clarify the effects of aggregate
crystalline PCBM on device properties are necessary.