The influence of dielectric screening on bimolecular recombination in binary and ternary organic solar cells

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The influence of dielectric screening on bimolecular recombination in binary and ternary organic solar cells

Guanran Zhang

Supervisors: Associate Professor Attila J. Mozer
Dr. Tracey M. Clarke

"This thesis is presented as part of the requirements for the award of the Degree of Doctor of Philosophy of the University of Wollongong"

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ABSTRACT

Semiconducting polymer-based solar cells (PSCs) have attracted great interest due to its potential for manufacturing at low cost and large quantity. While the performance of PSCs has significantly improved in the past twenty years, the state-of-the-art efficiency around 12% is still much lower than the theoretical efficiency limit, which is above 31%. One of the major bottlenecks to PSC efficiency is bimolecular recombination, which limits the active layer thickness and thus sunlight harvesting of the solar cell. Reduced bimolecular recombination, in which the bimolecular recombination rate is one to three orders of magnitude lower than predicted by a model based on Langevin theory, has been shown to have beneficial effects most notably allowing large fill factors at large active layer thicknesses. Reduced recombination has been observed only in a few confirmed cases of conjugated polymer/fullerene blends. Initially, this study was motivated to find additional examples of material systems with reduced recombination in order to establish general design guides for new high-performance materials.

This thesis focuses on a low bandgap diketopyrrolopyrrole polymer (DT-PDPP2T-TT) based PSC, which was reported to show high efficiency at large active layer thickness, thus having the potential of showing reduced recombination. Serendipitously, DT-PDPP2T-TT was found to exhibit exceptionally high dielectric constant of 16.8 in pristine polymer even at low frequency of 1 kHz in Chapter 5, which warranted further detailed experiments to investigate the effect of dielectric screening on bimolecular recombination.

The high dielectric constant in DT-PDPP2T-TT is of particular interest, because weak dielectric screening in polymer solar cells has been attributed to one of the major contributions to charge recombination. In polymer solar cells where charge mobility is relatively low, the charge recombination is typically assumed to be limited by charge carrier diffusion in the bulk heterojunction blend. Due to the weak dielectric screening ($\varepsilon_r$ between 3 - 4), the Coulomb capture radius is around 5 nm, which is on the same magnitude of the domain sizes in bulk heterojunction blends. By increasing the dielectric constant to 10, the Coulomb capture radius reduces to around 1 nm. Thus the probability for charge carriers to meet and recombine is reduced. Due to the lack of high dielectric constant materials, however, this theory could not be put to test until now.
This thesis is structured as follows:

Firstly, the experimental techniques used to measure dielectric constant, bimolecular recombination kinetics and charge carrier mobility are established in Chapter 3 on a well-studied polymer: fullerene acceptor system, poly(3-hexylthiophene-2,5-diyl): [6,6]-Phenyl C₆₁ butyric acid methyl ester (P3HT: [60]PCBM). The aim of this chapter is to establish the characterization methodology for dielectric constant, charge carrier mobility and recombination kinetics, which are essential for studies of bimolecular recombination.

Bimolecular recombination in DT-PDPP2T-TT: PCBM blend solar cells is studied in Chapter 4. Using the methodology established in Chapter 3, a high dielectric constant of 7 and high charge mobility of $1.8 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is measured in the device. The recombination kinetics in DT-PDPP2T-TT: PCBM is found to be diffusion-dominated, however a recombination reduction factor of 0.04 is observed which suggests reduced recombination compared to diffusion-dominated kinetics. Since bimolecular recombination is controlled by the mobility of the charge carriers as well as the strength of dielectric screening, the need for a methodology to assess bimolecular recombination at matched charge mobility is raised.

Chapter 5 compares frequency modulated and time-resolved techniques for geometric capacitance measurement to establish the accuracy and validity of the obtained dielectric constant values. The frequency dependence of geometric capacitance, the selection of equivalent circuit for impedance spectrum modelling and the applied bias dependence of geometric capacitance are studied in detail for the first time in literature. The effect of device geometry, material batch dependence and the effects of processing environment on dielectric constant are also investigated for the first time in literature. An experimental guideline is proposed for accurate geometric capacitance measurement. A large batch-to-batch dependence of the measured dielectric constant is observed, which is a complication for the studies carried out in this thesis. For consistency, all comparison studies are carried out using the same polymer batch, and the dielectric constant, charge mobility, and recombination kinetics in DT-PDPP2T-TT based devices using different polymer batches are characterized and studied independently. It is further observed that the exposure to air and moisture decreases the dielectric constant in DT-PDPP2T-TT, possibly due to oxygen and water induced doping.
In Chapter 6, three well-established polymer: PCBM systems with low dielectric constant are compared in terms of recombination kinetics with DT-PDPP2T-TT: PCBM. By comparing the bimolecular recombination coefficient normalized to charge mobility in these systems, one of the main findings in this thesis is made: at saturated charge density, DT-PDPP2T-TT: PCBM showed the lowest normalized recombination coefficient value and longest charge carrier lifetime at the same open circuit voltage compared to other systems with lower dielectric constant.

Chapter 7 aims at exploiting the benefit of enhanced dielectric screening in DT-DPP2T-TT in a novel polymer solar cell design. Ternary blend solar cells are used to enhance panchromatic photon harvesting in a single junction bulk heterojunction solar cell by mixing two polymer donors with different absorption profiles to increase solar spectrum coverage. One of the limitations in ternary solar cells is the active layer thickness, which is limited by the recombination within the ternary blend layer. In this sense, the high dielectric constant DT-PDPP2T-TT is a promising candidate for ternary blend solar cells which could potentially reduce bimolecular recombination when blended with a low dielectric constant polymer thereby allowing thicker active layer to be made. For this purpose, poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-B;3,4-B’]dithiophene)-alt-4,7(2,1,3-benzothiadiazole)] (PCPDTBT) is selected which has a dielectric constant of 3.5 and diffusion-dominated recombination. The energy offset between PCPDTBT and DT-PDPP2T-TT allows hole carriers to be transported predominantly in PCPDTBT domains, therefore in principle the influence of dielectric constant could be evaluated independent of mobility.

Transient absorption spectroscopy was used to examine hole transfer mechanism in the ternary blends, where spectroscopic evidence was observed suggesting hole transfer from DT-PDPP2T-TT to PCPDTBT. The dielectric constant values in ternary blend devices with varying DT-PDPP2T-TT contents are measured, showing dielectric constant values between 3 and 4 are obtained. The low dielectric constants suggest that the ternary blends using PCPDTBT: DT-PDPP2T-TT: PCBM have weak dielectric screening similar to that in PCPDTBT: PCBM, therefore the bimolecular recombination kinetics are expected to be similar to that in PCPDTBT: PCBM. Surprisingly, the ternary blend devices show lower bimolecular recombination coefficient normalized to mobility compared to PCPDTBT: PCBM. This suggests reduced recombination in ternary blend devices,
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<th>Description</th>
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<tr>
<td>A</td>
<td>Acceptor</td>
</tr>
<tr>
<td>BHJ</td>
<td>Bulk Heterojunction</td>
</tr>
<tr>
<td>CB</td>
<td>Chlorobenzene</td>
</tr>
<tr>
<td>CELIV</td>
<td>Charge extraction by Linearly Increasing Voltage</td>
</tr>
<tr>
<td>CF</td>
<td>Chloroform</td>
</tr>
<tr>
<td>CT</td>
<td>Charge transfer</td>
</tr>
<tr>
<td>D</td>
<td>Donor</td>
</tr>
<tr>
<td>DIO</td>
<td>1,8-diiodooctane</td>
</tr>
<tr>
<td>EQE</td>
<td>External quantum efficiency</td>
</tr>
<tr>
<td>ETL</td>
<td>Electron transport layer</td>
</tr>
<tr>
<td>FF</td>
<td>Fill factor</td>
</tr>
<tr>
<td>FRET</td>
<td>Forster resonance energy transfer</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>HTL</td>
<td>Hole transport layer</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>Jsc</td>
<td>Short circuit current density</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>NIR</td>
<td>Near-infrared</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>OD</td>
<td>Optical density</td>
</tr>
<tr>
<td>o-DCB</td>
<td>Ortho-dichlorobenzene</td>
</tr>
<tr>
<td>PCE</td>
<td>Photo-conversion efficiency</td>
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<tr>
<td>PEDOT:PSS</td>
<td>Poly-(ethylenedioxythiophene): poly(styrene sulfonate)</td>
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<td>PCPDTBT</td>
<td>Poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta [2,1-b;3,4-b’]dithiophene)-alt-4,7(2,1,3-benzothiadiazole)]</td>
</tr>
<tr>
<td>PSC</td>
<td>Polymer solar cells</td>
</tr>
<tr>
<td>RPM</td>
<td>revolution per minute</td>
</tr>
<tr>
<td>rr-P3HT</td>
<td>regioregular- Poly(3-hexylthiophene-2,5-diyl)</td>
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<td>TAS</td>
<td>Transient absorption spectroscopy</td>
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<td>Time-resolved charge extraction</td>
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Chapter 1 Introduction
1.1 Motivation

The application of \( \pi \)-conjugated polymers in photovoltaic devices has been extensively investigated over the past 30 years due to their flexible nature and solution processibility, potentially allowing low-cost large scale production.\(^{[1]} \) The first polymer solar cells (PSCs) were composed of a transparent conducting electrode, a layer of conducting polymer and the counter electrode with efficiency generally below 0.1 \%.\(^{[2]} \) The first leap in PSC development was in 1992,\(^{[3]} \) when the discovery of photoinduced charge transfer between a soluble conducting polymer, poly[1-methoxy,5-(2’-ethyl-hexyloxy)-p-phenylenevinylene] (MEH-PPV), and buckminsterfullerene (C\(_{60} \)) led to the application of fullerene in a bilayer heterojunction.\(^{[3]} \) The bilayer MEH-PPV: C\(_{60} \) PSC device showed a power conversion efficiency of 0.04 \% under 514 nm illumination with low intensity of 1 mW cm\(^{-2} \).\(^{[4]} \) As C\(_{60} \) has a larger electron mobility and higher electron affinity and ionization potential than the polymer, it absorbs strongly at wavelengths between 300 and 500 nm\(^{[5]} \) and acts as an electron acceptor. The semiconducting polymer MEH-PPV absorbs predominantly between 370 nm and 600 nm\(^{[3]} \) and acts as electron donor.

The second leap in PSC efficiency came from the concept of bulk heterojunction (BHJ) which is achieved by intimately blending the polymer donor and the fullerene acceptor to form a nanometre-scale interpenetrating network.\(^{[2b]} \) Such interpenetrating BHJ structure allows large charge generation interface area and selective charge collection at corresponding electrodes; thus, in principle, charge separation efficiency and collection efficiency near unity can be achieved. In 2001, 2.5 \% efficiency was achieved using poly[2-methoxy-5-(3’,7’-dimethyloctyloxy)-p-phenylenevinylene] (MDMO-PPV) and 3’-phenyl-3’H-cyclopropa[1,9](C60-Ih)[5,6] fullerene-3’-butanoic acid methyl ester ([60]PCBM) BHJ blend.\(^{[6]} \) The active layer morphology was modified by changing the blend solution solvent from toluene to chlorobenzene, resulting in much more uniform mixing of the components and eventually leading to over two-fold increase in device efficiency. These contributions have sparked a wide spread research focusing on BHJ solar cells.

Since then, the BHJ solar cells have seen rapid developments, with state-of-the-art devices exceeding 12 \% in efficiency.\(^{[7]} \) Although current research on PSCs has made remarkable progress, the performance in PSC is still much lower than the theoretical upper limit of 31% predicted from Shockley-Queisser theory.\(^{[8]} \) The efficiency loss comes
from several aspects including optical loss, recombination loss, and low mobility, where non-radiative recombination loss has been shown to account for the largest part of efficiency loss.\cite{9} Therefore, to overcome the efficiency limit in PSC, it is necessary to reduce non-radiative recombination.

The understanding of recombination between photo-generated free carriers in PSCs, i.e. bimolecular recombination, has been one of the research focuses in the field of polymer solar cells. The Langevin theory, originally proposed for mobility dependent recombination of ions in gases in 1903, was first used to approximate the bimolecular recombination kinetics in a trap-free PSC system.\cite{10} While Langevin theory has been used to describe bimolecular recombination in a number of systems, strongly reduced recombination kinetics from that described by Langevin recombination has also been observed in a number of systems.\cite{11} One of the most famous examples of non-Langevin systems is rr-P3HT: PCBM, where bimolecular recombination coefficient was reported four orders of magnitude smaller than the Langevin recombination coefficient.\cite{11a} The research on bimolecular recombination in PSC systems was then divided into two branches. One is to experimentally study recombination behaviour in different PSC systems looking for efficient systems with reduced bimolecular recombination; the other is to develop physical models to explain the observed deviation from Langevin behaviour.

To experimentally study bimolecular recombination kinetics in PSC systems, a number of steady state and transient techniques has been used to obtain charge mobility, bimolecular recombination coefficient, and charge carrier lifetime in PSC systems. Bimolecular recombination kinetics have been investigated in a wide range of systems, where reduced recombination compared to Langevin recombination was claimed for a number of systems.\cite{12} Several approaches have been demonstrated to contribute to reduced bimolecular recombination in PSC systems, such as controlling the film morphology\cite{12d, 13} and polymer structure.\cite{12b} However, despite the effort devoted, very few systems demonstrated clear features of non-Langevin behaviour.

For theoretical development aiming to explain reduced bimolecular recombination, rr-P3HT: PCBM is typically used as the model system. A number of explanations has been proposed to account for the non-Langevin behaviour in P3HT: PCBM, including the disordered potential landscape theory proposed by Arkhipov,\cite{14} multiple trapping theory suggested by Nelson,\cite{15} two-dimensional Langevin recombination theory,\cite{16} among
others. These theories succeeded in simulating recombination kinetics and device performance in some of the model systems, however due to the large difference in chemical structure, film morphology and electronic properties in different semiconducting polymers further understanding is required to develop a more universal theory.

In terms of overcoming efficiency limit in PSC devices, novel approaches such as multiple junction solar cells and ternary blend PSCs have been proposed. These approaches aims not to reduce recombination in PSC devices but to enhance photon harvesting within the device, thereby increasing $J_{SC}$ and thus device efficiency. The concept of tandem photovoltaic devices is to apply semiconductors with complementing absorption windows in different sub-cells, and by connecting these sub-cells in parallel or series the current or voltage output can be significantly enhanced compared to single-junction solar cells. High efficiency tandem solar cells have been successfully fabricated using inorganic semiconductors, where efficiency as high as 50 % has been achieved by applying semiconductors of different bandgap in four sub-cells.\textsuperscript{[17]} Organic tandem cells have also shown enhanced efficiency compared to single junction PSC, where efficiency above 12 % has been reported.\textsuperscript{[18]} However, one of the technical problems with tandem solar cells is the complicated device design, where interfacial layers between sub-cells need to be carefully engineered to allow light transmission while blocking charge injection. Ternary solar cells have thus been proposed as a simplified alternative to tandem cells, where polymers with different bandgaps are intimately mixed with the acceptor to form bulk heterojunction structure. In ternary solar cells, the device architecture is the same as binary bulk-heterojunction solar cells, thus making the device fabrication much more straight forward and commercially achievable than tandem devices. Efficiencies above 11 % have been successfully achieved in ternary solar cells by selecting structurally compatible polymers with complimentary absorption.\textsuperscript{[19]} One of the major efficiency limitations in ternary solar cells is the small active layer thickness between 80 to 100 nm due to bimolecular recombination. As the principle of ternary solar cells is to enhance photon absorption, the small thickness significantly limits absorption of the active layer thus rendering the benefit of enhanced absorption in ternary design.

One of the promising approaches to reduce bimolecular recombination is by increasing the dielectric screening in the PSC. Due to the intrinsically low dielectric constant in
semiconducting polymers caused by the lack of long range order, several consequences in terms of the nature of charge carrier generation, transport, and recombination are present in organic solar cells. As a result of weak carrier screening and localized nature of the electronic states in disordered polymers, after photoexcitation the electrons and holes are bound by the Coulomb force, forming so-called excitons. The strong Coulomb interaction leads to additional energy required to separate bounded electron and hole pairs, which not only limits charge generation efficiency but also contributes to charge recombination. Increasing the strength of dielectric screening thus has the potential of increasing charge generation efficiency and reducing charge recombination, allowing larger active layer thickness and higher efficiency. In a simulation study reported by Koster et al., over an order of magnitude decrease in exciton binding energy and close to 100 % increase in device performance can be achieved by increasing the dielectric constant in PSC device from 3 to 10. However, PSC systems demonstrating strong dielectric screening are scarce, and thus very few studies have been carried out regarding the dielectric effect on the photophysics in PSCs.

This thesis is thus motivated by the open question: What is the effect of dielectric screening on bimolecular recombination? More specifically, this thesis is aimed at answering the following questions:

1) How to accurately characterize the strength of dielectric screening in PSCs?
2) How to independently study the dielectric effect on bimolecular recombination, taking into account the difference in charge density, mobility and other parameters?
3) How does the bimolecular recombination kinetics change in a ternary blend PSC in the presence of a high dielectric constant polymer?

1.2 Influence of dielectric screening on polymer solar cell operation

1.2.1 The importance of dielectric screening

The dielectric constant of most semiconducting polymers is within the range of 3 - 5. These values are much lower compared to the dielectric constants of inorganic semiconductors such as silicon, which has a dielectric constant of 11.4. The low dielectric constant of semiconducting polymers has several consequences in terms of the
nature of charge carrier generation, transport, and recombination processes in organic semiconductor devices such as solar cells:

The Coulomb energy $E_C$ of a bound electron and hole pair is inversely proportional to the dielectric constant $\varepsilon_r$:

$$E_C = \frac{e^2}{4\pi\varepsilon_r\varepsilon_0 r_0}$$

(1.1)

where $e$ is the elementary charge, $\varepsilon_0$ is the vacuum permittivity and $r_0$ is the electron-hole separation distance. In inorganic semiconductors, the high dielectric constant and highly delocalized electrons lead to $E_C$ on the same order of magnitude as the thermal energy $k_B T$ ($k_B T = 0.026$ eV at $T = 297$ K). In organic semiconductors, however, due to the relatively low dielectric constant and more localized electrons, the $E_C$ is usually large ($0.1$ eV to $1$ eV). As a result, charge separation of electron and hole pairs is not spontaneous. Therefore, additional energy is needed for efficient charge separation.[22] For this purpose, fullerene derivatives are commonly used in semiconducting polymer: fullerene blends as an electron acceptor, forming the so-called bulk heterojunction (BHJ) photovoltaics. In these BHJ devices the energy offset between the LUMO of semiconducting polymer and fullerene derivative need to be sufficiently large (typically above $0.2$-$0.3$ eV,[23]) in order to provide the required driving force. However, electron transfer from the donor to the acceptors leads to a loss of the electrochemical energy of the electrons and holes, lowering the maximum attainable power conversion efficiency. New semiconducting polymers with high dielectric constant would potentially remove this limitation making single junction organic semiconductor layers with increased charge separation efficiency possible.[20]

Once successfully separated, electrons and holes may still undergo bimolecular recombination, which is the recombination of dissociated carriers. In diffusion-limited bimolecular recombination (aka Langevin recombination), the recombination coefficient $\beta_L$ is calculated as:

$$\beta_L = \frac{e\mu}{\varepsilon_0\varepsilon_r}$$

(1.2)
where $\mu$ is the charge mobility. Charge screening is weak in the photo-active layer of PSC devices thus charge recombination is expected to be fast. There are several consequences of fast recombination: i) if free carriers are lost through recombination, the open circuit voltage ($V_{oc}$) is reduced; ii) the lower free carrier yield leads to lower quantum efficiency, which in turn leads to reduced short circuit current ($J_{sc}$); iii) the fill factor ($FF$) of the device will also be reduced if the carrier mobility is low, i.e. the extraction of carriers is slower than recombination; iv) due to strong charge recombination and low mobility, the optimum active layer thickness in most PSC systems is limited to between 80 – 100 nm.\(^{[24]}\)

When the active layer thickness is increased, the $V_{oc}$ as well as $FF$ decrease significantly, resulting in decreased device performance. In an active layer with weak dielectric screening, the screening of charged defects is weak. As a result, charge carrier transport is affected and the charge mobility is low (on the order of $10^{-5} – 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$,\(^{[24d, 25]}\)) in most low dielectric constant organic materials. The low charge mobility further contributes to carrier recombination and the active layer thickness limitations.

In order to provide a comprehensive theoretical understanding of dielectric effect on bimolecular recombination, in the following subsections the influence of dielectric screening on charge photogeneration, geminate recombination and bimolecular recombination are introduced in sequential order.

### 1.2.2 Charge photogeneration in PSC

Photovoltaic devices operate by converting photon energy into electrical energy. The charge photogeneration in PSCs is generalized into subsequent steps as follows (Figure 1.1). If the energy of a photon exceeds the bandgap of a semiconductor, the photon energy is absorbed to form an excited state. Unlike photovoltaics based on inorganic semiconductors where electrons at excited states readily dissociate into free electrons,\(^{[9b]}\) the weak dielectric screening (dielectric constant $\varepsilon_r$ in the range of 3 - 4) in semiconducting polymers results in a strong Coulomb attraction between the photogenerated electron and hole (Equation 1.1). As a result, a Coulombically bound electron-hole pair, or exciton, is formed after photoexcitation. The hot exciton thermalises (typically within the exciton lifetime), until the electron decays back to the ground state and recombines or reaches a donor-acceptor interface with a certain distance (thermalisation length) between electron and hole. The bound electron-hole pair at the
D/A interface separated by the thermalisation length is typically referred to as a charge-transfer (CT) state.

As a result, additional driving force is required to separate the CT state and yield free charge carriers. This is achieved by the presence of an energy offset between the electron affinity of the polymer donor and acceptor (see Figure 1.2). The D/A electron affinity offset is selected such that there is enough driving force for charge separation while the voltage loss due to electron transfer is minimized.\textsuperscript{23c} The most commonly adopted structure in PSCs is bulk-heterojunction, where the polymer electron donor (D)\textsuperscript{27} and the electron acceptor (A) are intimately blended to form a interpenetrating network (Figure 1.1).\textsuperscript{2b} The interpenetrating BHJ structure creates large D/A interface areas, which allows the separated charge carriers to diffuse to the transport domain before the recombination takes place.
The formation of Coulombically bound excitons is inherently correlated with the low dielectric constant in semiconducting polymers. In inorganic semiconductors, the high dielectric constant and highly delocalized electrons lead to $E_C$ on the same order of magnitude as the thermal energy $k_B T$ ($k_B T = 0.026 \text{ eV at } T = 297 \text{ K}$). In organic semiconductors, however, due to the relatively low dielectric constant and more localized electrons, the $E_C$ is usually large (0.1 eV to 1 eV). As a result, charge separation of electron and hole pairs is not spontaneous. New semiconducting polymers with high dielectric constant would potentially remove this limitation making single junction organic semiconductor layers with increased charge separation efficiency possible.\cite{20}

1.2.3 Geminate recombination in BHJ solar cells

Charge carrier recombination is typically separated into geminate recombination and bimolecular recombination in literature.\cite{28} Geminate recombination of bound electron-hole pairs (i.e. CT state) takes place between opposite charge carriers generated from the same exciton. Geminate recombination is typically quantified by the dissociation probability $P(E)$, at which the charge carrier can escape from the Coulomb force and become fully dissociated. The dissociation probability model was first suggested by Onsager in 1938, which considered the recombination of CT state in the presence of an external electric field. Onsager theory proposed that, after the CT state is generated it either recombines under the Coulomb force, or dissociates into free charge carriers under...
the thermal energy $k_B T$. The probability of dissociation thus depends on the competition between thermal energy and the energy caused by Coulomb force. Onsager proposed a Coulomb capture radius $r_c$, which is the minimum distance required between the bound pair in order to dissociate.\[26\]

$$r_c = \frac{e^2}{4\pi \varepsilon_0 \varepsilon_r k_B T}$$  \hspace{1cm} (1.3)$$

where $e$ is the elementary charge, $\varepsilon_0$ is the vacuum permittivity, $\varepsilon_r$ is the dielectric constant of the medium, $k_B$ is the Boltzmann’s constant and $T$ is the temperature. When the thermalisation distance exceeds $r_c$ the charge carriers are considered dissociated. If the thermalisation distance is smaller than $r_c$, the charge carriers will dissociate at a probability of $P(E)$, while geminate recombination can also take place at a probability of 1 - $P(E)$. The dissociation probability given by Onsager theory depends on the applied electric field $E$, the thermalisation distance $a$ and the temperature $T$ (at low field strength):\[26\]

$$P(E) = \exp\left(-\frac{r_c}{a}\right)(1 + \frac{er_c}{2k_B T}E)$$  \hspace{1cm} (1.4)$$

As Onsager theory was first proposed to describe charge dissociation in a weak electrolyte, a number of limitations are present when it is used to describe charge generation in conjugated polymers. For example, Onsager theory assumes recombination to take place spontaneously when the distance between electron and hole approaches zero. This assumption did not consider the finite lifetime of the CT state. Braun\[29\] modified the Onsager theory by introducing a CT state lifetime, and within the lifetime dissociation of the CT state into free carriers is a reversible process which may occur multiple times. Wojcik and Tachiya introduced a finite intrinsic recombination rate at which electron and hole with non-zero separation will recombine, which allows the Onsager theory to be more readily applied in semiconducting polymers.\[26\]

Since the Coulomb capture radius $r_c$ is inversely proportional to $\varepsilon_r$ the low $\varepsilon_r$ in most of the semiconducting polymer systems ($\varepsilon_r$ between 3 and 4) leads to large $r_c$ and thus low $P(E)$. This is a direct indication of weak dielectric screening reducing charge generation efficiency and inducing strong geminate recombination. The influence of dielectric screening on exciton binding has been reported previously, where the dielectric constant
in N,N0-bis(1-naphthyl)-N,N0-diphenyl-1,10-biphenyl-4,40-diamine (NPD): C₆₀ blend was controlled by varying the polymer: C₆₀ blending ratio. As εr increased, a redshift in the electroluminescence spectra peak was observed for the NPD: C₆₀ blends, indicating a reduction in the energy of CT state.³⁰

1.2.4 Bimolecular recombination mechanisms in PSC

Bimolecular recombination involves the recombination between fully dissociated charge carriers originating from two different excitons. In the photo-excited BHJ layer at open circuit the mobile charge carriers diffuse within their transport domains, until the distance between an electron and hole is small enough for them to be captured by the Coulomb force and recombine. The recombination rate is thus dependent on the charge carrier concentration of electrons and holes:

\[
\frac{dn}{dt} = \frac{dp}{dt} = -\beta np
\]

where \(n\) and \(p\) are the concentration of electrons and holes, respectively and \(\beta\) is the recombination coefficient.³¹

Langevin theory was first suggested to describe recombination between free electron and a free hole.²⁶ According to Langevin theory, in a trap-free three-dimensional system charge recombination occurs when the distance between electron and hole is smaller than \(r_c\). The Langevin theory proposed a recombination coefficient \(\beta\), aka Langevin coefficient \(\beta_L\), which is determined by the mobility of opposite charge carriers and the dielectric constant of the media (Equation 1.2).¹⁰ However, in many cases the calculated \(\beta_L\) value is much larger than experimentally obtained \(\beta\). To describe bimolecular recombination in PSC systems where \(\beta\) deviation is present, a bimolecular recombination reduction factor \(\xi\) was introduced. Hence the bimolecular recombination kinetics can be described using a corrected equation, see Figure 1.3. The bimolecular recombination coefficient \(\beta\) is thus dependent on three different parameters: the charge carrier mobility \(\mu\), the reduction factor \(\xi\) and the dielectric constant \(\varepsilon_r\). The charge carrier mobility \(\mu\) determines how fast can electrons and holes encounter within the Coulomb capture radius, the reduction factor \(\xi\) determines how likely is the electron and hole recombine once they come into the Coulomb capture radius, and the dielectric constant \(\varepsilon_r\) determines the length of Coulomb capture radius \(r_c\).
Figure 1.3 Schematic of parameters influencing bimolecular recombination coefficient $\beta$, where $\zeta$ is the Langevin reduction factor, $\mu$ is charge carrier mobility and $\varepsilon_r$ is dielectric constant. The arrows show the processes that each parameter is related to in bimolecular recombination.

In order to evaluate the influence of dielectric screening on bimolecular recombination independent of other parameters, the influence of charge mobility, reduction factor and dielectric screening on recombination are discussed in detail below.

1.2.4.1 Charge carrier mobility

Charge carrier mobility in a PSC device characterizes the charge transport property within the active layer. As illustrated in Figure 1.3, charge carrier mobility of electrons and holes determines how fast they can diffuse to a donor / acceptor interface to be captured by their mutual Coulomb force. In this sense, slower mobility will directly lead to smaller $\beta$, leading to reduced recombination. However, high mobility is essential for efficient charge collection at the electrodes. After photogeneration, the charge carriers need to be
transported to the electrodes to be collected. Under the presence of an electric field, the electrons and holes drift through the active layer within their lifetime $\tau$ until they reach the collecting electrodes or recombine. The drift length of charge carriers, $l_d$, under an electric field $E$ is determined as:

$$l_d = \mu \cdot \tau \cdot E$$  \hspace{1cm} (1.6).

For charge carriers to be efficiently extracted from the device within the carrier lifetime, long drift length is necessary thus requiring high mobility.

The hole mobility in different polymers can vary over three orders of magnitude, from $10^{-5}$ to $10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$ (see Table 1.1). Such large difference in charge mobility in semiconducting polymer is affected by a number of properties, including sidechain structure, molecular weight and regioregularity. In some polymer: acceptor systems the electron and hole mobility can be different by over an order of magnitude. The unbalanced electron and hole mobility can lead to the accumulation of carriers with lower mobility in the active layer, which will result in a space-charge region at the slow carrier collecting electrode. As a result, the charge collection efficiency will be reduced, resulting in lower performance of the device. In systems where the electron and hole mobilities are largely unbalanced, S-shaped J-V curves can appear. In terms of recombination, the Langevin theory suggested $\beta_L$, dependent on the sum of electron and hole mobilities ($\mu_e + \mu_h$). However, Groves and Greenham has shown that while Langevin theory correctly established the dependence of $\beta$ on mobility, the use of a sum mobility fails to consider the anisotropic charge transport and two-dimensional charge transport. While modified Langevin theories using spatially averaged mobility and slower carrier mobility have been put forward, neither theory provided very good fit to experimental data. This failure partly arises from the fact that most of the OPV systems are not purely Langevin by nature, which means that deviation in their bimolecular recombination coefficient from the Langevin recombination coefficient is expected due to the presence of trap states and energetic barriers. In this thesis, the Langevin recombination coefficient is calculated using mobility values obtained directly from photo-CELIV, which is described in further details below.
The charge carrier mobility $\mu$ can be obtained from a number of steady state and transient techniques, including photogenerated charge extraction by linearly increasing voltage (photo-CELIV), surface-generation time-of-flight (TOF), space-charge limited current (SCLC) or field-effect transistor (FET). Surface-generation TOF requires large active layer thickness with high optical density ($OD > 10$) to ensure only the surface of the film is photo-excited. SCLC technique (steady state or dark injection) measures a monopolar device, i.e. only one type of carrier is present. FET devices have very different architecture compared to other techniques which use conventional PSC architecture, where bottom-gate bottom-contact configuration using Si/SiO$_2$ as bottom gate/contact and Au or Ag as top source-drain is commonly used. Photo-CELIV uses working PSC devices, thus the obtained mobility can be readily correlated with other characteristics measured from the same device. It allows the measurement of charge carrier mobility under varying delay time, excitation density and maximum to investigate the dependence of mobility on charge relaxation, charge carrier concentration and electric field. Another benefit of photo-CELIV is that from the extraction transients the charge density could be calculated, thus providing additional information on charge density decay kinetics and recombination. The main disadvantage with photo-CELIV measurements is that it only measures the faster carriers in the device, and the sign of the dominant carrier (electron or hole) producing the photo-CELIV transients cannot be determined. In an OPV system where the electron and hole mobilities are balanced, the extraction transients of electrons and holes in photo-CELIV measurements cannot be distinguished due to the proximity of extraction timeframe. As a result, the charge carrier mobility obtained from such photo-CELIV transients is an averaged value. In devices where the electron and hole mobilities are unbalanced, e.g. the mobility of fast and slow carriers vary by over an order of magnitude, two transient peaks may be observed in photo-CELIV measurements. Therefore, the mobility obtained from photo-CELIV is only relevant to bimolecular recombination when it’s measured at timescales corresponding to the recombination process, i.e. from sub-microsecond to microsecond timescales. In this thesis photo-CELIV is selected to measure charge carrier mobility, and the mobility dependence on delay time, excitation density and electric field will be discussed in Chapter 4.

1.2.4.2 Reduction factor

The bimolecular recombination reduction factor $\zeta$ is introduced to account for the difference between experimentally obtained $\beta$ and Langevin recombination coefficient $\beta_L$. 
The reduction factor $\xi$ has been widely used to evaluate whether a system has non-Langevin recombination. Here non-Langevin recombination refers to bimolecular recombination which cannot be described by diffusion-dominated kinetics, and have a reduction factor significantly smaller than 1. The term reduced recombination is also used in this thesis, which refers to bimolecular recombination kinetics slower than Langevin recombination kinetics, but not necessarily caused by non-Langevin behaviour.

A number of explanations have been proposed to explain non-Langevin recombination. The majority of proposed mechanisms for non-Langevin recombination are from two aspects: energetic and morphology considerations. Arkhipov et al. take the disordered energy landscape in semiconducting polymers into consideration and suggested that the presence of an energetic barrier at D/A interface, which is formed by the presence of interfacial dipoles in an ordered phase, reduces recombination.$^{[14]}$ Recombination via tail states was proposed by Nelson in 2003,$^{[15]}$ who suggested a multiple trapping and detrapping process of charge carriers dominating charge transport, and the recombination rate is controlled by thermal activation of trapped carriers. Another mechanism by Hilczer and Tachiya suggested that recombination of free electrons and holes lead to the formation of CT state.$^{[31]}$ Therefore, electron and hole encounters do not necessarily lead to charge annihilation and the recombination after the formation of CT state is essentially the same between geminate recombination and bimolecular recombination.$^{[39]}$

Morphology based mechanisms, such as 2D Langevin recombination,$^{[40]}$ has also been proposed, which suggested that in P3HT: PCBM films with highly ordered lamella or fibril-like structure the probability for charges to meet is reduced. Clarke et al. proposed that in a silole-based copolymer PDTSiTTz: PCBM bulk heterojunctions, the reduced bimolecular recombination is due to an energetic barrier formed by an amorphous polymer and/or PCBM phase at the donor / acceptor phase.$^{[41]}$

When the bimolecular recombination is well described by Langevin theory, the reduction factor $\xi$ is close to 1. In non-Langevin systems such as P3HT: PCBM, the reduction factor $\xi$ can be as small as $10^{-4}$. However, in practice the difference between non-Langevin and Langevin systems is ambiguous when using $\xi$ as the sole judgement. It is noted that a large variation in $\xi$ has been reported for P3HT: PCBM, depending strongly on morphology.$^{[42]}$ For example, after thermal annealing $\xi$ decreased by approximately two orders of magnitudes in rr-P3HT: PCBM,$^{[43]}$ which has been attributed to lateral phase
separation between crystalline P3HT and PCBM domains.\textsuperscript{[44]} Even in P3HT: PCBM devices with similar thermal annealing treatment, a large difference in reported $\xi$ has been observed. Armin et al. reported $\xi = 0.059$ in annealed rr-P3HT: PCBM device,\textsuperscript{[45]} which was over an order of magnitude higher than that reported by Hamilton et al.\textsuperscript{[46]} In systems with Langevin recombination, while $\xi$ between 0.1 and 1 is typically observed,\textsuperscript{[11b, 25c]} lower $\xi$ has also been reported. For example, Albrecht et al. reported a lower $\xi = 0.05$ in PCPDTBT: PCBM when processed with 1,8-diiodooctane (DIO), compared to $\xi = 0.15$ when processed without DIO.\textsuperscript{[47]} The lower $\xi$ was achieved by an increase in charge mobility in devices processed with DIO, rather than a decrease in $\beta$. To determine bimolecular recombination kinetics in a PSC system, the $\xi$ value is typically used in combination with other kinetic features, which will be discussed in further detail in Section 1.3.

\subsection*{1.2.4.3 Dielectric constant}

The value of dielectric constant is influenced by different dielectric loss processes depending on the investigated timescales. There are five dielectric loss mechanisms in polymers, known as polarization processes, and taking place on different timescales.

1) Electronic polarization, which is caused by the distortion of electron cloud under an external electric field. This is the most fundamental polarization mechanism that exists in all materials.

2) Vibrational polarization, which refers to the displacement of atoms under an applied field in a molecule.

3) Dipolar polarization is the reorientation of dipoles towards the direction of the applied field, and is only present in materials with permanent dipoles.

4) Ionic polarization in polymers involves the physical transport of ions within polymers.

5) Interfacial polarization is the accumulation of charge carriers at interfaces under an electric field within a heterogeneous system.

As the scale of dielectric displacement increases from electronic polarization to interfacial polarization, the time it requires for the displacement to take place also increases. As a
result, these polarization mechanisms are directly related to the frequency of the electric field, thus time. The dielectric constant of a material is directly related to polarizability through Clausius-Mossotti equation,[48] and thus the frequency dependent polarization mechanisms translate into frequency dependent dielectric constant. Figure 1.4 shows these polarization mechanisms on different frequency domains. The typical timescale of charge generation and recombination processes in organic solar cells are also shown.[26]

As the focus of this thesis is on charge recombination processes in PSC, the dielectric constant value on the same timescale of recombination process is of relevance. Bimolecular recombination typically takes place on the nanosecond to millisecond timescale;[26] therefore the dielectric constant measured in the $10^3 - 10^9$ Hz range is the most relevant. As will be shown, measuring the dielectric relaxation processes at frequencies above $10^9$ Hz is difficult due to the limited time resolution of the RC circuit employing typical organic solar cell devices. The dielectric constant values are characterized on the kHz to MHz range in this thesis. Measurement techniques for obtaining dielectric constants at higher frequencies, such as terahertz spectroscopy or microwave conductivity will not be discussed.
The bimolecular recombination is limited by weak dielectric screening following the same argument of strong Coulomb interaction as mentioned in Section 1.2.1. The Langevin theory describes a recombination coefficient $\beta_L$ inversely proportional to $\varepsilon_r$ (Equation 1.2), thus fast diffusion-dominated recombination is expected if $\varepsilon_r$ is low. Although the influence of dielectric screening on reduced bimolecular recombination was less frequently discussed, theories considering energetic barriers at interfaces, such as Arkhipov theory, do take into consideration of the interfacial dipole and charge screening within the donor and acceptor phases. Theoretical studies as well as experimental studies have shown that, by increasing the dielectric constant the recombination rate is reduced while the charge carrier lifetime is increased.\textsuperscript{[12b, 49]}

Due to the weak screening of charged defects, charge carrier transport is affected and the charge mobility is low (on the order of 10$^{-5}$ – 10$^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$,\textsuperscript{[24d, 25]} in most low dielectric constant organic materials. The low charge mobility further contributes to carrier recombination and the active layer thickness limitations.

Due to the lack of long range order in semiconducting polymers, the molecular orbitals are highly localized, resulting in hopping charge transport of charges instead of band transport of free carriers in inorganic materials. As thermal activation is required for the hopping process, the charge transfer is expected to be slower than band transport in inorganic materials. Increased dielectric screening may also affect the average electrochemical energy of the polarons in semiconducting polymer, which may affect the activation energy for charge carrier hops. It was also suggested that increased dielectric screening effectively smoothes the energy landscape in a disordered system, leading to faster transport.\textsuperscript{[50]}

The space charge, which is a distribution of free carriers accumulated adjacent to the electrodes due to the presence of external electric field, is also influenced by the strength of dielectric screening. Under an extraction bias, the photogenerated carriers drift under the external field towards the collecting electrodes where the drift length $l_d$ is given by
Equation 1.6.\cite{51} When the active layer thickness is larger than $l_d$, the carriers accumulated at the electrodes will screen the external field within the active layer, forming a zero-field space charge region. The formation of space charge significantly limits the extracted photocurrent because charge carriers within the space charge region cannot be extracted and are lost to recombination. This effect is minor in devices with active layer thickness similar to or smaller than $l_d$, which is typically between 100-200 nm in systems with moderate mobility ($10^{-5}$ - $10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$).\cite{11b, 24b, 52} However in devices with active layer thickness larger than $l_d$ the space charge effect can lead to reduced photocurrent, thereby lowering device performance. The space-charge limited current $J_{SCL}$ is calculated as:

$$J_{SCL} = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{(V - V_{bi})^2}{L^3}$$ (1.7)

where $V-V_{bi}$ is the applied voltage corrected by the built-in voltage of the device, and $L$ is the length of the space charge region.\cite{53} The space-charge limited current is thus directly proportional to the dielectric constant $\varepsilon_r$.

While theoretical studies and simulations correlating increased dielectric screening to enhancement in device performance were reported,\cite{20, 30, 49a} very few experimental studies are present regarding the dielectric effect on PSC devices. This is mainly due to the rarity of high dielectric constant semiconducting polymers. Several attempts have thus been made to increase dielectric constant in PSC systems. A diketopyrrolopyrrole (DPP) based polymer PIDT-DPP-CN with a polar nitrile side-chain was synthesized by Cho et al. with dielectric constant of 5 (measured at 1 kHz).\cite{12b} Increase in $V_{OC}$, fill factor and efficiency was observed in PIDT-DPP-CN based PSC devices comparing to the counterpart with non-polar side-chain,. A longer small-perturbation lifetime was reported, which was attributed to reduced bimolecular recombination. Side chain modification approach was also used by Torabi et al. to increase dielectric constant without sacrificing mobility or solubility.\cite{54} The dielectric constant of thiophene-quinoxaline (TQ) was increased from 4.5 to 5.7 (measured at 1kHz) by fluorination, as reported by Lu et al.\cite{55} The fluorinated copolymer FTQ showed a larger bandgap and an increased $V_{OC}$. 
As shown above, bimolecular recombination in PSC systems is influenced by a combination of charge mobility, reduction factor and dielectric screening. The techniques to characterize each parameter are introduced in the following section and demonstrated using rr-P3HT: [60]PCBM in Chapter 3. To study the influence of dielectric screening on bimolecular recombination, a key challenge is to separate the influence of dielectric screening from the other two parameters. This is achieved by comparing the bimolecular recombination coefficient normalized to charge mobility ($\beta/\mu$), which will be demonstrated in detail in Chapter 6.

1.3 Techniques to characterize bimolecular recombination and its influencing parameters

1.3.1 Bimolecular recombination kinetics

The overall bimolecular recombination kinetics can be evaluated from charge density decay kinetics and bimolecular recombination coefficient, both of which can be obtained directly using optoelectronic techniques such as time-resolved charge extraction (TRCE) and photo-induced charge extraction by linearly increasing voltage (photo-CELIV) or estimated from optical density decay using transient absorption spectroscopy (TAS). Optoelectronic techniques such as TRCE and photo-CELIV measure the extraction current transients of a working PSC device at different delay times, and charge density at each delay time can be obtained from integrating the extraction transients. For TAS, a thin film sample is used to measure the transient absorption decay at different wavelengths from which the absorption spectrum as well as decay kinetics at a specific wavelength are obtained. The change in optical density ($\Delta OD$) is directly proportional to charge density ($\Delta OD \propto \varepsilon nd$), where $\varepsilon$ is the molar extinction coefficient at the specific wavelength, $n$ is the charge density and $d$ is the film thickness. With $\Delta OD$ and molar extinction coefficient, the charge density decay of the polaron can thus be calculated. As an optical technique, TAS has the advantage of probing different photo-generated species at different wavelengths, thus providing more detailed optical information on charge generation, transfer and recombination. As TAS is not limited by the RC time constant or charge extraction losses, it allows the measurement of early time recombination kinetics which cannot be obtained from TRCE or photo-CELIV. The main disadvantage of TAS
is that when the density of excited species is low, e.g. at long delay times or low excitation densities, the optical detection of the TA signal can be difficult. For this reason, TAS will be carried out as a supplementing technique in Chapter 7 to investigate charge transfer mechanism in ternary blend film samples.

Time-resolved charge extraction (TRCE) is used to measure the decay of carrier density within a working device. In this technique, the device is held at open circuit condition by applying high impedance. Then a laser pulse illuminates a small area of the device to create charge carriers. Photoexcitation outside the active area of the device should be avoided to control parasitic charge generation in the surrounding area. The photogenerated charges are then extracted under the built-in potential or an applied voltage bias after a certain delay time by applying low impedance to create short circuit condition. The carrier density decay is recorded using an oscilloscope as a voltage pulse. The change between high and low impedance modes are carried out using a nanosecond switch. As the carriers are kept inside the device at high impedance after photogeneration, the loss of charge during the delay time is solely due to recombination. Therefore, by measuring under various decay times TRCE allows direct observation of carrier density versus time at open circuit. Such data could be further analysed to obtain useful information on recombination kinetics and carrier lifetime. The experimental setup of TRCE is shown in Figure 1.5.

For photovoltage decay, the device is constantly held at high impedance and no switch is needed. Photovoltage decay is often used in conjunction with TRCE to study the relation between carrier density and photovoltage.
Figure 1.5 Experimental setup of time-resolved charge extraction (TRCE).

From charge density decays the time-dependent bimolecular recombination coefficient and charge carrier lifetime can be calculated:\textsuperscript{[56]}

\[ n(t) = \frac{n_0}{1 + n_0 \beta t} \]  \hspace{1cm} (1.8)

where \( n(t) \) is the time-dependent charge density, \( n_0 \) is the initial charge density, \( \beta \) is bimolecular recombination coefficient and \( t \) is time; and\textsuperscript{[56]}

\[ \tau = \frac{1}{n\beta} = -n\left(\frac{dn}{dt}\right)^{-1} \]  \hspace{1cm} (1.9).

The carrier lifetime can also be obtained from transient photovoltage (TPV) decays. In TPV a weak laser pump is used to generate a weak voltage transient in a device held at a known \( V_{OC} \). When the magnitude of voltage perturbation generated by the laser pump is much smaller than \( V_{OC} \) the transient decays exponentially and the small-perturbation carrier lifetime is the exponential decay time constant. The small perturbation lifetime is different from the overall carrier lifetime, as the small-perturbation technique measures the decay dynamics of free charge carriers instead of decay dynamics of the total charge carrier population. The total charge lifetime is further calculated as the multiplication of small-perturbation lifetime and the reaction order \( \varphi \) of bimolecular recombination:\textsuperscript{[56]}

\[ \tau_{tot} = \tau_{TPV} \cdot \varphi \]  \hspace{1cm} (1.10),

where \( \varphi \) is calculated from:\textsuperscript{[56]}

\[ \frac{dn}{dt} = -\beta n^\varphi \]  \hspace{1cm} (1.11).

Photogenerated charge extraction by linearly increasing voltage (photo-CELIV) has also been widely used to study photovoltaic devices. As shown in Figure 1.6, the photo-CELIV measurement involves photo-excitation using a laser pulse. After a certain delay
time a triangle extraction voltage bias (i.e. a reverse bias) is applied to the active layer. The current decay is measured through an oscilloscope.

Figure 1.6 Experimental setup of photo-generated charge extraction by linearly increasing voltage (photo-CELIV).

The charge carrier density can be obtained from photo-CELIV as a function of delay time; therefore it offers information on recombination behaviour as well as carrier lifetime. As shown in Figure 1.7, \( j(0) \) is the capacitive response of the device under bias in the dark, which reaches a constant value after the circuit RC time constant \( \tau_{RC} \). After charge photogeneration, the generated carriers will migrate to the electrodes under the applied bias, and the charge density can be calculated from the difference between integrated area of photo-CELIV and dark CELIV transients (shaded area in Figure 1.7). By changing the delay time between photoexcitation and extraction bias, the charge density as a function of time is obtained.
Figure 1.7 An example of photo-CELIV and dark-CELIV curves. $t_{\text{max}}$ corresponds to the time at which the current density reaches maximum value. $j(0)$ is the capacitive current response in the dark and $\Delta j$ is the difference between the peak current density under excitation and the dark current density. The shadowed area corresponds to the extracted charge under excitation.

Both TRCE and photo-CELIV allow charge extraction as a function of decay times, however there are a number of differences between the two techniques. In TRCE the charge carriers are extracted under the built-in potential of the device, and the extraction time is determined by the RC time constant of the circuit when thin films are used. In photo-CELIV, on the other hand, charge carriers are extracted under a linearly increasing extraction bias, and the extraction time is determined by the length of the applied bias, which is a fixed value. As a result, the tail of the extraction transient is truncated, leading to lower charge density. A detailed comparison between TRCE and photo-CELIV was reported by Clarke et al.\cite{56} where photo-CELIV gave lower charge densities over the investigated timescales and faster decay kinetics at delay time longer than 5 $\mu$s compared to TRCE. A comparison between charge density decay and $\beta$ obtained from TRCE and photo-CELIV will be carried out in Chapter 3 to determine the primary technique used to obtain charge density decay kinetics, $\beta$ and lifetime in this thesis.
1.3.2 Charge carrier mobility

Photo-CELIV is used to obtain charge carrier mobility in this thesis. To estimate the carrier mobility from photo-CELIV, three cases of material conductivity are considered:

Low conductivity case where $\Delta j \ll j(0)$ (see Figure 1.7):$^{[11a]}

$$\mu = \frac{2d^2}{3At_{max}^2} \quad (1.12)$$

where $\mu$ is the carrier mobility, $d$ is the active layer thickness, $A$ is the gradient of the voltage pulse ($A = \frac{U}{t_{pulse}}$) and the extraction time $t_{max}$ is the time for current transient to reach maximum.

Moderate conductivity case where $\Delta j \approx j(0):$ $^{[11a]}

$$\mu = \frac{2d^2}{3At_{max}^2[1 + 0.36 \frac{\Delta j}{j(0)}]} \quad (1.13)$$

and $j(0)$ is the RC circuit current step as shown in Figure 1.7.

High conductivity case where $\Delta j \gg j(0):$ $^{[11a]}

$$\mu = \frac{d^2j(0)}{At_{max}^2\Delta j} \quad (1.14)$$

The mobility dependence on electric field, delay time and excitation density can be obtained from photo-CELIV, which will be demonstrated in Chapter 3.

1.3.3 Recombination reduction factor

The bimolecular recombination reduction factor can be calculated from $\beta$ obtained from time-resolved charge extraction (TRCE) and $\beta_t$ calculated from carrier mobility and dielectric constant; or from bulk-generation time-of-flight (TOF).
The setup of time-of-flight (TOF) measurement is similar to that of photo-CELIV, except that instead of having a triangle voltage pulse, a constant extraction bias is applied to the device. The laser pulse is applied to the device, and the photocurrent decay is recorded with an oscilloscope. To obtain the reduction factor, TOF is measured in bulk generation mode \((\alpha d \ll 1, \alpha \text{ being the absorption coefficient of the material})\) where charge carrier is photogenerated throughout the whole active layer thickness.

Bulk-generation TOF uses a constant bias to extract photo-generated charge carriers within a PSC device. When the active layer is thin \((\alpha d \ll 1, \alpha \text{ being the absorption coefficient of the material})\) the charge carriers are considered to be generated throughout the whole active layer thickness and are redistributed instantaneously under the applied bias. When a constant extraction bias is applied to the device, it is screened by the photocarriers within the dielectric relaxation time \(\tau_\sigma = \varepsilon \varepsilon_0 / \sigma\) where \(\sigma\) is the bulk conductivity of the sample, creating a zero field region of free carrier reservoir. As the carriers are constantly extracted at the electrodes, the reservoir is slowly depleted resulting in an extraction transient decay. At high excitation intensities, the extracted charge will saturate due to bimolecular recombination. The extracted charge and extraction half time \(t_{1/2}\) can be obtained directly from the transients under different excitation densities from which the recombination reduction factor can be calculated:\(^{[11a]}\)

\[
\xi = \frac{\beta}{\beta_L} = \frac{C U_0 t_{tr}}{Q_e t_e} \tag{1.15},
\]

where \(C\) is the geometric capacitance, \(U_0\) is the applied bias, \(Q_e\) is the extracted charge, \(t_{tr} = \frac{d^2}{\mu U}\) is the transit time and the extraction time \(t_e\) is determined by the difference between \(t_{1/2}\) at high and low excitation densities.

In bulk generation mode, the TOF signal is normally plotted as a decay of photocurrent against time. For organic solar cells, the TOF photocurrent transient is often observed to saturate with increasing excitation density of the laser pulse, which is an indication of bimolecular recombination being the dominant recombination mechanism (as explained above). The ratio between extracted charge and capacitive charge \((Q_e/CU_0)\) as well as the time at which the photocurrent decay to half of the maximum value \((t_{1/2})\) are also key characteristics to understand the recombination behaviour. A plateau is often observed in
the TOF transient decay for polymers with non-Langevin recombination. Such plateau region originates from the accumulation of free charges as only $Q = CU_0$ can be extracted per transit time ($t_{tr}$). This is due to the space-charge limited conditions at high excitation density, where the extraction current is limited to the space-charge limited current $j_{SCLC}$ ($j_{SCLC} = CU_0/t_{tr}$). In contrast, no such plateau is observed for pure Langevin systems.[57]

Juška et al has shown that the extraction time $t_e$ is controlled by the loading resistance of the extraction circuit, especially when a large resistance is used.[58] By increasing the resistance used, the extraction time will substantially increase, leading to smaller reduction factor $\xi$. This was substantiated by a number of literature reports.[16, 58-59] Therefore, in this thesis the reduction factor values are only compared at the same resistance between different systems. The load resistance should also be small so that the drift time of carriers is shorter than the dielectric relaxation time. While in most of the systems 50 Ω resistance satisfies this requirement, in samples with large active layer thickness the capacitance can be much smaller, which would require a larger resistance.

1.3.4 Dielectric constant

1.3.4.1 Obtaining dielectric constant values in semiconducting polymers

The most common approach to characterize low frequency (sub-THz) dielectric constant in materials is dielectric spectroscopy. Dielectric spectroscopy measures the dielectric properties as a function of frequency in a sample material. The measured material is either placed inside a measuring probe or fabricated into a thin film polymer capacitor, and the frequency dependent dielectric constant is calculated using the complex capacitance obtained from the impedance response and the sample dimensions ($S$ stands for area and $d$ stands for film thickness).[60]

$$C = \varepsilon_0 \varepsilon_r \frac{S}{d}$$

(1.16)

The main difference in dielectric spectroscopy measurements using a measuring probe or a thin film capacitor device lies in sample preparation:

1. The dielectric measurement probe measures liquid and solid samples with thicknesses in micrometre to millimetre range. Such sample thicknesses are much larger than the typical thickness used in actual photovoltaic devices, which is typically around 100 nm.
Thick samples require several grams of the tested material. The commercial price for semiconducting polymers is as high as several thousand dollars per gram making it a very expensive measurement for speciality polymers.

2. The solid sample used in dielectric measurement probe is typically prepared by melting or pressing the dry sample into a disc, whereas the active layer prepared in PSC devices is casted from solution by doctor blading or spin coating. These differences in sample preparation are likely to result in differences in film morphology, which may affect the measured dielectric constant values, as it will be discussed later.

For these considerations, the dielectric constant will be determined using thin film devices in this thesis. The determination of dielectric constant values of a polymer film using a thin film capacitor raises several important considerations on device fabrication and measurement procedures. Here for the purpose of capacitance characterization, the device is called a capacitor; however practically speaking it behaves more like a diode where at forward bias the current flows and at reverse bias the current is blocked. In a thin film polymer capacitor, sandwich-type architecture is typically used where a thin layer of the polymer sample is placed between two conducting electrodes. To avoid charge injection into the polymer layers from the electrodes, a charge blocking layer is typically used. Figure 1.8a shows the device architecture used in this chapter, where pre-patterned ITO glass and aluminium are used as electrodes and a thin layer of PEDOT: PSS is used as electron blocking layer. In this architecture the area of the capacitor device is determined by the overlapping area of the ITO and Al electrodes ($S$). Using Equation 1.16, the dielectric constant can be calculated if the thickness ($d$) of the sample and the capacitance ($C$) of the device are measured.
Figure 1.8 Schematic of device architecture used in this chapter (a). Several aspects affecting dielectric constant value characterization, including thickness variation (b), pin holes (c), low electrode conductivity or lack of blocking layer (d) and stray capacitance (e), are also shown.

In order to accurately obtain the dielectric constant value, there following potential issues regarding device structure and samples preparation need to be considered:

1) Ideally, the polymer film should have a uniform thickness (see Figure 1.8b). When a thickness variation is present, the capacitance of the device can be interpreted as a series of parallel-connected smaller capacitors corresponding to different sample thicknesses. In the impedance spectra this could result in a depressed semicircle shape corresponding
to a distributed capacitance element, usually modelled using a constant phase element CPE. There is no straightforward way to take into account large variations in sample thickness in calculating the capacitance. Typically, in Equation 1.16, the average value of film thickness is used to calculate the dielectric constant. However, the average value is only applicable when the thickness variation is small. In the case of large thickness variation, the capacitance will be frequency dependent and make the analysis complicated. In case of more severe defects such as pin-holes, the capacitance values could be more significantly affected (Figure 1.8c), which can lead to over-estimation of the capacitance and thus dielectric constant value.

2) When measuring the capacitance of a diode, the presence of electrode or blocking layer / active layer interfaces could also influence the capacitive response of the device (Figure 1.8d). If the electrode conductivity is low, the contact response will act as an additional capacitance in series to the geometric capacitance, which can be observed in impedance spectroscopy.\textsuperscript{[61]} If a blocking layer is used, change in charge injection / extraction barriers may be introduced thereby changing the built-in potential of the device. Simulation study has shown that increasing the injection barrier at a fixed built-in potential can decrease the measured capacitance value comparing at a fixed reverse bias in bias-dependent capacitance measurements, although this phenomena may not be as pronounced when the measurement frequency is above the low frequency limit.\textsuperscript{[62]} This suggests that dielectric constant values determined using the same active layers but different contact layers may vary.

3) In the device architecture shown in Figure 1.8a, the device area is defined by the overlapping area of ITO and Al electrodes. Due to the high conductivity of PEDOT: PSS, current may flow outside of this overlapping electrode area (Figure 1.8e). Stray capacitance from such edge effects or the potential influence of neighbouring pixels on a multi-pixel device typically used should be investigated.

In a typical PSC design, the capacitance of the device is around $10^{-10} - 10^{-9}$ F due to the low dielectric constant, the small active area and film thickness. The low capacitance coupled with the high resistivity ($>\ M\Omega$) of the device pushes the capabilities of most commercially available electrochemical impedance units. Equipment induced errors can be significant when measuring such small capacitance especially at the high frequency
range. Ideally, the device should be as thin and have as large active area as possible. However, thin polymer films (below 100 nm) can easily lead to pin-holes due and large active area can further increase the thickness variation due to non-uniformity of coating processes by spin coating and doctor blading.

1.3.4.2 Considerations of material/sample preparation in thin-film organic semiconducting capacitor devices

There are a number of material considerations when fabricating thin-film capacitor devices using semiconducting polymers:

Unlike in high purity crystalline semiconductors, the dielectric constant of a polymer may be variable due to the disordered nature of semicrystalline or amorphous polymers. As a result, the dielectric response of a polymer sample shows a distribution of time constants. This can lead to frequency dependence (dispersion) of the dielectric constant values in addition to the frequency dependence of various contributions to polarization discussed above. For example, the electronic segments of conjugated polymers characterized by the “effective conjugation length” shows a distribution depending on morphology such as chain alignment. In turn, the polarizability of the electrons of the π-conjugated segments will also vary from chain to chain. The manifestation of this effect is the appearance of distributed capacitance element (constant phase element) needed to model the impedance spectrum. Calculation of the capacitance is therefore not straightforward.

The capacitance of a diode is also sensitive to the morphology of the polymer film. Change of film morphology between different samples may lead to variations between the measured capacitance and thus the obtained dielectric constant values. The film morphology can be affected by a number of factors, including film thickness, sample preparation method (spin coating/drop casting/dip coating etc.), thermal treatment and casting solvent, etc. In order to measure and compare the device capacitances, the polymer film morphology should be kept consistent. This means that the film thickness should be kept relatively constant, and the sample preparation conditions between for example a photovoltaic device and the thin-film polymer capacitor device should be as close as possible for the purposes of comparison.
When measuring the capacitive response of the device, the chemical capacitance originating from free carriers needs to be differentiated from the geometric capacitance $C_{geo}$. Free carriers giving rise to a chemical capacitance may originate from photogeneration or from charge carriers already existing in the dark. Dark carriers can be intrinsic (doping or impurities) or extrinsic (charge accumulation at interfaces, injected charge from contacts). In order to extract $C_{geo}$ of a device, the capacitance measurement should be conducted in the dark, and any possible contribution to chemical capacitance, e.g. air, moisture and strong light exposure, should be avoided.

### 1.3.4.3 Techniques for measuring capacitance in thin film polymer capacitors

The low frequency (< 1 MHz) capacitance of a thin film polymer device can be measured using impedance spectroscopy (frequency domain) or as the transient current response to a voltage change (time domain). For the latter, charge extraction by linearly increasing voltage (CELIV) has been frequently used and is well developed. Impedance spectroscopy is a steady state technique where a small AC voltage modulation is applied on top of a DC bias to obtain the complex-valued resistance (impedance) at a given bias and frequency. In CELIV, on the other hand, a linearly increasing voltage bias is applied to the device and the current response of the device is recorded. The benefit of this technique is that the capacitive response can be easily separated from contribution from chemical capacitance, such as extraction of intrinsic or extrinsic charge carriers.

#### 1) Impedance spectroscopy

There are two different approaches to obtain capacitance values using impedance spectroscopy. One is to keep the DC bias constant and measure the impedance at different AC frequencies. The modulus of the impedance and the phase shift can both be plotted as a function of frequency, giving the so called Bode plot; or the imaginary part of impedance can be plotted against the real part giving the Nyquist plot.

Figure 1.9a shows an example of Nyquist plot obtained from a P3HT only device with the device architecture of ITO/PEDOT: PSS/P3HT/Al. The real part of impedance ($Z'$) decreases under illumination due to the smaller bulk resistance as a result of photoconductivity. A semicircle-shaped impedance response was observed in both dark and illuminated conditions, which is indicative of an equivalent circuit containing a
resistor and a capacitor element in parallel. The impedance response was fitted to an equivalent circuit model (Figure 1.9b) where \( R_p \) is the bulk resistance of the P3HT layer and is corresponding to the diameter of the semicircle, \( C_p \) is the capacitance of the P3HT layer and \( R_s \) represents the series resistance from the electrodes and connections to the external circuit. Here \( C_p \) is the total capacitance of the bulk layer with contributions from both geometric and chemical capacitance, where the chemical capacitance arises from dark carriers and photo-generated charge. In the case of a semiconducting polymer with no dark carriers present, the capacitance \( C_p \) obtained from a dark impedance response would correspond to \( C_{geo} \).

In some cases the impedance spectra of polymer devices are not a semicircle, instead a depressed semicircle due to a frequency dependent capacitance caused by disordered nature of polymers or thickness variation in polymer film as explained above. When fitting such impedance spectra a constant phase element (CPE) is often used to account for the frequency dependence of the capacitance. A CPE can be considered as a non-ideal capacitance with a continuous distribution of RC time constant when put together with a resistor, and mathematically it can be described as:

\[
Y_C = A_0 (i\omega)^n
\]

(1.17)

where \( Y_C \) is the admittance of the CPE, \( A_0 \) is the magnitude of the CPE, \( \omega \) is the angular frequency and \( n \) is the exponent with value between 0 and 1.\(^{[62]}\) When \( n = 1 \) the CPE becomes an ideal capacitor and when \( n = 0 \) the CPE becomes a pure resistor. In a thin-film polymer capacitor, when there is no capacitance contributed from electrode interfaces, the \( n \) is expected to be close to unity. If \( n \) much lower than 1 is observed, it is typically a suggestion of more than one capacitance source present, and a different equivalent circuit will be needed. Once \( A_0 \) and \( n \) values are obtained from fitting, the equivalent capacitance value could be calculated as:

\[
C = \frac{Y_C}{i\omega} = A_0 \omega^{n-1}
\]

(1.18)

The capacitance \( C \) could also be calculated directly from the imaginary part of the impedance, \( Z' \):
\[ Z'' = \frac{1}{\omega C} \]

(1.19),

giving a frequency dependent capacitance.

Figure 1.9 (a) Impedance spectra of a P3HT only device measured in the dark and under 1 sun illumination, (b) the equivalent circuit model used to fit the impedance spectra.\textsuperscript{[61]} Reprinted with permission from Ref. \textsuperscript{[61]}, Copyright 2012, Wiley-VCH.

The other approach to obtain capacitance values in impedance spectroscopy is to measure the impedance of the device at a changing DC bias. This technique is carried out by stimulating the device with a small sinusoidal voltage perturbation at fixed frequency and measuring the impedance of the device. The DC bias is changed from forward to reverse bias and from the obtained impedance the capacitance is calculated assuming an RC equivalent circuit.
Figure 1.10 shows the capacitance-voltage plot of a pristine P3HT device, which was distinguished into three regions [63] with respect to built-in potential. At a large reverse bias ($V \ll V_{bi}$, section (1) in Figure 1.10), the active layer is fully depleted and the measured capacitance corresponds to the geometric capacitance $C_{geo}$. At forward bias above the built-in potential ($V > V_{bi}$, section (3)), the capacitance decreases as the injection is limited by the build-in potential. At forward bias below $V_{bi}$ and low reverse bias (section (2)), the capacitance increases due to the rapid current response at the Schottky barrier. The capacitance in a device with a Schottky barrier follows the Mott-Schottky equation from which the doping concentration can be determined.

While this technique is mostly used to determine the built-in potential and doping concentration, $C_{geo}$ could also be obtained at a large reverse bias. In the ideal case, $C_{geo}$ is independent of the bias applied; however in some cases a slow decrease in capacitance at increasing reverse bias is observed. This could be due to i) current injection caused by electrodes that are not perfectly blocking especially at larger reverse biases or ii) the presence of deep trapped carriers that are difficult to extract even at large bias.

Figure 1.10 shows an example of bias dependent capacitance measurement plot where a weak slope of capacitance versus applied bias was observed even at large reverse bias. Hereby a question arises: how to take the leakage current into account when obtaining $C_{geo}$? While typically $C_{geo}$ is taken at a large reverse bias (> 1 V), some literature also take the value at 0 V.[64] While taking $C_{geo}$ at large reverse bias fails to take leakage current into account, at 0 V the injected carriers are very often not fully depleted, leading to an overestimated $C_{geo}$ value. Another method is to extrapolate the plot at large reverse bias to 0 V and taking the extrapolated value as $C_{geo}$. By extrapolating the data and taking $C_{geo}$ at 0 V the leakage current is accounted for, giving a more accurate $C_{geo}$ value. When the leakage current is absent, the extrapolated value is identical to that at large reverse bias.
Figure 1.10 $1/C^2$ plotted as a function of applied bias, obtained from bias dependent impedance measurement on a pristine DT-PDPP2T-TT device, carried out at 1 kHz using a Gamry potentiostat. The solid line shows the determination of build-in potential by linear extrapolation at forward bias, and the numbers shown in figure list the different capacitance response regions with respect to the built-in potential.

2) Charge extraction by linearly increasing voltage (CELIV)

Unlike impedance spectroscopy, CELIV is a time-resolved technique that uses large capacitive response signals and therefore cannot represent steady-state conditions. In a CELIV experiment, a linearly increasing extraction bias (reverse bias) is applied to the sample to extract charge carriers inside a device. The resulting extraction current transients are recorded, shown in Figure 1.11a. CELIV probes the current response of the whole device, including all capacitive responses from geometric capacitance and chemical capacitance. For a pure capacitor under a linearly increasing voltage ramp, following a rise-time related to the circuit RC time constant $\tau_{RC}$, a constant displacement current, $I_0$, is reached:
\[ I_0 = \frac{U_{\text{max}} C}{t_{\text{pulse}}} \]  

(1.20)

where \( U_{\text{max}} \) is the maximum applied bias and \( t_{\text{pulse}} \) is the pulse width of the voltage ramp. Since \( U_{\text{max}} \) and \( t_{\text{pulse}} \) are both known parameters and \( I_0 \) is measurable using an oscilloscope, \( C \) can directly be obtained.

To obtain the geometric capacitance in CELIV, the measured PSC device should be kept in darkness throughout the measurements. If no free carriers or injection from electrodes are present in the device, Equation 1.20 applies and \( C = C_{\text{geo}} \). However, in systems with free carriers, the current transient is the combination of an extraction current and the displacement current. In PSC systems where conductivity is low, an extraction peak and the current decaying to the displacement current value can be observed in the current transient (see Figure 1.11b), indicating full depletion of the device active layer. When characterizing the device capacitance, the present of such peak indicates the presence of dark carriers. When dark carriers are present, it is still possible to obtain \( C_{\text{geo}} \) from the transient so long as the dark carriers are significantly less than the capacitive charge. In this case the dark carriers will have minor screening effect on the electric field and \( I_0 \) could be obtained at longer time when dark carriers are fully extracted. In some cases carrier injection from electrodes can occur, giving a current transient with increasing current value at time longer than \( \tau_{\text{RC}} \) (Figure 1.11c). Such current transient shape is typically observed when a non-blocking electrode is present or when the applied maximum bias \( U_{\text{max}} \) is too large.
Figure 1.11 (a) A typical dark CELIV transient, obtained from a 100 kHz linear voltage sweep with $U_{\text{max}} = 2$ V (the blue line); (b) CELIV transient of a device with the presence of dark carriers, where a weak transient peak could be observed; (c) CELIV transient of a device with injection current, characterized by the continuous rise of current after $\tau_{RC}$. The dash lines in figure a and b show the displacement current $I_0$. 

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1.3.5 Transient absorption spectroscopy to study charge transfer mechanism

Transient absorption spectroscopy (TAS) is widely used to study photogenerated transient species. To measure TAS, a pulsed laser light (pump) is used to irradiate the sample to excited states. The change in optical density (ΔOD) of the sample at specific wavelengths is measured using a second beam of light (probe) and monochromators. The signal is recorded over a period of time to obtain a transient decay signal. The plot of ΔOD-time at specific probe wavelengths is useful in studying kinetics of transient species while plotting ΔOD at constant delay time over various probe wavelengths will provide the excited state absorption spectrum, which contains information of energy bands of different transient species. The experimental setup of TAS is shown in Figure 1.12.

Figure 1.12 Experimental setup of transient absorption spectroscopy (TAS) measurement.

TAS can be measured on solution samples as well as film samples. The measurement can also be carried out under cryostat to obtain further dynamic information. Although TAS only provides information on optical properties of a sample, the magnitude of a signal at particular time is directly proportional to the charge carrier density. In a film sample, when the spectroscopic features are well defined, the magnitude of the polaron peak corresponding to free charge carriers can be calculated using ΔOD, which can be calculated from the change in measured voltage transient (ΔOD =
\[-\log_{10}\left(\frac{V_{\text{excited}}}{V_{\text{ground}}}\right)\] Therefore TAS could also be used as a supplementary technique to understand the kinetics of charge carrier decay.

In a TAS measurement, the obtained spectrum is contributed from four different processes:\[^{[65]}\]

1) Ground state bleaching is caused by the decrease in number of species at the ground state due to photoexcitation. Since the number of species at ground state is decreased, ground state bleaching gave a negative signal in \(\Delta \text{OD}\) at the wavelength range of ground state absorption.

2) Stimulated emission is caused by the probe passing through the photoexcited sample. The probe photon induces emission of another photon from an excited state, followed by the excited state returning to the ground state. Generally speaking, stimulated emission follows the shape of the fluorescence spectrum, and due to the presence of emitted photons a negative \(\Delta \text{OD}\) is produced. The stimulated emission is typically observed on the timescale from sub-nanosecond to tens of nanoseconds, which is similar to the photoluminescent lifetime.

3) Excited state absorption is observed when excited states are generated. The excited states observed in a TA spectrum include those directly generated by photoexcitation such as excited singlet states and states produced from relaxation, intersystem crossing, and other processes, such as charge transfer states, charge separated states and excited triplet states. These are often the focus of TAS studies on PSC systems, as the energetic and dynamics of all excited state species involved in charge photogeneration and recombination can be obtained. As the excited states are generated from ground states, the population of bleached ground states equals the sum of all excited state species. In a TA spectrum, this means the area enclosed by ground state bleaching should be similar to the area enclosed by excited state absorption spectrum.

4) Electro-absorption is caused by the Stark effect, which is shifting in energy levels of the ground and/or excited states under an electric field. The electro-absorption can be observed in TAS measurements when a localized field is present, which can be caused by a change in permanent dipole moment or polarizability induced by photoexcitation. It can
also be observed when an external field is applied, which has also been used to study charge generation in PSC systems.\textsuperscript{[66]} The electro-absorption EA induced by the electric field depends on the strength of the electric field $E$ and the ground state absorption $A(\lambda)$:

\[
EA = -\frac{dA(\lambda)}{d\lambda} \Delta pE - \frac{1}{2} \frac{dA(\lambda)}{d\lambda} \Delta \alpha E^2 + \frac{1}{2} \frac{d^2A(\lambda)}{d\lambda^2} (\Delta pE)^2 + \ldots
\]

(1.21)

where $\Delta \alpha$ is the polarizability and $\Delta p$ is the permanent dipole moment.\textsuperscript{[67]} In a polymer: PCBM BHJ blend the first term cancels itself when integrated over the bulk of the active layer. The second and third terms are proportional to the first or second order derivative of the ground state absorption spectrum.

As summarized above, a number of parameters are available to characterize charge density decay, bimolecular recombination coefficient, reduction factor, charge mobility and dielectric constant. The first aim of this thesis is therefore to establish characterization techniques and measurement conditions to obtain each parameter. This will be carried out in Chapter 3, which uses a widely studied system rr-P3HT: PCBM as a reference system to establish characterization techniques for recombination kinetic, geometric capacitance, charge mobility and reduction factor characterizations. A more detailed technique comparison on dielectric constant measurement on pristine polymer thin-film devices will be carried out in Chapter 5.

1.4 Design and development of PSCs for better performance

1.4.1 Materials used for PSCs

Since the discovery of photoinduced charge transfer between polymer and fullerene, hundreds of semiconducting polymers have been synthesized in hope of further enhancing the performance of PSCs. In general, the design of semiconducting polymers targets at 1) decreasing polymer bandgap and 2) increasing the polymer donor HOMO and fullerene acceptor LUMO offset. Early research on PSC was focused poly (p-phenylene vinylene) and polythiophene based polymers, which typically has a bandgap
The large bandgap in these polymers limits the harvesting of solar photon flux, which has a maximum around 1.8 eV, thus lowering the $J_{sc}$ of the PSCs. For this reason, semiconducting polymers with lower bandgap is desired. Also, as the theoretical maximum $V_{oc}$ is determined by the energy offset between the donor HOMO and the acceptor LUMO, the $V_{oc}$ in PSCs can be increased by tuning the HOMO and LUMO levels of the semiconducting polymers.

Several approaches are commonly used to tune the bandgap and HOMO, LUMO levels in semiconducting polymers, including the application of donor-acceptor structure, stabilizing the quinoid structure of conjugated units, controlling the polymer chain planarity and controlling the conjugated length. The most widely adopted approach is to use alternating electron donor and electron acceptor units, forming a so-called ‘push-pull’ structure. The push-pull structure provides a driving force facilitating electron delocalization and the formation of quinoid mesomeric structure on the polymer backbone. The electron delocalization leads to the hybridization of molecular orbitals between donor and acceptor units, resulting in narrower bandgap in the push-pull polymer. One of the successful examples of push-pull polymers is poly[2,6-(4,4-bis(2-ethylhexyl)-4H-cy-clopenta[2,1-b;3,4-b’]dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT), which contains 4H-cyclopenta[2,1-b:3,4-b’]dithiophene (CPDT) as donor and benzothiadiazole as acceptor units (Figure 1.13). PCPDTBT shows an optical bandgap of around 1.4 eV, with HOMO and LUMO levels of -5.3 and -3.57 eV, respectively, see Table 1.1.

Another widely used design strategy for low bandgap polymers is to stabilize the quinoid structure in the polymer backbone. There are two resonance structures in π-conjugated polymer backbones at ground state: the aromatic form where the π-electrons are localized within the aromatic structure, and the quinoid form where π-electrons are delocalized along the backbone, synchronously transferring double bonds into single bonds and single bonds into double bonds. The quinoid structure is energetically less stable than the aromatic form, thus having a lower bandgap. By using thieno[3,4-b]thiophene (TT) unit the quinoid structure can be stabilized, achieving lower bandgap. A successful example using this strategy is poly((4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b;4,5-b’]dithiophene-2,6-diyl){3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediy1}) (PTB7), which has an optical bandgap around 1.6 eV, a HOMO of -5.15 eV and LUMO of -3.31
Table 1.1 shows a non-exhaustive literature review of semiconducting polymers developed in recent years, where the HOMO and LUMO levels characterized from cyclic voltammetry, the optical bandgap of the polymer as well as hole mobility are listed in the second to fifth column. Table 1.2 lists the device performance from the polymers listed in Table 1.1. The chemical structures of representative polymers are listed in Figure 1.13.

Several interesting findings could be made from Table 1.1 and Table 1.2. Firstly, among the 42 polymers listed in the table, most of the optimized efficiencies were reported using an active layer thickness of 80-110 nm, while only 7 polymers showed high $FF$ above 0.6 with thickness above 200 nm. The low $FF$ at large active layer thickness (>200 nm) is caused by a number of reasons, including the space-charge effect resulted from unbalanced electron and hole mobility, charge recombination, and change in morphology at large thickness caused by film deposition techniques used. Secondly, the bandgap values do not necessarily correlate with $J_{sc}$ of fabricated devices. Despite the large difference in polymer bandgap ranging from 1.3 eV to 2.0 eV, the majority of $J_{sc}$ values reported for fabricated devices were between 10 to 13 mA cm$^{-2}$. This clearly shows that high $J_{sc}$ is also influenced by other parameters, such as charge mobility, polymer chain packing and inter-chain interactions. Thirdly, different device performance can be obtained in the same polymer donor: PCBM system by using different device architectures. For example, in P3HT: [60]PCBM blend with active layer thickness of 150 nm, when a conventional architecture was used (ITO/PEDOT:PSS/P3HT: PCBM/Al), a $J_{sc}$ of 5.4 mA cm$^{-2}$ was reported. When an inverted architecture (ITO/ZnO/P3HT: PCBM/Ag) was used a $J_{sc}$ of 9.2 mA cm$^{-2}$ was observed with the same active layer thickness. This suggests that the device architecture can largely influence the performance of a PSC.

As mentioned above, when searching for semiconducting polymers potentially showing reduced recombination, a strong indicator is high $FF$ achieved at large active layer thickness. Within the 42 polymers listed in Table 1.2, only four polymers showed $FF$ values above 0.6 when the active layer thickness exceeds 200 nm, and only one polymer, namely DT-PDPP2T-TT, is commercially available. Li et al first reported this diketopyrrolopyrrole-based push-pull polymer DT-PDPP2T-TT in 2013. It showed a low bandgap of 1.42 eV with HOMO level at -5.1 eV and an absorption onset of 920 nm allowing photon harvesting at near longer wavelengths. High $FF$ of 0.6 was reported at
active layer thickness above 300 nm. High hole mobility of 0.8 cm² V⁻¹ s⁻¹ was reported for this polymer, obtained from hole-only FET. The authors suggested that the high FF was due to reduced bimolecular recombination in the system, which was possibly caused by the fibrous morphology of crystalline polymer in the film. However, no recombination study was carried out for this polymer.

Therefore, one of the focuses of this thesis is to find out whether DT-PDPP2T-TT: PCBM BHJ blends have reduced bimolecular recombination. This is done by reproducing the devices and investigate the influences of $\mu$, $\varepsilon_r$ and $\zeta$ on $\beta$. A detailed study will be carried out in Chapter 4 and Chapter 6.
Figure 1.13 Chemical structures of some representative semiconducting polymers and fullerene acceptors for PSC application.

Table 1.1 Energy level, optical bandgap and hole mobility for some semiconducting polymers.
<table>
<thead>
<tr>
<th>Polymer</th>
<th>HOMO (CV, eV)</th>
<th>LUMO (CV, eV)</th>
<th>Band gap (optical, eV)</th>
<th>Hole mobility (cm²V⁻¹s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT</td>
<td>-5.2[75]</td>
<td>-3.2[76]</td>
<td>1.9[77]</td>
<td>2×10⁻⁴ (annealed)[78]</td>
</tr>
<tr>
<td>PSIF-DTB[36a]</td>
<td>-5.39</td>
<td>-3.57</td>
<td>1.82</td>
<td>~1×10⁻³ b</td>
</tr>
<tr>
<td>PCPD-TBT[79]</td>
<td>-5.3</td>
<td>-3.57</td>
<td>1.46</td>
<td>1×10⁻³ b</td>
</tr>
<tr>
<td>PBDTP-DTBT[80]</td>
<td>-5.35</td>
<td>-3.34</td>
<td>1.7</td>
<td>8.89×10⁻² c</td>
</tr>
<tr>
<td>Si-PCPD-TBT[81]</td>
<td>-5.05</td>
<td>-3.27</td>
<td>1.45</td>
<td>1×10⁻³ b</td>
</tr>
<tr>
<td>P1[82]</td>
<td>-5.36</td>
<td>-3.55</td>
<td>1.37</td>
<td>N/A</td>
</tr>
<tr>
<td>PBDTTT-C[83]</td>
<td>-5.12</td>
<td>-3.55</td>
<td>1.61</td>
<td>2×10⁻⁴</td>
</tr>
<tr>
<td>PBDTTT-CF[71]</td>
<td>-5.22</td>
<td>-3.45</td>
<td>1.77</td>
<td>7×10⁻⁴ c</td>
</tr>
<tr>
<td>PTB7[84]</td>
<td>-5.15</td>
<td>-3.31</td>
<td>1.57</td>
<td>5.8×10⁻⁴ c</td>
</tr>
<tr>
<td>PBDTT-DPP[85]</td>
<td>-5.3</td>
<td>-3.63</td>
<td>1.44</td>
<td>3.1×10⁻⁴ c</td>
</tr>
<tr>
<td>PCDTBT[86]</td>
<td>-5.5</td>
<td>-3.60</td>
<td>1.9</td>
<td>1×10⁻³ a</td>
</tr>
<tr>
<td>PBDT TBT[87]</td>
<td>-5.31</td>
<td>-3.44</td>
<td>1.75</td>
<td>N/A</td>
</tr>
<tr>
<td>PBnDT-FTAZ[88]</td>
<td>-5.36</td>
<td>-3.05</td>
<td>2.0</td>
<td>1.03×10⁻³ c</td>
</tr>
<tr>
<td>P2[89]</td>
<td>-5.4</td>
<td>N/A</td>
<td>1.73</td>
<td>N/A</td>
</tr>
<tr>
<td>PBDTTPD[90]</td>
<td>-5.56</td>
<td>-3.75</td>
<td>1.80</td>
<td>N/A</td>
</tr>
<tr>
<td>P3[91]</td>
<td>-5.66</td>
<td>-3.86</td>
<td>1.80</td>
<td>N/A</td>
</tr>
<tr>
<td>DT-PDPP2T-TT[74]</td>
<td>-5.1</td>
<td>-3.68</td>
<td>1.35</td>
<td>0.8 a</td>
</tr>
<tr>
<td>PDPP3T[92]</td>
<td>-5.17</td>
<td>-3.61</td>
<td>1.3</td>
<td>0.04 c</td>
</tr>
<tr>
<td>PDPPPTPT[92]</td>
<td>-5.35</td>
<td>-3.53</td>
<td>1.53</td>
<td>0.04 ± 0.01 a</td>
</tr>
<tr>
<td>PDT-DPB[93]</td>
<td>-5.26</td>
<td>-3.61</td>
<td>1.38</td>
<td>3.2 × 10⁻³ c</td>
</tr>
<tr>
<td>PBDT T-SeDPP[94]</td>
<td>-5.25</td>
<td>-3.7</td>
<td>1.38</td>
<td>6.9 × 10⁻⁴ c</td>
</tr>
<tr>
<td>PMDPP3T[91]</td>
<td>N/A</td>
<td>N/A</td>
<td>1.3</td>
<td>10⁻² - 10⁻³ a</td>
</tr>
<tr>
<td>P4[95]</td>
<td>-5.5</td>
<td>-3.7</td>
<td>1.75</td>
<td>N/A</td>
</tr>
<tr>
<td>P(Se)[96]</td>
<td>-5.49</td>
<td>-3.82</td>
<td>1.67</td>
<td>0.017 b</td>
</tr>
<tr>
<td>PDTGTPD[97]</td>
<td>-5.6</td>
<td>-3.5</td>
<td>1.69</td>
<td>N/A</td>
</tr>
<tr>
<td>PDTSTPD[98]</td>
<td>-5.57</td>
<td>-3.38</td>
<td>1.73</td>
<td>1 × 10⁻⁴ a</td>
</tr>
<tr>
<td>PTD2[99]</td>
<td>-5.24</td>
<td>N/A</td>
<td>1.68</td>
<td>1.69 × 10⁻⁴ c</td>
</tr>
<tr>
<td>PTAT-3[100]</td>
<td>-5.04</td>
<td>-3.28</td>
<td>1.76</td>
<td>1.69 × 10⁻⁴ c</td>
</tr>
<tr>
<td>PTBF[101]</td>
<td>-5.15</td>
<td>-3.31</td>
<td>1.68</td>
<td>4.1 × 10⁻⁴ c</td>
</tr>
<tr>
<td>PSeB2[102]</td>
<td>-5.04</td>
<td>-3.26</td>
<td>1.78</td>
<td>1.35 × 10⁻³ c</td>
</tr>
<tr>
<td>PBDT-DTNT[32a]</td>
<td>-5.19</td>
<td>-3.26</td>
<td>1.58</td>
<td>1.3 × 10⁻⁵ c</td>
</tr>
<tr>
<td>PBDTP-DTBT[79]</td>
<td>-5.35</td>
<td>-3.34</td>
<td>1.70</td>
<td>8.9 × 10⁻² c (pristine)</td>
</tr>
<tr>
<td>PTPD3T[103]</td>
<td>-5.55</td>
<td>-3.73</td>
<td>1.82</td>
<td>5.87 × 10⁻²b, 1.2 × 10⁻³c</td>
</tr>
</tbody>
</table>
Table 1.2 Device architecture and photovoltaic performances of some PSC devices.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Architecture</th>
<th>Active Layer Thickness (nm)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>$FF$ (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCPDTBT$^{[112]}$</td>
<td>ITO/PEDOT:PSS/polymer: [70]PCBM/Al</td>
<td>110</td>
<td>16.2</td>
<td>0.62</td>
<td>55</td>
<td>5.5</td>
</tr>
<tr>
<td>Si-PCPDTBT$^{[80]}$</td>
<td>ITO/PEDOT:PSS/polymer: [70]PCBM(1:1, w/w)/Ca/Al</td>
<td>80</td>
<td>12.7</td>
<td>0.68</td>
<td>55</td>
<td>4.7</td>
</tr>
<tr>
<td>PCDTBT$^{[85]}$</td>
<td>ITO/PEDOT:PSS/polymer: [70]PCBM(1:4, w/w)/TiO$_x$/Al</td>
<td>80</td>
<td>10.6</td>
<td>0.88</td>
<td>64</td>
<td>6.0</td>
</tr>
<tr>
<td>Sample</td>
<td>ITO/PEDOT:PSS/polymer:</td>
<td>N/A</td>
<td>17.3</td>
<td>0.57</td>
<td>61</td>
<td>5.9</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------</td>
<td>-----</td>
<td>------</td>
<td>------</td>
<td>----</td>
<td>-----</td>
</tr>
<tr>
<td><strong>P1</strong></td>
<td>[70]PCBM(1:1, w/w)/Al</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>PBDTTT-C</strong></td>
<td>[70]PCBM(1:1.5, w/w)/Ca/Al</td>
<td>80</td>
<td>14.7</td>
<td>0.7</td>
<td>64</td>
<td>6.6</td>
</tr>
<tr>
<td><strong>PBDTTT-CF</strong></td>
<td>[70]PCBM(1:1.5, w/w)/Ca/Al</td>
<td>N/A</td>
<td>15.2</td>
<td>0.76</td>
<td>67</td>
<td>7.4</td>
</tr>
<tr>
<td><strong>PTB7</strong></td>
<td>[70]PCBM (1:1.5, w/w)/MoO3/Al</td>
<td>80</td>
<td>17.2</td>
<td>0.754</td>
<td>72</td>
<td>9.15</td>
</tr>
<tr>
<td><strong>PBDTT-DPP</strong></td>
<td>[70]PCBM (1:2, w/w)/Ca/Al</td>
<td>100</td>
<td>13.5</td>
<td>0.74</td>
<td>65</td>
<td>6.5</td>
</tr>
<tr>
<td><strong>PBDTTTB</strong></td>
<td>[70]PCBM (1:2, w/w)/Ca/Al</td>
<td>80</td>
<td>10.7</td>
<td>0.92</td>
<td>58</td>
<td>5.5</td>
</tr>
<tr>
<td>PnDT-FTAHz</td>
<td>[60]PCBM (1:2, w/w)/Ca/Al</td>
<td>160</td>
<td>11.5</td>
<td>0.74</td>
<td>70</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>250</td>
<td>11.8</td>
<td>0.79</td>
<td>73</td>
<td>6.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>310</td>
<td>12.2</td>
<td>0.79</td>
<td>67</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td>13.3</td>
<td>0.74</td>
<td>58</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1000</td>
<td>14.0</td>
<td>0.74</td>
<td>54</td>
<td>5.6</td>
</tr>
<tr>
<td><strong>P2</strong></td>
<td>N/A</td>
<td>11.5</td>
<td>0.85</td>
<td>68</td>
<td>6.6</td>
<td></td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>Material</th>
<th>ITO/PEDOT-PSS/polymer:</th>
<th>Current Density (mA/cm²)</th>
<th>Fill Factor (%)</th>
<th>Efficiency (%)</th>
<th>Voc (V)</th>
<th>FF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBDTTPD[114]</td>
<td>[60]PCBM (1:1.5, w/w)/Ca/Al</td>
<td>100</td>
<td>11.2</td>
<td>0.94</td>
<td>69</td>
<td>7.3</td>
</tr>
<tr>
<td>PDTSTPD[115]</td>
<td>ITO/PEDOT-PSS/polymer: [70]PCBM (1:2, w/w)/BCP/Al</td>
<td>90</td>
<td>12.2</td>
<td>0.88</td>
<td>68</td>
<td>7.3</td>
</tr>
<tr>
<td>PDTGTPD[97]</td>
<td>ITO/ZnO/polymer: [70]PCBM/MoO₃/Ag</td>
<td>N/A</td>
<td>12.6</td>
<td>0.85</td>
<td>68</td>
<td>7.3</td>
</tr>
<tr>
<td>PDPPTPT[92]</td>
<td>ITO/PEDOT:PSS/polymer: [70]PCBM (1:2, w/w)/LiF/Al</td>
<td>80-90</td>
<td>10.8</td>
<td>0.8</td>
<td>65</td>
<td>5.5</td>
</tr>
<tr>
<td>PDTP-DFBT[93]</td>
<td>ITO/ZnO/polymer: [70]PCBM/MoO₃/Ag</td>
<td>100</td>
<td>17.8</td>
<td>0.68</td>
<td>65</td>
<td>7.9</td>
</tr>
<tr>
<td>PBDTT-SeDPP[94]</td>
<td>ITO/PEDOT:PSS/polymer: [70]PCBM/Ca/Al</td>
<td>100</td>
<td>16.8</td>
<td>0.69</td>
<td>62</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>ITO/PEDOT:PSS/polymer: [70]PCBM (1:3, w/w)(Fischer, #310)/PFN/Al</td>
<td>160</td>
<td>17.8</td>
<td>0.6</td>
<td>66</td>
<td>7</td>
</tr>
<tr>
<td>PMDPP3T[91]</td>
<td>ITO/PEDOT:PSS/polymer: [60]PCBM (1:3, w/w)/Ca/Al</td>
<td>108</td>
<td>14</td>
<td>0.61</td>
<td>66</td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>135</td>
<td>14.8</td>
<td>0.61</td>
<td>65</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>177</td>
<td>15.7</td>
<td>0.59</td>
<td>59</td>
<td>5.6</td>
</tr>
<tr>
<td></td>
<td>230</td>
<td>16.9</td>
<td>0.58</td>
<td>56</td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td>------------------</td>
<td>-----</td>
<td>------</td>
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<td>-----</td>
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</tr>
<tr>
<td>P3[90]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ITO/PEDOT:PSS/polymer: [70]PCBM (1:1, w/w)/TiO$_x$/Al</td>
<td>105</td>
<td>10.51</td>
<td>0.92</td>
<td>63</td>
<td>6.1</td>
<td></td>
</tr>
</tbody>
</table>

|                  |     |      |      |     |     |
| P(Se)[96]        |     |      |      |     |     |
| ITO/PEDOT:PSS/polymer: [70]PCBM (1:1, w/w)/Al | 75  | 9.71  | 0.87 | 63  | 5.35 |
|                  |     |      |      |     |     |
|                  | 95  | 10.74 | 0.88 | 62  | 5.79 |
|                  | 130 | 10.24 | 0.86 | 60  | 5.28 |
|                  | 200 | 9.79  | 0.84 | 50  | 4.07 |

|                  |     |      |      |     |     |
| PTDBD2[99]       |     |      |      |     |     |
| ITO/PEDOT:PSS/polymer: [70]PCBM (1:1.2, w/w)/Ca/Al | N/A | 13  | 0.89 | 65.3 | 7.6 |

|                  |     |      |      |     |     |
| PTAT·3[100]      |     |      |      |     |     |
| ITO/PEDOT:PSS/polymer: [60]PCBM (1:1, w/w)/Ca/Al | 100 | 15  | 0.66 | 58  | 5.62 |

|                  |     |      |      |     |     |
| PTBF1[101]       |     |      |      |     |     |
| ITO/PEDOT:PSS/polymer: [70]PCBM (1:1.5, w/w)/Ca/Al | 70-100 | 14.1 | 0.74 | 68.9 | 7.2 |

|                  |     |      |      |     |     |
| PSeB2[102]       |     |      |      |     |     |
| ITO/PEDOT:PSS/polymer: [70]PCBM (1:1.2, w/w)/Ca/Al | 100 | 16.8 | 0.64 | 64  | 6.46 |

|                  |     |      |      |     |     |
| PBDT-DTNT[32a]   |     |      |      |     |     |
| ITO/PEDOT:PSS/polymer: [70]PCBM (1:1, w/w)/Ca/Al | 80-90 | 11.71 | 0.8 | 61  | 6 |

<p>| | | | | | |
|                  |     |      |      |     |     |
| PSiF-DBT[78]     |     |      |      |     |     |
| ITO/PEDOT:PSS/polymer: [60]PCBM (1:2, w/w)/Al | 70  | 9.5  | 0.9 | 50.7 | 5.4 |</p>
<table>
<thead>
<tr>
<th>Material</th>
<th>ITO/PEDOT:PSS/polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[70]PCBM (1:1.5, w/w)/Ca/Al</td>
</tr>
<tr>
<td><strong>PBDTP-DTBT</strong>[^79]</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td>12.94</td>
</tr>
<tr>
<td></td>
<td>0.88</td>
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### 1.4.2 Device architecture of PSCs

Two types of device architectures are typically used in BHJ solar cells, as illustrated in Figure 1.14. The conventional architecture consists of a transparent conducting oxide, usually tin indium oxide (ITO), as hole collecting electrode, followed by a hole transport
layer (HTL), the BHJ active layer and an electron transport layer. Aluminium is typically used as the electron collecting electrode. The purpose of using hole/electron transport layer is to facilitate selective charge transport and extraction while enhancing contact quality to reduce surface recombination. Poly(3,4-ethylenedioxythiophene) polystyrene sulphonate (PEDOT:PSS) is the most commonly used HTL material. TiO$_x$, Ca, LiF and poly[(9,9-bis(3'-(N,N-dimethyl)-N-ethylammonium)propyl)-2,7-fluorene)-2,7-(9,9-dioctyfluorene)-4,7-(2,1,3-benzo selenadiazole)]dibromide (PFN) are among the most commonly used ETL materials.

One of the disadvantages for conventional device architecture is the poor long term stability. Due to the low work function of Al, it is easily attacked by oxygen in air, forming an electrically insulating oxidized layer. The penetrated oxygen and water also participate in photo-oxidation reactions with the donor and acceptor materials, leading to material degradation and formation of trap states. To avoid such issues, inverted architecture is used. The inverted architecture typically has a structure of ITO/ETL/donor: acceptor/HTL/hole collecting electrode. High work function metal such as Au or Ag is typically used as electrode, thus avoiding the degradation issue present in conventional architecture. Metal oxides, such as ZnO and TiO$_x$, are commonly used as ETL in inverted architecture, while polymers such as PFN and polyethylenimine ethoxylated (PEIE) have also been applied in inverted PSCs. For HTL, MoO$_x$ is one of the most commonly used materials due to its excellent air stability. Despite the benefits of inverted structure, the use of metal oxides in PSCs with inverted architecture suffers from some disadvantages as well. Dewetting issues can occur at the surface between inorganic and organic layer, which inhibits charge transfer at the organic/inorganic interface. For the purpose of electrochemistry characterizations in PSCs, the use of charge transport layers should also be limited to a minimum, as additional layers often lead to extra capacitive response in electrochemistry characterizations, which can largely complicate the analysis of results.
1.4.3 Influence of active layer morphology on device parameters

One of the fundamental requirements in BHJ solar cells is to form intermixing donor and acceptor domains in the active layer with controlled domain sizes. This makes the BHJ solar cells particularly sensitive to nanoscale morphology of the active layer. In many cases, by modifying the nanomorphology alone, the device performance can be considerably improved. In general, the nanomorphology in PSCs can be modified via 1) thermal annealing of active layer or 2) modifying the solvent, both of which has been widely applied in PSCs to enhance device performance.

The most well-known example of enhanced PSC performance through thermal annealing is rr-P3HT: PCBM blends. It has been shown that, by annealing rr-P3HT: PCBM film...
highly ordered P3HT phases are formed and larger PCBM aggregates were observed, compared to the film untreated.\[127]\) This was attributed to the diffusion of PCBM in the amorphous phase to PCBM aggregates at elevated temperature, allowing P3HT crystallization. After annealing treatment, the optical absorption onset of the blend film and charge mobility was increased and charge recombination was significantly reduced, leading to substantial increase in photocurrent and device efficiency.\[128]\) Modifying film morphology using different solvents is also a commonly used method. The purpose of solvent modification is to control the evaporation time of the solvent during the film casting process from solution, in order to control the domain size and crystallization of the sample. By adding a high boiling point solvent diiodooctane (DIO) into o-DCB solvent, the efficiency in PCPDTBT: PCBM was increased by a factor of two, from 2.8 % to 5.5 %.\[112]\) It has been proposed that the added DIO allows spatially more favourable side-chain arrangement and selective solubility of the fullerene component, leading to increased domain size, reduced geminate recombination loss and increased charge mobility.\[27a, 129]\)

To characterize nanomorphology in BHJ thin films, a variety of different techniques are used. Microscopic techniques such as atomic force microscopy (AFM) and transmission electron microscopy (TEM) allow direct observation of the film morphology on the nanometre scale, and information regarding domain size and intermixing of different phases can be obtained. However, more in-depth study on domain crystallinity and orientation of crystallite facet is often required in morphology studies. For such purposes, grazing incident X-ray scattering (GIXS) and grazing incident X-ray diffraction (GIXRD) techniques are used.\[130]\) As the crystallinity in polymer films are generally weak, accurate measuring the crystalline structure requires a strong X-ray source. For this reason, GIXS and GIXRD techniques are usually limited to the accessibility of synchrotron facilities. The vertical phase separation has also been studied using variable-angle spectroscopic ellipsometry and X-ray photoemission spectroscopy.\[130a]\)

While optimizing film morphology can lead to significant increase in device performance, the conditions of morphology control largely depends on the individual material used. Not only does the chemical structure strongly affect BHJ film morphology, the molecular weight,\[131]\) polydispersity,\[132]\) PCBM blending ratio\[68b]\) and film thickness\[12d]\) also affect morphology. As a result, the morphology optimization for PSCs is often case-by-case,
which is partly responsible for the large efficiency variation from the same system reported in different literatures. For detailed morphology study laborious effort and specialized equipment are required. Due to the limited timeframe and resources during the PhD study, film morphology will not be investigated in this thesis. Rather, as the device performance is highly sensitive to active layer morphology the device performance is characterized for all studied systems and compared to literature where applicable prior to further charge mobility and recombination measurements. The device performance will act as an indicator for film morphology, where comparable performance to literature indicates similar film morphology.

### 1.4.4 Performance of PSCs

The performance of PSCs is quantified using the power conversion efficiency (PCE), which is termed as the ratio of maximum power output to incident light power:

\[
\eta = \frac{P_{\text{max}}}{P_{\text{in}}} = \frac{FF \cdot J_{\text{SC}} \cdot V_{\text{OC}}}{P_{\text{in}}}
\]  

(1.22)

where \( FF \) is the fill factor, \( J_{\text{SC}} \) is the short circuit current and \( V_{\text{OC}} \) is the open circuit voltage. Hence, PCE represents the overall ability of a device to convert light into electrical power and can be easily obtained from a \( J-V \) curve (see Figure 1.15). For device characterization under a solar simulator, the incident power is 100 mW cm\(^{-2}\) with spectral intensity distribution calibrated to match that of solar illumination at 48.2 ° on the earth’s surface at 25 °C, or the Air Mass 1.5 (AM1.5) spectrum.
Figure 1.15 A typical current density-voltage curve measured under illumination. In figure the open circuit voltage, $V_{OC}$, is the intersect of the curve with the x axis; the short circuit current, $J_{SC}$, is the intersect of the curve with the y axis; $P_{max}$ corresponds to the point with maximum power output, with corresponding current density and voltage marked as $J_{max}$ and $V_{max}$.

The fill factor ($FF$) is by definition the ratio of maximum power output to the product of $J_{SC}$ and $V_{OC}$:

$$FF = \frac{P_{max}}{I_{SC}V_{OC}} = \frac{J_{max}V_{max}}{I_{SC}V_{OC}}$$

Various aspects during charge transport and collection can affect the $FF$. Charge carrier transport is always in competition with recombination and fast recombination would significantly decrease $FF$. $FF$ reflects the ‘squareness’ of a $J$-$V$ curve, therefore shunt resistance (which typically arises from fabrication defects such as pin-holes) and series resistance (which arises from charge transport within the active layer at electrode interfaces and within the electrodes) also plays an important role on the $FF$. The contacts between electrodes and active layer should be carefully designed to minimize series resistance and eliminate pin-holes to have maximized shunt resistance.
Another important parameter is the external quantum efficiency (EQE). EQE is defined as the ratio of the number of photogenerated charge collected at the contacts under short circuit condition to that of incident photons; hence it is synonymously called the incident photon-to-current efficiency (IPCE). By definition EQE is the product of the efficiency of each process during charge photogeneration and collection. For PSCs,

$$EQE = \eta_a \times \eta_{diff} \times \eta_{TC} \times \eta_{tr} \times \eta_{cc}$$ (1.24)

where the parameters correspond to the efficiency of photon absorption ($\eta_a$), exciton diffusion towards D/A interface ($\eta_{diff}$), exciton dissociation ($\eta_{TC}$), carrier transport towards electrodes ($\eta_{tr}$) and charge collection ($\eta_{cc}$).\[133\] EQE is a useful parameter in evaluating the charge photogeneration process within a specific device without taking into consideration the incident spectrum. The EQE is usually measured monochromatically to acknowledge the current response to photons of different energy.

The short circuit current density, $J_{SC}$, is by definition the photocurrent generated under illumination at short circuit. $J_{SC}$ is dependent on the incident light:

$$J_{SC} = q \int_0^\infty \eta_c(\hbar\omega) (1 - R(\hbar\omega)) a(\hbar\omega)b_s(\hbar\omega)d(\hbar\omega)$$

$$= q \int_0^\infty IPCE(\hbar\omega)b_s(\hbar\omega)d(\hbar\omega)$$ (1.25)

where $q$ is the elementary charge, $a(\hbar\omega)$ is the probability of a photon of energy $\hbar\omega$ to be absorbed, $R(\hbar\omega)$ is the probability of the photon to be reflected, $b_s(\hbar\omega)$ the solar photon flux on a surface and $\eta_c(\hbar\omega)$ is the probability of photogenerated electron to be collected.\[15\] From the equation it is clear that the value of $J_{SC}$ has taken into account both EQE and incident solar spectrum. Therefore $J_{SC}$ could also be calculated by integrating the EQE spectrum over the solar spectrum.

At open circuit, the open circuit voltage ($V_{OC}$) is the voltage when the photocurrent is at balance with the dark current, hence the net current density:

$$J = J_{SC} - J_{dark}(V_{OC}) = 0$$ (1.26)
For a photodiode,

\[ J = J_{SC} - J_0 \left( e^{qV/n_{id}kT} - 1 \right) \]  \hspace{1cm} (1.27)

where \( J_0 \) is the temperature dependent constant for a given material, \( k \) is the Boltzmann’s constant, \( T \) is temperature and \( n_{id} \) is the ideality factor which typically lies between 1 and 2.\(^{[15]} \) It was reported that \( J_0 \) could be experimentally determined from the electroluminescence of the charge-transfer band and the photovoltaic quantum efficiency, and a linear dependence of \( V_{OC} \) on spectral position of charge transfer band was observed.\(^{[134]} \)

Generally speaking, the open circuit voltage \( V_{OC} \) in a PSC is determined by the energy offset between the donor HOMO and the acceptor LUMO and additional \( V_{OC} \) loss:

\[ eV_{OC} = (E_{LUMO,A} - E_{HOMO,D}) - E_{loss} \]  \hspace{1cm} (1.28)

The dependence of \( V_{OC} \) on HOMO levels has indeed been observed. Scharber et al. showed that in 26 different BHJ solar cells using the same acceptor (PCBM), the experimentally measured \( V_{OC} \) followed a linear relation with the HOMO of the polymer donor.\(^{[135]} \) The \( V_{OC} \) loss has a number of origins, including charge carrier loss at electrode contacts,\(^{[136]} \) charge recombination,\(^{[27c]} \) weak dielectric screening\(^{[137]} \) and low CT state energy.\(^{[27c, 40a, 138]} \)

### 1.5 Ternary blend PSC – concept and development

#### 1.5.1 Approaches to enhance short circuit current

\( J_{SC} \) values below 15 mA cm\(^{-2} \) are typically observed in PSC devices, which is notably lower than the radiative limit predicted from Shockley-Queisser theory.\(^{[8, 139]} \) This is due to the relatively high band gap and narrow absorption window in semiconducting polymers. P3HT, for example, has an optical band gap of 1.9 eV with maximum absorption appearing at 517 nm.\(^{[76]} \) The full-width-half-maximum of the absorption spectrum is below 200 nm, which means that only photons with wavelength between 420 nm and 590 nm are most likely to be absorbed for carrier generation, while the rest will
not be efficiently utilized. On the contrary, inorganic semiconductors can have optical band gap as low as 0.26 eV \(^{[140]}\) with plateau absorption above the band gap, resulting in \(J_{sc}\) as high as 40 mA cm\(^{-2}\) in crystalline silicon solar cells. \(^{[141]}\) This intrinsic difference between organic and inorganic materials determines that to enhance PSC performance, a broadened absorption spectrum towards the near-infrared (NIR) is necessary.

There have been a few approaches addressing such need. Low band gap polymers with band gap as low as 1.0 eV have been synthesized.\(^{[142]}\) Li et al reported the synthesis and application of poly[2,5-bis(2-hexyldecyl-2,3,5,6-tetrahydro-3,6-dioxopyrrolo[3,4-c]pyrrole-1,4-diyl]-alt-[3’,3”-dimethyl-2,2’:5’,2’’-terthiophene]-5,5’’-diyl] (PMDPP3T)\(^{[143]}\) which has a small band gap of 1.3 eV with balanced electron and hole mobility in the range of 10\(^{-2}\) - 10\(^{-3}\) cm\(^2\) V\(^{-1}\) s\(^{-1}\). The fabricated devices using PMDPP3T: [70]PCBM blend showed \(J_{sc}\) of 17.8 mA cm\(^{-2}\) and efficiency of 7.0 %.

Another solution to the absorption limitation problem is the tandem cell, which involve two or more sub-cells that employ polymers of different band gaps and absorption windows. Typically, the polymer with larger band gap is used in the front cell (active layer directly on top of the transparent electrode) and the lower band gap polymer is used in the back cell with an interconnecting layer between the two. This is to allow more efficient photon harvesting, as the unabsorbed low energy photons could be transmitted to the back cell to be harvested. For example, PMDPP3T has been employed in tandem cell in conjunction with PCDTBT due to their complementary absorption profile (Figure 1.16).\(^{[143]}\) Using PCDTBT: [70]PCBM blend BHJ device as the front cell and PMDPP3T: [60]PCBM blend in back cell (architecture as shown in Figure 1.16b), the tandem device showed efficiency of 8.9 % with \(V_{oc}\) as high as 1.49 V. Using two PMDPP3T: [60]PCBM back cells (Figure 1.16c), the efficiency further increased to 9.64 % with remarkable \(V_{oc}\) value of 2.09 V. One of the most efficient tandem cells have been reported by the Yang Yang group using P3HT: indene-C60 bis-adduct (ICBA) front cell and PDTP-DFBT: [60]PCBM back cell.\(^{[93]}\) The best performing tandem device gave an efficiency of 10.61 %, which is the highest reported efficiency for tandem cells to date. However such devices usually require complicated multi-layer fabrication and parameters of each sub-cell as well as the intermediate layers between sub-cells has to be carefully optimized.\(^{[17]}\)
A novel approach to increase photon absorption in the active layer is by incorporating a third component to form ternary blend solar cells. A ternary blend device, as the name implies, involves three components forming a bulk heterojunction blend in the active layer. The design principle is to add a third component with complementary absorption to the donor polymer to the conventional polymer/fullerene blend in order to broaden the absorption window of the active layer to near-infrared. The ternary blend devices can therefore be fabricated using the same procedure as the donor/acceptor BHJ solar cells, making it a promising alternative to the tandem devices.
1.5.2 Charge transfer mechanisms in ternary PSC

As this thesis focuses on bimolecular recombination study in binary and ternary solar cells, it is crucial to first understand the charge transfer mechanisms within the ternary blend. The cascade charge transfer refers to charge dissociation and transfer under an energetic level relay in the ternary system. A number of publications\cite{145} have studied the charge transfer and transport mechanisms within ternary blend systems with cascade energy levels, and cascade charge transfer has indeed been one of the dominant charge generation mechanisms. However, having cascade energy structure does not necessarily lead to charge transfer. Förster resonance energy transfer (FRET) has also been observed in polymer/dye/fullerene \cite{146} as well as polymer/polymer/fullerene \cite{145a} ternary systems. For FRET to take place, spectral overlap between the donor emission and the acceptor absorption is necessary, however further energetics and morphology conditions, such as the intimate mixing of emitting sensitizer and the energy acceptor, also apply. In FRET, the charge carrier transport and recombination kinetics are essentially the same as in binary D/A PSCs, therefore the energy transfer mechanism will not be discussed further.

For cascade charge transfer to take place, the electron energy levels of the third component should lie between the donor and acceptor so that carriers generated in this component could be successively transferred to the donor and acceptor phase to be collected. This raises two requirements: the driving force for carrier dissociation should be large enough to separate the electron-hole pair generated within the third component, and the energy levels should be carefully selected to avoid exciton and charge trapping. It should also be noted that within a ternary blend system, the types of interfaces increase from one in a binary system (donor/acceptor interface) to three. At each interface carrier dissociation and recombination may occur, therefore each charge recombination pathway should be evaluated carefully. Theoretically, in a donor / acceptor blend with cascade energy levels, the electrons always transfer to a lower energy level and hole transfer is always from low to a high energy level. The same rule applies to charge transfer in ternary blend systems. As a result, the electron transport is predominantly through the acceptor and the hole transport through the polymer component with shallower HOMO level. Therefore, charge carrier recombination, which takes place at interfaces between electron and hole transport domains, will take place primarily between the polymer with highest HOMO and the acceptor. This has indeed been observed in a ternary blend containing
P3HT, [60]PCBM and a low bandgap polymer poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b’]-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT). Figure 1.17 illustrates the charge transfer pathways within P3HT: PCPDTBT: [60]PCBM system. P3HT may transfer an electron to either PCPDTBT or [60]PCBM. [60]PCBM could transfer a hole to P3HT or to PCPDTBT, while PCPDTBT could only transfer the electron to [60]PCBM and the hole to P3HT. With multiple charge transfer pathways, multiple recombination processes would also take place between the components.

Figure 1.17 Scheme of cascade charge transfer in a P3HT: PCPDTBT: [60]PCBM ternary blend solar cell. The arrows indicate potential pathways for charge transfer. Aluminium-doped zinc oxide [23c] is used as the hole blocking layer. Reprinted with permission from Ref. [17]. Copyright 2017, Wiley.

Koppe et al. have reported cascade charge transfer between P3HT, PCPDTBT and [60]PCBM based on photo-induced absorption [148] spectroscopy study, [147] which uses a frequency modulated laser pulse (pump) to excite the sample film and another monochromatic beam to measure the change in absorption, either at different wavelengths (to obtain a transient absorption spectrum) or at a specific wavelength (to study the signal decay kinetics). Upon photoexcitation below P3HT band gap (pump energy 1.59 eV), a pronounced absorption band at 1.25 eV was observed in P3HT: PCPDTBT: [60]PCBM (0.8: 0.2: 1, w/w) blend (Figure 1.18), indicating the generation of P3HT+ polarons. Bulk generation time-of-flight was also measured on binary and ternary blend devices. In annealed ternary blend device, the j-TOF curve shows a distinct transition time $t_{tr}$ and a bimolecular recombination coefficient similar to that of the annealed P3HT: [60]PCBM
P3HT is among the few polymers that follow non-Langevin recombination. These results suggest that the photo-generated charges within PCPDTBT are efficiently transferred to and transported via P3HT and [60]PCBM phases.

Figure 1.18 (a) Photo induced absorption spectra of annealed binary and ternary blend thin films and (b) integrated mode time-of-flight of annealed and unannealed ternary blends, excited at 1.59 eV using long pass cut-off filter at 1.59 eV. Reprinted with permission from Ref.147. Copyright 2017, Wiley.

The study was also extended to Si-PCPDTBT, a Si analogue of PCPDTBT. The charge transfer mechanism of the ternary blend is similar to that of PCPDTBT, where fast hole transfer time of a few hundred picoseconds was observed. Fitting using intensity dependent measurement results reveal that hole transfer from Si-PCPDTBT to P3HT competes with bimolecular recombination of holes in Si-PCPDTBT with electrons from [60]PCBM.
1.6 Aim and objectives of this thesis

The aim of this thesis is to understand the effect of dielectric screening on bimolecular recombination in PSCs. To do so, a number of questions need to be answered, as demonstrated above:

1) How to accurately measure charge recombination kinetics in a system? This involves the characterization of parameters influencing bimolecular recombination, i.e. charge mobility, dielectric constant and Langevin reduction factor.

2) How to accurately measure the dielectric constant in semiconducting polymers and PSCs;

3) Does DT-PDPP2T-TT based PSC devices show non-Langevin type recombination, if not, why can it be fabricated with large thickness without sacrificing fill factor?

4) How does dielectric screening influence charge mobility and recombination kinetics in PSCs;

5) How does a polymer with high dielectric constant affect overall dielectric constant and charge recombination kinetics in a ternary blend system.

To answer these questions in a logical order, this thesis is structured as follows:

1) The techniques used to characterize bimolecular recombination kinetics and its influencing parameters are established in Chapter 3. Different techniques used to obtain bimolecular recombination coefficient will be compared to determine the methodology for the rest of the thesis;

2) The dielectric constant, device performance, charge mobility and recombination kinetics in a high dielectric constant polymer DT-PDPP2T-TT: [60]PCBM devices are studied in Chapter 4;

3) Techniques used to characterize device geometric capacitance are compared using a high dielectric constant polymer, and the dependence of dielectric constant on sample processing conditions are compared in Chapter 5;
4) The charge mobility and recombination kinetics in different systems with high and low dielectric constant are compared to understand the effect of increased dielectric screening on bimolecular recombination in Chapter 6;
5) The high dielectric constant polymer is added into a low dielectric constant polymer: PCBM host system to study possible effect of high dielectric constant polymer on ternary device performance, charge mobility and recombination kinetics in Chapter 7.

The main body of this thesis is focused on a low bandgap polymer, DT-PDPP2T-TT, which is one of the very few commercially available low bandgap polymers which can be fabricated at large thickness while maintaining performance (See Table 1.2). The large active layer thickness makes it promising for large scale PSC production. The high FF maintained at large thickness is also very interesting research-wise, as it suggests recombination slower than charge extraction in the system. High dielectric constant is also observed in pristine polymer and polymer: PCBM blend devices measured in the work presented in this thesis. These properties make DT-PDPP2T-TT an intriguing and unique candidate for recombination study. For comparison, three systems with low dielectric constant, namely P3HT: PCBM, PCPDTBT: PCBM and PTB7: PCBM, are also studied. These systems are chosen because they are three of the few commercially available PSC systems the dielectric constant values of which have been reported.[137, 150] Due to the lack of study on dielectric effect in PSCs, the dielectric constant of a polymer: PCBM blend is often assumed but not experimentally measured. Also, the selected systems have been extensively studied with well-established recombination kinetics. The annealed rr-P3HT: PCBM devices showed significantly reduced bimolecular recombination,[11a] whereas PCPDTBT: PCBM and PTB7: PCBM showed diffusion-dominated recombination.[27] The different recombination kinetics in selected systems provides a good diversity for comparison with DT-PDPP2T-TT: PCBM system.

The conventional device architecture of ITO/PEDOT: PSS/polymer: PCBM/Al is used for all devices in the studies carried out in this thesis. This simple architecture is selected, because it consists of only one interlayer between the active layer and electrodes while allowing reasonable device performance. As is mentioned in Section 1.4.2, the use of transport layers often lead to additional capacitive response in the impedance measurements. The characterization of dielectric constant using impedance spectroscopy
is fundamental for the studies carried out in this thesis; therefore it is important to minimize additional influences on the obtained impedance results.

The purpose of studying ternary blend system is to investigate the influence of high dielectric constant DT-PDPP2T-TT on a low dielectric constant polymer: PCBM system. In order to study the influence of dielectric screening alone on bimolecular recombination, a host system with diffusion-dominated recombination is desired, and the recombination in the ternary blend is preferred to be dominated by the host system. For the ternary blend system investigated in this thesis, PCPDTBT: PCBM is selected as the host system. The system is selected based on 1) diffusion dominated recombination reported for the system and 2) the cascade energy structure in PCPDTBT: DT-PDPP2T-TT: PCBM blend which allow hole transfer from DT-PPDP2T-TT to PCPDTBT. This will be further explained in Chapter 7.

1.7 References


Chapter 2 Experimental Methods
2.1 Materials

Poly(3-hexylthiophene-2,5-diyl) (P3HT, Mw = 82 kg/mol, PDI = 1.5 regioregularity > 95%), poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-B;3,4-B’]dithiophene)-alt-4,7(2,1,3-benzothiadiazole)] (PCPDTBT, Mw = 40 kg/mol, PDI = 1.15) and [6,6]-Phenyl C61 butyric acid methyl ester ([60]PCBM) were purchased from Solaris Chem Inc. Poly([4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b’]dithiophene-2,6-diyl]{3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl}) (PTB7, OS0007) and DT-PDPP2T-TT (OS0300) were purchased from 1-Material. Analytical grade anhydrous chlorobenzene, 1,2-dichlorobenzene, toluene and 1,8-octanediol were purchased from Sigma Aldrich. Acetone and isopropanol were purchased from Chem-supply. All chemical and solvents were used as purchased. Poly-(ethyleneoxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Clevios P, VP Al 4083) was purchased from Heraeus. A list of polymers used in this thesis is shown in Table 2.1.

Table 2.1 A list of DT-PDPP2T-TT polymer batches used in this thesis.

<table>
<thead>
<tr>
<th>LOT#</th>
<th>Mw (kg mol⁻¹)</th>
<th>PDI</th>
<th>Trace Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>P61 YY6278</td>
<td>61</td>
<td>2.4</td>
<td>99.99+ %</td>
</tr>
<tr>
<td>P80 YY9052DB</td>
<td>80</td>
<td>2.5</td>
<td>99.99+ %</td>
</tr>
<tr>
<td>P33 YY8020CH</td>
<td>33</td>
<td>2.4</td>
<td>99.99+ %</td>
</tr>
<tr>
<td>P78 SX7126DB</td>
<td>78</td>
<td>2.6</td>
<td>99.99+ %</td>
</tr>
<tr>
<td>P45 SX7126CB</td>
<td>45</td>
<td>2.5</td>
<td>99.99+ %</td>
</tr>
<tr>
<td>P60 YY9248CB</td>
<td>60</td>
<td>2.5</td>
<td>N/A</td>
</tr>
</tbody>
</table>
2.2 Sample preparation

2.2.1 Solution preparation

Device preparation was as follows: P3HT: [60]PCBM (1:1 w/w) solution was dissolved in chlorobenzene at 80 °C. PCPDTBT: [60]PCBM (1:2 w/w) solution was dissolved in dichlorobenzene with 3 vol% 1,8-octanedithiol as additive. PTB7: [60]PCBM (1:1.5, w/w) was dissolved in hot chlorobenzene with 3 vol% 1,8-octanedithiol. The PCPDTBT: PCBM and PTB7: PCBM solutions were dissolved at 120 °C and stirred overnight using a magnetic stirring hotplate, carried out in a glovebox. Pristine and PCBM blended DT-PDPP2T-TT solutions were dissolved in chloroform with 7.5 vol% dichlorobenzene. The solutions were dissolved at 45 °C and stirred overnight in a glovebox. The PCPDTBT: DT-PDPP2T-TT: PCBM ternary blend solutions were prepared in chloroform with 8.3 vol% o-DCB.

2.2.2 Substrate preparation

2.2.2.1 ITO substrate

Patterned ITO glass substrates (15 Ω/m²) were purchased from Xinyan Technology Ltd, with four 2 mm-wide pixel fingers on each substrate. The substrate design is shown in Figure 2.1a, and the transmission profile provided by manufacturer was shown in Figure 2.1b. The substrates were cleaned by sonicating in detergent, DI water, acetone and isopropanol, each for 15 minutes then blow dry with nitrogen and treated with UV-Ozone for twenty minutes. A Novascan PSD UV-O3 treatment system was used to create a hydroxyl rich surface using UV light.

The substrate for single pixel devices is the same as shown in Figure 2.1a.
Figure 2.1 (a) Design of patterned ITO substrates used in this thesis. The bright yellow regions correspond to ITO covered regions while the pale yellow regions are glass. (b) Transmission profile of the purchased ITO substrate provided by the manufacturer.

2.2.2.2 Glass substrate

For ground state absorption and transient absorption spectroscopy measurements, transparent glass substrates are used. Microscopic slides (Sail Brand, clear glass, 1.2 mm thick) were used. Square substrates with 1.5 cm × 1.5 cm dimension were cut from the microscopic slides using a tile cutter. The glass substrates were first blowed with compressed air to remove any broken glass, then cleaned by sonicating in soapy water, distilled water, acetone and isopropanol, each for 15 minutes. After washing, the glass
substrates were blow dried, and then were placed in the UV-Ozone treatment system and treated for 20 minutes before using.

### 2.3 Device fabrication

#### 2.3.1 PEDOT:PSS deposition

Once the ITO substrates were cleaned following the steps in Section 2.2.2.1, the substrate was blowed with N\(_2\) to remove any dust attached to the substrate surface then PEDOT: PSS (Heraeus Clevios Al 4083) was spin coated on top of the treated substrates at 4500 rpm for 15 seconds. The PEDOT: PSS coated substrates were then subsequently annealed at 140 °C for ten minutes in air using a hotplate to achieve a dry thickness of around 30 nm.

#### 2.3.2 Active layer deposition

The photoactive layer was deposited via spin coating hot polymer solutions in air. Solutions containing DT-PDPP2T-TT were kept at 45 °C prior to deposition, whereas P3HT: PCBM, PCPDTBT: PCBM and PTB7: PCBM solutions were kept at 70 °C. This is because the primary solvent used to dissolve DT-PDPP2T-TT is chloroform, which has a boiling point around 60 °C. At room temperature, high molecular weight DT-PDPP2T-TT solutions in chloroform form polymer gels which prohibit further processing into polymer films. Heating the solutions prevent the forming of aggregations and gels by increasing polymer solubility, which can improve the quality of the obtained active layer films.

For polymer: PCBM devices, the active layer were deposited on heated substrates through spin coating, where thickness was controlled via changing spin speed. For DT-PDPP2T-TT: [60]PCBM (1:3 w/w) samples with polymer concentration of 4 mg/mL, a spin speed of 2000 rpm was used to achieve a thickness around 260 nm. The above fabrication processes were carried out under ambient condition. After active layer deposition, the substrates were immediately transferred into the glovebox to minimize exposure to ambient air.
For pristine DT-PDPP2T-TT devices studied in Chapter 5, the polymer films were casted inside the glovebox via drop casting unless specified. The annealed PEDOT: PSS coated substrates were transferred into the glovebox and placed flat on the glovebox bench. 55 μL of DT-PDPP2T-TT solution was carefully drop casted on top of the PEDOT: PSS layer. This should give a fully covered substrate with observable surface tension, but without any solution leaking out. The casted substrates were then left in the glovebox until completely dried. For environmental influence studies in Chapter 5, identical drop casting procedure was used but the process was carried out in ambient air, inside a fume hood. The substrates were either prepared in a covered Petri dish or on a flat hotplate with cover.

2.3.3 Determining active layer thickness

The active layer thickness was measured using a Dektak stylus profilometer on a separate film sample prepared on a cleaned glass substrate under nominally identical conditions as the active layer prepared on ITO substrate. A blunt tweezer edge was used to make 2 - 4 scratches at the centre of the film to enable the determination of the step height between the active layer film and the substrate. The scratched sample was then placed on the stage of the profilometer to obtain a thickness profile. The edge region (3 mm from each side) should be avoided for thickness measurements, as large thickness deviation often exist at the edges which significantly increases the measurement error.

2.3.4 Thermal annealing

For rr-P3HT: PCBM devices, thermal annealing was carried out inside a glovebox following spin coating. The substrates were heated to 140 °C for 10 minutes.

2.3.5 Thermal evaporation

For electron collecting electrode deposition, aluminium was chosen due to its low work function. The deposition was carried out once the vacuum inside the evaporation chamber has reached approximately $1 \times 10^{-6}$ mbar. The evaporation rate was controlled by following these three steps to obtain an aluminium thickness of 100 nm.

1) For the first 0 - 5 nm thick aluminium layer, the evaporation rate was 0.1 Å/s.
2) For the next 5 - 10 nm, the evaporation rate was increased to 0.5 Å/s
3) For the final 10 - 100 nm, the evaporation rate was approximately 1.2 Å/s.

Once finished, the material was allowed to cool down for 1 hour before returning the chamber to atmospheric pressure.

2.3.6 Device encapsulation

Once retrieved from thermal evaporator, the complete devices were immediately transferred into a glovebox where the device encapsulation was carried out. A drop of UV curable epoxy added on top of the evaporated Al, then a glass slide was carefully placed on top to ensure no air bubbles were trapped between the substrate and the cover slide. A UV gun was used to cure the epoxy for 40 seconds. The encapsulated devices were kept in the glovebox for an additional 30 minutes to ensure the epoxy is completely dried.

2.3.7 Device area

The device area was defined by the overlay area between ITO fingers and the aluminium electrode, which is 0.06 cm$^2$ for each device pixel. The complete device architecture is shown in Figure 2.2a. For single pixel devices, the active layer deposition was identical as listed in Section 2.3.2. After spin coating, the active layer was carefully cleaned using a toluene soaked cotton tip to leave only one strip of active layer coated on top of an ITO finger, whereas the rest of the film was removed. The aluminium was evaporated on top of the active layer only (Figure 2.2b), and the overlay between the aluminium and ITO defines the active area, which is 0.06 cm$^2$. 
2.4 Characterization

2.4.1 UV-Vis Absorption spectroscopy

UV-Vis absorption spectra were measured using a UV-3600 spectrometer, Shimadzu. Film samples were prepared via spin-coating on clean glass substrates as explained above.
2.4.2 Current-Voltage Measurement

Current-Voltage characterizations were carried out using Solar cell I-V curve testing system model IV21L, PV measurements. The solar simulator was calibrated using a reference Si diode prior to each measurement. To determine the solar cell performance, the solar cell I-V curve measurement systems model IV16 (L) was employed to measure the current-voltage characteristic of the solar cell under continuous white light illumination.

There are two main components for device testing measurement: (i) solar simulator and (ii) the I-V curve measurement system. The latter comprises the electronic load and the data acquisition (e-DAQ) system controlled by the software developed by PV Measurements Inc. The e-DAQ (Keithley 2400) applies the potential to the solar cell device under light illumination, then measures the actual current for each voltage applied. PSC devices were measured under 100mW cm\(^{-2}\), AM1.5 spectrum from the calibrated solar simulator.

2.4.3 Quantum Efficiency

External quantum efficiency characterizations were carried out using QE-X10, PV measurements. The devices were illuminated using a monochromatic light with tuneable wavelength, and the electrical current output was measured at each wavelength which can be calculated into percentage of absorbed photons compared to incident photons. A wavelength step of 5 nm was used and a wavelength range from 400 nm to 1000 nm was used. From the EQE spectrum \(J_{SC}\) can be calculated by converting the percentage of photon absorbed to total number of photons harvested using the solar spectrum, which is used to cross examine with the current-voltage measurements.

2.4.4 Impedance spectroscopy

Impedance spectroscopy was carried out using Zahner IM6 electrochemical workstation and Gamry Reference 600 potentiostat. AC oscillation amplitude of 5 mV was used. The voltage bias between -2 V and 2 V and frequency between 1 kHz and 500 kHz was applied when measuring bias dependent impedance. For impedance spectrum, the measurements were carried out at 0 V and frequency range between 0.01 – 100 kHz. All equivalent circuit fitting was carried out using ZView. The measurement limit for capacitance values
was determined for both potentiostat, where the lowest capacitance measurement limit for Gamry is 100 pF and that for Zahner is 390 pF.

2.4.5 Different lasers used in this thesis

Two different lasers were employed for the study of this thesis. A Q-switched Nd-YAG laser (532 nm, 10 Hz, INDI Quanta-Ray, Spectra-Physics) was used to measure P3HT: PCBM and PTB7: PCBM samples. Another high energy output Q-switched Nd-YAG laser (355 nm, Spectra Physics Quanta Ray Lab 170) was used in conjunction with a Quanta Ray MOPO to generate laser output with tuneable wavelength. Samples containing DT-PDPP2T-TT and PCPDTBT were characterized using this laser. A polarizer and a quarter waveplate were used for both lasers to modify the output energy.

2.4.6 Charge extraction by linearly increasing voltage

The experimental setup for CELIV measurements are shown in Figure 1.6.

Dark CELIV was carried out using a function generator (WF 1974, NF). A voltage ramp was generated using the function generator, applying a reverse bias to the device. The measurements were carried out in the dark and the devices were covered using a black cloth to block any stray light. Time zero for the recorded transient was set at the start of the extraction bias ramp using a delay generator. The extraction current transients were recorded using an oscilloscope (Tektronics, DPO4054) over 50 Ω build-in resistor.

For photo-CELIV, a pulsed laser was used to generate charge carriers within measured devices. Excitation pulse of 650 nm was used for DT-PDPP2T-TT: PCBM and PCPDTBT: PCBM devices and 532 nm for P3HT: PCBM devices. The delay time between photoexcitation and voltage ramp application was controlled using a nanosecond switch (2.2 MΩ impedance, Asama Lab) and a delay generator (Stanford Research DG535). The extraction current was recorded using an oscilloscope (Tektronics, DPO4054), using either the build-in 50 Ω impedance on oscilloscope or a homemade 13.5 Ω resistor in parallel with the 1 MΩ input impedance on oscilloscope, depending on the device capacitance.
2.4.7 Time-resolved charge extraction

TRCE measurements were carried out as follows. A pulsed laser was used to generate charge carriers within measured devices. Excitation pulse of 650 nm was used for DT-PDPP2T-TT devices and 532 nm for P3HT devices. The devices were initially held at high impedance using a nanosecond switch (2.2 MΩ impedance, Asama Lab). After a controllable delay time using a digital delay generator (Stanford Research DG535), the switch was opened and the devices were at short circuit condition. The extracted current was measured using an oscilloscope (Tektronics, DPO4054) as a function of time (input impedance 50 Ω). The dark response was subtracted to remove the switch noise.

2.4.8 Photovoltage decay

The devices were photo-excited using a pulsed laser at open circuit, which was realized by using the 1 MΩ high impedance of the oscilloscope (Tektronics, DPO4054). The voltage decay was recorded as a function of time. Four measurements were carried out for each photovoltage decay curve on different timescales.

2.4.9 Time-of-flight

The device was photo-excited using a laser pulse same as above while biased by applying 2 V reverse bias using a function generator. The extraction currents were recorded using an oscilloscope (Tektronics, DPO4054). The circuit impedance was controlled by applying resistors in parallel to the 1 MΩ input impedance of oscilloscope. The excitation density of the device was altered by using different neutral density filters, with the highest excitation density of 1000 μJ cm².

2.4.10 Sub-microsecond transient absorption spectroscopy

Transient absorption spectroscopy was carried out as follows: the absorption spectra of spin-coated films were first measured to make sure the absorbance at excitation wavelength is between 0.3-0.5. The samples were then transferred into the glovebox and sealed in a custom-made quartz cuvette for transient absorption measurements. A pulsed laser was used as pump excitation source. Excitation pulse of 650 nm was used for DT-PDPP2T-TT and PCPDTBT devices and 532 nm for P3HT and PTB7 devices. A Xe lamp (Edinburgh Instruments, Xe900) was used as probe light, where a 425 nm long pass filter was placed in front of the lamp to prevent device heating and UV light degradation. The
probe light wavelength was adjusted using a monochromator. The probe light was detected using a silicon photodiode (Femto, HCA-S-200M-SI) for probe wavelength below 1000 nm or an InGaAs photodiode (Femto, HCA-S-200M-IN) for probe wavelength above 1000 nm. The signal from the photodiode was amplified (Femto, DHPVA-200) then collected using a oscilloscope (Tektronics, DPO4054). The data collection in the oscilloscope was synchronized from a trigger signal from the pump laser using a photodiode (Newport, 818-BB-40).

2.4.11 Femtosecond transient absorption spectroscopy

Picosecond transient absorption spectroscopy was carried out on pristine DT-PDPP2T-TT as well as DT-PDPP2T-TT: [60]PCBM 1:3w/w blend films at Imperial College, London, under the guidance of Dr. Tracey Clarke. Picosecond transient absorption spectroscopy was carried out using a commercially available transient absorption spectrometer, HELIOS (Ultrafast systems). Samples were excited with a pulse-train generated by an optical parametric amplifier, TOPAS (Light conversion). Both the spectrometer and the parametric amplifier were seeded with a 1 kHz, 800 nm, 100 fs Solstice Ti: sapphire regenerative amplifier (Newport Ltd.). An excitation wavelength of 650 nm was used. Samples were kept in a cuvette under nitrogen atmosphere.

2.4.12 Atomic force microscopy

Atomic force microscopy was carried out using a tapping mode AFM, which was kindly carried out by Ms. Tian Zheng.
Chapter 3 Characterizing Bimolecular Recombination in an PSC Device: Establishing Methodology using a P3HT: PCBM Device
3.1 Introduction

3.1.1 Background

The main focus of this thesis is to study the influence of dielectric screening on bimolecular recombination in PSC devices. As demonstrated in Chapter 1, a number of parameters including charge carrier lifetime, bimolecular recombination coefficient and recombination reduction factor can be used to describe the bimolecular recombination in PSC devices. The charge density decay can be characterized using time-resolved charge extraction (TRCE) and photogenerated charge extraction by linearly increasing voltage (photo-CELIV), both of which are transient optoelectronic techniques allowing charge extraction at controllable delay times. In TRCE the charge carriers are extracted under the built-in potential of the device, and the extraction time is determined by the RC time constant of the circuit. In photo-CELIV, on the other hand, charge carriers are extracted under a linearly increasing extraction bias, and the extraction time is determined by the length of the applied bias, which is a fixed value. From charge density decay bimolecular recombination coefficient can be calculated:

\[ n(t) = \frac{n_0}{1 + n_0 \beta t} \]  \hspace{1cm} (3.1)

where \( n(t) \) is the time-dependent charge density, \( n_0 \) is the initial charge density, \( \beta \) is bimolecular recombination coefficient and \( t \) is time; and

\[ \tau = \frac{1}{n\beta} = -n\left(\frac{dn}{dt}\right)^{-1} \]  \hspace{1cm} (3.2)

The bimolecular recombination reduction factor \( \xi \) can be calculated from \( \beta \) obtained from Equation 3.1 (\( \xi = \beta / \beta_L \)) or from bulk generation time-of-flight (TOF):

\[ \xi = \frac{\beta}{\beta_L} = \frac{CU_0}{Q_e} \frac{t_{tr}}{t_e} \]  \hspace{1cm} (3.3)

where \( C \) is the geometric capacitance, \( U_0 \) is the applied bias, \( Q_e \) is the extracted charge, \( t_{tr} = \frac{d^2}{\mu U} \) is the transit time and the extraction time \( t_e \) is determined by the difference
between extraction transient decay half time $t_{1/2}$ at high and low excitation densities. The reduction factor can vary depending on the device architecture and morphology, where $\xi$ between $10^{-4}$ and 0.06 has been reported for rr-P3HT: PCBM.$^{[1]}$

The Langevin recombination coefficient $\beta_L$ is determined by the charge mobility $\mu$ and dielectric constant $\varepsilon_r$:

$$\beta_L = \frac{e\mu}{\varepsilon_0 \varepsilon_r}$$

(3.4).

The charge carrier mobility is obtained using photo-CELIV transients:

$$\mu = \frac{2d^2}{3At_{max}^2 [1 + 0.36 \frac{\Delta j}{j(0)}]}$$

(3.5)

where $d$ is the active layer thickness, $A$ is the slope of the extraction voltage ramp, $t_{max}$ is the time for photo-CELIV transient to reach maximum, $j(0)$ is the capacitive displacement current and $\Delta j$ is the difference between the maximum extraction current and $j(0)$ when $\Delta j \approx j(0)$.

These parameters are very often difficult to compare between different polymers and sometimes even different devices using the same polymer: acceptor blend. For example, in annealed regioregular poly(3-hexylthiophene-2,5-diyl): [6,6]-Phenyl C61 butyric acid methyl ester (rr-P3HT: [60]PCBM) PSCs, the bimolecular recombination coefficient $\beta$ values between $1.5 \times 10^{-14}$ - $3 \times 10^{-12}$ cm$^3$ s$^{-1}$ have been reported. Such a large variation of $\beta$ over two orders of magnitudes has a number of origins, including the difference in active material (e.g. molecular weight and regioregularity of P3HT, difference in P3HT: PCBM blending ratio), different device architecture used for the study (conventional vs. inverted structure) and different techniques used to obtain the $\beta$ values. In a system with enhanced dielectric screening which is likely to influence recombination process, accurately characterising bimolecular recombination kinetics is expected be more challenging. Therefore, this chapter will first establish the characterization techniques and methodology used to study device performance, dielectric constant, charge mobility, bimolecular recombination kinetics and reduction factor in P3HT: PCBM which is
selected as a model system. As a large variation in $\beta$ and reduction factor has been reported for P3HT: PCBM, this chapter will also compare $\beta$ values obtained using different techniques in the same device. This will help understanding the influence of different techniques on obtained recombination kinetic results, from the knowledge of which the technique used in this thesis to obtain $\beta$ will be determined.

Active layer thickness has also been reported to show a strong influence on PSC performance and recombination. In an optical modelling study on P3HT: PCBM, two maxima in $J_{SC}$ was reported when increasing active layer thickness up to 350 nm, the first one around active layer thickness of 80 nm and the second one around 230 nm.\[^2\] Similar results were obtained in another device performance modelling study.\[^3\] Both studies suggested that, by increasing the active layer thickness to above 200 nm the device performance could be substantially increased. However, this is contradicting experimental study, which characterized over 10 devices with active layer thickness increasing from 35 nm to 155 nm, where the best performance was observed in the 63 nm device.\[^4\] In terms of bimolecular recombination, as the thickness increase the time it takes for dissociated charge carriers to reach the collecting electrode increases, resulting in more recombination. The poor performance at the second optical maxima was attributed to unbalanced charge mobility and doping, both of which lead to strong space charge effect.\[^5\] This raises a problem when comparing bimolecular recombination kinetics, as devices fabricated using different materials very often have different thickness. For the purpose of comparison between systems, this chapter will also study the influence of active layer thickness on bimolecular recombination kinetics.

### 3.1.2 Aim and objectives

As concluded in Chapter 1 and further demonstrated above, it is necessary to establish characterisation procedures for bimolecular recombination kinetics in PSC devices with a consistent and accurate methodology. Therefore, the aim of this chapter is to establish the methodology for bimolecular recombination kinetic characterizations, its influencing parameters (dielectric constant, charge mobility and reduction factor) and device performance for further studies in this thesis.
The device performance is first studied using current-voltage measurement and quantum efficiency measurements, which is compared to literature to ensure the quality of the device. The dielectric constant of polymer: PCBM blend is studied using impedance spectroscopy and dark-CELIV. The charge carrier mobility is measured using photo-CELIV under varying excitation densities and delay times. The charge density decay kinetics, bimolecular recombination coefficient and charge carrier lifetime is primarily characterized using time-resolved charge extraction (TRCE), whereas photo-CELIV is also used for comparison. Langevin reduction factor is characterised using bulk-generation time-of-flight (TOF) and reduction factors calculated from $\beta$ obtained in TRCE and photo-CELIV are also used for comparison. Each technique listed above is carried out on a rr-P3HT: PCBM device, and the obtained result is compared to selected literature and the consistency between literature and experimental results are discussed for each technique. The influence of active layer thickness on recombination kinetics is compared, and the bimolecular recombination coefficients experimentally obtained from TRCE and TOF are compared to examine the consistency between techniques.

The mixture of regioregular poly(3-hexylthiophene-2,5-diyl) and [6,6]-Phenyl C61 butyric acid methyl ester (P3HT: [60]PCBM) is selected to use as reference system in this chapter, as it is the most studied donor: acceptor blend for PSC devices. To compare the results measured in this chapter to literature, ideally it is desirable to find literature that use nominally identical device fabrication methods with very similar device performance. More specifically, there are three selection criteria for the comparing literature:

1) The literature used the same techniques as in this chapter;
2) The device architecture are the same between literature and device used in this chapter;
3) The blending ratio and film morphology between literature and this chapter should be similar.

Based on these criteria, a thorough literature review was done on publications focusing on characterization of bimolecular recombination in P3HT: PCBM. Between 2003 and 2016, over 1800 publications can be found focusing on P3HT: PCBM blend PSC devices, among which 349 publications mentioned charge mobility and 75 mentioned charge recombination (search result from Web of Science). Device performance in these publications showed a large variation, where device efficiencies from below 0.5 % to over
6 %, and charge mobility varying between $10^{-5}$ and $10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ was reported. No publication was found satisfying all three criteria listed above. As a result, it is practically impossible to compare a single literature with all experimental results. Therefore, the device performance in this chapter is compared with the publication by Koppe et al.$^{[6]}$ which used the same device architecture. An active layer thickness of 120 nm was used, giving a $V_{OC} = 0.57$ V, $J_{SC} = 7.1$ mA cm$^{-2}$, $FF = 0.63$ and $PCE = 2.8$ %. As the performance in PSC devices are extremely sensitive to film morphology, by achieving comparable performance the active layer morphology in fabricated devices can be examined. The charge mobility and reduction factor are compared to that reported by Sliaužys et al.$^{[1b]}$ who used photo-CELIV and TOF to obtain charge mobility and reduction factor, respectively, in a device with the same architecture as used here.

3.2 Experimental

Poly(3-hexylthiophene-2,5-diyl) (P3HT, Mw = 82 kg/mol, PDI = 1.5 regioregularity > 95%), and [6,6]-Phenyl C61 butyric acid methyl ester ([60]PCBM) were purchased from Solaris Chem Inc. Chlorobenzene was purchased from Sigma Aldrich. All chemical and solvents were used as purchased.

Device preparation was as follows: P3HT: [60]PCBM (1:1 w/w) solution was dissolved in chlorobenzene, heated to 80 ºC and stirred overnight. Pre-patterned ITO substrates with active area of 0.06 cm$^2$ were cleaned by sonicating in detergent, DI water, acetone and isopropanol, each for 15 minutes then blow dry with nitrogen and treated with UV-Ozone for 20 mins. Poly-(ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT:PSS) (Clevios P, VP Al 4083) was spin coated on the substrates then subsequently annealed at 140 ºC for 10 minutes to achieve a dry thickness of around 30 nm. The photoactive layer was deposited via spin coating the hot solutions. Active layer thickness was controlled via changing spin speed and measured using Dektak160 stylus profilometer. The above processes are carried out under ambient condition except polymer solution preparation, which was prepared in an Argon filled glovebox. Al counter electrode was deposited by thermal evaporation at $\sim$1$\times$10$^{-6}$ mbar to achieve thickness around 100 nm. The complete devices were encapsulated with cover glass using UV-curable epoxy in glovebox for characterizations under ambient conditions.
UV-Vis absorption spectra were measured using a UV-3600 spectrometer, Shimadzu. Film samples spin-coated on clean glass substrates were used for absorption spectra measurements. Current-voltage curves were measured on encapsulated devices using Solar cell I-V curve testing system model IV211, PV measurements. The solar simulator used was calibrated prior to measurement, and a Si irradiance monitor was used throughout the measurements to account for irradiation fluctuation of the simulator. The voltage between -1.5 and 1.5 V was applied. Voltage dependent capacitance and impedance spectroscopy were measured using a Zahner IM6 electrochemical workstation using AC oscillation amplitude of 5 mV.

Photo-CELIV was measured using a pulsed laser (532 nm, Spectra Physics Quanta Ray Lab 170) to generate charge carriers. A function generator (WF 1974, NF) was used to apply an extraction voltage ramp after photoexcitation of device. The decay time between photoexcitation and extraction voltage ramp was controlled using a nanosecond switch (2.2 MΩ impedance, Asama Lab) and a delay generator (Stanford Research DG535). The extraction current was recorded using an oscilloscope (Tektronics, DPO 4054) with a 50 Ω impedance.

Time-resolved charge extraction was carried out as follows. A pulsed laser (532 nm, Spectra Physics Quanta Ray Lab 170) was used to generate charge carriers within measured devices. The devices were initially held at high impedance using a nanosecond switch (2.2 MΩ impedance, Asama Lab). After a controllable delay time using a digital delay generator (Stanford Research DG535), the switch was opened and the devices were at short circuit condition. The extracted current was recorded using an oscilloscope (Tektronics, DPO 4054, and input impedance 50 Ω). The dark response was subtracted to remove the switch noise.

Bulk-generation time-of-flight was carried out by photo-excitation a device using a 532 nm pulsed laser while applying a constant extraction bias using a function generator (WF 1974, NF). The extraction transient was recorded with an oscilloscope (Tektronics, DPO 4054) using a 50 Ω impedance. The excitation density was varied by applying different neutral density filters with the highest excitation density of 1000 μJ cm⁻².
3.3 Results

3.3.1 Photovoltaic performance of P3HT: [60]PCBM devices

An annealed rr-P3HT: [60]PCBM device with active layer thickness of 65 nm, 110 nm and 306 nm (after annealing) was fabricated as described in Section 3.2, and the device performance were characterized under 100 mW cm$^{-2}$ illumination and in the dark to obtain the current-voltage curves. Figure 3.1 shows the current-voltage curves measured in the dark (dash line) and under illumination (solid line), and the performance parameters obtained from Figure 3.1 are listed in Table 3.1. The 306 nm device showed the largest short-circuit current density ($J_{SC}$) of 9.6 mA cm$^{-2}$, whereas the 110 nm device showed a $J_{SC} = 8.1$ mA cm$^{-2}$ and the 65 nm device showed a $J_{SC} = 7.8$ mA cm$^{-2}$. This is in agreement with more efficient photon harvesting at larger thickness, as reported previously.$^{[2]}$ A slight increase in open-circuit voltage ($V_{oc}$) was also observed with increased thickness, where a $V_{oc} = 0.57$ V was observed for 306 nm device, while $V_{oc}$ between 0.53 V and 0.54 V was observed for the other thinner devices. The higher $V_{oc}$ and $J_{SC}$ in the 306 nm device resulted in a higher $FF$ of 0.5 and the highest $PCE$ of 2.7 % among the three fabricated devices, whereas the thinner devices gave lower $FF$ between 0.44 and 0.46, and lower $PCE$ around 1.9 %. The lower $FF$ in 65 nm and 110 nm devices compared to that in 306 nm devices is likely due to the low shunt resistance in the device, evidenced by the increased current density at large reverse bias. The highest performance obtained in the 306 nm device is also in agreement with previous thickness dependent study in P3HT: PCBM.$^{[3]}$

These performance parameters were compared to literature values reported by Koppe et al. which used the same device architecture and an active layer thickness of 120 nm,$^{[6]}$ also listed in Table 3.1. The $V_{oc}$ in 65 nm and 110 nm devices were slightly lower than the literature value of 0.57 V, whereas the 306 nm device showed close to identical $V_{oc}$. The $J_{SC}$ in all fabricated devices reported here were larger than that reported in literature (7.1 mA cm$^{-2}$). The fabricated devices showed lower $FF$ compared to $FF = 0.63$ reported in literature. The literature device gave a $PCE$ of 2.5 %, which was slightly lower than that obtained here for the 306 nm device but higher than the 110 nm device, which has similar film thickness with literature device. Although the 306 nm device showed comparable performance to literature, the 110 nm device which has very similar thickness with the literature device showed a lower $V_{oc}$ and performance compared to literature.
This can be caused by the difference in material source and molecular weight of the polymer used, as the literature reported a molecular weight of 50 kg mol$^{-1}$ whereas the rr-P3HT polymer used here has molecular weight of 82 kg mol$^{-1}$. Nonetheless, the high performance observed in the 306 nm device indicates comparable device morphology, allowing further characterisations.

For the demonstration of further characterisations in this chapter, the 65 nm device will be used. This is because as mentioned in Section 3.1.1, large thickness leads to substantially more significant space charge effect, influencing recombination kinetics. Comparison of recombination kinetics between these devices will also be carried out, and will be discussed in detail in Section 3.3.6 below.

![Figure 3.1](image.png)

Figure 3.1 Current-Voltage characterization of P3HT: PCBM devices with thickness of 65 nm, 110 nm and 306 nm, carried out in the dark (dash line) and under AM1.5 illumination (solid line).

<table>
<thead>
<tr>
<th>Voltage (V)</th>
<th>65 nm_light</th>
<th>65 nm_dark</th>
<th>110 nm_light</th>
<th>110 nm_dark</th>
<th>306 nm_light</th>
<th>306 nm_dark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current density (mA cm$^{-2}$)</td>
<td>-0.4</td>
<td>-0.2</td>
<td>0.0</td>
<td>0.2</td>
<td>0.4</td>
<td>0.6</td>
</tr>
<tr>
<td>-40</td>
<td>-20</td>
<td>0</td>
<td>20</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.1 Device performance parameters obtained from Figure 3.1 compared with literature values.
The external quantum efficiency was characterized for a 65 nm device, as shown in Figure 3.2 together with the absorption spectrum of 1:1 w/w P3HT: PCBM blend measured on glass substrate. The absorption peak was observed at 510 nm, which was attributed to the absorption of P3HT. The increase in absorbance at wavelength below 400 nm was attributed to the absorption of PCBM. A maximum EQE of 56 % was observed at 515 nm, which matches the peak absorption wavelength since most efficient charge generation is expected to take place when photon absorption is strongest. By integrating the EQE spectrum over the whole wavelength range, the short circuit current $J_{sc}$ could also be calculated. The integrated $J_{sc}$ was 7.2 mA cm$^2$, which is close to the $J_{sc}$ of 7.8 mA cm$^2$ obtained from $J$-$V$ measurements. In literature the maximum EQE of 55 % was observed at 500 nm, which has a very similar peak EQE value to the results shown in Figure 3.2 but the wavelength reported in literature is shorter.

<table>
<thead>
<tr>
<th>WaveLength (nm)</th>
<th>EQE (±)</th>
<th>$J_{sc}$ (mA cm$^2$)</th>
<th>$V_{oc}$ (±)</th>
<th>$F因子$ (±)</th>
</tr>
</thead>
<tbody>
<tr>
<td>65 ± 5 nm</td>
<td>0.54 ± 0.003</td>
<td>7.8 ± 0.5</td>
<td>7.2</td>
<td>0.46 ± 0.007</td>
</tr>
<tr>
<td>110 ± 7 nm</td>
<td>0.531 ± 0.007</td>
<td>8.1 ± 0.5</td>
<td></td>
<td>0.441 ± 0.005</td>
</tr>
<tr>
<td>306 ± 11 nm</td>
<td>0.571 ± 0.003</td>
<td>9.6 ± 0.4</td>
<td></td>
<td>0.50 ± 0.03</td>
</tr>
<tr>
<td>Literature [6]</td>
<td>0.57</td>
<td>7.1</td>
<td></td>
<td>0.63</td>
</tr>
</tbody>
</table>
Figure 3.2 The absorption spectrum of P3HT: PCBM film, plotted with EQE spectrum obtained from the P3HT: PCBM device same as shown in Figure 3.1.

3.3.2 Geometric capacitance and dielectric constant

As one of the key parameters influencing bimolecular recombination, the dielectric constant is characterized by measuring the geometric capacitance of the P3HT: PCBM device. The geometric capacitance of the active layer was characterized using bias dependent impedance spectroscopy. The dark impedance of the device was measured under a bias sweep at fixed frequency. The capacitance $C$ value was calculated from the impedance $Z$ at given bias and frequency:

$$Z = 1/j\omega C$$ (3.6)

where $\omega$ is the angular frequency.

Figure 3.3a shows the $1/C^2$ - bias plots of five P3HT: PCBM devices, four of which has the same film thickness of 110 nm and one with a smaller thickness of 65 nm, measured at 1 kHz using a Zahner potentiostat. The geometric capacitance $C_{geo}$ could be obtained by linear extrapolation of the plot at large reverse bias (dash line in figure) and taking the
intersect at 0 V. Using the obtained $C_{geo}$ and measured active layer thickness $d$, the dielectric constant value is calculated:

$$C_{geo} = \epsilon_0 \epsilon_r \frac{S}{d}$$

(3.7).

$C_{geo}$, thickness and dielectric constant values are listed in Table 3.2. The five devices shown in Figure 3.3a gave an average $\epsilon_r$ of 3.6 ± 0.2, where the error is likely due to thickness variation. It was noted that at -1 V, depletion of capacitive charge was not reached, which can lead to underestimation of $1/C^2$ value and thus overestimation of $C_{geo}$ and $\epsilon_r$. The charge carriers at large reverse bias can either be the dark carriers in P3HT:PCBM device [7] or injection carriers from the electrodes. It is also noted that in the 65 nm device in Figure 3.3a, the $1/C^2$ drop-off appeared at lower bias compared to thicker devices. This is because at lower thickness, the electrode capacitance has a stronger influence than the doping carriers, and the $1/C^2$ drop-off appears at lower bias. [16]
Figure 3.3 (a) $1/C^2$-Bias plots for P3HT: PCBM device measured at 1 kHz measured using a Zahner potentiostat. The dash lines showed the linear extrapolation of the bias – $1/C^2$ plot at reverse bias and the obtained capacitance was labelled in figure. (b) Dark CELIV transients obtained in a P3HT: PCBM device under different $U_{max}$ and $t_{pulse}$ conditions.
Table 3.2 List of device capacitance values obtained using bias dependent impedance measurements at 1 kHz as shown in Figure 3.3a, and calculated dielectric constant values. Five P3HT: PCBM devices with different active layer thicknesses were measured, where the thickness values were also listed in the table.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>$C_{geo}$ (nF)</th>
<th>$\varepsilon_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>110 ± 7</td>
<td>1.7 ± 0.1</td>
<td>3.5 ± 0.2</td>
</tr>
<tr>
<td>110 ± 7</td>
<td>1.7 ± 0.1</td>
<td>3.5 ± 0.2</td>
</tr>
<tr>
<td>110 ± 7</td>
<td>1.8 ± 0.1</td>
<td>3.7 ± 0.2</td>
</tr>
<tr>
<td>110 ± 7</td>
<td>1.8 ± 0.1</td>
<td>3.8 ± 0.2</td>
</tr>
<tr>
<td>65 ± 5</td>
<td>2.9 ± 0.2</td>
<td>3.5 ± 0.3</td>
</tr>
</tbody>
</table>

Charge extraction by linearly increasing voltage (CELIV) was also used to measure the device capacitance in the P3HT: PCBM device with 65 nm active layer. In a CELIV measurement, a linear voltage ramp was applied to the devices at set frequency with a voltage ramp maximum $U_{max}$ and a pulse duration $t_{pulse}$, while the device was kept in the dark. The current step response reached:

$$j(0) = C_P U_{max}/t_{pulse}$$

in the circuit time constant $\tau_{RC}$ for an $RC$ circuit. The time constant $\tau_{RC}$ was controlled below 200 ns by applying different resistors depending on the device capacitance. Figure 3.3b shows the dark CELIV transients of P3HT: PCBM obtained at various $U_{max}$ and $t_{pulse}$ in the dark measured using the 50 Ω input impedance of the oscilloscope. A small current peak was observed in the CELIV transients at $t_{pulse} = 20$ μs or $U_{max} = 1$ V, and then the current transients decay back to $j(0)$. The presence of a small peak in the CELIV dark transient is due to the presence of dark carriers in P3HT: PCBM, which has been reported previously.\(^7\) Using Equation 3.7 and Equation 3.8, an average $C_{P, CELIV} = 2.7 \pm 0.2$ nF and dielectric constant value of $3.3 \pm 0.2$ is calculated. The capacitance values obtained from impedance ($C_{P, EIS}$) and CELIV ($C_{P, CELIV}$) showed a 7% variation, see Table 3.3.
During the literature review of dielectric constant in P3HT: PCBM films, very little experimental study on dielectric constant characterization was found despite numerous mention of low dielectric constant between 3 – 4 in P3HT: PCBM films.[8] The dielectric constant \( \varepsilon_r \) in P3HT: PCBM (1:1 w/w) blend is typically assumed to be 3.5 based on a dielectric constant of 3 for P3HT and 3.9 for PCBM,[9] however experimental support for such assumption was scarce. Chen et al. reported a dielectric constant of 4.2 ± 0.2 in 1:1 w/w P3HT: [70]PCBM blend device characterized in vacuum using a LRC meter at 100 kHz,[10] which was notably larger than typical assumptions and the dielectric constant value obtained here. The 20 % higher \( \varepsilon_r \) reported by Chen et al. can come from a number of reasons, including the different fullerene derivative acceptor used, difference in polymer source, film preparation and device fabrication method.

Considering the importance of dielectric screening on charge generation and recombination, accurately and reproducibly characterizing the dielectric constant is of key importance for charge recombination studies. Several aspects need to be further addressed for accurate measurement of dielectric constant, including the different capacitance values obtained from impedance and CELIV techniques, the frequency dependence of geometric capacitance obtained from impedance techniques, the \( U_{max} \) and \( t_{pulse} \) dependence of capacitance values obtained from CELIV. Therefore, Chapter 5 is dedicated to accurately characterize the dielectric constant value in DT-PDPP2T-TT and to establish an experimental procedure for dielectric constant characterization.

Table 3.3 List of P3HT: PCBM 1:1 device capacitance values obtained from Figure 3.3 and calculated dielectric constant value.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>( C_{geo} ) (nF)</th>
<th>( \varepsilon_r )</th>
<th>( C_{geo} ) (nF)</th>
<th>( \varepsilon_r )</th>
<th>( \varepsilon_{r, literature} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>65 ± 5</td>
<td>2.9 ± 0.2</td>
<td>3.5 ± 0.3</td>
<td>2.7 ± 0.2</td>
<td>3.3 ± 0.2</td>
<td>4.2 ± 0.2</td>
</tr>
<tr>
<td>110 ± 7</td>
<td>1.8 ± 0.1</td>
<td>3.6 ± 0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.3.3 Charge carrier mobility

Photo-induced charge extraction by linearly increasing voltage (photo-CELIV) was carried out on the fabricated P3HT: PCBM device with the active layer thickness of 65 nm to characterize charge carrier mobility. The experimental setup and experimental procedure for this technique is shown in Chapter 2. The P3HT: PCBM device transients measured under maximum extraction bias ($U_{\text{max}}$) of 1 V and bias duration ($t_{\text{pulse}}$) of 50 µs at changing delay times are shown in Figure 3.4. The $U_{\text{max}}$ and $t_{\text{pulse}}$ values were chosen such that the applied extraction field is large enough to produce clear signals with good signal-to-noise ratio without injection. In Figure 3.4, it is observed that with increasing delay time, a decrease in $t_{\text{max}}$ is present. At short delay time of 5 µs, the extracted charge was 1.5 times the capacitive charge characterized by the difference between area under the extraction transient and the dark transient. Similar features of large extracted charge and decreasing $t_{\text{max}}$ at long delay times have been observed before and are associated with reduced bimolecular recombination.$^{[11]}$ This is because in systems with reduced bimolecular recombination, the charge carrier lifetime is longer than the extraction time, leading to accumulation of charge density much larger than charge stored on the contacts and the extraction of the accumulated charge further lead to shorter $t_{\text{max}}$. This is indeed the case here. The charge density at 5 µs was calculated by integrating the extraction transient and subtracting the capacitive charge, giving a charge density of $4.8 \times 10^{16}$ cm$^{-3}$. The charge carrier lifetime at this charge density is on the scale of tens of microseconds (as will be shown in Section 3.3.5), which is indeed much longer than the $t_{\text{pulse}}$ used here.
Figure 3.4 Photo-CELIV transients obtained at various delay times using $t_{pulse}$ of 50 µs and $U_{max}$ of 1 V.

The charge carrier mobility $\mu$ could be calculated from the photo-CELIV transients using Equation 3.5 in the case of moderate conductivity ($\Delta j \approx j(0)$). Figure 3.5 shows the calculated charge mobility at different excitation density or delay time while keeping the other parameters constant. The charge mobility showed over an order of magnitude increase when increasing delay time from 5 µs to 1 ms (Figure 3.5a), which is in agreement with the observed decrease in $t_{max}$ in Figure 3.4. An order of magnitude decrease in the calculated mobility was observed at increasing excitation density.
Figure 3.5 Charge carrier mobility plotted as a function of delay time (at 100 $\mu$J cm$^{-2}$) (a) and excitation density (at 5 $\mu$s delay time) (b), while keeping other parameters constant.

It is noted that at high excitation density or short delay time, the extracted charge exceeds the capacitive charge ($\Delta j > j(0)$), thus these transients are not suitable for mobility calculation using Equation 3.5. Selecting transients with small extracted charge ($\Delta j \leq j(0)$) for mobility calculation, the mobility was calculated for each transient and an averaged charge mobility value was obtained, as shown in Table 3.4. The mobility value obtained here is approximately six times smaller than the photo-CELIV mobility reported by Sliaužys et al. using a 1:1 P3HT: PCBM device.$^{[1b]}$ Decreasing $t_{\text{max}}$ at increasing delay time was reported in literature, which was similar to that observed in Figure 3.4. The large difference between experimentally obtained mobility and literature value is because the
carrier mobility in a system is strongly related to the film morphology, which is in turn affected by a number of aspects including molecular weight of the polymer, film annealing temperature and solvent used for dissolving polymer, just to name a few. The lower mobility obtained here is likely caused by i) in literature no thermal annealing was carried out on the rr-P3HT: PCBM device, whereas the P3HT: PCBM device used in photo-CELIV measurements here was annealed for 10 minutes at 140 ºC, which can result in different active layer morphology between these devices; ii) exposure of active layer in air during device preparation, which increases the level of doping and thus carrier trapping. Using the charge mobility obtained here and the dielectric constant obtained in Section 3.4, the Langevin recombination coefficient is calculated using Equation 3.4, giving $\beta_L = 2.5 \times 10^{-11}$ cm$^3$s$^{-1}$ (also listed in Table 3.4).

In terms of mobility characterization in this thesis, photo-CELIV transients with $\Delta j \leq j(0)$ are used to calculate mobility using Equation 3.5, and an averaged mobility value is used for further calculations. Despite the strong delay time and excitation density observed in P3HT: PCBM, weak or no dependence of mobility on delay time and excitation density is typically observed in Langevin-type systems. This is due to the faster recombination than extraction which prohibits the accumulation of charge carriers in the active layer. This is further confirmed in Chapter 6 by comparing the delay time dependence of mobility in four different polymer: PCBM systems.

<table>
<thead>
<tr>
<th>Table 3.4</th>
<th>Charge carrier mobility as well as Langevin recombination coefficient calculated for the fabricated P3HT: PCBM device as well as from literature.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mobility (cm$^2$V$^{-1}$s$^{-1}$)</td>
<td>$\varepsilon_r$</td>
</tr>
<tr>
<td>Measured here</td>
<td>4.83 $\times$ 10$^{-5}$</td>
</tr>
<tr>
<td>Literature$^{[1b]}$</td>
<td>3 $\times$ 10$^{-4}$</td>
</tr>
</tbody>
</table>

### 3.3.4 Charge density decay and bimolecular recombination coefficient

The charge density decay kinetics in the 65 nm device were characterized using time-resolved charge extraction (TRCE) using a nanosecond switch. The experimental setup
and methodology for the TRCE measurement are given in Chapter 1. Figure 3.6a shows the TRCE transients of a P3HT: PCBM device obtained in the dark and under 100 µJcm$^{-2}$ excitation at different delay times. The transient with largest peak magnitude corresponded to the shortest delay time of 100 ns. By increasing the delay time, the extraction current transient decreased in magnitude until the transient reached similar magnitude to the dark transient at 10 ms delay time. The charge density could be calculated from Figure 3.6a by subtracting the dark transient then integrating the extraction transients at each delay time. The obtained charge density could then be plotted as a function of time, giving Figure 3.6b. At early timescales prior to 1 µs, a strong excitation density dependence of charge density was observed. The excitation density dependence weakens until no excitation density dependence could be observed at long timescales beyond 200 µs. At timescales beyond 10 µs, power law decay of charge density was observed with a power law gradient of 0.5. The observed charge density decay was dominated by bimolecular recombination rather than geminate recombination, because i) geminate recombination in P3HT: PCBM takes place on the timescale of picoseconds, where a recombination time constant of ~ 800 ps has been reported;[12] ii) geminate recombination has first order kinetics and is excitation density independent.
Figure 3.6 (a) The dark and 100 μJ cm\(^{-2}\) photo-excited TRCE transients for the 65 nm P3HT: PCBM device obtained at different delay times, and (b) charge density decay in P3HT: PCBM obtained under a series of excitation densities. The dashed line in Figure b shows the power law fitting, giving a gradient of 0.5.
The time-dependent bimolecular recombination coefficient $\beta(t)$ could be calculated from the charge density decay:

$$\beta(t) = -\frac{dn}{dt} \frac{1}{n^2} \quad (3.9).$$

From Figure 3.6b, $\beta$ was calculated using charge density decay at different excitation densities and plotted as a function of time, as shown in Figure 3.7. No excitation density dependence was observed for $\beta$ at each delay time. A time-dependent $\beta$ with decreasing value at longer time was observed. The time dependence, and thus charge density dependence of $\beta$, is due to the presence of trap states at different hopping rates.\textsuperscript{[13]} As demonstrated by Eng et al, assuming the trap distribution to be exponential, the bimolecular recombination coefficient is dependent on the ratio between localized carrier density ($n_L$) and free carrier density ($n_F$) ($\beta(n) \propto \frac{1}{1+n_L/n_F}$).\textsuperscript{[13]} Eng et al suggested a charge density dependent $\beta$ which reaches a constant value when charge density is large, i.e. when the majority of extracted carriers are free carriers, and a $\beta$ being power law dependent on charge density when the charge density is low. This is in agreement with the time dependent $\beta$ observed in Figure 3.7.

For consistency between different systems, the calculation and comparison of charge density decay and $\beta$ in the rest of this thesis will be carried out at the saturated excitation density, which allows the comparison of maximum charge density at each delay time across different systems. In this thesis saturation is observed above 10 $\mu$J cm\(^{-2}\) for all studied devices, therefore only excitation density above 10 $\mu$J cm\(^{-2}\) will be used for further comparison.
Figure 3.7 Bimolecular recombination coefficient $\beta$ in P3HT: PCBM device, calculated from Figure 3.6b using Equation 3.9 at various excitation densities.

### 3.3.5 Charge carrier lifetime

Charge carrier lifetime could also be calculated from Equation 3.2. Figure 3.8a shows calculated charge carrier lifetime plotted as a function of charge density at various excitation densities calculated from Figure 3.6b. At excitation densities above 10 $\mu$J cm$^{-2}$, the calculated lifetimes are independent of excitation density, which is in agreement with the saturated charge density observed in Figure 3.6b. At lower excitation densities, shorter carrier lifetime was observed at the same charge density, compared to saturated lifetimes. One of the possibilities for the observed shorter lifetime at low excitation densities is due to non-uniform distribution of charge carriers across the active layer thickness. At the open circuit condition at which the device was kept during the delay time, the electron concentration is higher at the aluminium side and hole concentration at ITO side. At lower excitation densities such non-uniform charge distribution is less pronounced, resulting in more uniformly distributed charge carriers and longer observed lifetime.$^{[14]}$ At saturated excitation density and charge density ($2 \times 10^{17}$ cm$^{-3}$), P3HT: PCBM device showed a carrier lifetime of 3 $\mu$s. The charge carrier lifetime is also plotted as a function of $V_{OC}$ (Figure 3.8b), which was obtained from photovoltage decay and...
matched to charge density at the same delay time. Good agreement in charge carrier at the same $V_{OC}$ was observed for all excitation densities above 0.3 μJ cm$^{-2}$.

![Figure 3.8](image)

Figure 3.8 (a) Charge carrier lifetime plotted as a function of charge density on a log-log scale, and (b) charge carrier lifetime plotted as a function of $V_{OC}$.

Charge density decay, bimolecular recombination coefficient and lifetime can be calculated from photo-CELIV as well, following similar methodology as TRCE. The obtained charge density decay and lifetime at saturated excitation density of 10 μJ cm$^{-2}$ from TRCE and photo-CELIV are compared in Figure 3.9. A lower charge density was obtained from photo-CELIV, which is due to the fixed extraction pulse width in photo-
CELIV measurements. As seen in Figure 3.9, at early delay times the extraction transient tail of photo-CELIV was truncated by the fixed pulse width. As the delay time became longer, the truncated extraction tail also became smaller which is in agreement with the smaller difference in charge density obtained from TRCE and photo-CELIV at longer delay times, see Figure 3.10. When an extraction tail is present in measurements, the fixed pulse width will truncate the extraction tail leading to smaller charge density. This is more pronounced at short delay times where the charge density is high, whereas at long delay times the difference between charge density from two techniques is smaller. Comparing the calculated charge carrier lifetime, slightly shorter lifetime values were obtained in photo-CELIV (Figure 3.10b). This is in agreement with literature where a shorter lifetime was obtained from photo-CELIV compared to TRCE.\textsuperscript{[15]} The reason for the shorter lifetime obtained from photo-CELIV is most likely due to the short integration time as mentioned above. Since the calculated charge density in photo-CELIV is smaller than the actual charge density during the measurement, the charge carrier lifetime is underestimated in photo-CELIV.

![Comparison of photo-CELIV obtained at t\textsubscript{pulse} of 50 μs and dark CELIV transients. The dash lines indicate the truncated extraction transient tail.](image_url)
For above reasons, TRCE will be used to obtain charge density decay and charge carrier lifetime in this thesis. A comparison of $\beta$ obtained from different techniques will be carried out in Section 3.4.3.

Figure 3.10 Comparison between charge density decay (a) and charge carrier lifetime plotted as a function of charge density (b) obtained using TRCE and photo-CELIV, both excited at 10 μJ cm$^{-2}$. 
3.3.6 Recombination reduction factor

The bimolecular recombination reduction factor in the 65 nm device is obtained using bulk-generation TOF using variable resistances. The purpose of using different loading resistors is that the decay time of TOF transients are determined by the RC time constant of the extraction circuit, and by using a series of different resistors the charge extraction time is varied. Figure 3.11 shows the TOF transients measured on P3HT: PCBM device using a resistor of 50 Ω at changing excitation densities. Current transients showed saturation above excitation density of 10 μJ cm\(^{-2}\), which is a clear characteristic of bimolecular recombination. A shoulder in TOF transients could be observed in the saturated transients, which corresponds to the time to deplete the reservoir under the applied bias. This is characteristic of non-Langevin recombination, which is only present when the extraction time is longer than the transit time required for the carriers to travel through the sample thickness under the applied bias (\(U\)). Similar transient shape with a transient kink was reported in literature as shown in Figure 3.11, where transient saturation was also observed at large excitation density.\(^{[1b]}\)

![Figure 3.11 TOF transients in P3HT: PCBM device obtained at a series of excitation densities, measured using a 50 Ω resistor.](image)

From the TOF transients, the bimolecular recombination reduction factor \(\xi\) could be calculated from Equation 3.3. \(Q_e\) could be obtained by integrating the time-of-flight transients under the specific excitation density, and \(t_e\) is determined by the difference of half-maximum decay time \(t_{1/2}\) at high and low excitation densities. Figure 3.12 shows the ratio between extracted charge and capacitive charge \(Q_e/CU\) and \(t_{1/2}\), plotted as a function...
of excitation density and Table 3.4 shows the obtained $\xi$ using 50 $\Omega$ and 1 k$\Omega$ resistor. At maximum excitation density $Q_e/CU$ ratio of 5.3 was observed for the 50 $\Omega$ TOF. $Q_e/CU$ ratio above 1 is typically observed in non-Langevin systems due to the reduced recombination. As the extraction time is limited by the RC constant, when measuring with a larger resistor, typically the extracted charge $Q_e$ will be less due to recombination. The obtained $Q_e/CU$ at 1 k$\Omega$ is indeed smaller than that at 50 $\Omega$. From Figure 3.12 $\xi$ is calculated, as listed in Table 3.5. Reduction factor $\xi$ values of 0.07 and 0.025 were obtained at 50 $\Omega$ and 1 k$\Omega$, respectively. While $\xi$ much smaller than 1 is characteristic of reduced bimolecular recombination, the $\xi$ values obtained here are larger than that reported in literature ($\xi = 3.4 \times 10^{-4}$).\cite{1b} The $\beta$ values calculated here (Table 3.5) are also larger than that in literature by approximately an order of magnitude ($\beta = 1.5 \times 10^{-14}$ cm$^3$ s$^{-1}$). One of the possible origins for the larger $\xi$ and $\beta$ values obtained here is the difference in active layer thicknesses between literature and measured devices. This is likely the case, as the device in reference literature has a thickness of 1.2 $\mu$m whereas in the device measured here the active layer is 65 nm thick. The difference in thickness can affect the drying speed of spin-coated film which in turn can lead to difference in vertical segregation of phases, giving different film morphology.

For comparison of TOF results in this thesis, the results should be obtained under the same resistance. As mentioned in Chapter 1, another requirement for the resistance used in TOF is that the RC time constant should be longer than the dielectric relaxation time $\tau_\sigma = \varepsilon\varepsilon_0/\sigma$. Due to the large active layer thickness and high dielectric constant in DT-PDPP2T-TT: PCBM device which will be shown in the next chapter, a resistance of 50 $\Omega$ does not satisfy this requirement. Thus for further comparison in this thesis, a resistance of 1 k$\Omega$ will be used.
Figure 3.12 The $Q_e/CU$ ratio and $t_{1/2}$ values plotted as a function of excitation density obtained in P3HT: PCBM device, using both 50 Ω and 1 kΩ resistors.

Table 3.5 Extraction time $t_e$, $Q_e/CU$, ratio, reduction factor $\xi$, and $\beta$ obtained from TOF measurements for P3HT: PCBM.

<table>
<thead>
<tr>
<th>$R$ (Ω)</th>
<th>$t_e$ (s)</th>
<th>$Q_e/CU$</th>
<th>$\xi$</th>
<th>$\beta$ (cm$^3$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>$1.07 \times 10^{-6}$</td>
<td>5.3</td>
<td>0.07</td>
<td>$1.73 \times 10^{-12}$</td>
</tr>
<tr>
<td>1000</td>
<td>$5.05 \times 10^{-6}$</td>
<td>3.2</td>
<td>0.025</td>
<td>$6.18 \times 10^{-13}$</td>
</tr>
</tbody>
</table>
3.4 Discussion

3.4.1 Establishing characterization techniques

The charge carrier mobility, charge density decay kinetics, carrier lifetime, recombination reduction factor as well as photovoltaic performance are obtained experimentally in a 1:1 w/w P3HT: PCBM device and are each compared to literature. Between experimental results and literature data, difference in device $V_{OC}$, charge mobility and reduction factor were observed. The charge carrier mobility was lower than reported in literature (Table 3.4). Larger $\xi$ and $\beta$ values were obtained experimentally using TOF compared to literature (Table 3.5), suggesting faster recombination in the measured device compared to reference. These differences are likely caused by the difference in material source and film morphology of the polymer, both of which has been shown to strongly affect the recombination kinetics in P3HT: PCBM. These observed differences further demonstrate that, to compare recombination kinetics between different systems, experimentally obtained results from one system cannot be compared directly to that from another system reported in literature.

The main body of this thesis is focused on the bimolecular recombination kinetics study on binary and ternary blends using DT-PDPP2T-TT, PCPDTBT, PTB7 and PCBM. For this purpose, establishing consistent methodology for performance and recombination kinetic characterisations is necessary, which is the main focus of this chapter. The differences between literature values and experimental results carried out on P3HT: PCBM device show that, comparison between devices with different structure, fabrication method and characterization parameters can be difficult, even for the same material. Therefore, in order to compare recombination kinetics between different binary and ternary blends, the device architecture is kept consistent between different systems. To reduce the influence of contact capacitance on the geometric capacitance measurements, the number of charge transport layers is kept to a minimum. It should be mentioned that at open circuit the bimolecular recombination within the device is independent of contact barriers, therefore the possible difference in contact energetics of these systems are not
expected to influence the interpretation of the obtained recombination kinetics. Therefore, result comparison is only to be carried out between devices with same architecture and the fabricated devices are pre-tested using their J-V curves to make sure no current injection from electrode or S-shape curves are present.

The device performances are to be carried out on fabricated solar cells first to eliminate devices with poor contact quality. To compare dielectric constant values and apply them in Langevin recombination coefficient calculation, the geometric capacitance characterization were carried out using the same technique under the same conditions. For carrier mobility characterization, photo-CELIV is carried out under $U_{\text{max}}$ and $I_{\text{pulse}}$ values such that the applied extraction field is large enough to produce clear signals without carrier injection, and only photo-CELIV transients with $\Delta j \leq j(0)$ are used for mobility calculations.

For the characterization of bimolecular recombination kinetics, TRCE will be primarily used in this thesis. This is because it provides multiple parameters in one technique, and comparison between experimentally obtained TRCE results, literature values and results from other techniques showed good consistency. Comparison between time dependent charge density and $\beta$ in different systems are to be carried out only at saturated excitation due to the excitation density dependence of charge density and charge density decay kinetics, and the carrier lifetimes are to be compared at the same charge density since $\beta$ and thus $\mu$ are strongly charge density dependent. To clarify whether the bimolecular recombination has Langevin or non-Langevin characteristics in certain systems, TOF is carried out to examine the presence of non-Langevin characteristics.

### 3.4.2 Key features in a non-Langevin system

When examining whether a system has non-Langevin or Langevin type recombination, a number of key features can be used as evaluating criteria. Reduction factor $\xi$ has been widely used to determine non-Langevin recombination, where $\xi \ll 1$ indicates non-Langevin-type recombination. However, the reduction factor can vary largely within a system, depending on the film morphology, sample resistance and thickness. As mentioned in Section 3.1.1, $\xi$ values between $10^{-4}$ and 0.06 have been reported for P3HT:
PCBM. Here, $\zeta = 0.07$ was obtained from TOF using a 50 $\Omega$ resistor, which is over two orders of magnitude higher than previously reported value using TOF and close to that obtained from injected-CELIV. Such large difference between $\zeta$ obtained using the same technique strongly suggests that the $\zeta$ value alone is not reliable to determine whether a system is Langevin or non-Langevin.

Apart from a low reduction factor $\zeta$, non-Langevin systems have a number of features to differentiate from Langevin systems.

1) In photo-CELIV transients of a non-Langevin system, the extracted charge largely exceeds the capacitive charge, and at saturated excitation density and short delay time $\Delta j >> j(0)$ (Figure 3.4). Another non-Langevin feature in photo-CELIV is the delay time dependence of $t_{max}$, where a strong decrease is observed when increasing delay time at fixed excitation density, $U_{max}$ and $t_{pulse}$, also observed in Figure 3.4. As explained in Section 3.3.3, this is due to the accumulation of charge carriers at the contact as a result of bimolecular recombination slower than charge extraction.

2) In TOF transients measured for P3HT: PCBM device, a distinct extraction time $t_e$ was observed. The presence of such $t_e$ is caused by bimolecular recombination slower than charge extraction, which is characteristic of non-Langevin systems. In non-Langevin systems like P3HT: PCBM, the calculated $Q/CU >> 1$ (Figure 3.12) due to the same reason as $\Delta j >> j(0)$ observed in saturated photo-CELIV transients.

### 3.4.3 Obtaining bimolecular recombination coefficient $\beta$

The bimolecular recombination coefficient $\beta$ is obtained from TRCE, photo-CELIV and TOF. In TRCE and photo-CELIV, time-dependent $\beta$ values are calculated from charge density, whereas in TOF a single $\beta$ value is obtained under one loading resistance. To compare $\beta$ obtained between three techniques, the $\beta$ values obtained from all techniques are plotted in the same figure as a function of time, as shown in Figure 3.13. Comparing between $\beta$ obtained from TRCE and photo-CELIV, at 20 $\mu$s similar $\beta$ was obtained from both techniques, while TRCE gave higher $\beta$ at 5 $\mu$s and 10 $\mu$s and photo-CELIV gave higher $\beta$ above 50 $\mu$s. Stronger time dependence was observed for $\beta$ obtained from TRCE, where TRCE obtained $\beta$ decreased by a factor of 3 when delay time increased from 10 $\mu$s.
to 100 μs while the photo-CELIV obtained β decreased by a factor of 1.3. These differences are most likely caused by the fixed extraction pulse width in photo-CELIV, which truncates the extraction tail leading to smaller extracted charge density and distortion of decay kinetics. The β values calculated from TOF showed consistency with that obtained from TRCE.

These results suggest that the TRCE is a suitable technique to obtain time dependent β. In the following of this thesis, bimolecular recombination coefficient β will be characterized using TRCE for recombination kinetic studies.

![Figure 3.13 Comparison between β obtained from TRCE and TOF, plotted as a function of time. The TOF obtained β are marked in figure as dash lines.](image)

3.5 Conclusions

Experimental techniques for device performance, geometric capacitance, carrier mobility, bimolecular recombination kinetics and reduction factor have been carried out on 1:1 w/w P3HT: [60]PCBM devices to establish the methodology for dielectric constant, charge mobility and recombination kinetic characterizations. Device performance comparable to
literature was obtained. A charge mobility of $4.83 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was obtained in the 65 nm device which was lower than literature value of $3 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, possibly due to difference in material source, molecular weight and film morphology. Strong evidence of reduced bimolecular recombination was observed in P3HT: PCBM, which was in agreement with its non-Langevin characteristics reported in previous publications.

The methodology for further mobility, recombination kinetics and reduction factor characterisations were established in this chapter:

1) Charge mobility in this thesis will be carried out using photo-CELIV. The photo-CELIV transients with $\Delta j \leq j(0)$ will be used for mobility calculation. In non-Langevin systems, strong excitation density and delay time dependence of mobility will be present, by selecting transients with $\Delta j \approx j(0)$ only transients at low excitation density or long delay time will be used. The transients satisfying this requirement will be averaged to give an average mobility for the calculation of Langevin recombination coefficient $\beta_L$, when no notable electric field dependence is present in the averaged values (as is indeed the case in this thesis).

2) The charge density decay, bimolecular recombination coefficient and carrier lifetime will be obtained using TRCE. As shown in this chapter, TRCE gave higher charge density and longer lifetime compared to photo-CELIV. For comparison between different systems, results obtained at saturated excitation density (above 10 $\mu$J cm$^{-2}$ in this thesis) will be used. Thickness dependence in charge density and $\beta$ was observed, where devices with thicker active layer gave lower charge density and larger $\beta$. On the other hand, the lifetime versus $V_{OC}$ plot was insensitive to different thicknesses between the devices, allowing direct comparison between different devices.

3) The reduction factor was obtained from TOF, which showed similar value to that calculated from TRCE. However, it was demonstrated in this chapter that the reduction factor value alone is insufficient in determining the bimolecular recombination mechanism in a system (Langevin versus non-Langevin). To determine whether a system has non-Langevin recombination, transient features in photo-CELIV ($\Delta j \gg j(0)$ at saturated excitation and short delay time and strong delay time dependence of mobility) and TOF (clearly observable $t_e$ feature in transient and $Q/CU \gg 1$) should be considered.
For the geometric capacitance and dielectric constant characterisation, a small difference was observed between bias-dependent impedance measurements and dark CELIV. Considering the strong influence of dielectric screening on bimolecular recombination, the geometric capacitance and dielectric constant characterisations will be further studied in Chapter 4 and Chapter 5.

### 3.6 References


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Chapter 4 Bimolecular Recombination in a High Dielectric Constant Diketopyrrolopyrrole-based Low Bandgap Polymer: PCBM Blend
4.1 Background and motivation

Based on the methodology established in Chapter 3, the initial aim in this chapter is to investigate whether the DT-PDPP2T-TT: PCBM system has non-Langevin recombination. As mentioned in Chapter 1, one of the approaches to enhance PSC performance is to reduce the recombination loss within the device, and systems demonstrating reduced bimolecular recombination have been a research focus in recent years. While very few systems showed clear features of significantly reduced bimolecular recombination,\(^1\) a common feature in these systems is that high FF can be achieved in PSC devices with large active layer thickness. In search for systems potentially having reduced bimolecular recombination, a diketopyrrolopyrrole-based push-pull polymer DT-PDPP2T-TT was noticed (see Table 1.1 and Figure 1.13). This low bandgap polymer DT-PDPP2T-TT not only showed high FF of 0.6 at active layer thickness above 300 nm, but is also commercially available. Furthermore, DT-PDPP2T-TT has a low bandgap of 1.42 eV and an absorption onset of 920 nm,\(^2\) allowing photon harvesting at near-infrared region. High hole mobility of 0.8 cm\(^2\) V\(^{-1}\) s\(^{-1}\) was reported for this polymer, obtained from hole-only FET. The authors suggested that the high FF was due to slower bimolecular recombination in the system, which was possibly caused by the fibrous morphology of crystalline polymer in the film. However, no recombination study was carried out for this polymer. Furthermore, no dielectric constant value was reported for this polymer. As explained in Chapter 1, enhanced dielectric screening can potentially reduce bimolecular recombination. Therefore, the primary objective of this chapter is to reproduce the published high FF devices using the commercially sourced polymer and evaluate the dielectric constant, charge mobility, charge carrier recombination kinetics and reduction factor using the techniques established in Chapter 3.

A key issue is that there is a large difference in molecular weight between the polymer reported in literature (447 kg mol\(^{-1}\)) and the commercially sourced polymer batch (67 kg mol\(^{-1}\)). The effect of molecular weight difference on device performance has been widely studied in a number of polymer: PCBM blend systems.\(^3\) Molecular weights of semiconducting polymers showed strong effect on blend film morphology, which in turn affect the charge carrier recombination and transport in the active layer and further reflect in molecular weight dependent device performance. Devices fabricated using high Mn (121 kg mol\(^{-1}\)) rr-P3HT showed an order of magnitude lower hole mobility compared to
that in low Mn (13 kg mol$^{-1}$) device,$[^{3a}]$ leading to over 50% decrease in device fill factor in the high Mn device. This was attributed to the much lower crystallinity and highly intertwined polymer backbones in high Mn blend. Contrary to rr-P3HT, in poly [N-9''-heptadecanyl-2,7'-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT), poly (di(2-ethylhexyloxy) benzo [1,2-b:4,5-b'] dithiophene -co- octylthieno[3,4-c]pyrrole-4,6-dione) (PBDTTPD) and poly [(5,6-difluoro -2,1,3 – benzothiadiazol -4,7-diyl) -alt- (3,3'''- di(2-octyldecyl) 2,2';5',2'';5'',2'''- quaterthiophen-5,5'''-diyl)] (PffBT4T-2OD) blends, devices fabricated using high Mn polymer showed higher carrier mobility, reduced bimolecular recombination and higher performance, which was attributed to more ordered polymer domains with higher domain purity in high Mn devices.$[^{3b},^{3h},^{3i}]$ The above literature show that the effect of molecular weight on PSC device performance is not universal and depends on the polymer blend studied.

As will be shown in this and the following chapters, the DT-PDPP2T-TT polymer has a high dielectric constant in pristine film as well as in polymer: PCBM blends. Strong dielectric screening could have profound influences on charge generation and recombination processes. The use of a high dielectric constant polymer in PSC systems has a very high significance and novelty in the field of organic photovoltaics. To summarise, the above properties make DT-PDPP2T-TT a very interesting candidate for recombination study in PSC systems.

This chapter therefore specifically aims to:

1. Reproduce the high FF published in the literature using the commercially sourced polymer;
2. Measure dielectric constant, charge carrier mobility, carrier lifetime, bimolecular recombination coefficient and reduction factor using the techniques established in Chapter 3;

With further measurements, the results obtained in this chapter are then used to explain the effect of dielectric screening on charge recombination kinetics.

To achieve the above aims, DT-PDPP2T-TT: [60]PCBM 1:3 w/w blend devices were fabricated and the solar cell performance were evaluated. The geometric capacitance of fabricated blend devices was characterized using bias and frequency dependent
impedance measurements and dark CELIV to obtain the dielectric constant. Charge carrier mobility was characterized using photo-CELIV and the recombination reduction factor was obtained using TOF. Charge density decay kinetics, bimolecular recombination coefficient and charge carrier lifetime were obtained using TRCE to calculate bimolecular recombination coefficient and charge carrier lifetime.

4.2 Experimental

4.2.1 Materials

DT-PDPP2T-TT was purchased from 1-Material (OS0300, Lot# YY6278, Mw = 67 kg mol⁻¹ PDI = 2.4). [60]PCBM and [70]PCBM were purchased from Solaris.

4.2.2 Device fabrication

Photovoltaic devices were fabricated as follows: pre-patterned indium tin oxide (ITO) substrates with active area of 0.06 cm² were cleaned by sonicating in detergent, DI water, acetone and isopropanol, each for 15 minutes then blow dried with nitrogen and treated with UV-Ozone for twenty minutes. Poly-(ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT:PSS) (Clevios P, VP Al 4083) was spin coated on the substrates then subsequently annealed at 140 °C for ten minutes to achieve a dry thickness of around 30 nm. The active layer was prepared following the exact procedure as described in literature: DT-PDPP2T-TT and [60]PCBM (1:3, w/w) were dissolved in a solvent of CHCl₃ with 7.5 vol% o-DCB to obtain a concentration of 16 mg/mL. The solution was stirred at 45 °C for a minimum of 5 hours, until the polymer was completely dissolved. The photoactive layer was then deposited via spin coating the hot solution on PEDOT:PSS at around 2500 nm to achieve a dry thickness of around 260 nm. The spin speed was altered to achieve different active layer thicknesses. Active layer thickness was measured using Dektak stylus profilometer. The above processes were carried out under ambient condition except polymer solution preparation, which was prepared in an argon filled glovebox. An aluminium cathode was deposited by thermal evaporation at ~ 1 × 10⁻⁶ mbar to achieve thickness around 100 nm. The complete devices were encapsulated with cover glass using UV-curable epoxy in glovebox for characterizations under ambient conditions.
4.2.3 Characterisation

Current-voltage characterisations were carried out using Solar cell I-V curve testing system model IV21L, PV measurements. The solar simulator was calibrated using a Si reference cell before each measurement, and the irradiation intensity was monitored during measurements using a Si diode. Dark tapes were used to mask out unmeasured pixels on the substrate during current-voltage measurements. Film thickness was measured using Dektak stylus profilometer. For active layer thickness measurements, film samples were spin-coated on two identical cleaned glass substrates in parallel to the device using the same solution and spin-coating conditions and the thickness measurements were carried out on glass substrate samples. Each measurement was carried out over a scan length of 3000 μm with a stylus force of 0.1 mg. For each film three scans were carried out for an averaged thickness.

Bias and frequency dependent capacitance: Voltage and frequency dependent capacitance was measured using a Gamry Reference 600 potentiostat. AC oscillation amplitude of 5 mV was used. The voltage bias between -2 V and 2 V and frequency between 1 kHz and 500 kHz was applied.

Charge Extraction by Linearly Increasing Voltage: CELIV was carried out using a function generator (WF 1974, NF) and the extraction current was recorded using an oscilloscope over 50 Ω impedance.

Photogenerated Charge Extraction by Linearly Increasing Voltage: A pulsed laser (532nm, Spectra Physics Quanta Ray Lab 170) and a Quanta Ray MOPO was used to photoexcite the samples at 650 nm. The delay time between photoexcitation and voltage ramp application was controlled using a nanosecond switch (2.2 MΩ impedance, Asama Lab) and a delay generator (Stanford Research DG535). The extraction current was recorded using an oscilloscope (Tektronics, DPO4054), using the built-in 50 Ω impedance on oscilloscope.

Bulk Generation Time-of-Flight: The device was photo-excited using a laser pulse same as above while biased by applying 2 V reverse bias using a function generator. The extraction currents were recorded using an oscilloscope. The circuit impedance was controlled by applying resistors in parallel to the 1 MΩ input impedance of oscilloscope. The excitation density of the device was altered by using different neutral density filters, with the highest excitation density of 1000 μJ cm⁻².
Time-Resolved Charge Extraction: TRCE measurements were carried out as follows. A pulsed laser (532 nm, Spectra Physics Quanta Ray Lab 170) and a Quanta Ray MOPO was used to photoexcite the samples at 650 nm. The device was initially held at high impedance using a nanosecond switch (2.2 MΩ impedance, Asama Lab). After a controllable delay time using a digital delay generator (Stanford Research DG535), the switch was opened and the devices were at short circuit condition. The extracted current was measured using an oscilloscope as a function of time (input impedance 50 Ω). The dark response was subtracted to remove the switch noise.

4.3 Results

4.3.1 Device performance

To check the reproducibility of high $FF$ and large $V_{OC}$ reported by Li et al. using the commercially obtained polymer, an ITO/PEDOT:PSS/DT-PDPP2T-TT: [60]PCBM/Al device with active layer thickness of 267 ± 8 nm was fabricated. The thickness error was calculated by averaging 3 scans on different spots of a film sample prepared on a glass substrate. The averaged photovoltaic parameters are displayed in Table 4.1 alongside with the parameters for the most efficient (4 %) device in parenthesis. The device performance reported by Li et al using DT-PDPP2T-TT: [60]PCBM blend of the same blending ratio and similar thickness at 260 nm.\textsuperscript{[2]} The current-voltage curve of the fabricated device with 4 % efficiency is shown in Figure 4.1. An open circuit voltage $V_{OC}$ of 0.71 V was obtained, which is in agreement with the publication by Li et al. (see Table 4.1). A short circuit current $J_{SC}$ of 9.2 mA cm$^{-2}$ and a $FF$ of 0.62 were obtained for the most efficient device, leading to an overall efficiency of 4.0 %. The $FF$ reported by Li et al. is 0.67, which is slightly higher than the value measured here possibly due to the use of a LiF electron transport layer in their device architecture. Hence the first aim of this chapter, namely reproducing the high $FF$ reported using commercially sourced polymer batch, was achieved despite the difference in polymer molecular weight.

Table 4.1 Average performance parameters in fabricated DT-PDPP2T-TT: [60]PCBM devices with 267 ± 8 nm active layer, compared to that reported by Li et al.\textsuperscript{[2]} The measured parameters are averaged from a total of eight pixels from two devices. Values in brackets are from device with highest efficiency.
<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>$FF$</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured here</td>
<td>267</td>
<td>0.706 ± 0.004</td>
<td>8 ± 1 (9)</td>
<td>0.64 ± 0.03 (0.62)</td>
</tr>
<tr>
<td>Literature$^{[2]}$</td>
<td>260</td>
<td>0.68</td>
<td>12.9</td>
<td>0.67</td>
</tr>
</tbody>
</table>

Figure 4.1 Current-voltage characterization of the fabricated DT-PDPP2T-TT: [60]PCBM 1:3 device, measured under AM1.5 illumination and in the dark.

On the other hand, the $J_{SC}$ obtained here is lower than the value (12.9 mA cm$^{-2}$) in the literature with similar active layer thickness of 260 nm. The lower $J_{SC}$ is the main reason for the lower efficiency of 4% compared to the literature value of 5.8%. To understand the cause of lower $J_{SC}$, the absorption spectrum of the DT-PDPP2T-TT: PCBM film and the external quantum efficiency spectrum of the device were measured and compared to literature. Figure 4.2a shows the absorption spectrum of DT-PDPP2T-TT pristine film (reproduced from literature) and the absorption spectra of DT-PDPP2T-TT pristine film and the DT-PDPP2T-TT: [60]PCBM (1:3 w/w) film obtained here, all normalized to the
maximum absorption peak of the polymer. No blend film absorption spectrum was provided in the literature for comparison. The maximum absorption around 830 nm and the absorption peaks at 750 nm and 430 nm were consistent between the literature results and the spectrum reported here. Similar spectral shapes were observed in the pristine film absorption given in the literature and measured here, although the maximum absorption in the sample measured here is slightly redshifted compared to the literature, from 820 to 830 nm, leading to stronger absorption between 830 and 920 nm. Stronger absorption below 700 nm is also observed in the pristine film measured here. The strong absorption at wavelengths shorter than 550 nm observed in the DT-PDPP2T-TT: PCBM sample is attributed to the absorption by the PCBM acceptor. While a weak absorption tail at wavelengths longer than 900 nm is observed in the pristine films both in literature and in measured sample, it is not observed in the blend film. Possible origins of the low energy absorption include the presence of a carrier tail, possibly caused by low concentration oxygen/moisture doping or charge-transfer (CT) state absorption.
Figure 4.2 (a) Absorption spectrum of DT-PDPP2T-TT pristine and DT-PDPP2T-TT:PCBM (1:3) blend film prepared from purchased polymer, compared with pristine DT-PDPP2T-TT film reported in Reference [2]; (b) EQE spectrum of DT-PDPP2T-TT:PCBM device fabricated here compared with Reference.

The EQE spectra published in the literature and obtained for the devices fabricated here are compared in Figure 4.2b. The $J_{SC}$ values obtained by integrating the EQE spectra are 12.9 and 9.1 mA cm$^{-2}$ in the literature and the device fabricated here, respectively, both consistent with that obtained from current-voltage measurements. So the differences in
$J_{SC}$ can be attributed to the difference in shape and magnitude of the EQE spectra. The onset of EQE in literature data was extended further to the NIR. On the other hand, the maximum EQE values at peak absorption wavelength were similar between the literature data (40 % at 820 nm) and the one reported here (37 % at 830 nm). At shorter wavelength, however, larger EQE values were observed in literature data by up to 20 %. The literature data also showed an additional EQE peak at 600 nm, which was absent in the absorption spectra and in the EQE of the device reported here.

The larger values of EQE in literature data could arise from i) more efficient photon harvesting at shorter wavelengths due to optical cavity effects, ii) more efficient charge separation and/or iii) charge collection. The higher EQE at short wavelengths between 350-550 nm in literature also suggests stronger PCBM absorption in the device reported in literature. A device architecture of ITO/PEDOT:PSS/DT-PDPP2T-TT: PCBM/LiF/Al was used in literature, which was different from the architecture used in this chapter which didn’t use the LiF layer. As the LiF layer used in literature had a thickness of 1 nm, it is unlikely that this layer affects the optical field distribution in the active layer significantly. The appearance of the additional peak at 600 nm peak in the literature therefore cannot be explained. Considering the similar absorption spectra shown in Figure 4.2a, the larger EQE at shorter wavelength$^{[2]}$ is most likely due to more efficient charge separation. This could be the result of more segregated PCBM domains in literature device, evidenced by finer domain sizes and more fibrous features observed in atomic force microscopy images, see Figure 4.3. As the device fabricated here was prepared following exactly the same experimental method published in literature, the difference in morphology could be the result of the lower molecular weight (67 kg mol$^{-1}$) in the commercially sourced polymer. The shorter EQE onset wavelength in the device reported here is possibly caused by difference in active layer morphology between literature and fabricated device as well, which can be the result of different molecular weight of DT-PDPP2T-TT used.

Despite the difference in $J_{SC}$ and EQE spectra, high $FF$ and large $V_{OC}$ were successfully reproduced in the fabricated device using a commercially obtained polymer. Therefore, the fabricated device is used in the following bimolecular recombination studies.
Figure 4.3 Atomic force microscopy images compared between literature\(^2\) and device fabricated here. (a) and (c) are the height and phase images from literature, respectively, and (b) and (d) are those measured on the fabricated device, kindly carried out by Ms. Tian Zheng.

4.3.2 Dielectric constant in DT-PDPP2T-TT: PCBM blends

The geometric capacitance \(C_{geo}\) of the device was characterized using bias and frequency dependent impedance measurements to obtain the dielectric constant of the DT-PDPP2T-TT: PCBM (1:3) blend. Figure 4.4 shows the \(I/C^2\) values plotted as a function of applied bias, measured at frequencies between 500 Hz and 500 kHz. The \(C_{geo}\) values were calculated by extrapolating the \(I/C^2\) plot at large reverse bias to zero volts (indicated by dash line in figure), and the dielectric constant values were calculated using Equation 3.7. The calculated dielectric constant values were plotted as a function of measurement...
frequency, as shown in Figure 4.5b. A weak frequency dependence of $\varepsilon_r$ was observed, where $\varepsilon_r$ decreased from 7.5 at 500 Hz to 5.9 at 500 kHz. At low frequencies of 500 Hz and 1000 Hz, larger measurement noise in $1/C^2$ was observed compared to that measured at higher frequencies. The most likely reason for larger noise at low frequencies is that the magnitude of out of phase signal decreases at lower frequencies, which significantly increases the difficulty to accurately measure the phase shift. The results here and in Chapter 3 shows that the $C_{geo}$ values are bias and frequency dependent, where smaller capacitance is observed at larger reverse bias and higher frequency. The bias dependence is likely the result of current injection or charges that are trapped and therefore are not extracted at lower applied voltages, while the frequency dependence could be the result of disordered nature of polymers, time dependence of polarization processes (see Figure 1.4), or film thickness variation. A more detailed study on the voltage and frequency dependence of the capacitance is shown in Chapter 5.
The dielectric constant value obtained here is over twice the dielectric constant value of 3.5 obtained in P3HT:PCBM (Chapter 3), and is higher than any other previously reported dielectric constant values in polymer: PCBM blends. This finding is very significant for this thesis, as it provides the opportunity to determine the influence of using a high dielectric constant polymer in ternary polymer: PCBM blends (see Chapter 7). Therefore, great effort is spent in this thesis to check the measurements and sample preparation conditions for accurately determining the dielectric constant value (Chapter 7).
4 and 5) and to understand the origin of such high dielectric constant in a polymer: PCBM blend.

Figure 4.5 (a) Four dark CELIV transients measured at different tpulse and Umax values, and (b) dielectric constant values calculated from bias dependent impedance and CELIV, plotted as a function of frequency.
First, to examine whether this high dielectric constant value is reproducible between various techniques and samples, the capacitance measurement was carried out using an alternative technique and on other devices, by considering the following questions:

1) Is the bias dependent impedance measurement accurate for \(C_{\text{geo}}\) measurement?
2) Is the dielectric constant value thickness dependent?
3) Is the dielectric constant value influenced by stray capacitance?
4) Is the dielectric constant value reproducible if a different acceptor material is used?

To examine the accuracy of the \(C_{\text{geo}}\) value obtained using impedance measurement, the capacitance was also calculated from CELIV. Unlike the impedance measurement which is a steady-state measurement using small AC voltage modulation, CELIV is a time-resolved technique and measures the transient current response to an applied linearly increasing voltage. The \(C_{\text{geo}}\) values were calculated from CELIV transients carried out on the same device as above, measured at different \(t_{\text{pulse}}\) and \(U_{\text{max}}\) values using Equation 3.7 (Figure 4.5a). The dielectric constant was calculated using the obtained capacitance values, and were also plotted as a function of voltage bias frequency (1/\(t_{\text{pulse}}\)). The dielectric constant values obtained from CELIV were within 2\% error compared to that obtained from impedance measurements. Similar to bias dependent impedance measurement results, a frequency dependent dielectric constant was also observed. These experiments using principally different techniques therefore confirm the accuracy and suitability of the techniques for the measurements of \(C_{\text{geo}}\) and thus dielectric constant.

To examine whether the dielectric constant value is thickness dependent, two devices with active layer thickness of 200 ± 12 nm and 250 ± 13 nm were fabricated and the \(C_{\text{geo}}\) of these devices were characterized using bias dependent impedance measurements at 1 kHz. The obtained \(C_{\text{geo}}\) as well as calculated dielectric constant values are listed in Table 4.2, along with that from the 267 nm device shown above. The capacitance values are inversely proportional to thickness as is expected according to Equation 3.7, see Figure 4.6. The active layer thickness dependence of the measured \(C_{\text{geo}}\) confirms that the measured capacitance is indeed the geometric capacitance of the active layer, and therefore it can be used to calculate the dielectric constant. Due to the limited number of devices fabricated because of limited amount of material, no further study was carried out.
on this subject. However, due to the significance of such dielectric constant observed in organic polymer: PCBM system, it is necessary to validate the accuracy of the measured values, which requires the establishing of dielectric constant characterisation methodology. In Chapter 5 pristine DT-PDPP2T-TT devices were fabricated with much larger thickness variation (100 nm – 630 nm), and linear dependence of $C_{geo}$ on film thickness was observed, giving dielectric constant values within experimental error.

Table 4.2 List of $C_{geo}$ and dielectric constant values obtained from DT-PDPP2T-TT: [60]PCBM 1:3 devices with three different active layer thickness.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>$C_{geo}$ (nF)</th>
<th>Dielectric constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>200 ± 12</td>
<td>2.0 ± 0.1</td>
<td>7.5 ± 0.3</td>
</tr>
<tr>
<td>250 ± 13</td>
<td>1.5 ± 0.3</td>
<td>7.2 ± 0.4</td>
</tr>
<tr>
<td>267 ± 8</td>
<td>1.4 ± 0.1</td>
<td>6.8 ± 0.1</td>
</tr>
</tbody>
</table>

Figure 4.6 Geometric capacitance values measured in three devices plotted as a function of active layer thickness.

To check the influence of stray capacitance (possible influence of neighbouring pixels on the same substrate), two devices were fabricated with only one aluminium strip.
evaporated leading to only one pixel on the substrate. The geometric capacitance were characterized using bias dependent impedance measurement at 1 kHz, and the obtained capacitance as well as calculated dielectric constant values are shown in Table 4.3. High dielectric constant values of 8.0 and 7.0 were obtained in these singe-pixel devices, which is consistent with dielectric constant value obtained from multi-pixel devices. As a result, no influence of stray capacitance on dielectric constant is observed.

Table 4.3 Geometric capacitance as well as calculated dielectric constant values of two single pixel DT-PDPP2T-TT: [60]PCBM 1:3 devices.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>Capacitance (nF)</th>
<th>Dielectric constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>295 ± 16</td>
<td>1.5 ± 0.1</td>
<td>8.0 ± 0.4</td>
</tr>
<tr>
<td>300 ± 11</td>
<td>1.2 ± 0.1</td>
<td>7.0 ± 0.8</td>
</tr>
</tbody>
</table>

To examine whether the choice of different fullerene acceptors have any effect on dielectric constant values in blend devices, a device was fabricated using DT-PDPP2T-TT: [70]PCBM 1:3 blend with active layer thickness of 107 ± 15 nm, following the exact same procedure as the devices using [60]PCBM. $C_{geo}$ of 3.4 ± 0.4 nF was obtained using bias dependent impedance at 1 kHz, giving dielectric constant value of 6.9 ± 0.9. This is in agreement with dielectric constant values obtained in DT-PDPP2T-TT: [60]PCBM devices assuming same dielectric constant in [70]PCBM and [60]PCBM. This result demonstrated the reproducibility of high dielectric constant value using different fullerene derivative acceptors.

From above results, it is concluded that a dielectric constant value of 7 has been obtained in this DT-PDPP2T-TT: PCBM 1:3 blend with accuracy and reproducibility. The high dielectric constant of 7 raises some interesting questions unanswered in the literature:

1) Does the high dielectric constant correlate with a high dielectric constant of pristine DT-PDPP2T-TT polymer, or is it only observed in blends?

2) What is the physical origin of such a high dielectric constant? Is the high dielectric constant reproducible between polymer batches with various molecular weights?
3) How does the high dielectric constant affect bimolecular recombination kinetics in DT-PDPP2T-TT: PCBM blend?

To answer these questions, Chapter 5 details the characterization techniques to determine the dielectric constant values in pristine DT-PDPP2T-TT devices with the aim of investigating the possible origins of the observed high dielectric constant. The following sections of this chapter will focus on establishing the mobility and bimolecular recombination kinetics in the DT-PDPP2T-TT: [60]PCBM blend. Chapter 6 compares the bimolecular recombination kinetics shown in this chapter with that of three low dielectric constant blends, namely P3HT: PCBM, PTB7: PCBM and PCPDTBT: PCBM to study the effect of dielectric constant in bimolecular recombination in PSC systems with the aim of uncovering any possible contributions to the recombination kinetics of the strength of dielectric screening.

4.3.3 Charge carrier mobility and Langevin recombination coefficient

Photo-CELIV measurements were carried out on the 4 % device to determine the charge carrier mobility. Figure 4.7 shows photo-CELIV transients measured at (a) various delay times at laser intensity of 10 μJ cm$^{-2}$ and (b) at various laser intensities and at a fixed 5 μs delay time. The $U_{max}$ was 1 V and the $t_{pulse}$ was 10 μs.
Figure 4.7 Photo-CELIV transients obtained at (a) various delay times and (b) various excitation densities using tpulse of 10 µs and Umax of 1 V.

Charge carrier mobility in some disordered semiconducting polymers has been reported to depend on delay time, charge density and applied field.\textsuperscript{[4]} Based on the results in
Chapter 3, photo-CELIV transients were obtained at weak electric field (similar to working conditions, \( F_{\text{max}} < 7.5 \text{ kV cm}^{-1} \)), short delay time \( t_{\text{del}} \) (< 1 ms) and at small extracted current density compared to the geometric capacitance \( Aj \lesssim j(0) \)\(^4\) to calculate mobility. A total number of 15 transients were recorded with varying \( U_{\text{max}} \) and \( t_{\text{del}} \). An average mobility value of \((1.8 \pm 0.6) \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\) was obtained, which is among the highest mobility value obtained using photo-CELIV technique.\(^{1b, 4a, 5}\) The mobility obtained using photo-CELIV here is lower than the mobility reported by Li et al. \((0.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})\)\(^2\) which was carried out on pristine polymer FET. The smaller value is possibly due to the difference in the measured sample (blend vs. pristine film in the literature) and the measurement technique (Photo-CELIV vs. FET), as has been reported in the literature.\(^6\) Using the obtained dielectric constant and mobility, the Langevin recombination coefficient \( \beta_L = 4.7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}\) was calculated using Equation 3.4, as listed in Table 4.4.

<table>
<thead>
<tr>
<th>Mobility (cm(^2) V(^{-1}) s(^{-1}))</th>
<th>Dielectric constant</th>
<th>( \beta_L ) (cm(^3) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1.8 \times 10^{-3})</td>
<td>7.0</td>
<td>(4.7 \times 10^{-10})</td>
</tr>
</tbody>
</table>

No strong dependence of the time to reach maximum extraction current \( t_{\text{max}} \) on delay time or excitation density was observed in the measured DT-PDPP2T-TT: PCBM device (Figure 4.7). This is in contrast to the P3HT: PCBM device shown in Chapter 3, which showed a decreased \( t_{\text{max}} \) at longer delay times. The decreased \( t_{\text{max}} \) with increasing delay time is typically observed in systems with significantly reduced bimolecular recombination\(^7\) due to the longer charge carrier lifetime than charge extraction time, leading to the accumulation of charge density much larger than the charge stored on the contacts. \( t_{\text{max}} \) independent of delay time suggests that charge carrier lifetime is not longer than the charge extraction time in DT-PDPP2T-TT: PCBM device, which is typical of systems with Langevin-type diffusion controlled recombination. This raises the possibility that the large active layer thickness achieved in DT-PD2PT-TT: PCBM devices is not due to non-Langevin recombination kinetics, but because of enhanced dielectric screening. Thus a challenge rises for the remaining of this chapter, which is to
evaluate the influence of enhanced dielectric screening on bimolecular recombination kinetics independent of charge mobility.

4.3.4 Charge density decay, bimolecular recombination and charge carrier lifetime

In order to obtain bimolecular recombination coefficient $\beta$ and carrier lifetime $\tau$, time-resolved charge extraction (TRCE) was carried out on the 267 nm device following the methodology established in Chapter 3. Charge density decay was obtained from TRCE measurements under different excitation densities as shown in Figure 4.8a. The bimolecular recombination coefficient $\beta$ was calculated from charge density decay at 100 $\mu$J cm$^{-2}$ using Equation 3.9 and was plotted as a function of time, shown in Figure 4.8b. The $\beta$ was constant at delay times below 1 $\mu$s and decreased at longer timescales. The time-independent $\beta$ at early timescales is attributed to recombination during charge extraction in TRCE measurements,[8] which is also confirmed by the charge carrier lifetime (see below, Figure 4.9) which is on the same timescale as the extraction time observed in the extraction transients (see discussion in Section 4.4). The bimolecular recombination coefficient $\beta$ of DT-PDPP2T-TT: PCBM was $1.95 \times 10^{-11}$ cm$^3$ s$^{-1}$ at delay times shorter than 1 $\mu$s.
Figure 4.8 (a) Charge density decay in DT-PDPP2T-TT: PCBM device measured under different excitation densities; (b) bimolecular recombination coefficient $\beta$ calculated from charge density decay at 100 $\mu$J cm$^{-2}$ plotted as a function of time.

The charge carrier lifetime was calculated using Equation 3.2 and plotted as a function of charge density, as shown in Figure 4.9. At saturated charge density, charge carrier lifetime of 3.4 $\mu$s was obtained. Comparing to charge lifetime in the 306 nm P3HT: PCBM device
at the same charge density measured in Chapter 3, P3HT: PCBM gave longer lifetime of 12 μs. The longer lifetime in P3HT: PCBM device suggests comparatively more reduced recombination in P3HT: PCBM. The carrier lifetime increased by almost two orders of magnitude (220 μs) as the charge density decreased from $1 \times 10^{16}$ cm$^{-3}$ to $4 \times 10^{15}$ cm$^{-3}$. Such strong dependence of lifetime on charge density is the result of charge density dependent $\beta$ as mentioned above. The bimolecular recombination mechanism will be discussed in detail in Section 4.4.1.

![Figure 4.9](image)

Figure 4.9 Charge carrier lifetime calculated from charge density decay at 100 μJ cm$^{-2}$, plotted as a function of charge density.

Compared with P3HT: PCBM devices shown in Chapter 3, similar biphasic kinetics was observed in charge density decay in the DT-PDPP2T-TT: PCBM system as shown in Figure 4.8a. The $\beta$ value at saturated charge density in DT-PDPP2T-TT: PCBM was approximately an order of magnitude higher than that observed in P3HT: PCBM device ($1.07 \times 10^{-12}$ cm$^3$ s$^{-1}$), which is an indication of faster bimolecular recombination in the DT-PDPP2T-TT: PCBM device. Comparing at the same charge density of $1.2 \times 10^{16}$ cm$^{-3}$, the lifetime in P3HT: PCBM device is over two orders of magnitude longer than that in DT-PDPP2T-TT: PCBM.
4.3.5 TOF and recombination reduction factor

As demonstrated in Chapter 3, TOF is very useful in evaluating the bimolecular recombination behaviour in a PSC. It was shown that in case of strongly reduced, non-Langevin recombination, the extraction time \( t_e \) is longer than transit time \( t_v \) due to slower bimolecular recombination than charge extraction in the reservoir. This results in i) the presence of a plateau in the TOF transient and ii) strong excitation density dependence of half decay time \( t_{1/2} \). Due to the slow recombination and thus long carrier lifetime, the extracted charge \( Q_e \) at high excitation density can exceed the capacitive charge \( C U \) by over an order of magnitude. If DT-PDPP2T-TT: PCBM has strongly reduced recombination as suggested by Li et al.,\cite{9} these characteristics are expected in TOF measurements.

Bulk-generation time-of-flight (TOF) was carried out on the 4 % DT-PDPP2T-TT: PCBM device using external resistors of 1 kΩ and 10 kΩ. The TOF transients obtained at different excitation densities using 1 kΩ and 10 kΩ resistors are shown in Figure 4.10. TOF transients obtained at 50 Ω are not shown because using a 50 Ω resistor the RC time constant is shorter than transit time \( t_v \), making it invalid for integral mode TOF, as has been explained in Chapter 1. At high laser intensity, causing saturation of the extraction current, the decay time was approximately 10 μs using the 1 kΩ resistor and 80 μs using the 10 kΩ resistor. The extraction transients were limited by the RC time constant, and the longer decay time observed using large resistors is due to the larger RC constant of the circuit. No distinct feature of \( t_e \) was observed in the TOF transients. The ratio between extracted charge and capacitive charge \( Q_e/C U_0 \) and the time for the transient to decay to half its maximum magnitude \( t_{1/2} \), plotted as a function of excitation density, are shown in Figure 4.11. The maximum \( Q_e/C U_0 \) reached 2.7 using the 1 kΩ resistor and 2.2 using the 10 kΩ resistor. The extraction time \( t_e \) was also found to depend on the resistance, where \( t_e = 1.04 \mu s \) at 1 kΩ and \( t_e = 5.94 \mu s \) at 10 kΩ was observed. The reduction factor \( \xi = \beta/\beta_L \) was calculated using Equation 3.3, giving 0.07 at 1 kΩ and 0.015 at 10 kΩ, see Table 4.5. Bimolecular recombination coefficient \( \beta \) values calculated from the reduction factor are also listed in Table 4.5. Reduction factor \( \xi \ll 1 \) was calculated for the measured device, which suggests reduced bimolecular recombination compared to Langevin type recombination. However, typical non-Langevin characteristics were absent in the photo-CELIV and TOF transients. These results are contradicting to each other and will be further discussed in Section 4.4.
Figure 4.10 Bulk-generation TOF measured using loading resistor of 1 kΩ (a) and 10 kΩ (b). The arrows in figure correspond to increasing excitation density.
Figure 4.11 The $Q_e/CU$ ratio and $t_{1/2}$ values plotted as a function of excitation density obtained in DT-PDPP2T-TT: PCBM device, using both 1 kΩ and 10 kΩ resistors.

Table 4.5 List of extraction time $t_e$, $Q_e/CU$ ratio and Langevin reduction factor obtained using loading resistors of 1 kΩ and 10 kΩ.

<table>
<thead>
<tr>
<th>$R$ (Ω)</th>
<th>$t_e$ (s)</th>
<th>$Q_e/CU_0$</th>
<th>$\xi$</th>
<th>$\beta$ (cm$^3$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>$1.04 \times 10^{-6}$</td>
<td>2.7</td>
<td>0.07</td>
<td>$3.3 \times 10^{-11}$</td>
</tr>
<tr>
<td>10000</td>
<td>$5.94 \times 10^{-6}$</td>
<td>2.2</td>
<td>0.015</td>
<td>$7.1 \times 10^{-12}$</td>
</tr>
</tbody>
</table>
4.4 Discussion

As shown above, a reduction factor of 0.07 was obtained in DT-PDPP2T-TT: PCBM device using 1 kΩ resistor. The TOF transients at excitation conditions leading to saturation lack the distinctive $t_e$ feature in DT-PDPP2T-TT: PCBM device, and the $Q_e/CU_0$ ratio was 2.7 at 1 kΩ. As seen in Figure 4.7, no delay time dependence in $t_{max}$ was observed in the photo-CELIV transients, and the integrated extracted current even at maximum excitation was equal to the capacitive charge. Despite a reduction factor smaller than 0.1, the transient features in DT-PDPP2T-TT: PCBM device are strong indications of Langevin type recombination in DT-PDPP2T-TT: PCBM.

These are in stark contrast to P3HT: PCBM, the recombination of which was demonstrated in Chapter 3 showing clear features of a non-Langevin system. Figure 4.12 compares the photo-CELIV transients in DT-PDPP2T-TT: PCBM and P3HT: PCBM, both excited at 100 μJ cm$^{-2}$ at varying delay times. Several striking differences can be observed: first, in DT-PDPP2T-TT: PCBM, even at the shortest delay time $Δj$ is similar to $j(0)$, indicating extracted charge and capacitive charge being similar in magnitude. In P3HT: PCBM, on the other hand, $Δj$ is significantly larger than $j(0)$, which is a clear indication of recombination slower than extraction, as explained in Chapter 3. Also, in DT-PDPP2T-TT: PCBM $t_{max}$ is roughly consistent at increasing delay times, whereas in P3HT: PCBM a clear decrease in $t_{max}$ is present when delay time increase. As has been explained in Chapter 3, the delay time dependent $t_{max}$ is also a strong indication of non-Langevin behaviour, whereas the lack of such feature typically suggests Langevin type recombination.
Figure 4.12 Comparison between photo-CELIV transients at different delay times in DT-PDPP2T-TT: PCBM (a) and P3HT: PCBM (b), both excited at 100 μJ cm⁻².

Figure 4.13 compares the saturated TOF transients obtained in DT-PDPP2T-TT: PCBM and P3HT: PCBM, both measured using a 1 kΩ resistor. The TOF transient obtained in P3HT: PCBM is notably longer in time compared to DT-PDPP2T-TT: PCBM. Also, the transient obtained from P3HT: PCBM showed an observable feature of extraction time $t_e$, which is clearly absent in DT-PDPP2T-TT: PCBM transient. The observed difference in
TOF as well as photo-CELIV transients clearly shows that, unlike P3HT: PCBM, DT-PDPP2T-TT: PCBM has diffusion dominated, Langevin type recombination.

Figure 4.13 Saturated TOF transients measured at 1 kΩ, obtained from DT-PDPP2T-TT: PCBM and P3HT: PCBM.

Despite being a Langevin system, high FF was achieved in DT-PDPP2T-TT: PCBM device with active layer as thick as 267 nm. This suggests that reduced recombination is present, but is not reduced by being a non-Langevin system. Considering the high mobility obtained in the system, the reduced recombination can only be contributed by the strong dielectric screening in DT-PDPP2T-TT: PCBM, evidenced by the high dielectric constant. As will be shown in Chapter 6, despite being diffusion-dominated, the bimolecular recombination was reduced as a result of strong dielectric screening within the device. The Coulomb capture radius is smaller in a system with strong dielectric screening, as a result the charge carriers are screened within the respective domains leading to reduced recombination at donor/acceptor interfaces. This hypothesis will be
examined and by comparing the recombination kinetics in DT-PDPP2T-TT: PCBM with three low dielectric constant systems, namely P3HT: PCBM, PCPDTBT: PCBM and PTB7: PCBM in Chapter 6.

### 4.5 Conclusion

To examine whether DT-PDPP2T-TT: PCBM has non-Langevin recombination, PSC devices with 267 nm thick active layer were fabricated and the performance, charge mobility, dielectric constant and recombination kinetics were characterised following the methodology established in Chapter 3. High $FF$ of 0.6 with active layer thickness of 267 nm was reproduced in ITO/ PEDOT:PSS/ DT-PDPP2T-TT: [60]PCBM (1:3 w/w)/ Al solar cell using commercially sourced DT-PDPP2T-TT. An exceptionally high dielectric constant value of 7 was observed, which was consistently reproduced using two different capacitance characterization methods, in multiple devices with different active layer thicknesses, different substrate design and using [70]PCBM instead of [60]PCBM. High charge carrier mobility of $1.8 \times 10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$ was measured using photo-CELIV, which is among highest mobility reported using photo-CELIV and is consistent with the high FET mobility reported.

Contrary to the initial expectation, bimolecular recombination in the DT-PDPP2T-TT: [60]PCBM device showed clear features of Langevin type recombination, evidenced by the delay time independence of $t_{\text{max}}$ in the photo-CELIV transients and the maximum extracted current being equal to the capacitive charge. TOF transients obtained in DT-PDPP2T-TT: PCBM also showed clear features of Langevin type recombination, where no distinctive $t_e$ was observed. Therefore, the high FF achieved in the thick DT-PDPP2T-TT: PCBM cannot be due to non-Langevin recombination. Considering the exceptionally high dielectric constant measured, it is likely that the high FF was achieved due to bimolecular recombination reduced by strong dielectric screening.

Two particularly significant findings were made in this chapter, namely 1) the high dielectric constant of 7 in DT-PDPP2T-TT: PCBM blend and 2) high FF achieved with thick active layer despite the absence of significantly reduced recombination. These findings raise some new questions:
1) Does the high dielectric constant correlate with a high dielectric constant of pristine DT-PDPP2T-TT polymer, or is it only observed in blends?

2) What is the physical origin of such a high dielectric constant? Is the high dielectric constant reproducible between polymer batches with various molecular weights?

3) How does the high dielectric constant affect bimolecular recombination kinetics in DT-PDPP2T-TT: PCBM blend?

In the following chapters, Chapter 5 will focus on answering question 1 and 2, focusing on characterization of pristine DT-PDPP2T-TT dielectric constant values. Chapter 6 will answer question 3, comparing recombination kinetics established here with three low dielectric constant systems, namely P3HT: PCBM, PTB7: PCBM and PCPDTBT: PCBM.

4.6 Reference


Chapter 5 Obtaining Dielectric Constant from a Thin Film Device: A Comparative Study of Characterization Techniques and Device Preparation Conditions
5.1 Introduction

5.1.1 Background

As shown in Chapter 4, an exceptionally high dielectric constant was observed in DT-PDPP2T-TT: PCBM. This discovery of high dielectric constant immediately raised a number of new questions:

1) Is the high dielectric constant originated from high dielectric constant in the pristine DT-PDPP2T-TT, or is it only observed in the blend?

2) How to accurately characterise dielectric constant in a thin film polymer device?

3) What is the origin of the high dielectric constant observed? Is it consistent between different polymer batches, or does it vary from batch to batch?

To answer these questions, this chapter focuses on the characterisation of dielectric constant in semiconducting polymer devices. As introduced in Chapter 1, there are a number of challenges in determining the geometric capacitance from a thin film polymer device. First the thickness variation will lead to a depressed semicircle shape in the impedance spectrum, corresponding to a distributed capacitance element. Due to the thickness variation, the calculated capacitance of the device is frequency dependent. Second, the presence of interfaces between semiconducting polymer and electrode and the presence of additional charge blocking layers will introduce additional capacitances to the overall capacitance of the device. This can be a problem when the electrode conductivity is low or if impurities are present at the polymer: electrode interface. Third, due to the use of highly conductive PEDOT: PSS stray capacitance from outside of the active area defined by the overlay of ITO and aluminium electrodes may contribute to the measured capacitance of the device. Other influences, such as pin-hole in the device, will lead to injection of carriers into the device, which may influence the measured capacitance of the device. The disordered nature of polymers will lead to a distribution of time constant in the dielectric response, also resulting in a frequency dependent capacitive response. The presence of dark carriers in the polymer will give rise to a chemical capacitance which can be difficult to differentiate from the geometric capacitance. Also, the capacitance of a diode is sensitive to the film morphology, and changing morphology
between different samples can lead to variation between obtained dielectric constant values.

To characterise geometric capacitance at low frequency (< 1 MHz) in a thin film polymer device, impedance spectroscopy, bias dependent impedance measurement and CELIV can be used. These techniques cover both the frequency domain and the time domain, thus can provide capacitive information of different aspects. The impedance techniques measure at steady state conditions. It provides the complex-valued impedance at a known frequency and bias. CELIV, on the other hand, is a transient technique which allows the separation of geometrical capacitive response from chemical capacitive response. In order to establish the preferred method for dielectric constant characterisation, all these techniques will be used in this chapter for a detailed comparison.

5.1.2 Aim of this chapter

As described above, there are a number of consideration regarding sample preparation, device fabrication and characterization when measuring dielectric constant values of semiconducting polymers:

1) The polymer film morphology should be consistent across different devices when comparing dielectric constant values, which requires careful control over sample preparation conditions and film thicknesses between different devices;

2) The polymer film thickness variation should be reasonably small to reduce frequency dependence in capacitance;

3) The chemical capacitance should be separated from geometric capacitance, and the contribution of photo-carriers and dark chemical capacitance sources should be eliminated when characterizing geometric capacitance;

4) The device architecture should be consistent when comparing dielectric constant values calculated from different devices;

5) The device should be free of pin-holes with high conductivity electrodes and blocking layers;
6) Stray capacitance should be avoided.

In order to elucidate the origin of high dielectric constant observed in DT-PDPP2T-TT: PCBM blend devices (Chapter 4), this chapter aims at characterizing dielectric constant value in pristine DT-PDPP2T-TT thin film devices. Pristine DT-PDPP2T-TT devices are fabricated and the dielectric constant values are characterized using the techniques outlined above. The experiments in this chapter are aimed at answering the following questions:

1) Is the dielectric constant value reproducible in different polymer batches?

2) What method is most appropriate to measure the geometric capacitance values in pristine DT-PDPP2T-TT thin-film devices? What are the limitations and benefits of each technique and how do the dielectric constant obtained from these methods compare?

3) How will the measured dielectric constant be affected by film thickness, air and light exposure and heating treatment?

4) What are the possible origins of batch-to-batch variations in the dielectric constant of pristine DT-PDPP2T-TT?

In order to answer above questions, this chapter is structured as follows:

1) Pristine DT-PDPP2T-TT devices are fabricated in an inert atmosphere and characterized using impedance spectroscopy and CELIV techniques in Section 5.3.4. The obtained results are compared and the frequency dependence of dielectric constant is examined, and a general practice for geometric capacitance characterization in thin-film polymer devices is proposed;

2) The dielectric constant obtained from pristine polymer devices fabricated in inert atmosphere will be compared to that of fabricated in ambient conditions and with or without thermal treatment to check possible effect of morphology and material, device degradation in Section 5.3.5;

3) Polymer thickness and device area dependence of the measured dielectric constant values are examined in Section 5.3.2;
4) Batch-to-batch variation in pristine DT-PDPP2T-TT dielectric constant will be examined in Section 5.3.1.

5.2 Experimental

DT-PDPP2T-TT (OS0300, batch information see Table 5.1) was purchased from 1-Material. Chloroform (analytical grade, 99.8 %) was purchased from Chem-Supply, o-DCB (anhydrous, 99 %) from Sigma-Aldrich.

Table 5.1 List of pristine DT-PDPP2T-TT batches used in this chapter. Data obtained from manufacturer.

<table>
<thead>
<tr>
<th>ID</th>
<th>LOT#</th>
<th>Mw (kg mol⁻¹)</th>
<th>PDI</th>
<th>Trace Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>P61</td>
<td>YY6278</td>
<td>61</td>
<td>2.4</td>
<td>99.99+ %</td>
</tr>
<tr>
<td>P80</td>
<td>YY9052DB</td>
<td>80</td>
<td>2.5</td>
<td>99.99+ %</td>
</tr>
<tr>
<td>P33</td>
<td>YY8020CH</td>
<td>33</td>
<td>2.4</td>
<td>99.99+ %</td>
</tr>
<tr>
<td>P78</td>
<td>SX7126DB</td>
<td>78</td>
<td>2.6</td>
<td>99.99+ %</td>
</tr>
<tr>
<td>P45</td>
<td>SX7126CB</td>
<td>45</td>
<td>2.5</td>
<td>99.99+ %</td>
</tr>
</tbody>
</table>

Thin-film polymer devices were fabricated with the same architecture as polymer: PCBM solar cells using the same substrate design. Pre-patterned indium tin oxide (ITO) substrates with active area of 0.06 cm² were cleaned by sonicating in detergent, DI water, acetone and isopropanol, each for 15 minutes then blow dried with nitrogen and treated with UV-Ozone for twenty minutes. Poly-(ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT:PSS) (Clevios P, VP Al 4083) was spin coated on the substrates then subsequently annealed at 140 °C for ten minutes to achieve a dry thickness of around 30 nm. The pristine polymer films were drop-casted from 45 °C polymer solution (5 mg/mL in chloroform with 7.5 vol% o-DCB) in a glovebox, where 60 mL of solution was dropped
on the substrate to cover the whole substrate area and left untouched until completely dry. The air-exposed devices were prepared in a fume-hood using the same procedure.

The polymer film thickness was characterized using a Dektak150 stylus profilometer. The film thickness was not measured on the actual device but on a parallel film prepared under identical conditions as the device on a clean glass substrate. There were two purposes for doing so: 1) the film thickness could be checked during device fabrication to ensure the device active layer was at desired film thickness; 2) the devices were encapsulated immediately after fabrication to avoid ambient exposure, and measuring active layer thickness on the actual device cannot be done without breaking the device apart. Aluminium electrode was deposited by thermal evaporation at ~$1 \times 10^{-6}$ mbar to achieve thickness around 100 nm. The complete devices were encapsulated with cover glass using UV-curable epoxy (Ossila) in glovebox. One drop of epoxy was added between the aluminium contact and a thin cavity glass slide. The epoxy was then cured using a UV light torch for 40 s and left in glovebox until the epoxy had completely dried. The effect of epoxy and UV light exposure on the measured dielectric constant values of thin-film polymer devices was examined by measuring the capacitance of devices before and after epoxy encapsulation and UV exposure. As the data shows in Appendix, no difference in device capacitance (hence dielectric constant) was observed with up to 2 minutes of UV light exposure.

Bias sweep impedance measurement was carried out using a Zahner IM6 electrochemical workstation or a Gamry Reference 600 potentiostat. Both potentiostat were tested before the measurements using reference dummy cells provided by the manufacturer. AC oscillation amplitude of 5 mV was used in all measurements. Frequency sweep impedance measurement was carried out using the same potentiostat, measured over a frequency range of 0.01 Hz – 1 MHz. The encapsulated devices were measured in air, while open devices were measured in an Argon purged box.

Charge extraction by linearly increasing voltage (CELIV) was carried out using a function generator (WF 1974, NF). The device was measured in a dark room and covered with dark cloth to eliminate photo-carrier generation. The extraction transient was recorded using an oscilloscope (Tektronics, DPO 4054) over the built-in 50 Ω impedance.
Atomic force microscopy was carried out by Miss Tian Zheng on the DT-PDPP2T-TT:PCBM blend samples.

5.3 Results

5.3.1 Comparing two potentiostat and examining measurement limits

As mentioned in Section 5.2, a Gamry Reference 600 potentiostat and a Zahner IM6 electrochemical workstation were both used to characterize the device capacitance. In this section, the equipment accuracy and measurement limits of the two potentiostat are first compared using a home-built RC circuit. The RC circuit used in this section consists of ten 10 MΩ resistors connected in series (100 MΩ), connected in parallel with a 100 pF capacitor, which represents an upper limit of instrument requirements in terms of resistance and capacitance values of the studied thin-film capacitor devices.

The impedance spectra measured using Gamry and Zahner potentiostat are shown in Figure 5.1. The impedance spectra were measured at 0 V bias over the frequency range of 0.1 Hz to 1 MHz using both potentiostat. The impedance spectra obtained from both potentiostat showed semicircle shape, although the data obtained from Zahner has more noise between 10 Hz and 100 Hz. Both impedance spectra were fitted using the equivalent circuit shown in Figure 5.6 inset, and the fitted resistance and capacitance values are listed in Table 5.2. The dash line in Figure 5.6 is the fitting result of the Gamry dataset with $R = 100.3 \ \text{MΩ}$ and $C = 101.5 \ \text{pF}$. For the Zahner dataset, a larger capacitance value of 126.4 pF was obtained. This is due to the observed noise in Zahner dataset, which was most likely caused by interference of the 50 Hz AC power.
Figure 5.1 Impedance spectra of a homemade parallel RC circuit with a 100 MΩ resistor and a 100 pF capacitor, characterized at 0 V using Gamry and Zahner potentiostat. The dash lines show the corresponding equivalent circuit fit, the used equivalent circuit model and the fitted resistance and capacitance value from Gamry spectrum are shown in inset.

<table>
<thead>
<tr>
<th>$R$ (MΩ)</th>
<th>$C$ (pF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>100</td>
</tr>
<tr>
<td>Gamry</td>
<td>100.3</td>
</tr>
<tr>
<td>Zahner</td>
<td>99.9</td>
</tr>
</tbody>
</table>

The circuit was also measured at fixed frequencies under changing bias to obtain the parallel capacitance. The capacitance should be bias independent and remain constant.
within the equipment error. The obtained average capacitance values at each measurement frequency are listed in Table 5.3. No frequency dependence was observed in the average capacitance values obtained using Gamry potentiostat. The capacitance variation was within 0.3 % in all measured frequencies. When measuring using the Zahner potentiostat, capacitance values notably larger than the reference values were observed. At 200 Hz, the average capacitance was 50 % higher than the reference value, with over 100 % error. At higher frequencies, both deviation of average capacitance from reference and error decreased, however at the highest measured frequency of 10 kHz, the average capacitance was still 25 % higher than the reference value.

Table 5.3 Parallel capacitance values obtained at a series of frequencies from bias dependent impedance measurements, measured using both Gamry and Zahner potentiostat.

<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
<th>C_Gamry (pF)</th>
<th>C_Zahner (pF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>101.6±0.1</td>
<td>151±190</td>
</tr>
<tr>
<td>500</td>
<td>101.50±0.02</td>
<td>136±49</td>
</tr>
<tr>
<td>1k</td>
<td>101.3±0.2</td>
<td>128±14</td>
</tr>
<tr>
<td>2k</td>
<td>101.5±0.3</td>
<td>128±7</td>
</tr>
<tr>
<td>5k</td>
<td>101.6±0.2</td>
<td>127±1</td>
</tr>
<tr>
<td>10k</td>
<td>101.5±0.1</td>
<td>126±2</td>
</tr>
</tbody>
</table>

The higher capacitance measured using Zahner potentiostat as shown in Table 5.3 suggests that 100 pF is below the measurement limit of the equipment. To test measurement limit of the Zahner potentiostat, two capacitors with marked capacitance of 390 pF and a 530 pF characterized using Zahner potentiostat. The obtained capacitance values were shown in Table 5.4. When measuring using a 390 pF capacitance, the measurement error significantly decreases to below 2 %, and the measurement error further decreased to 0.5 % when using a 530 pF capacitor. The small error obtained at these capacitance values demonstrate that the capacitance measurement limit is below
390 pF, and characterisations of parallel capacitance values above 390 pF is reliable using Zahner potentiostat.

Table 5.4 Parallel capacitance values obtained at 1 kHz and 10 kHz from bias dependent impedance measurements, measured using Zahner potentiostat.

<table>
<thead>
<tr>
<th>Reference capacitance value (pF)</th>
<th>Frequency</th>
<th>$C_{\text{Zahner}}$ (pF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>390</td>
<td>1 kHz</td>
<td>383 ± 1</td>
</tr>
<tr>
<td></td>
<td>10 kHz</td>
<td>385 ± 2</td>
</tr>
<tr>
<td>530</td>
<td>1 kHz</td>
<td>530 ± 1</td>
</tr>
<tr>
<td></td>
<td>10 kHz</td>
<td>528 ± 3</td>
</tr>
</tbody>
</table>

The above results show that for devices with capacitance around 100 pF and resistance around 100 MΩ, the capacitance values could be accurately obtained using the Gamry potentiostat. Assuming a dielectric constant of 3 and device area of 0.06 cm², this corresponds to film thickness around 1.59 μm. In polymers with higher dielectric constant, this limit on thickness value may further increase. Therefore it is concluded that the capacitance in devices with an area of 0.06 cm² can be accurately measured using the Gamry potentiostat, given that the polymer films used in this study all have thicknesses below 1.59 μm. The impedance spectrum obtained using the Zahner potentiostat gave a similar spectrum shape as that of the Gamry, but the fitted capacitance values were overestimated by approximately 25%. The bias dependent measurements using Zahner gave both larger capacitance values and larger error when the measured capacitance is below 390 pF, while an accurate measurement of parallel capacitance with measurement error below 2% could be obtained for higher capacitance values. As the smallest capacitance value measured in this chapter is 510 pF, both potentiostat can be used to provide accurate capacitance measurements.

5.3.2 Measuring the Film Thickness

5.3.2.1 Effect of substrate

As explained in Section 5.2, the polymer film thickness was determined by preparing a film in parallel with device fabrication on a cleaned glass substrate and by measuring the thickness of this film using a stylus profilometer. The procedure was implemented to
avoid the exposure of the sample to ambient / air before sealing the device in the glove box. Because of the presence of the epoxy sealant in the final device, the film thickness used in the actual devices could not be measured after completing all the electrical characterisation by for example, device disassembly and measurement. The implemented procedure using films prepared in parallel could have some drawbacks. Firstly, the substrate used was different from device fabrication where the polymer film was casted on a 30 nm thick PEDOT: PSS coated ITO glass to smooth the contact between ITO glass and the polymer layer to prevent electrical shorts. In order to compare the effect of different substrate on film thickness, two films were cast using the same conditions on glass and on PEDOT: PSS coated ITO glass. The obtained profilometer scans are shown in Figure 5.2. The film casted on PEDOT: PSS coated ITO has an averaged thickness of 701 nm (Figure 5.2a) and the film casted on glass gave a thickness of 686 nm (Figure 5.2b). The thickness difference between the two samples gave a 2.2 % error, which is within the error range typically obtained from drop-casting. Note that the PEDOT: PSS layer has a thickness of 30 nm (separately measured using Dektak) and the presence of PEDOT:PSS layer might contribute to the obtained thickness in Figure 5.2a as well. In this case the thickness variation between polymer films on PEDOT: PSS coated ITO and glass substrates will be smaller.
Figure 5.2 Film thickness measured on two parallel drop-casted polymer samples prepared on (a) PEDOT: PSS coated ITO glass and (b) cleaned glass substrate. The dash lines show the averaged thickness values of 701 nm (a) and 686 nm (b).

5.3.2.2 Reproducibility of drop-casted film thickness values

Drop-casting inside a glovebox was used to prepare pristine polymer films studied in this chapter to avoid exposure to ambient environment. As the drop-casting method was known to have a larger thickness variation between samples, the reproducibility of drop-casted film thickness was examined in this section. Eight polymer films were prepared using the same deposition process. The thicknesses were measured using a stylus profilometer. The overlay of the scan results is shown in Figure 5.3. The film thickness varied between 613 nm and 497 nm, giving an average thickness of $555 \pm 58$ nm. This corresponds to a thickness error of 20 %; therefore the calculated dielectric constant is
displayed with an error bar of 20%. The observed thickness variation has a number of effects on capacitance characterization as mentioned in Section 5.1.1, including variation of capacitance and thus dielectric constant values between different samples, the frequency dependence of capacitance and the sub-unity $n$ value in impedance spectra when fitting to an R-CPE model.

Figure 5.3 Overlay of film thickness measurements on eight parallel drop-casted samples.

5.3.3 Determining Dielectric Constant Values in Pristine DT-PDPP2T-TT

5.3.3.1 High Dielectric constant observed in pristine DT device

In the previous chapter, a high dielectric constant of 7 was measured in DT-PDPP2T-TT: PCBM blends using P61. The current question of interest is whether the high dielectric constant value in the blend can be correlated with the high dielectric constant of the pristine polymer used. To answer this question, the same batch of polymer was used to fabricate two single-pixel DT-PDPP2T-TT devices with an active area of 0.06 cm$^2$. The device capacitance was measured using the bias-sweep impedance method at 1 kHz. The obtained results are shown in Figure 5.4. The $1/C^2$ values in both devices reached constant
values at reverse bias, indicating full depletion of the polymer layer with no leakage current. The $C_{geo}$ values in these devices were therefore taken at 0 V (see Section 5.1.1 and Chapter 1), where $C_{geo} = 3.1$ nF and 4.2 nF were obtained in devices with polymer film thickness of 289 nm and 200 nm, respectively. The dielectric constant in these pristine films was calculated:

$$C = \varepsilon_0 \varepsilon_r \frac{S}{d}$$  \hspace{1cm} (5.1)

and the results are shown in Table 5.5. High dielectric constant values of 16.8 and 15.8 were obtained in devices with polymer thickness of 289 nm and 200 nm, giving an average dielectric constant of 16.3 ± 0.5. This is by far the highest dielectric constant value in semiconducting polymers reported to date. Given the importance of dielectric screening influencing the nature of charge recombination and transport processes in organic semiconductor devices, there is of particular interest to further investigate the accuracy of the measurements and the possible origin of the obtained high dielectric constant.

Figure 5.4 Bias dependent impedance measurements at 1 kHz carried out on two P61 single pixel thin-film polymer devices using Gamry potentiostat.
Table 5.4 List of capacitance values obtained from Figure 5.4 and the calculated dielectric constant values.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>Capacitance (nF)</th>
<th>$\varepsilon_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>200 ± 11</td>
<td>4.2 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>16 ± 1</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>289 ± 7</td>
<td>3.1 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>16.8 ± 0.7</td>
<td></td>
</tr>
</tbody>
</table>

5.3.3.2 Batch-to-batch variation of dielectric constant values

The entire remaining polymer sample from the above batch was used to measure the effect of enhanced dielectric screening in the photovoltaic blend as shown in the previous chapter and Chapter 6. For further studies in this chapter, a different polymer batch was needed. For this purpose, four new polymer batches were purchased from the same source (the same batch was no longer available). The device capacitance was characterized using bias-sweep impedance measurements and the $1/C^2 - V$ plots of these devices measured at 1 kHz are shown in Figure 5.5. The obtained capacitance, film thickness as well as dielectric constant values are listed in Table 5.6. Note that these devices were fabricated using patterned ITO substrates with four ITO pixels on each substrate and measured using the Zahner potentiostat, while P61 ($\varepsilon_r = 16.8$ batch) was fabricated into single pixel devices and were measured using the Gamry potentiostat. A minimum number of 6 devices were fabricated using each polymer batch with different film thicknesses. For better comparison, the bias sweep impedance data were presented selectively by choosing devices with similar thickness. All devices were prepared in a glovebox. Due to the lack of availability of a spin coater in the glovebox, all polymer films were drop-casted from solution. This made the accurate control of film thickness more difficult compared to spin-coating or doctor-blading. As a result, thickness variation (between 160 nm and 350 nm) in between various different batches was observed. Note that within the range of 100 – 630 nm using the same polymer batch, no thickness dependence of dielectric constant was observed, see Appendix. The observed thickness variation between different batches is likely caused by the different solution concentration used when preparing polymer films due to different solubility between batches.
A strong batch-to-batch variation in the measured capacitance values hence the dielectric constant was observed, where the P61 batch (see Section 5.3.3.1) showed the highest dielectric constant of 16.8, P80 showed dielectric constant of 7.7, and P78, P45 and P33 showed dielectric constant around 3. Table 5.6 clearly shows that, the high dielectric constant of 16.8 in P61 was not reproduced in other batches. As explained in Section 5.1.1, there are various aspects that might affect the measurement of capacitance values even for the same material, including doping, impurities, domain size and crystallinity of material. All polymer batches have purity of > 99.99 % (company provided value), which means that drastic change in the dielectric constant from trace inorganic impurity is unlikely. The presence of organic impurities has been tested in three different batches using 1H NMR, the data is shown in Appendix. The NMR spectra were consistent with the polymer structure with no detectable organic impurity. These results suggest that the batch-to-batch variation of dielectric constant in DT-PDPPP2T-TT arises not from impurities. Further discussions on batch-to-batch variation in measured dielectric constant values are presented in Section 5.4.1.

Among the measured polymer batches, P80 showed the second highest dielectric constant of 7.7. Although lower than the P61 batch, this value is still higher than other dielectric constant values reported in publications up to date. For this reason, it was selected to carry out further detailed studies in the following sections of this chapter.
Figure 5.5 Bias dependent capacitance measurements of encapsulated thin-film polymer capacitors fabricated using different polymer batches, characterized using Zahner and Gamry potentiostat and measured at 1 kHz. It is noted that the lowest capacitance value measured here is above measurement limit for both potentiostat.

<table>
<thead>
<tr>
<th>Mw (kg mol(^{-1}))</th>
<th>Thickness (nm)</th>
<th>Capacitance (nF)</th>
<th>(\varepsilon_r)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P80 80</td>
<td>220 ± 10</td>
<td>1.9 ± 0.2</td>
<td>7.7 ± 0.9</td>
</tr>
<tr>
<td>P78 78</td>
<td>182 ± 11</td>
<td>0.88 ± 0.07</td>
<td>3.0 ± 0.2</td>
</tr>
<tr>
<td>P45 45</td>
<td>350 ± 7</td>
<td>0.51 ± 0.05</td>
<td>3.4 ± 0.3</td>
</tr>
<tr>
<td>P33 33</td>
<td>162 ± 8</td>
<td>1.00 ± 0.08</td>
<td>3.1 ± 0.3</td>
</tr>
<tr>
<td>P61 61</td>
<td>289 ± 7</td>
<td>3.1 ± 0.1</td>
<td>16.8 ± 0.7</td>
</tr>
</tbody>
</table>

5.3.4 Measuring the Capacitance: A Comparison Study

5.3.4.1 Impedance spectroscopy

Impedance spectroscopy was carried out using the Zahner potentiostat in the dark at 0 V on a thin film device with polymer layer (P80) thickness of 630 nm. The parallel capacitance values measured here are above the measurement limit of 390 pF for Zahner potentiostat. The obtained impedance spectrum and fitted results are shown in Figure 5.6. The obtained Nyquist plot showed a semicircle, which is characteristic of parallel RC circuit. The impedance spectrum was therefore fitted to an equivalent circuit of parallel RC with a series resistance (see inset of Figure 5.6a). The parallel RC model assumes the most simplified case, where the circuit consist of a resistance \(R_S\) which accounts for the voltage loss from electrodes and external contacts, in series with the parallel resistance \(R_P\) which corresponds to the bulk resistance of the polymer film and a parallel capacitance \(C_P\) which is the bulk geometric capacitance.\(^{[1]}\) Figure 5.6a shows the fitted curve using this parallel RC model, and the fitting parameters are listed in Table 5.7. The parallel RC
model gave a reasonable fit at frequencies above 300 Hz, however at lower frequencies the measured spectrum deviates from the fitted semicircle. Using the parallel RC model, a capacitance $C_P = 0.63 \text{ nF}$, $R_P = 1.10 \text{ M}\Omega$ and $R_S = 201.5 \text{ } \Omega$ was obtained. The large $R_P$ value was likely due to large active layer thickness and the lack of free carriers. Using Equation 5.1, the dielectric constant was calculated using fitted $C_P$ value, giving $\varepsilon_r = 7.5$.

As mentioned in Section 5.1.1, the dielectric constant is often frequency dependent in disordered materials such as polymers. To account for the frequency dependence, a constant phase element (CPE) is often used instead of a capacitance. A parallel R-CPE model was therefore used to fit the impedance spectrum, as shown in Figure 5.6b. The R-CPE model gave identical $R_S$ and $R_P$ as the parallel RC model, with $A_0 = 0.82 \text{ nS}$ and $n = 0.97$. The fitted curve from R-CPE model showed better fit at frequency above 300 Hz compared to the parallel RC model. The equivalent capacitance of the CPE was also calculated:

$$C = \frac{Y_c}{i\omega} = A_0\omega^{n-1}$$  \hspace{1cm} (5.2),

where $Y_c$ is the admittance of the CPE, $A_0$ is the magnitude of the CPE, $\omega$ is the angular frequency and $n$ is the exponent with value between 0 and 1. A capacitance value of $C = 0.67 \text{ nF}$ is calculated, which is similar to the $C_P$ value obtained from parallel RC model. A dielectric constant of 7.9 was calculated from the equivalent capacitance.

Apart from equivalent circuit model fitting, the parallel capacitance could also be calculated using the imaginary part of the impedance, $Z''$:

$$Z'' = \frac{1}{\omega C}$$  \hspace{1cm} (5.3).

The calculated capacitance and dielectric constant was plotted as a function of frequency, as shown in Figure 5.7. The dash line shows the fitted capacitance value and dielectric constant obtained from parallel RC model. The capacitance obtained from equivalent circuit fitting was obtained at 5 kHz. This is another indication that the fitted capacitance is the low frequency geometric capacitance. Frequency dependent capacitance (and thus dielectric constant) was observed, where the capacitance value at 100 kHz was 18 % lower than that at 1 kHz. This is likely due to the disordered nature of polymers and thickness variation (see Section 5.1.1 and Chapter 1). As shown in Section 5.3.2, the
thickness variation is around 20\%, which is comparable to the magnitude of the dielectric constant decrease at higher frequencies.

From the above results, it can be concluded that the low frequency geometric capacitance of a thin-film polymer device can be obtained from fitting the impedance spectra with parallel RC or R-CPE equivalent circuit models. R-CPE model gave better fitting compared to RC model, and both models gave similar geometric capacitance values. The capacitance and dielectric constant values obtained from $Z''$ showed frequency dependence where high frequency (100 kHz) values showed approximately 18\% decrease compared to low frequency (1 kHz) values.
Figure 5.6 Impedance spectrum of a 630 nm thick thin-film polymer capacitor measured at 0 V using Zahner potentiostat. Figure a and b show the spectrum fitted with a parallel RC model and an R-CPE model (fitting shown in dash lines), with equivalent circuit models shown in corresponding figure inset.

Table 5.6 Fitted parameters of RC and R-CPE models as shown in Figure 5.6.

<table>
<thead>
<tr>
<th>Model</th>
<th>$R_S$ ($\Omega$)</th>
<th>$R_P$ (M$\Omega$)</th>
<th>$C_P$ (nF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RC</td>
<td>201.5</td>
<td>1.1</td>
<td>0.63</td>
</tr>
<tr>
<td>R-CPE</td>
<td>201.5</td>
<td>1.1</td>
<td>0.822</td>
</tr>
</tbody>
</table>

Figure 5.7 Capacitance values and dielectric constant values calculated from impedance spectrum using Equation 5.3 plotted as a function of frequency. The dash lines show the fitted capacitance and dielectric constant value obtained from parallel RC model.
5.3.4.2 Bias dependent impedance measurement

The bias dependent impedance is carried out on a pristine DT-PDPP2T-TT device with a 220 nm thick polymer layer (P80), using the Zahner potentiostat. As shown in Section 5.3.1, the capacitance measurement limit is 390 pF for Zahner potentiostat, which is much lower than capacitance values measured here. The DC bias was varied between -2 V to 1.5 V, and the measurement was carried out at a series of frequencies between 500 Hz and 100 kHz. The obtained results at 500 Hz, 1 kHz, 5 kHz, 20 kHz and 100 kHz are shown in Figure 5.8. The plot obtained at 500 Hz was notably noisier than others, which is likely due to the small AC current response of the impedance measurements at low frequency. At higher frequencies the signal gets larger, resulting in less pronounced noise.

Typically the scientific literature describes the $1/C^2$-$V$ response at large reverse bias to be constant due to the depletion of the free charge.\[^{[3]}\] However, in Figure 5.8 a weak dependence of $1/C^2$ on reverse bias was observed for all measured frequencies. At larger reverse bias the $1/C^2$ values are slightly higher, which corresponds to a lower capacitance. This is attributed to the leakage current caused by injection from non-blocking contacts (see Section 5.1.1 and Chapter 1), as shown in Figure 5.8, where the $1/C^2$ - $V$ plot obtained at 1 kHz (a) as well as the corresponding DC current-voltage curve (b) of the measurement was shown. Due to the presence of leakage current (Figure 5.9b), the capacitive charge modulated by the external voltage stimuli decreases. As a result, by increasing the DC bias the leakage current also increases, leading to an increasing $1/C^2$ value. This is illustrated in Figure 5.9a with a red dash line indicating the bias dependence.

To compare the three procedures to obtain the $C_{geo}$ value, the capacitance values obtained by i) averaging capacitance at large reverse bias (between -2 and -1 V), ii) capacitance at 0 V and iii) capacitance from extrapolation were obtained for bias sweep impedance results measured at all frequencies. The capacitance as well as calculated dielectric constant values is shown in Figure 5.10. The capacitance values obtained by averaging at reverse bias gave higher capacitance (and thus dielectric constant values) at frequencies below 2 kHz and lower values at higher frequencies. The capacitance values taken at 0 V and by extrapolation were in agreement except the point at 500 Hz, due to the noise in the measurement. While the capacitance values at 0 V and averaged capacitance both showed larger values at lower frequencies in Figure 5.10, the values obtained by the extrapolation method yielded more consistent values. It is also observed that when the frequency
increase, the capacitance values decrease, independent of the method used. Compared to the capacitance at 500 Hz (taking the extrapolation value), the capacitance decreased by 8% at 100 kHz. Such dependence of capacitance (and thus dielectric constant) on frequency was seen in the impedance spectrum and has been observed in other polymers,[4] which is likely the combined result of dipolar polarization, the disordered nature of polymers and film thickness variation.

To summarise, using bias dependent impedance measurements $C_{geo}$ could be obtained. The measurement frequency above 1 kHz is optimal while lower frequency measurements gave noisy results due to low current response. Linear extrapolation of the $1/C^2$ - $V$ data at large reverse bias ($> -1$ V) to 0V intersect provided the most consistent $C_{geo}$ value, minimising the effects of leakage current observed at large negative bias. A (weak) frequency dependence of the obtained geometric capacitance and dielectric constant was observed, where high frequency (100 kHz) dielectric constant showed approximately 20% lower values compared to the 1 kHz value.
Figure 5.8 Bias dependent capacitance measurements carried out at a series of frequencies on a 220 nm thick encapsulated thin-film polymer capacitor, measured using Zahner potentiostat.
Figure 5.9 (a) Bias dependent impedance measurement carried out at 1 kHz, and (b) the DC current-bias plot corresponding to figure a.
Figure 5.10 Capacitance values and dielectric constant values calculated from Figure 5.8, using linear extrapolation of capacitance at large reverse bias, taking the average value at large reverse bias and taking at 0 V.

5.3.4.3 CELIV

CELIV measurements were carried out on a 630 nm thick pristine polymer film device, which was fabricated in the same batch as the device used in Section 5.3.4.1. Figure 5.11 shows a series of CELIV transients measured in the dark, under different maximum applied biases and pulse widths of the voltage ramp. All transients showed a flat transient after the RC time, suggesting the absence of dark carriers being extracted or carriers being injected from the electrodes, and thus the capacitive response obtained from CELIV corresponds to the geometric capacitance. For a pure capacitor under a linearly increasing
voltage ramp, following a rise-time related to the circuit RC time constant $\tau_{RC}$, a constant displacement current, $I_0$, is reached:

$$I_0 = \frac{U_{max}C}{t_{pulse}}$$

(5.4),

where $U_{max}$ is the maximum applied bias and $t_{pulse}$ is the pulse width of the voltage ramp. Since $U_{max}$ and $t_{pulse}$ are both known parameters and $I_0$ is measurable using an oscilloscope, $C$ can directly be obtained. As shown in Equation 5.4, the displacement current is only dependent on two experimental parameters, namely $U_{max}$ and $t_{pulse}$. The current value is proportional to $U_{max}$ and inversely proportional to $t_{pulse}$, therefore the voltage transient plateau should scale linearly with $U_{max}$ and $1/t_{pulse}$. These two parameters were therefore varied to evaluate their effects on the obtained capacitance values, shown in Figure 5.11. When $t_{pulse}$ was kept constant at 10 $\mu$s in Figure 5.11a, the current transient plateau $I_0$ scaled linearly with $U_{max}$ below 2 V; when $U_{max}$ increased above 3 V, $I_0$ was lower than predicted from a linear dependence (linearly scale values shown in dash lines). When $U_{max}$ was kept constant at 3 V while changing $t_{pulse}$, a similar behaviour was observed (Figure 5.11b): at long $t_{pulse}$ above 20 $\mu$s the $I_0$ values scaled inversely proportional to $t_{pulse}$. At short $t_{pulse}$ of 10 $\mu$s, however, $I_0$ was lower than predicted from a linear dependence (linearly scale value shown in dash lines). When $U_{max}$ further increased to 4 V, the deviation of $I_0$ started to appear at longer $t_{pulse} = 20$ $\mu$s. Such deviation of $I_0$ from the predicted from a linear dependence was observed when $t_{pulse}$ was short and $U_{max}$ was large, see Figure 5.12a. The dash lines in Figure 5.12a shows the linear relation of $I_0$ at low $U_{max}$ and long $t_{pulse}$, and the deviation at large $U_{max}$ and short $t_{pulse}$ could clearly be observed.

To further analyse the effect of measurement parameters on obtained capacitance, the dielectric constant $\varepsilon_r$ values were calculated from the measured transients and were plotted as a function of $U_{max}/t_{pulse}$, as shown in Figure 5.12b. The majority of $\varepsilon_r$ values obtained at $U_{max}/t_{pulse}$ values below $2 \times 10^5$ V s$^{-1}$ were between 6.94 and 6.04, giving an average value of 6.37. At $U_{max}/t_{pulse}$ above $2 \times 10^5$ V s$^{-1}$, the calculated $\varepsilon_r$ values were much lower, between 4.90 and 5.04, which were caused by the observed deviation of $I_0$ from the predicted linear dependence. One of the possible reasons for the deviation of $I_0$ at high $U_{max}/t_{pulse}$ could be the voltage loss caused by series resistance, which becomes
more pronounced when the bias ramp is large. The results suggest that measuring CELIV at low $U_{max}/t_{pulse}$ gives more accurate capacitance results.

Figure 5.11 (a) CELIV transients carried out on a 630 nm polymer capacitor, with $t_{pulse} = 10 \, \mu s$ and $U_{max}$ increasing from 1 V to 4 V; (b) CELIV transients obtained at $U_{max} = 3 \, V$ and $t_{pulse}$ increasing from 10 $\mu s$ to 100 $\mu s$. The dash lines in figure show the predicted from a linear dependence.
Figure 5.12 (a) $I_0$ plotted as a function of $U_{\text{max}}$, with dash lines showing linear scale; (b) dielectric constant dependence on $\frac{U_{\text{max}}}{t_{\text{pulse}}}$. 


Comparing between frequency depended impedance, bias dependent impedance and CELIV measurements to obtained $C_{geo}$ and $\varepsilon_r$

As shown above, capacitance and dielectric constant values were obtained from both impedance spectroscopy and CELIV techniques. The obtained capacitance and dielectric constant values using the above methods are summarised in Table 5.8. The dielectric constant obtained from impedance spectrum fitting was 7.9 and bias dependent impedance measurement at 1 kHz gave dielectric constant of 7.5, whereas CELIV gave an average dielectric constant of 6.4 which is 15% lower than the bias dependent impedance result at 1 kHz. It is noted that the dielectric constant from CELIV was obtained from averaging results measured at $t_{pulse}$ between 10 μs and 100 μs, corresponding to frequency between 10 kHz and 100 kHz. To compare at the same frequency, the dielectric constant calculated from bias dependent impedance measured at 100 kHz was also listed in Table 5.8, which showed a higher value than that from CELIV.

<table>
<thead>
<tr>
<th>Method</th>
<th>Capacitance (nF)</th>
<th>Thickness (nm)</th>
<th>$\varepsilon_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Impedance spectra (fitted)</td>
<td>0.63</td>
<td>630</td>
<td>7.9</td>
</tr>
<tr>
<td>Bias dependent impedance measurement (1 kHz)</td>
<td>1.81</td>
<td>220</td>
<td>7.5</td>
</tr>
<tr>
<td>Bias dependent impedance measurement (100 kHz)</td>
<td>1.69</td>
<td>220</td>
<td>7.0</td>
</tr>
<tr>
<td>CELIV</td>
<td>0.54</td>
<td>630</td>
<td>6.4</td>
</tr>
</tbody>
</table>

Comparing the different capacitance measurement methods, the main advantage of using the frequency dependent impedance measurement is that it allows the direct observation of the circuit elements of the device. The number of semicircles (arcs) corresponds to the number of RC or R-CPE elements in the device (as long as their time constant is very different). This provides key information on different capacitive responses in the device, from which the geometric capacitance and other capacitive responses could be differentiated. Another benefit of obtaining capacitance from the impedance spectra is that the frequency dependence of the capacitance and dielectric constant could be easily
obtained in a single measurement within minutes. However, obtaining capacitance from impedance spectra requires an equivalent circuit model that fits the impedance results well and has a clear physical meaning, which can be challenging in some cases.

The bias sweep impedance technique provides a simple and direct method to obtain the device capacitance at low frequencies. This method allows the extraction of geometric capacitance while the built-in potential can also be obtained. This method also allows the measurement of frequency dependent geometric capacitance, although multiple measurements are required.

CELIV is principally different from impedance spectroscopy and it provides a different approach to obtain the capacitance in a polymer thin-film device. The advantages of CELIV techniques are i) the shape of the CELIV transients provides direct observation of some features in a device, e.g. whether dark carriers are present in a device or if there are non-blocking electrodes; ii) CELIV allows much larger voltage modulation compared to impedance spectroscopy (on the magnitude of several volts in CELIV as opposed to millivolts in impedance techniques), making the measurement of capacitance in thick samples possible which would otherwise be too small to be measured by impedance techniques.

Thus it is concluded that the methods shown above are useful in revealing different aspects of capacitive response within a polymer device, and should be used in combination to obtain accurate dielectric constant values. When measuring the geometric capacitance in a polymer thin-film device, CELIV could first provide a direct evaluation on whether the device has dark carriers or non-blocking electrodes. Then the impedance spectra could be used, which provide basic information on capacitive responses within the device. Once the equivalent circuit model is fitted to the impedance spectrum, bias dependent impedance measurement could be carried out at frequency range corresponding to the geometric capacitance, which could be obtained from the impedance spectrum.

Based on above discussions, a general practice for capacitance characterization in a thin-film semiconducting polymer capacitor is proposed:
1) Measure CELIV transients to check whether dark carriers or charge injection from electrodes are present. An estimation of device capacitance could also be obtained. The linearity of the current response versus $U_{max}/t_{pulse}$ should be evaluated;

2) Measure the impedance spectrum at 0 V and fit the spectrum to RC or R-CPE equivalent circuit models. Appearance of more than one semicircle suggests additional capacitance contributed from electrode interfaces. When fitting with R-CPE model, the exponent $n$ should be close to 1 and the equivalent capacitance should be close to the capacitance value obtained from RC model. An exponent value much lower than 1 suggests there might be more than one capacitive response on the measured frequency range, and a different equivalent circuit model will be needed;

3) Once the impedance spectrum is fitted to a suitable equivalent circuit model, the bias dependent impedance measurement could be carried out on the frequency range corresponding to the semicircle of the geometric capacitance. If weak injection at reverse bias is present, the capacitance value could be taken by linearly extrapolating the $1/C^2$ value to zero bias and take the intersect value.

5.3.5 Comparing Device Preparation Conditions: The Effect of Ambient Environment on Dielectric Constant

When fabricating thin-film polymer capacitors using different polymer batches, the devices were first fabricated in air using a spin-coater. However, significantly lower dielectric constant compared to batch P61 was observed in all measured batches. In order to find out the origin of such decrease, the fabrication conditions were controlled to eliminate possible contributions from ambient environment. When device fabrication conditions were systematically controlled, an interesting observation was made: when the P80 devices were prepared in the glovebox, the obtained dielectric constant was notably higher than that in devices fabricated in air (see below for details). In order to understand the underlying reason for this observation and to further explore the effect of polymer film preparation conditions on the measured dielectric constant values, thin-film devices were prepared under different conditions. First, devices were fabricated with pristine polymer films drop-casted in air and in glovebox with (nominally) the same film thickness. The film cast in air was left in ambient environment for 30 minutes before transferring to
a glovebox. As shown in Figure 5.13a, smaller $1/C^2$ value was observed for the glovebox-casted device, corresponding to a higher capacitance and thus dielectric constant. The device prepared in the glovebox showed a constant $1/C^2$ value at reverse bias, whereas the air casted device showed a large slope. The strong slope observed in air-casted device suggest that, not only is the dielectric constant of the film is decreased, but the degree of doping is also increased by exposing the polymer film to air. The doping most likely originates from oxygen and / or moisture exposure, which has been observed in regioregular poly(3-hexylthiophene-2,5-diyl) (rr-P3HT). Oxygen was reported to interact with thiophene ring, causing local perturbation and re-orientation of thiophene backbone. This re-orientation further facilitates interaction of H$_2$O-O$_2$ complexes with the polymer backbone, leading to doping of rr-P3HT.

Figure 5.13b compares the effect of heating on geometric capacitance and dielectric constant. Two identical devices were prepared in air. One of the devices was heated at 50 ºC for 10 minutes while the other was kept at room temperature. The heated device showed a larger $1/C^2$ value compared to the room temperature device. Furthermore, the drop of $1/C^2$ values caused by the injection of carriers at forward bias around the build-in potential was not observed in the heated device. This can be caused either by the change of build-in potential or by a drastic decrease of carrier mobility or an additional injection barrier due at the contact. Change in build-in potential of the polymer film could be caused by morphological change due to heating. Decrease in charge mobility can be caused by the change in film morphology or by increased mid-gap trap states. It has been reported that in p(DTG-TPD): [70]PCBM devices, the electron mobility decreased from $5 \times 10^{-4}$ to $2 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ and the hole mobility decreased from $1.6 \times 10^{-4}$ to $3 \times 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$ when active layer was processed in air instead of N$_2$. The decrease of hole mobility by almost an order of magnitude was attributed to water and oxygen doping. The effect of film morphology on mobility is another possibility.

Figure 5.13c compares the effect of room light on geometric capacitance and dielectric constant. Again, two parallel devices were fabricated in air, one exposed to room light while the other covered in the dark. No notable difference in capacitance was observed between the two devices, suggesting that room light has only a minor or no effect on the measured dielectric constant. Note that the close to identical capacitance values in two separate devices suggest that the reproducibility of capacitance is reasonable.
The capacitance values at 1 kHz obtained from Figure 5.13 were used to calculate the dielectric constant, as listed in Table 5.9. The highest dielectric constant of 7.7 at was observed in the Ar cast device, while the device prepared in air showed a reduced dielectric constant of 6.1, corresponding to a 19% decrease. As mentioned in Section 5.3.2, the thickness measurement gave a 20% error; therefore the lower dielectric constant is within experimental error. The dielectric constant further decreased to 5.0 in devices exposed for 60 minutes, with and without room light exposure. The lowest dielectric constant was observed in the heat-treated device, which gave a dielectric constant of 4.1. The reduced dielectric constant seen in 60 minutes air exposed devices confirms that the ambient exposure leads to reduced dielectric constant, which is further exacerbated by heating the sample. The exact origin of the reduced values of dielectric constant under ambient air and heat exposure is not yet known. One of the possibilities for reduced dielectric constant in ambient is chemical degradation, e.g., fragmentation of the polymer backbones. Another possible origin for decreased dielectric constant is the change in polymer dipoles. For example, if the high dielectric constant of the polymer originates from delocalization of polymer segments, the re-orientation of polymer backbone caused by O₂ doping could immobilize such segments or block delocalisation, resulting in reduced dielectric constant.
Figure 5.13 Bias dependent impedance measurements carried out at 1 kHz on (a) parallel devices fabricated in glovebox and in air, exposed for 30 minutes; (b) parallel devices in air, 30 minutes; (c) parallel devices in air, room temperature and 50 degrees for 10 minutes; (d) parallel devices in air, dark and light for 60 minutes.
fabricated in air at room temperature and under 50 ºC heating for 10 minutes and (c) parallel devices fabricated in air, in dark or under room light illumination for 60 minutes. All measurements carried out using Gamry potentiostat.

<table>
<thead>
<tr>
<th>Prep conditions</th>
<th>Dielectric constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon, dark, 21 ºC</td>
<td>7.5</td>
</tr>
<tr>
<td>Air, dark, 30 minutes 21 ºC</td>
<td>6.1</td>
</tr>
<tr>
<td>Air, dark, 10 minutes 50 ºC</td>
<td>4.1</td>
</tr>
<tr>
<td>Air, dark, 60 minutes 21 ºC</td>
<td>5.0</td>
</tr>
<tr>
<td>Air, light, 60 minutes 21 ºC</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Table 5.8 Dielectric constant values obtained from Figure 5.13.

5.4 Discussion

5.4.1 Batch-to-batch variation in dielectric constant

Figure 5.5 and Table 5.6 showed that a strong batch-to-batch dependence in dielectric constant was present in pristine DT-PPDPP2T-TT samples. This can have several possible origins.

Changing morphology, including domain size and crystallinity, are expected to affect the dipolar polarization which will be reflected in the dielectric constant values. Therefore it is suggested here that the batch-to-batch variation of dielectric constant might be caused by the change in thin film morphology. To test this hypothesis, film morphology of pristine polymers was examined using polarized optical microscope on two batches with different molecular weight, as shown in Figure 5.14. The low dielectric constant sample (P33) showed fine segregated domains, whereas the high dielectric constant sample (P80) showed no observable segregation but rather a fibril-like structure, which was absent in the low Mw sample. These differences in film morphology might be able to explain the dielectric constant difference between batches; however definitive conclusion requires detailed morphology study, which is beyond the scope of this thesis.
When polymers of different batches were synthesized, there might be procedural differences between batches which caused some batches to be more prone to degradation or H₂O/O₂ doping than other batches. Such difference could be minor, even undetectable using regular polymer characterisation techniques such as NMR; however the results in Section 5.3.5 suggest that a short period of exposure to air or mild heat could lead to drastic change in dielectric constant. The validation of this would require systematic study of synthesis conditions and a detailed degradation study.

(a) Low $\varepsilon_r$ (P33)

(b) High $\varepsilon_r$ (P80)
Figure 5.4.14 Optical microscopy images obtained from pristine polymer films prepared on glass substrates using a low molecular weight (a) and a high molecular weight (b) polymer batch.

5.4.2 The significance of this chapter

Three significant outcomes are demonstrated in this chapter.

1) High dielectric constant of 16.8 and 7 was obtained for two different batches of DT-PDPP2T-TT pristine polymer, P61 and P80. Both values are higher than other dielectric constant values reported to date, where P61 showed a dielectric constant over two times larger than highest value reported in literature. The importance of high dielectric constant in DT-PDPP2T-TT is that, it provides opportunities to study the influence of dielectric screening on charge generation, transport and recombination processes which has been limited to theoretical analysis before. With such high dielectric constant, experimental studies of influence of dielectric screening on charge-photogeneration and recombination processes become possible for the first time, making this polymer a unique material in semiconducting polymers.

2) For the first time in literature, three experimental techniques for geometric capacitance measurement are studied in detail and are compared. No such study has been carried out in literature before, which makes the comparison between dielectric constant values obtained from different techniques at question. In this chapter, not only were three different characterization techniques compared, the measurement conditions at which geometric capacitance could be accurately measured were proposed for the first time. This chapter provides an experimental guideline for geometric capacitance characterization in thin-film polymer devices including but not limited to semiconducting polymers, and is thus beneficial for the field of polymer devices in a broader context.

3) The influence of sample processing conditions on dielectric constant is demonstrated, where ambient air and heating exposure showed a detrimental effect on dielectric constant. This is an important observation, which suggests that other semiconducting polymers may also suffer from oxygen and water doping leading to the low dielectric constant values typically observed. While the effect of ambient conditions on charge mobility and long term stability in semiconducting polymers have been studied,
This chapter shows that ambient environment affects the fundamental dielectric property of a semiconducting polymer, which will have a wide range of influences including charge generation and recombination in semiconducting polymers.

5.5 Conclusion

This chapter focuses on the characterization of dielectric constant in pristine DT-PDPP2T-TT films and answers the questions raised at Section 5.1:

1) High dielectric constant of 16.8 was measured reproducibly in polymer batch P61, which is the highest reported dielectric constant value for semiconducting polymers up to date. Batch-to-batch variation of dielectric constant was observed, giving dielectric constant values between 16.8 and 3.0.

2) Three different techniques were used to characterize the geometric capacitance of pristine polymer thin-film devices. The bias dependent impedance technique was most suitable in obtaining low frequency (between 1 kHz and 10 kHz) capacitance values in devices with sample thickness below 1 μm. Dark CELIV was used to examine the linearity of displacement current, which allowed determining the quality of a device. It is also useful in obtaining geometric capacitance especially when the film thickness exceeds 1 μm and the device capacitance is too small to be measured from impedance. It is suggested for the first time in this thesis that when measuring geometric capacitance in a thin-film polymer capacitor device or PSC device, CELIV should be carried out first to check whether dark carriers or electrode injection current is present in the device. Then the impedance spectrum should be measured and fitted to suitable equivalent circuits. Once the frequency range corresponding to geometric capacitance is obtained, the bias dependent impedance measurement could be carried out.

3) The effect of sample preparation conditions on the measured dielectric constant of pristine DT-PDPP2T-TT, namely ambient air exposure, heat exposure and room light exposure, were examined. A decrease in the dielectric constant value was observed when the polymer film was exposed in air for more than 30 minutes, and a larger decrease was observed when heating polymer sample at 50 °C in air. Room light exposure showed no
effect on dielectric constant. The dielectric constant decrease when processed in ambient air or heated is possibly caused by O\textsubscript{2} and H\textsubscript{2}O doping.

4) While the origin of batch-to-batch variation of dielectric constant values in DT-PDPP2T-TT remains unclear, several possibilities including morphology, doping and material degradation were proposed.

The findings in this chapter are important to check the effect of dielectric screening on charge recombination in this thesis. It also has some broader implications in the field of organic semiconductor characterisation. The high dielectric constant obtained in pristine DT-PDPP2T-TT confirmed the dielectric constant of 7 measured in DT-PDPP2T-TT: PCBM blend shown in Chapter 4, further supporting the hypothesis that strong dielectric screening in DT-PDPP2T-TT contributes to reduced bimolecular recombination in the fabricated PSC device. The geometric capacitance characterization guideline proposed in this thesis also benefits general audience in the field of thin-film semiconducting devices.

This chapter also raises some open questions, such as the origin of batch-to-batch variation in dielectric constant in DT-PDPP2T-TT, and the possible mechanisms for smaller dielectric constant measured after ambient air and heat exposure. Further experiments, including detailed degradation and morphology studies, are required to answer these questions.

5.6 References

Chapter 6 Distinguishing the Effect of Dielectric Screening: A Comparative Study of Bimolecular Recombination Kinetics between Four Polymer: PCBM Blend Systems
6.1 Introduction

6.1.1 Background

As mentioned in Chapter 1, recombination of charge carriers (both geminate and bimolecular) is one of the major efficiency loss mechanisms in organic photovoltaic devices. The charge recombination through Coulomb interaction in three-dimensional systems can be described using the Langevin theory, where in the trap-free case the recombination coefficient can be calculated as:

\[ \beta_L = \frac{e\mu}{\varepsilon_0\varepsilon_r} \]  

(6.1)

where \( \beta_L \) is the Langevin recombination coefficient, \( \mu \) is the charge carrier mobility and \( \varepsilon_0 \) and \( \varepsilon_r \) are the vacuum permittivity and relative dielectric constant, respectively. The charge density decay following Langevin recombination will therefore have a second order decay kinetics and \( \beta_L \) will only depend on the carrier mobility \( \mu \) and the dielectric constant of the material \( \varepsilon_r \).

To reduce the bimolecular recombination in an PSC system without sacrificing mobility, two approaches are thus possible: one is to have a system which has non-Langevin recombination, i.e. bimolecular recombination is significantly reduced compared to diffusion-dominated recombination; the other approach is to increase the dielectric constant. The reduced bimolecular recombination is characterized using TOF, from which the reduction factor is obtained. In a non-Langevin system, the bimolecular recombination coefficient is described as:

\[ \beta = \xi \cdot \beta_L = \xi \cdot \frac{e\mu}{\varepsilon_0\varepsilon_r} \]  

(6.2)

where the reduction factor \( \xi \) has a maximum of 1 for Langevin recombination (\( \beta = \beta_L \)). In a system with significantly reduced bimolecular recombination, the reduction factor \( \xi \) can be several orders of magnitude smaller than 1, as observed in rr-P3HT: PCBM.[1] A number of mechanisms has been proposed to explain such deviation from Langevin theory. Nelson suggested recombination via tail states as a possible mechanism for reduced bimolecular recombination, in which case the recombination rate is controlled by thermal activation of trapped carriers rather than diffusion.[2] It has also been suggested that recombination of charge carriers takes place through an intermediate CT state, which
is formed upon free electron and hole encounter but could again separate into free carriers.\cite{3} Morphology based theories such as two-dimensional Langevin recombination has also been proposed suggesting reduced probability for charges to meet in P3HT: PCBM films with highly ordered lamella or fibril-like structure.

Increasing dielectric constant in PSC systems has also been investigated, where several approaches have been reported to successfully increase the dielectric constant in semiconducting polymers from below 4 to 5 – 6. Diketopyrrolopyrrole (DPP) based polymer PIDT-DPP-CN with dielectric constant of 5 (1 kHz) was successfully synthesized by introducing polar side-chain in a semiconducting polymer.\cite{4} The increased dielectric constant has been reported to lead to longer small-perturbation lifetime and increased \( V_{OC} \). Fluorination has also been used to increase the dielectric constant in semiconducting polymer, where the dielectric constant showed an increase from 4.5 in thiophene-quinoxaline (TQ) to 5.7 in the fluorinated polymer FTQ.\cite{5} However, a detailed study on the effect of increased dielectric screening on recombination is still lacking, most likely due to the lack of high dielectric constant polymers available.

### 6.1.2 Aim and Objectives

The aim of this chapter is to investigate the effect of dielectric screening on bimolecular recombination in PSC devices independent of other parameters. This is done by comparing the recombination kinetics in PSC systems with different dielectric constant values. It has been established in Chapter 4 and 5 that DT-PDPP2T-TT shows high dielectric constant values between 7 and 16 in pristine polymer films and high dielectric constant of 7 in polymer: PCBM blends, thus it is used as the high dielectric constant system for comparison in this chapter.

The challenge for this chapter is to separate the parameters influencing bimolecular recombination in a polymer: PCBM system, namely dielectric screening, reduction factor, and charge mobility. For a comprehensive comparison, PSC systems are selected based on these parameters. DT-PDPP2T-TT: PCBM has high dielectric constant of 7, thus the other systems should have low dielectric constant between 3 and 4. As DT-PDPP2T-TT: PCBM has very high charge mobility, other systems with low mobility and moderate mobility should be selected as well. To compare systems with Langevin and non-
Langevin recombination, systems with different bimolecular recombination mechanisms should also be selected. The selection criteria for comparing systems thus are:

1) Commercial available;
2) Recombination kinetics well reported in literature, where Langevin type and non-Langevin recombination systems should both be included;
3) The selected systems should have different mobility.

Three low dielectric constant systems, namely PCPDTBT: [60]PCBM, P3HT: [60]PCBM and PTB7: [60]PCBM are selected based on these requirements. The energy diagram of the used polymer donors and [60]PCBM acceptor is shown in Figure 6.1. Among the selected systems, PCPDTBT: PCBM and PTB7: PCBM have been reported to show diffusion-dominated recombination, whereas P3HT: PCBM is a well reported non-Langevin system. As shown in Chapter 4, the recombination in DT-PDPP2T-TT: PCBM has Langevin characteristics. PCPDTBT: PCBM and PTB7: PCBM will be characterised using methodology established in Chapter 3.

![Energy diagram of polymer systems](image)

**Figure 6.1** The energy diagram of P3HT,[6] PTB7,[7] PCPDTBT,[8] DT-PDPP2T-TT,[9] and [60]PCBM.[10]

In this chapter, as the key focus is on the effect of dielectric screening on bimolecular recombination, recombination kinetics and charge carrier mobility in DT-PDPP2T-TT: PCBM are compared with low dielectric constant systems. As demonstrated in Chapter
1, dielectric screening can influence a number of properties within a PSC, however as the focus of this chapter is on bimolecular recombination, other potential dielectric effects will not be discussed here. A literature review on the influence of dielectric screening on charge generation and geminate recombination was given in Chapter 1. The device performance, dielectric constant values and bimolecular recombination in P3HT: PCBM (established in Chapter 3), PCPDTBT: PCBM, and PTB7: PCBM are characterized and compared to that in DT-PDPP2T-TT: PCBM. The charge density decay kinetics, recombination coefficient $\beta$ values, carrier lifetimes and reduction factor $\zeta$ values are compared between the four systems. In order to compensate for the difference in mobility, a new methodology of normalizing bimolecular recombination coefficient to mobility ($\beta/\mu$) is proposed.

6.2 Experimental

Poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-B:3,4-B’]dithiophene)-alt-4,7(2,1,3-benzothiadiazole)] (PCPDTBT, Mw = 40 kg mol$^{-1}$, PDI = 1.15) and [6,6]-Phenyl C61 butyric acid methyl ester ([60]PCBM) were purchased from Solaris Chem Inc. Poly([4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediy]) (PTB7, OS0007) and DT-PDPP2T-TT (OS0300) were purchased from 1-Material. Analytical grade anhydrous chlorobenzene, 1,2-dichlorobenzene, toluene and 1,8-octanedithiol were purchased from Sigma Aldrich. Acetone and isopropanol were purchased from Chem-supply. All chemical and solvents were used as purchased. Poly-(ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT:PSS) (Clevios P, VP Al 4083) was purchased from Heraeus.

Device preparation was as follows: PCPDTBT: [60]PCBM (1:2 w/w) solution was dissolved in dichlorobenzene with 3 vol% 1,8-octanedithiol as additive. PTB7: [60]PCBM (1:1.5, w/w) was dissolved in hot chlorobenzene with 3 vol% 1,8-octanedithiol. The above solutions were dissolved at 120 °C and stirred overnight, carried out in a glovebox. DT-PDPP2T-TT: [60]PCBM 1:3 w/w solutions were dissolved in chloroform with 7.5 vol% dichlorobenzene. The solutions were dissolved at 45 °C and stirred overnight in a glovebox.
Patterned ITO glass substrates were cleaned by sonicating in detergent, DI water, acetone and isopropanol, each for 15 minutes then blow dry with nitrogen and treated with UV-Ozone for twenty minutes. PEDOT:PSS was spin coated at 4500 rpm on the substrates then subsequently annealed at 140 °C for ten minutes to achieve a dry thickness of around 30 nm. The photoactive layer was deposited via spin coating the hot solutions. Active layer thickness was controlled via changing spin speed and measured using Dektak stylus profilometer, the procedure of which will be introduced below. The above fabrication processes were carried out under ambient condition. The device area was defined by the overlay area between ITO fingers and the aluminium electrode, which is 0.06 cm² for each device pixel.

For UV-Vis absorption spectroscopy and transient absorption spectroscopy, polymer films were spin-coated on cleaned glass substrates from 45 °C solutions. The glass substrates were cut into 15 mm ×15 mm size and cleaned following the same procedure as the ITO substrates. For TAS measurements, the casted films were encapsulated in an argon filled quartz cuvette to measure in inert atmosphere.

Film thickness was measured using Dektak stylus profilometer. Each measurement was carried out over a scan length of 3000 μm with a stylus force of 0.1 mg. For each sample multiple scans were carried out for an averaged thickness. UV-Vis absorption spectra were measured using a UV-3600 spectrometer, Shimadzu. Film samples were prepared via spin-coating on clean glass substrates as explained above. Current-Voltage characterizations were carried out using Solar cell I-V curve testing system model IV21L, PV measurements. The solar simulator was calibrated using a reference Si diode prior to each measurement. Internal and external quantum efficiency characterizations were carried out using QE-X10, PV measurements.

Impedance spectroscopy was carried out using Zahner IM6 electrochemical workstation and Gamry Reference 600 potentiostat. AC oscillation amplitude of 5 mV was used. The voltage bias between -2 V and 2 V and frequency between 1 kHz and 500 kHz was applied when measuring bias dependent impedance.

For photo-CELIV, a pulsed laser (Spectra Physics Quanta Ray Lab 170) and a Quanta Ray MOPO were used to generate the laser pump signal for photoexcitation. Excitation pulse of 650 nm was used for DT-PDPP2T-TT: PCBM and PCPDTBT: PCBM devices.
and 532 nm for PTB7:PCBM device. The delay time between photoexcitation and voltage ramp application was controlled using a nanosecond switch (2.2 MΩ impedance, Asama Lab) and a delay generator (Stanford Research DG535). The extraction current was recorded using an oscilloscope (Tektronics, DPO4054), using either the built-in 50 Ω impedance on oscilloscope or a homemade 13.5 Ω resistor in parallel with the 1 MΩ input impedance on oscilloscope, depending on the device capacitance.

TRCE measurements were carried out as follows. A pulsed laser (Spectra Physics Quanta Ray Lab 170) and a Quanta Ray MOPO were used to generate the laser pump signal for photoexcitation. Excitation pulse of 650 nm was used for DT-PDPP2T-TT: PCBM and PCPDTBT: PCBM devices and 532 nm for PTB7: PCBM device. The devices were initially held at high impedance using a nanosecond switch (2.2 MΩ impedance, Asama Lab). After a controllable delay time using a digital delay generator (Stanford Research DG535), the switch was opened and the devices were at short circuit condition. The extracted current was measured using an oscilloscope (Tektronics, DPO4054) as a function of time (input impedance 50 Ω). The dark response was subtracted to remove the switch noise.

To measure photovoltage decay, the devices were photo-excited using a pulsed laser (same as above) at open circuit, which was realized by using the 1 MΩ high impedance of the oscilloscope (Tektronics, DPO4054). The voltage decay was recorded as a function of time. Four measurements were carried out for each photovoltage decay curve on different timescales. The $V_{OC}$ values were matched to the charge density and lifetime by reading voltage values at the same delay time.

### 6.3 Results

#### 6.3.1 Device performance

PCPDTBT: PCBM 1:2 w/w devices and PTB7: PCBM 1:1.5 w/w devices were fabricated as described in Section 6.2. The blending ratios were selected based on optimized performance reported in literature.\cite{11} The current-voltage characterization of fabricated devices was carried out under AM1.5 and in the dark, and the obtained curves are shown in Figure 6.2a, in comparison with P3HT: PCBM device studied in Chapter 3 and DT-
PDPP2T-TT: PCBM studied in Chapter 4. The performance parameters of shown devices are listed in Table 6.1. The highest $V_{OC}$ of 0.71 V was obtained in DT-PDPP2T-TT: PCBM while PCPDTBT: PCBM gave a $V_{OC}$ of 0.64 V and PTB7: PCBM a $V_{OC}$ of 0.62 V. The lowest $V_{OC}$ of 0.54 V was observed in P3HT: PCBM. Figure 6.2b shows the EQE spectra of the measured devices, where the maximum EQE wavelength shows good agreement with the bandgap of the polymer and with literature. The $J_{sc}$ values integrated from the EQE spectra are also in agreement with the $J_{sc}$ values obtained from $J-V$ measurements.
Figure 6.2 (a) Current-voltage curved of fabricated PTB7: PCBM and PCPDTBT: PCBM devices, compared with that in DT-PDPP2T-TT: PCBM and P3HT: PCBM; (b) EQE spectra measured in PTB7: PCBM, PCPDTBT: PCBM, DT-PDPP2T-TT: PCBM and P3HT: PCBM devices.

Table 6.1 List of performance parameters obtained from Figure 6.2.

<table>
<thead>
<tr>
<th></th>
<th>D:A ratio</th>
<th>Thickness (nm)</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ ($J_{EQE}$) (mA cm$^{-2}$)</th>
<th>$FF$</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT: PCBM</td>
<td>1:1</td>
<td>65 ± 5</td>
<td>0.54</td>
<td>7.8 (7.2)</td>
<td>0.46</td>
<td>1.9 %</td>
</tr>
<tr>
<td>PTB7: PCBM</td>
<td>1:1.5</td>
<td>94 ± 14</td>
<td>0.62</td>
<td>12.4 (12.0)</td>
<td>0.45</td>
<td>3.5 %</td>
</tr>
<tr>
<td>PCPDTBT: PCBM</td>
<td>1:2</td>
<td>96 ± 17</td>
<td>0.64</td>
<td>8.9 (9.0)</td>
<td>0.42</td>
<td>2.4 %</td>
</tr>
<tr>
<td>DT-PDPP2T-TT: PCBM</td>
<td>1:3</td>
<td>267 ± 8</td>
<td>0.71</td>
<td>9.2 (9.1)</td>
<td>0.62</td>
<td>4.0 %</td>
</tr>
</tbody>
</table>

6.3.2 Dielectric constant in studied systems

The geometric capacitance in PTB7: PCBM and PCPDTBT: PCBM are characterized using bias-dependent impedance measurements at 1 kHz, and the obtained $1/C^2$-bias plots are shown in Figure 6.3 in comparison to P3HT: PCBM and DT-PDPP2T-TT: PCBM. The geometric capacitance values are taken following the methodology shown in Chapter 5 and the obtained $C_{geo}$, as well as film thickness and calculated dielectric constant using Equation 3.7, are listed in Table 6.2. A dielectric constant of 4.0 in PTB7: PCBM and 3.1 in PCPDTBT: PCBM was calculated and both of which are in line with typically assumed values around 3 - 4.$^{[12]}$
Figure 6.3 1/C²-voltage plots measured in PTB7: PCBM and PCPDTBT: PCBM devices, compared with that in DT-PDPP2T-TT: PCBM and P3HT: PCBM devices. All devices were measured at 1 kHz.

Table 6.2 List of geometric capacitance and calculated dielectric constant values calculated from Figure 6.2.

<table>
<thead>
<tr>
<th></th>
<th>C_{geo} (nF)</th>
<th>Thickness (nm)</th>
<th>ε_r</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT: PCBM</td>
<td>2.9 ± 0.2</td>
<td>65 ± 5</td>
<td>3.5 ± 0.3</td>
</tr>
<tr>
<td>PTB7: PCBM</td>
<td>2.3 ± 0.3</td>
<td>94 ± 14</td>
<td>4.0 ± 0.6</td>
</tr>
<tr>
<td>PCPDTBT: PCBM</td>
<td>1.8 ± 0.3</td>
<td>96 ± 17</td>
<td>3.1 ± 0.5</td>
</tr>
<tr>
<td>DT-PDPP2T-TT: PCBM</td>
<td>1.35 ± 0.05</td>
<td>267 ± 8</td>
<td>6.8 ± 0.1</td>
</tr>
</tbody>
</table>

6.3.3 Charge carrier mobility

Charge carrier mobility in PTB7: PCBM and PCPDTBT: PCBM are characterized using photo-CELIV and the obtained photo-CELIV transients under varying delay times are shown in Figure 6.4 in comparison with P3HT: PCBM and DT-PDPP2T-TT: PCBM. Both PCPDTBT: PCBM and PTB7: PCBM transients shown in Figure 6.4 were measured
under $U_{\text{max}}$ of 2 V and $t_{\text{pulse}}$ of 10 µs, while P3HT: PCBM transient were measured under $U_{\text{max}}$ of 1 V and $t_{\text{pulse}}$ of 5 µs and DT-PDPP2T-TT: PCBM transients were measured under $U_{\text{max}}$ of 1 V and $t_{\text{pulse}}$ of 10 µs. With increasing delay time, a strong decrease in $t_{\text{max}}$ was observed in P3HT: PCBM device while PCPDTBT: PCBM and DT-PDPP2T-TT: PCBM devices showed no strong delay time dependence, and PTB7: PCBM showed an increase in $t_{\text{max}}$ at longer delay time. This delay time dependence of $t_{\text{max}}$ and thus mobility can be better demonstrated in Figure 6.5 where the mobility is plotted as a function of delay time for the four devices. Unlike the P3HT: PCBM device which showed a decreasing $t_{\text{max}}$ at longer delay times, the $t_{\text{max}}$ in the other three devices are relatively independent of delay time, suggesting diffusion controlled recombination as demonstrated in Chapter 3. In PTB7: PCBM a slight decrease in mobility was observed at increasing delay times. This is most likely due to the relaxation of free carriers into the trap states.

Using Equation 3.5 the charge carrier mobility for PTB7: PCBM and PCPDTBT: PCBM are calculated and listed in Table 6.3 together with that in P3HT: PCBM and DT-PDPP2T-TT: PCBM. Among the four devices compared, DT-PDPP2T-TT: PCBM showed the highest mobility of $1.8 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$, and PCPDTBT: PCBM has carrier mobility over an order of magnitude lower than DT-PDPP2T-TT: PCBM. PTB7: PCBM showed a carrier mobility of $8.25 \times 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$, which is slightly higher than that in P3HT: PCBM. The mobility values obtained from PTB7: PCBM and PCPDTBT: PCBM are similar to literature values, where a mobility of $1.3 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ for PTB7: [70]PCBM$^{[13]}$ and $4 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ for PCPDTBT: [60]PCBM$^{[14]}$ was reported. Using the obtained mobility, the Langevin recombination coefficient $\beta_L$ could also be calculated for the four devices (Equation 3.4), and the obtained values are also listed in Table 6.3.
Figure 6.4 Photo-CELIV transients characterized in PTB7: PCBM (b) and PCPDTBT: PCBM (c) devices under increasing delay times at 100 µJ cm\(^2\), compared with that P3HT: PCBM (a) and DT-PDPP2T-TT: PCBM (d). PCPDTBT: PCBM and PTB7: PCBM were measured under \(U_{\text{max}}\) of 2 V and \(t_{\text{pulse}}\) of 10 µs, while P3HT: PCBM was measured under \(U_{\text{max}}\) of 1 V and \(t_{\text{pulse}}\) of 5 µs and DT-PDPP2T-TT: PCBM was measured under \(U_{\text{max}}\) of 1 V and \(t_{\text{pulse}}\) of 10 µs.
Figure 6.5 Carrier mobility on the log scale plotted as a function of delay time, compared between four measured devices. Mobility values calculated from transients shown in Figure 6.4 using Equation 3.5.

Table 6.3 List of calculated carrier mobility, dielectric constant and Langevin recombination coefficient $\beta_L$ in four devices.

<table>
<thead>
<tr>
<th>Material</th>
<th>Mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)</th>
<th>$\varepsilon_r$</th>
<th>$\beta_L$ ($\text{cm}^3\text{s}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT:PCBM</td>
<td>$4.83 \times 10^{-5}$</td>
<td>3.5</td>
<td>$2.8 \times 10^{-11}$</td>
</tr>
<tr>
<td>PTB7:PCBM</td>
<td>$8.25 \times 10^{-5}$</td>
<td>4.0</td>
<td>$3.7 \times 10^{-11}$</td>
</tr>
<tr>
<td>PCPDTBT:PCBM</td>
<td>$1.32 \times 10^{-4}$</td>
<td>3.1</td>
<td>$7.7 \times 10^{-11}$</td>
</tr>
<tr>
<td>DT-PDPP2T-TT:PCBM</td>
<td>$1.8 \times 10^{-3}$</td>
<td>6.9</td>
<td>$4.7 \times 10^{-10}$</td>
</tr>
</tbody>
</table>

6.3.4 Charge density decay kinetics

TRCE was carried out on PTB7: PCBM and PCPDTBT: PCBM devices, and the charge density decay at saturated excitation (10 $\mu$J cm$^{-2}$) is shown in Figure 6.6 in comparison with P3HT: PCBM and DT-PDPP2T-TT: PCBM, also under 10 $\mu$J cm$^{-2}$ excitation. Largest charge carrier density was observed in the P3HT: PCBM device up to 500 $\mu$s,
followed by PTB7: PCBM. PCPDTBT: PCBM showed slightly higher charge carrier density than DT-PDPP2T-TT: PCBM, the latter of which has the lowest charge density over the whole investigated timescale in the four systems compared. Biphasic kinetics is observed in P3HT: PCBM, PTB7: PCBM and PCPDTBT: PCBM devices, where a change in kinetics appears at 5 μs. The biphasic kinetics in DT-PDPP2T-TT: PCBM, although present (see Chapter 4), was much less pronounced compared to the other three devices. It is noted that the low charge density could be caused by the larger thickness of the device compared to other devices, which has been shown to decrease the charge density.[15]

6.3.5 Bimolecular recombination coefficient $\beta$

The bimolecular recombination coefficient $\beta$ calculated from Figure 6.6 using Equation 3.9 is shown in Figure 6.7a. The $\beta$ values of the four devices at 500 ns are listed in Table 6.4. Similar $\beta$ values were observed in PCPDTBT: PCBM and DT-PDPP2T-TT: PCBM devices at 500 ns whereas smaller $\beta$ values were observed in PTB7: PCBM, and the smallest $\beta$ was observed in P3HT: PCBM. At longer timescale the difference in $\beta$ between four devices decreased, and after 100 μs all four devices showed $\beta$ of similar magnitudes.
The smaller $\beta$ values at early timescale observed in P3HT: PCBM is in agreement with reduced bimolecular recombination in P3HT: PCBM caused by slow mobility and non-Langevin behaviours. PTB7: PCBM also showed $\beta$ smaller than PCPDTBT: PCBM and DT-PDPP2T-TT: PCBM, suggesting slower recombination in the system.

The large $\beta$ value observed in DT-PDPP2T-TT: PCBM device suggests fast bimolecular recombination, however the large FF achieved at large thickness in the same device suggests charge extraction faster than bimolecular recombination due to the high mobility in the system. The large $\beta$ observed in DT-PDPP2T-TT: PCBM is most likely due to its high mobility, which is over an order of magnitude higher than other devices (Table 6.4). In order to account for the effect of carrier mobility, $\beta$ is normalized to mobility $\mu$ for each system and the obtained values are plotted as a function of time, as shown in Figure 6.7b. The $\beta/\mu$ values calculated using $\beta$ at 500 ns are also listed in Table 6.4, along with $\beta/\beta_L$ values. When the difference in mobility is accounted for, DT-PDPP2T-TT: PCBM showed the smallest $\beta/\mu$ values throughout the investigated timescale. P3HT: PCBM showed higher $\beta/\mu$ value compared to DT-PDPP2T-TT: PCBM, which was approximately 2 times larger than that in DT-PDPP2T-TT: PCBM at early timescale of 500 ns. PTB7: PCBM device showed a $\beta/\mu$ value approximately an order of magnitude higher than that in DT-PDPP2T-TT: PCBM device at 500 ns, and PCPDTBT: PCBM device showed a $\beta/\mu$ value two times that in PTB7: PCBM at 500 ns. The time dependence of $\beta/\mu$ values is different between P3HT: PCBM and the other devices, where weaker time dependence was observed in P3HT: PCBM device while the other three devices showed similar time dependence with a larger decrease in $\beta/\mu$ at long timescale. It is noted that the bimolecular reduction factor $\xi$ for P3HT: PCBM ($\beta = 1.7 \times 10^{-12}$, $\xi = 0.07$, see Chapter 3) was not as low as previously published ($\beta = 2 \times 10^{-13}$, $\xi = 10^{-4.76}$), which might be due to the difference in film morphology between literature and fabricated here. In an optimized P3HT: PCBM device the $\beta/\mu$ values should be lower than measured here, but the overall trend remains unchanged.

When normalized to mobility, DT-PDPP2T-TT: PCBM device showed the smallest $\beta/\mu$ values. This is also supported by the small $\beta/\beta_L$ value listed in Table 6.4. As shown in Chapter 4, the DT-PDPP2T-TT: PCBM device did not show the typical characteristics of systems with significantly reduced recombination. Thus, the low $\beta/\mu$ value in the device is attributed to the high dielectric constant. This can be understood from the Equation 3.4,
which suggests that $\beta$ in the case of trap-free three dimensional diffusion dominated recombination is only dependent on mobility and dielectric constant. The high dielectric constant balances high mobility, as a result similar $\beta$ values were obtained in DT-PDPP2T-TT: PCBM and PCPDTBT: PCBM.

As demonstrated in Chapter 3, the difference in active layer thickness influences the experimentally obtained charge density and $\beta$ values, leading to apparent defence in recombination kinetics. Here it is demonstrated again that the comparison between $\beta$ values should be carried out carefully, as $\beta$ values alone are insufficient to determine the difference between recombination kinetics in these systems. As shown in Chapter 3, higher $\beta$ was observed when the active layer thickness is large. This suggests that in a DT-PDPP2T-TT: PCBM device with thinner active layer around 100 nm, the obtained $\beta$ and $\beta/\mu$ values will likely be lower than observed here. In DT-PDPP2T-TT: PCBM devices with thinner active layer, therefore, more reduced recombination will be observed, which further supports the conclusions made here. The thickness dependence of $\beta$ was indeed observed where thinner devices showed lower $\beta$ values, see Figure A-4 in Appendix.
Figure 6.7 (a) $\beta$ plotted as a function of time, calculated from Figure 6.6; (b) $\beta$ values normalized to charge carrier mobility, plotted as a function of time. Mobility values listed in Table 6.3 were used.

<table>
<thead>
<tr>
<th></th>
<th>$\beta_L$ ($\text{cm}^3\text{s}^{-1}$)</th>
<th>$\beta_{500\text{ns}}$ ($\text{cm}^3\text{s}^{-1}$)</th>
<th>$\beta_{500\text{ns}}$/Mobility ($\text{cm}^3\text{V}^{-1}\text{s}^{-1}$)</th>
<th>$\beta_{500\text{ns}}/\beta_L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT: PCBM</td>
<td>$2.8 \times 10^{-11}$</td>
<td>$1.8 \times 10^{-12}$</td>
<td>$3.7 \times 10^{-8}$</td>
<td>0.064</td>
</tr>
<tr>
<td>Blend</td>
<td>Charge carrier density (cm^{-3})</td>
<td>Lifetime (µs)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------------</td>
<td>---------------------------------</td>
<td>---------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PTB7: PCBM</td>
<td>$3.7 \times 10^{-11}$</td>
<td>$0.24$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCPDTBT: PCBM</td>
<td>$7.7 \times 10^{-11}$</td>
<td>$0.36$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DT-PDPP2T-TT: PCBM</td>
<td>$4.7 \times 10^{-10}$</td>
<td>$0.045$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 6.3.6 Charge carrier lifetimes

Charge carrier lifetimes in the four devices calculated from Figure 6.6 using Equation 3.2 are plotted as a function of charge density in Figure 6.8a. The charge density between four devices showed a large variation over two orders of magnitude. In DT-PDPP2T-TT: PCBM, the charge carrier density saturates at $1 \times 10^{16}$ cm^{-3} whereas the saturated charge density in P3HT: PCBM is over an order of magnitude higher. In P3HT: PCBM, PTB7: PCBM and DT-PDPP2T-TT: PCBM, weaker dependence of carrier lifetime on charge density was observed at low charge densities compared to that at higher charge densities. Therefore, carrier lifetime between the studied four systems at the same charge density are incomparable, where P3HT: PCBM is at low charge density regime and DT-PDPP2T-TT: PCBM is at high charge density regime. For this reason the carrier lifetime was plotted as a function of $V_{OC}$, which was characterized from photovoltage decay and are matched to the charge density values. Charge carrier lifetimes plotted as a function of $V_{OC}$ for all four devices are shown in Figure 6.8. At $V_{OC}$ above 0.6 V, the smallest lifetime values were obtained in PTB7: PCBM device. PCPDTBT: PCBM showed slightly longer lifetime than PTB7: PCBM, and DT-PDPP2T-TT: PCBM showed the longest lifetime at $V_{OC}$ below 0.7 V. Very similar lifetime values around $4 \mu s$ were observed between P3HT: PCBM and DT-PDPP2T-TT: PCBM at $V_{OC}$ above 0.7 V. At lower $V_{OC}$, P3HT: PCBM showed the shortest lifetime, while PTB7: PCBM and PCPDTBT: PCBM showed carrier lifetime of similar values and DT-PDPP2T-TT: PCBM showed the longest lifetimes. The long lifetime at high $V_{OC}$ corresponds to the lifetime of free carriers, thus suggesting slow recombination of free carriers in DT-PDPP2T-TT: PCBM compared to PTB7: PCBM and PCPDTBT: PCBM. This is in agreement with the findings in Section 6.3.5, where the high dielectric constant in DT-PDPP2T-TT has been shown to reduce the bimolecular recombination in the system.
It has been reported that the charge carrier lifetime is also dependent on active layer thickness, where longer lifetime was observed for thinner devices comparing at the same charge density.\cite{15} This was attributed to the increased spatial separation between electrons and holes under the built-in potential in thinner devices, whereas in thick devices the charge carriers are more homogeneously distributed. For this reason the thickness difference in devices shown in Figure 6.8 is considered here. The DT-PDPP2T-TT: PCBM device has a notably larger thickness of 267 nm compared to other devices with active layer thickness around 100 nm. For this reason DT-PDPP2T-TT: PCBM as well as P3HT: PCBM devices with different active layer thickness were also characterized, where no notable lifetime dependence on active layer thickness was observed in the lifetime-Voc plot (see Appendix Figure A-5). These results suggest that conclusions made above on charge carrier lifetime are still valid when thickness difference is taken into consideration.
Figure 6.8 (a) Charge carrier lifetime calculated from Figure 6.6 for the four devices, plotted as a function of charge density; (b) carrier lifetime plotted as function of $V_{oc}$, which was measured from photovoltage decay.
6.4 The effect of dielectric screening on bimolecular recombination

Figure 6.7b shows that DT-PDPP2T-TT: PCBM system had the lowest bimolecular recombination coefficient to mobility ratio. As has been shown in Chapter 4, DT-PDPP2T-TT: PCBM has Langevin recombination, therefore the low $\beta/\mu$ values in DT-PDPP2T-TT: PCBM can only be explained by the effect of strong dielectric screening on Coulomb capture radius $r_c$:

$$r_c = \frac{e^2}{4\pi\varepsilon_0\varepsilon_r kT}$$  \hspace{1cm} (6.3).

Increased dielectric screening in DT-PDPP2T-TT: PCBM leads to a smaller Coulomb capture radius $r_c$ of around 2 nm compared to $r_c$ around 4 nm in low dielectric constant systems (3.6 nm for P3HT: PCBM, 4.1 nm for PCPDTBT: PCBM and 3.2 nm in PTB7: PCBM). In turn, the smaller $r_c$ leads to smaller $\beta$, as it takes longer for the electrons and holes to diffuse close to each other to be captured by their Coulomb interaction. The effect of faster mobility caused by faster charge transport is already considered in this analysis, as the measured $\beta$ is normalized to mobility.

The effect of dielectric screening on charge transport can be further analyzed by comparing the diffusion time of free carriers and charge lifetime. The diffusion of carriers can be calculated from diffusion coefficient $D$ following Einstein’s relation:

$$D = \mu k_B T / e$$  \hspace{1cm} (6.4)

Using obtained carrier mobility in Table 6.3, a diffusion coefficient value of $4.6 \times 10^{-5}$ cm$^2$ s$^{-1}$ for DT-PDPP2T-TT: PCBM, $3.4 \times 10^{-6}$ for PCPDTBT: PCBM, $1.2 \times 10^{-6}$ cm$^2$ s$^{-1}$ for P3HT: PCBM and $2.1 \times 10^{-6}$ cm$^2$ s$^{-1}$ for PTB7: PCBM is calculated. Using a one dimensional diffusion equation (Fick’s first law, Equation 6.5), the time it takes for charges to diffuse over half the typical domain size in efficient organic photovoltaic devices (5 nm) can be calculated:

$$J = -D \frac{\delta n}{\delta x}$$  \hspace{1cm} (6.5).

The exact charge distribution and therefore the charge concentration gradient under open circuit conditions cannot be determined from the measurements. For simplicity, it is
assumed that $\delta n$ equals the maximum charge density measured at saturation laser density at 1 μs (Figure 6.6; $1 \times 10^{16}$, $3.5 \times 10^{16}$, $5.2 \times 10^{16}$ and $3 \times 10^{17}$ cm$^{-3}$ for DT-PDPP2T-T: PCBM, PCPDTBT: PCBM, PTB7: PCBM and P3HT: PCBM, respectively) and $\delta x$ equals the thickness of the photoactive layer. From the diffusion current, the diffusion velocity $v$ is calculated as $v = J/n$, from which the time to diffuse over a 5 nm distance is calculated. The values are 290 ns, 1.5 μs, 2.2 μs and 2.9 μs for DT-PDPP2T-TT: PCBM, PCPDTBT: PCBM, PTB7: PCBM and P3HT: PCBM, respectively. The calculated diffusion time in DT-PDPP2T-TT: PCBM device is significantly shorter compared to the other systems, agreeing with the high diffusion coefficient originated from high carrier mobility. It is noted that outside the Coulomb capture radius at open circuit voltage, the average diffusion distance for electrons and holes could be much longer than the typical domain size since charges are likely to follow random paths. Nevertheless, an interesting observation is that only in DT-PDPP2T-TT: PCBM system is the calculated diffusion time significantly shorter than the carrier lifetime of 4 μs. The carrier lifetime in PCPDTBT: PCBM and PTB7: PCBM and P3HT: PCBM blends (1.1 μs and 1.2 μs, respectively) are shorter than the calculated diffusion times, and the charge lifetime of 3.1 μs in P3HT: PCBM is slightly longer, but comparable to the charge diffusion time. The charge carrier lifetime much longer than diffusion time suggests that, the probability for charges to meet and recombine is reduced despite the fast charge diffusion in DT-PDPP2T-TT: PCBM devices.

The reduced recombination due to strong dielectric screening is kinetically different from reduced recombination in non-Langevin systems. In a non-Langevin system such as P3HT: PCBM, the TOF transient showed a distinct extraction time $t_e$ whereas in diffusion-dominated systems an exponential decay without distinctive $t_e$ is typically observed. This is indeed observed in a comparison of TOF results between P3HT: PCBM, PCPDTBT: PCBM and DT-PDPP2T-TT: PCBM, as shown in Figure 6.9. The longest TOF transient is observed in P3HT: PCBM device with a clear $t_e$ feature. On the other hand, PCPDTBT: PCBM and DT-PDPP2T-TT: PCBM devices showed exponential decay transients much shorter TOF transients compared to P3HT: PCBM. Furthermore, in saturated photo-CELIV transients of a non-Langevin system, the reduced bimolecular recombination leads to photo-CELIV transients with extracted charge largely exceeding the capacitive charge ($Q_e/CU_0 >> 1$), and a decrease in $t_{max}$ at increasing delay times is expected (Figure 6.4). This is because the time to reach extraction current maximum $t_{max}$
in a non-Langevin system is controlled by the extraction time rather than the transit time. As charge density decreases with increasing delay time due to recombination, $t_{\text{max}}$ shifts to shorter time scales. Whereas in systems with diffusion-dominated recombination, the extracted charge is similar to the capacitive charge and $t_{\text{max}}$ is expected to be relatively constant at all light intensities and delay times. This is indeed observed in Figure 6.5, where relatively constant mobility was observed at increasing delay times for DT-PDPP2T-TT: PCBM, PCPDTBT: PCBM and PTB7: PCBM, all of which showed diffusion-dominated recombination. In summary, the results further confirmed that bimolecular recombination in DT-PDPP2T-TT: PCBM is not of non-Langevin characteristics, and the reduced recombination can only be caused by the increased dielectric screening.

![Figure 6.9 Comparison of saturated TOF transients measured in DT-PDPP2T-TT: PCBM, PCPDTBT: PCBM and P3HT: PCBM. All shown transients are measured using a loading resistor of 1 kΩ and an extraction bias of 2 V.](image)
6.5 Conclusion

This chapter answered the question raised at the end of Chapter 4 regarding the effect of high dielectric constant in bimolecular recombination kinetics. Bimolecular recombination kinetics in four different systems was compared. Bimolecular recombination coefficient values similar to PCPDTBT were observed at early timescales using a charge extraction technique, despite the order of magnitude higher charge mobility (1.8 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}). When the difference in carrier mobility is considered, DT-PDPP2T-TT: PCBM which has the highest dielectric constant showed \( \beta/\mu \) values a factor of two lower than that in P3HT: PCBM and over an order of magnitude lower than that in PTB7: PCBM and PCPDTBT: PCBM. The recombination kinetics in DT-PDPP2-TT: PCBM showed clear characteristics of diffusion-dominated recombination despite having a low reduction factor \( \xi \). The reduced recombination is explained by the strong dielectric screening, and as a result large thickness can be achieved without sacrificing charge transport properties. Thus increasing dielectric constant in the PSC system can be particularly useful especially when the carrier mobility is high, and can potentially lead to efficient PSC devices with large thickness.

As shown in this chapter, the smaller \( \beta/\mu \) caused by increased dielectric screening is particularly beneficial for systems with high charge carrier mobility and diffusion-controlled recombination. Enhanced dielectric screening balances the increased \( \beta \) caused by high mobility in DT-PDPP2T-TT: PCBM, leading to very similar \( \beta \) at 1 \( \mu \text{s} \) in DT-PDPP2T-TT: PCBM and PCPDTBT: PCBM was observed despite DT-PDPP2T-TT: PCBM having a one order of magnitude higher mobility. This raises an interesting question: can bimolecular recombination in a low dielectric screening system be reduced by the addition of a high dielectric constant polymer like DT-PDPP2T-TT?

Ideally, if everything in the host system remains unchanged after adding in the DT-PDPP2T-TT polymer, the dielectric screening of the active layer media will be increased and the bimolecular recombination will be reduced. In order to effectively increase the dielectric screening of the media, the amount of DT-PDPP2T-TT added into the system need to be large enough to affect the whole active layer assuming even distribution of DT-PDPP2T-TT over the whole film. This will inevitably affect the absorption profile of the host system and the film morphology, which will likely change the recombination kinetics in the host system. In order to independently investigate the effects of increased
dielectric screening on a low dielectric constant system without changing charge transport and recombination in the host system, cascade hole transfer from DT-PDPP2T-TT to the host system polymer is desired so that the recombination kinetics in the ternary blend will be dominated by the host system. The selection of the host system, the examination of hole transfer, and further studies on dielectric screening and recombination kinetics in DT-PDPP2T-TT containing ternary blend will be carried out in Chapter 7.

6.6 References

Chapter 7 Recombination in Ternary Blend Solar Cells with a High Dielectric Constant Polymer
7.1 Introduction

7.1.1 Background

As demonstrated in the previous chapters, high dielectric constant in DT-PDPP2T-TT polymer and its PCBM blends was measured. Reduced recombination was observed in DT-PDPP2T-TT: [60]PCBM devices, which was caused not by non-Langevin behaviour but by enhanced dielectric screening decreasing the Coulomb capture radius. Based on these conclusions, in this chapter a further question is raised: when a high dielectric constant polymer is added into a host PSC system with low dielectric constant, how does the high dielectric constant polymer influence dielectric screening and bimolecular recombination in the ternary blend?

The influence of enhanced dielectric screening in a ternary system is expected to be much more complicated, because the presence of three different components in the same BHJ blend not only increases the number of bimolecular recombination pathways from one to three compared to the binary system, but also significantly complicates the characterisation of film morphology. Also, enhanced dielectric screening may lead to smoothing of the energetic landscape[1] and reduce the activation energy for charge carrier hops,[2] potentially leading to increased charge mobility in the system. To investigate the influence of increased dielectric screening independent of charge transport and recombination kinetics in different components, it is desired to have a system where charge transport and recombination is dominated by the host system instead of DT-PDPP2T-TT: PCBM. In this case hole carriers generated in DT-PDPP2T-TT will transfer to the host system donor and electrons to the acceptor, and the charge carrier transport and recombination is expected to be dominated by the host polymer: acceptor blend.

As introduced in Chapter 1, in a donor1: donor2: acceptor (D1: D2: A) type ternary blend system, the hole transfer has two types of mechanisms:[3] hole transfer is either present between the two polymer donors, or hole transfer between polymers is absent and hole transport is independently carried out within each donor phase (Figure 7.1). For hole transfer to take place in a D1 : D2: A type ternary blend system, cascade energy levels with an energetic offset has been suggested necessary in order to provide sufficient driving force. However, no literature support was found suggesting a minimum driving force required for charge transfer between two semiconducting polymers. Theoretically,
in a donor / acceptor blend with cascade energy levels, the electrons always transfer to a lower energy level and hole transfer is always from low to a high energy level. The same rule applies to charge transfer in ternary blend systems, as illustrated in Figure 7.1a. As a result, the electron transport is predominantly through the acceptor and the hole transport through the polymer component with shallower HOMO level. Therefore, charge carrier recombination, which takes place at interfaces between electron and hole transport domains, will take place primarily between the polymer with highest HOMO and the acceptor. This has indeed been observed in P3HT:PCPDTBT: [60]PCBM\cite{4,5} and P3HT: Si-PCPDTBT: [60]PCBM,\cite{6} where rapid hole transfer from the low HOMO PCPDTBT to the high HOMO P3HT was observed starting at less 1 ps, with a characteristic relaxation time of 140 ps. Koppe et al. investigated the bimolecular recombination in P3HT: PCPDTBT: PCBM using bulk-generation TOF,\cite{5} where ternary blend devices after thermal annealing showed a TOF transient with distinctive $t_e$ which is characteristic of systems with significantly reduced recombination, while the device without thermal annealing showed a transient lacking such feature. Non-Langevin characteristics after thermal annealing are characteristic of recombination in rr-P3HT: PCBM. This is a clear indication that the charge recombination in P3HT: PCPDTBT: PCBM ternary blend is dominated by the P3HT: PCBM pathways, further confirming the presence of charge transfer between PCPDTBT and P3HT.

On the other hand, if the HOMO offset between D1 and D2 is not large enough to drive hole transfer (as in Figure 7.1b), charge carrier transport will be carried out independently at D1: A and D2: A interfaces. In this case the ternary blend is essentially equivalent to two binary blend subcells connected in parallel in a tandem device, where hole carriers generated in each polymer donor transport within the donor phase without transferring to the other polymer phase.\cite{7} Since the hole carriers are transported through the domains they are generated in, the recombination between each polymer component and acceptor is independent, and the observed recombination kinetics would be a simple overlay of the two.

Above considerations are based on the energy level offset. However, there are also a number of morphological requirements in the ternary system. Due to the different solubility of polymers in different solvents and the difference in polymer compatibility, the film morphology and domain sizes in ternary devices can be vastly different from that
in binary devices. In order to facilitate charge transfer in the ternary system, ideally D2 should locate at the interface between D1 and the acceptor, in which case it acts as a sensitizer; in systems with no charge transfer between D1 and D2, on the other hand, three percolating networks of D1, D2 and A should be present for electron and hole transport.

Figure 7.1 (a) Schematic of a D1: D2: A ternary system with charge transfer between polymer donors; (b) schematic of a D1: D2: A system where charge transfer between polymer donors is absent.

In order to independently investigate the effects of increased dielectric screening on a low dielectric constant system without changing charge transport and recombination in the host system, a basic requirement is that the HOMO of the host system polymer should be shallower than that in DT-PDPP2T-TT so that the recombination kinetics in the ternary blend will be dominated by the host system. A low band gap polymer with a HOMO level of -4.9 eV, namely PCPDTBT, is used as the host system donor. The energetics in the ternary blend device consisting of PCPDTBT, DT-PDPP2T-TT and PCBM is shown in Figure 7.2. The HOMO level offset between PCPDTBT and DT-PDPP2T-TT is estimated to be 0.2 eV calculated from reported energy levels (see Figure 7.2), allowing holes to transfer from DT-PDPP2T-TT to PCPDTBT while blocking hole transfer from PCPDTBT to DT-PDPP2T-TT. The cascade energy levels allow the hole transfer between DT-PDPP2T-TT and PCPDTBT to take place. If hole transfer is indeed present from DT-PDPP2T-TT to PCPDTBT and hole transport is dominated by the PCPDTBT domains, the charge carrier mobility in ternary blends will be relatively unaffected by the addition of high mobility DT-PDPP2T-TT. On the other hand, to effectively increase the dielectric
screening of the media, the amount of DT-PDPP2T-TT added into the system need to be large enough to affect the whole active layer, assuming an even distribution of DT-PDPP2T-TT over the whole film. This will inevitably affect the absorption profile of the host system and the film morphology, which will likely change the charge mobility and recombination kinetics in the host system.

When studying charge carrier transport and recombination kinetics in the PCPDTBT: DT-PDPP2T-TT: PCBM ternary system, several parameters are used to determine the charge transfer mechanism. In transient absorption spectroscopy, transient species generated from different ternary blend components can be distinguished if their polaron absorptions have different wavelengths. Charge transfer processes are reflected in the change of different polaron concentrations, which are in turn reflected in the increase and decrease of relative magnitude of corresponding polaron peaks in the TAS spectra. Charge transfer can thus be characterized by comparing the TAS spectra between ternary blends with different blending ratio and the binary blends.

The ternary blend $V_{OC}$ strongly depends on the charge transport mechanism, and two types of $V_{OC}$ dependence on ternary content ratio has been reported in D1: D2: A type ternary blends.\[8\] The first type is tuneable $V_{OC}$ with values intermediate between two binary systems, the mechanism of which is still under debate. One of the plausible explanations is the formation of alloy-like microstructure between two donors, resulting in CT state energy tuneable by the alloy component.\[9\] The formation of alloy structure would require similar chemical structure and good miscibility between ternary components. The second type is the pinning of ternary blend $V_{OC}$ to the $V_{OC}$ in one of the two binary systems.\[10\] In a PCPDTBT: DT-PDPP2T-TT: PCBM ternary blend, if hole transport is dominated by PCPDTBT, the $V_{OC}$ of the ternary blend will likely be determined by the $V_{OC}$ in PCPDTBT: PCBM binary blend devices; if carrier transfer is absent, the $V_{OC}$ is likely to scale with the ternary blending ratio. For the charge carrier mobility measurement, as two donors are present in the ternary blend, theoretically speaking three different mobility values exist in the ternary system: the hole mobility in PCPDTBT and DT-PDPP2T-TT, and electron mobility in PCBM. Therefore analysing photo-CELIV mobility in the ternary blend can be complicated, as the measured mobility will not only be affected by mobility within individual binary blends, the change in morphology will also affect the measured mobility. In an ideal case, assuming the domain
morphology in PCPDTBT, DT-PDPP2T-TT and PCBM unchanged; the measured mobility will largely depend on the charge transfer mechanism. If hole transfer from DT-PDPP2T-TT to PCPDTBT is present resulting in PCPDTBT dominating hole transport, the carrier mobility will be close to that in the PCPDTBT: PCBM binary blend. If hole transport is carried out independently in PCPDTBT and DT-PDPP2T-TT, the ternary blend mobility will likely have a value between that of PCPDTBT: PCBM and DT-PDPP2T-TT: PCBM binary blends, depending on the blending ratio. For recombination kinetic characterizations, as binary PCPDTBT: PCBM and DT-PDPP2T-TT: PCBM showed very similar recombination coefficient values in Chapter 6, the \( \beta \) in PCPDTBT: DT-PDPP2T-TT: PCBM ternary blend devices are also expected to be similar.

![Energy diagram of ternary PCPDTBT: DT-PDPP2T-TT: PCBM blend](image_url)

Figure 7.2 Energy diagram of ternary PCPDTBT: DT-PDPP2T-TT: PCBM blend, along with the energy level of the device electrodes and electron blocking layer. The HOMO and LUMO values in PCPDTBT were taken from reference\(^8\), DT-PDPP2T-TT from reference\(^9\) and [60]PCBM from reference\(^10\). The HOMO and LUMO levels in both PCPDTBT and DT-PDPP2T-TT were determined from cyclic voltammetry, where 0.1 mM tetrabutylammonium hexafluorophosphate solution in acetonitrile was used as electrolyte, platinum as working electrode, Ag/AgCl as reference electrode and calibrated to Fc/Fc+. The HOMO and LUMO levels in PCBM was determined from cyclic voltammetry using a glassy carbon working electrode, platinum as counter electrode and a standard calomel electrode as reference electrode.\(^10\)
7.1.2 Aim and objectives

This chapter aims to investigate the effect of enhanced dielectric screening in ternary blend solar cells using the high dielectric constant polymer DT-PDPP2T-TT. More specifically, this chapter will answer the following questions:

1) Is there hole transfer between DT-PDPP2T-TT and PCPDTBT in PCPDTBT: DT-PDPP2T-TT: PCBM ternary blends? If cascade charge transfer is present, how does it affect the dielectric constant, $V_{OC}$, charge mobility and recombination kinetics in the ternary blends?

2) Will the dielectric constant in PCPDTBT: DT-PDPP2T-TT: PCBM ternary blends increase with increasing the DT-PDPP2T-TT ratio? If so, will the dielectric constant scale with increasing DT-PDPP2T-TT ratio?

3) Does the high dielectric constant in DT-PDPP2T-TT reduce bimolecular recombination in PCPDTBT: DT-PDPP2T-TT: PCBM ternary blend?

To answer these questions, the concentration of DT-PDPP2T-TT in PCPDTBT: DT-PDPP2T-TT: PCBM ternary devices was systematically varied and ternary blend devices with different DT-PDPP2T-TT ratios were fabricated. The dielectric constant values will be characterized using bias-dependent impedance measurements, device performance will be obtained from current-voltage curve at AM1.5, charge mobility will be characterized using photo-CELIV and recombination kinetics will be studied using TRCE technique, all of which were established in Chapter 3 and 4. To examine whether hole transfer is present, transient absorption spectroscopy (TAS) is carried out on ternary blend films, and the ternary blending ratio dependence of $V_{OC}$ and mobility in devices was also examined. To examine possible effects of DT-PDPP2T-TT on ternary blend recombination kinetics, the bimolecular recombination coefficient $\beta$ normalized to mobility and charge carrier lifetime was compared between ternary devices with different DT-PDPP2T-TT ratios.

7.2 Experimental

PCPDTBT (Mw = 40kDa, PDI = 1.15) and [60]PCBM were purchased from Solaris. DT-PDPP2T-TT (OS0300, Lot# YY8090DB, Mw = 72kDa, PDI = 2.5) was purchased from 1-Material. Chloroform (analytical grade, 99.8 %) was purchased from Chem-Supply, o-DCB (anhydrous, 99 %) from Sigma-Aldrich.
Photovoltaic devices were fabricated as follows: pre-patterned ITO substrates with an active area of 0.06 cm$^2$ were cleaned by soninating in detergent, DI water, acetone and isopropanol, each for 15 minutes then blow dried with nitrogen and treated with UV-Ozone for twenty minutes. Poly-(ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT:PSS) (Clevios P, VP Al 4083) was spin coated on the substrates then subsequently annealed at 140 °C for ten minutes to achieve a dry film thickness of around 30 nm. The photoactive layer was deposited via spin coating the hot solution (donor: [60]PCBM ratio is 1:3 by weight in all devices, DT-PDPP2T-TT: [60]PCBM prepared in chloroform with 7.5 vol% o-DCB, the ternary blends prepared in chloroform with 8.3 vol% o-DCB. PCPDTBT: [60]PCBM in CB with 3 vol% diodooctane (DIO)). The active layer thickness was controlled via changing spin speed and measured using a Dektak stylus profilometer. The above processes are carried out under ambient conditions except the polymer solution preparation, which was prepared in an Argon filled glovebox. The Al counter electrode was deposited by thermal evaporation at $\sim 1 \times 10^{-6}$ mbar to achieve thickness of around 100 nm. The complete devices were encapsulated with cover glass using UV-curable epoxy in glovebox for characterizations under ambient conditions. The thickness of the active layer was measured by preparing a film on cleaned glass substrate which is nominally identical as the active layer. The thickness of the film was then measured using Dektak profilometer where a minimum of three scans were taken and the film thickness was calculated as the average of all measured scans.

Film samples for TAS was prepared as follows: glass substrates were cleaned by sonicating in detergent, DI water, acetone and isopropanol, each for 15 minutes then blow dried with nitrogen and treated with UV-Ozone for twenty minutes. Film samples were spin-coated from solutions prepared same as above onto cleaned glass substrates. The spin speed was controlled to make sure the absorbance of the film at excitation wavelength is between 0.3-0.5. The samples were then transferred into the glovebox and sealed in a custom-made quartz cuvette for transient absorption measurements.

Current-Voltage characterizations were carried out using Solar cell I-V curve testing system model IV21L, PV measurements.
Voltage and frequency dependent capacitance was measured using a Zahner IM6 electrochemical workstation. AC oscillation amplitude of 5 mV was used. The voltage bias between -2 V and 2 V and frequency between 1 kHz and 500 kHz was applied.

TRCE measurements were carried out as follows. A pulsed laser (532 nm, Spectra Physics Quanta Ray Lab 170) is used to generate charge carriers within measured devices. A Quanta Ray MOPO was used to tune the pump wavelength for photoexcitation. Excitation pulse of 650 nm was used. The devices were initially held at high impedance using a nanosecond switch (2.2 MΩ impedance, Asama Lab). After a controllable delay time using a digital delay generator (Stanford Research DG535), the switch is opened and the devices are at short circuit condition. The extracted current is measured using an oscilloscope as a function of time (input impedance 50 Ω). The dark response is subtracted to remove the switch noise.

For photovoltage decay, the devices were photoexcited at open circuit (1 MΩ impedance). The voltage decay was recorded as a function of time. The extracted charge is then matched with $V_{OC}$ at each delay time.

To measure photogenerated charge extraction by linearly increasing voltage (photo-CELIV), a pulsed laser (532 nm, Spectra Physics Quanta Ray Lab 170) is used to generate charge carriers within measured devices. A Quanta Ray MOPO was used to tune the pump wavelength for photoexcitation. Excitation pulse of 650 nm was used. The delay time between photoexcitation and voltage ramp application is controlled using a nanosecond switch (2 MΩ impedance, Asama Lab) and a delay generator (Stanford Research DG535). The extraction current is recorded using an oscilloscope, using either the built-in 50 Ω impedance on oscilloscope or a homemade 13.5 Ω resistor in parallel with the 1 MΩ input impedance on oscilloscope (loading resistance $\approx$ 13.5 Ω), depending on the device capacitance.

Sub-microsecond transient absorption spectroscopy was carried out as follows: A pulsed laser (Spectra Physics Quanta Ray Lab 170) and a Quanta Ray MOPO were used to generate the laser excitation signal. Excitation wavelength of 640 nm was used for PCPDTBT: PCBM and 500 nm for ternary PCPDTBT: DT-PDPP2TPTT: PCBM blend films, and excitation wavelength of 650 nm was used for DT-PDPP2T-TT: PCBM films. A Xe lamp (Edinburgh Instruments, Xe900) was used as probe light, where a 425 nm
long pass filter was placed in front of the lamp to prevent device heating and UV light degradation. The probe light wavelength was adjusted using a monochromator. The probe light was detected using a silicon photodiode (Femto, HCA-S-200M-SI) for probe wavelength below 1000 nm or an InGaAs photodiode (Femto, HCA-S-200M-IN) for probe wavelength above 1000 nm. The signal from the photodiode was amplified (Femto, DHPVA-200) then collected using a oscilloscope (Tektronics, DPO4054). The data collection in the oscilloscope was synchronized from a trigger signal from the pump laser using a photodiode (Newport, 818-BB-40).

Picosecond transient absorption spectroscopy was carried out on pristine DT-PDPP2T-TT as well as DT-PDPP2T-TT: [60]PCBM 1:3 w/w blend films at Imperial College, London, under the guidance of Dr. Tracey Clarke. Picosecond transient absorption spectroscopy was carried out using a commercially available transient absorption spectrometer, HELIOS (Ultrafast systems). Samples were excited with a pulse-train generated by an optical parametric amplifier, TOPAS (Light conversion). Both the spectrometer and the parametric amplifier were seeded with a 1 kHz, 800 nm, 100 fs Solstice Ti: sapphire regenerative amplifier (Newport Ltd.). An excitation wavelength of 650 nm was used. Samples were kept in a cuvette under nitrogen atmosphere.

7.3 Spectroscopy evidence of charge transfer between DT-PDPP2T-TT and PCPDTBT

7.3.1 Selecting pump wavelength for TAS studies

In order to select suitable excitation wavelength for TAS measurements, ground state UV/visible absorption spectra of samples used for TAS measurements were first measured. Figure 7.3a shows the pristine DT-PDPP2T-TT and DT-PDPP2T-TT: [60]PCBM 1:3 w/w blend films, and Figure 7.3b shows PCPDTBT: [60]PCBM as well as ternary blend PCPDTBT: DT-PDPP2T-TT: [60]PCBM films with DT-PDPP2T-TT/ total polymer weight ratio of 20 %, 57 % and 90 %. In typical transmission mode TAS measurements, photoexcitation of the sample is selected at a wavelength where a fraction of polymer molecules is promoted to the excited state. Due to the use of thin film samples (around 100 nm) in TA measurements, the change in optical signal can be extremely small. To
enhance signal to noise ratio, a typical conduct is to choose an excitation pump wavelength at which the ground state optical density of the film is moderate (around or below 0.5) while controlling the output energy of the excitation pump during the measurement. In this way a reasonable signal size can be obtained while avoiding excited state annihilation and saturation effects. Another consideration for excitation wavelength is to avoid overlapping between the transient absorption signal wavelength and the harmonic frequencies generated by the monochromator. While notch filters specifically blocking the harmonics of 532 nm Nd: Yag laser are commercially available, the availability of notch filter in non-standard laser line wavelengths is limited. For the pristine DT-PDPP2T-TT and DT-PDPP2T-TT: [60]PCBM films, as transient absorption features at 1100, 1200 and 1500 nm were observed (see Figure 7.5 and 7.10), the excitation wavelength above 600 below 750 nm should be used. Also, the output wavelength of the MOPO is between 400 and 690 nm. For above considerations an excitation wavelength of 650 nm was used for DT-PDPP2T-TT pristine and PCBM blend samples. The excitation wavelength for binary PCPDTBT: PCBM was selected at 640 nm to avoid the overlay of harmonics generated by the monochromators with the polaron absorption at 1300 nm (see Figure 7.13) by using a 1300 ± 12 nm bandpass filter.
Figure 7.3 (a) UV/visible absorption in pristine DT-PDPP2T-TT and 1:3 w/w DT-PDPP2T-TT: [60]PCBM films and (b) absorption spectra in DT-PDPP2T-TT: PCBM, PCPDTBT: PCBM binary blend films as well as PCPDTBT: DT-PDPP2T-TT: PCBM ternary blends with 90 %, 57 % and 20 % DT-PDPP2T-TT.

To investigate charge transfer in ternary PCPDTBT: DT-PDPP2T-TT: PCBM blends, the best approach is selective photoexcitation of one of the polymers. However, selective excitation of DT-PDPP2T-TT requires excitation wavelength above 800 nm. While the idler beam produced from the MOPO can produce 800 nm output, it requires
rearrangement of the optical setup used for other TAS measurements, which would require repeating of the binary blends TA measurements on the new optical setup. This is a large amount of work and is unpractical considering the timespan of the PhD. Another option is to choose a pump wavelength where both polymers have similar absorption coefficient. In this case the fraction of photoexcited PCPDTBT and DT-PDPP2T-TT depends on the blending ratio, i.e. the larger ratio of a polymer in the blend, the larger fraction of it will be excited. By varying the blending ratio, hole transfer at different generation scenarios, namely the majority of hole carriers generated from DT-PDPP2T-TT, PCPDTBT or equally from both polymers, can be studied. In order to select an appropriate excitation wavelength in the ternary blend, the absorption coefficient, which is defined as the absorbance per unit path length, was calculated from the ground state absorbance ($A$) and thickness ($d$) on the same sample (absorption coefficient = $A/d$). The absorption coefficient for pristine DT-PDPP2T-TT and PCPDTBT films are shown in Figure 7.4. PCPDTBT showed larger absorption coefficient than DT-PDPP-TT between 507 nm and 690 nm, which means that excitation wavelength around 640 – 650 nm, which was used for binary blends, is unsuitable for ternary blends. At 507 nm and 690 nm the absorption coefficient in DT-PDPP2T-TT and PCPDTBT are identical. As 690 nm is very close to the absorption peak of PCPDTBT, the ground state bleaching signal could not be measured using a 690 nm pump wavelength due to weak transmission. For this reason, excitation wavelength at 500 nm is selected for the ternary blends. At 500 nm, the absorption coefficients for PCPDTBT and DT-PDPP2T-TT are 6953 cm$^{-1}$ and 8324 cm$^{-1}$, respectively. It is noted that PCBM also absorbs at 500 nm, evidenced from the strong absorption below 600 nm of the DT-PDPP2T-TT: [60]PCBM sample in Figure 7.3a. From absorption spectra of the polymer: [60]PCBM blend films, the absorption coefficient of PCBM at 500 nm is estimated to be 3855 cm$^{-1}$. The photoexcited PCBM may therefore contribute to hole generation in the ternary blends, where hole transfer from PCBM to both PCPDTBT and DT-PDPP-TT are possible. This will be discussed in further detail below.

To study hole transfer in ternary PCPDTBT: DT-PDPP2T-TT: PCBM, three blending ratios with DT-PDPP2T-TT to total polymer ratio of 90 %, 57 % and 20 % were used, while the total polymer to PCBM ratio was kept constant at 1:3. The fraction of polymer absorption at 500 nm was calculated from polymer blending ratio and absorption coefficient values, as shown in Table 7.1. As the PCBM concentration is kept constant in
all ternary blends, the overall hole contribution from PCBM should also be constant in all ternary blends, at approximately 50%. By using three blending ratios of 90%, 57%, and 20%, three different hole generation scenarios where stronger excitation in DT-PDPP2T-TT, approximately equal in both polymers and stronger excitation in PCPDTBT are included. By comparing TAS spectra and kinetics in these three scenarios the presence of hole transfer from DT-PDPP2T-TT and the dependence of hole transfer on relative blending ratio are obtained.

Figure 7.4 Absorption coefficient calculated for pristine DT-PDPP2T-TT and PCPDTBT films. The dash lines mark 500 nm and 690 nm as a guide for the eye.

Table 7.1 Percentage of light absorption at 500 nm in PCPDTBT: DT-PDPP2T-TT: PCBM ternary blend with three blending ratios.

<table>
<thead>
<tr>
<th></th>
<th>DT-PDPP2T-TT</th>
<th>PCPDTBT</th>
<th>PCBM</th>
</tr>
</thead>
<tbody>
<tr>
<td>90% DT-PDPP2T-TT</td>
<td>47%</td>
<td>4%</td>
<td>49%</td>
</tr>
<tr>
<td>57% DT-PDPP2T-TT</td>
<td>31%</td>
<td>19%</td>
<td>50%</td>
</tr>
<tr>
<td>20% DT-PDPP2T-TT</td>
<td>11%</td>
<td>37%</td>
<td>52%</td>
</tr>
</tbody>
</table>
7.3.2 Sub-microsecond TAS in DT-PDPP2T-TT: [60]PCBM

Sub-microsecond TAS was carried out on a binary DT-PDPP2TPTT: [60]PCBM 1:3 w/w blend films using the selected pump wavelength of 650 nm at excitation density of 10 μJ cm⁻². The obtained TAS spectrum in DT-PDPP2T-TT: PCBM sample is shown in Figure 7.5a. Three absorption peaks were observed in the figure around 900 nm, 1100 nm and 1500 nm. Similar peak magnitude was observed for the 1100 nm and 1500 nm peaks at all plotted timescales, whereas the 900 nm absorption feature showed stronger time dependence. A possible origin for the absorption feature around 900 nm is the Stark effect, which is a shift in energy levels of the ground and/or excited states under an electric field. The Stark effect can be observed in transient absorption measurements when there is a change in permanent dipole moment and/or polarizability induced by photoexcitation (i.e. charge carrier generation). The electro-absorption EA induced by the electric field depends on the strength of the electric field \( E \) and the ground state absorption \( A(\lambda) \):

\[
EA = \frac{dA(\lambda)}{d\lambda} \Delta p E - \frac{1}{2} \frac{dA(\lambda)}{d\lambda} \Delta \alpha E^2 + \frac{1}{2} \frac{d^2A(\lambda)}{d\lambda^2} (\Delta p E)^2 + \ldots
\]  

(7.1)

where \( \Delta \alpha \) is the polarizability and \( \Delta p \) is the permanent dipole moment.[11] In a polymer: PCBM BHJ blend the first term cancels itself when integrated over the bulk of the active layer. The second and third terms are proportional to the first or second order derivative of the ground state absorption spectrum. Stark effect has been PSC systems such as poly(2,5-bis(3-hexadecylthiophen-2-yl) thieno[3,2-b]thiophene (pBTTT): PCBM blend,[11] where an electro-absorption (EA) feature was observed at 630 nm. The spectrum shape of the EA feature in pBTTT: PCBM showed similarity to the first order derivative of the absorption, and the EA amplitude was quadratically proportional to the applied field, suggesting the origin of the Stark effect to be the change in polarizability in pBTTT at ground and excited state.

Following similar methodology as above mentioned literature, to further examine whether the 900 nm feature observed in Figure 7.5a was due to the Stark effect, the normalized TAS spectrum at 200 ns was compared to the first and second order derivative of the absorption spectrum. As thin film samples were used for TAS studied carried out in this chapter, no EA measurement under applied bias was carried out. In Figure 7.5b, it was observed that the first order derivative of the absorption spectrum showed a peak around 847 nm and the second order derivative showed a peak at slightly longer
wavelength of 856 nm. Compared to the 900 nm feature in the TA spectrum, both first and second order derivative peaks showed approximately 50 nm blue shift. It is noted that due to the limited wavelength availability of bandpass filters and the cut-off of band shape due to ground state bleaching, the TA spectrum cannot provide an accurate measurement of the peak wavelength, thus limiting the comparison of TA spectrum and differentiated ground state spectra in detail. Nonetheless, Figure 7.5b suggests the possibility that the 900 nm peak observed in TA spectrum could be caused by Stark effect induced by charge generation.

The possibility of Stark effect present at microsecond timescale is particularly interesting. The presence of Stark effect up to microsecond timescale suggests the strong effect of local electric field even in the bimolecular recombination regime, possibly due to electron-hole pairs with a fixed distance present at microsecond timescale. This can be caused by strengthened dipole moment or stronger polarization which is also correlated with the dielectric screening of the samples. Another interesting observation is that the strong TA signal around 900 nm was observed not only in DT-PDPP2T-TT: PCBM blends but also in pristine DT-PDPP2T-TT films, which will be discussed in further detail below (see Figure 7.10). Due to the lack of an electron acceptor, no driving force for charge separation is present in the pristine polymer film, therefore the strength of the localized field will be much weaker than in polymer: PCBM blends and the presence of TA feature around 900 nm is unexpected. However, a strong signal at 900 nm was observed in the pristine DT-PDPP2T-TT film. One of the possible explanations is the generation of CT states or dissociated charge carriers in the pristine DT-PDPP2T-TT film due to the high dielectric constant.
Figure 7.5 (a) Sub-microsecond TAS spectra at different times for DT-PDPP2T-TT: [60]PCBM 1: 3 w/w blend film, excited at 650 nm under the excitation density of 10 µJ cm\(^{-2}\). (b) Overlay of normalized TA spectrum at 200 ns overlaid with first and second order derivative of the ground state absorption of the measured film. The spectra were measured using bandpass filters.

The decay kinetics of 1100 nm and 1500 nm transient absorption were further characterized to assign these features. The sub-microsecond to microsecond transient decay in DT-PDPP2T-TT: PCBM film at 1100 nm and 1500 nm were measured under a series of excitation densities, as shown in Figure 7.6. Power law kinetics were observed...
at both wavelengths. Power law gradients \( \alpha \) of 0.44 and 0.41 were obtained for the 1100 nm and 1500 nm decays, respectively, suggesting close to identical decay kinetics. Excitation density dependence for the 1100 nm and 1500 nm decay were observed at short timescales prior to 5 μs, where slower decay kinetics was observed at excitation densities below 1 μJ cm\(^{-2}\). At longer timescales, the difference in decay kinetics between high and low excitation densities became much smaller.

Figure 7.6 Transient decay kinetics under a series of excitation densities at (a) 1100 nm and (b) 1500 nm in the DT-PDPP2T-TT: [60]PCBM film, excited at 650 nm. The decay transients were measured using 1100 nm and 1500 nm bandpass filters. The solid lines in figure show fittings to power law decays.
In general, three types of transient species can be observed on microsecond timescales: 1) the polymer polarons, 2) the PCBM anions and 3) the polymer or [60]PCBM triplet excitons. PCBM cations and polymer anions have also been observed, depending on the doping and/or energetics of the system. While geminate recombination has also been observed on microsecond timescales, the power law decay kinetics up to sub-millisecond timescale observed at 1100 nm and 1500 nm strongly suggest that the observed decay cannot be attributed to geminate recombination. The possibility of [60]PCBM triplet is excluded, as the [60]PCBM triplet absorption peaks at 720 nm with a shoulder around 800 nm. To examine if these transient species at 1100 nm and 1500 nm are polymer triplet excitons, the 1100 nm and 1500 nm transients were also measured in air. If polymer triplet excitons are present at either wavelength, the presence of singlet oxygen in air will usually quench the triplet excitons leading to faster decay kinetics in air. As shown in Figure 7.7, no change in decay kinetics was observed at either wavelength, clearly indicating the absence of triplet exciton absorption at these wavelengths. The possibility of these absorption features being DT-PDPP2T-TT triplet excitons is thus excluded.
Figure 7.7 Oxygen quenching kinetics of DT-PDPP2T-TT: [60]PCBM at 1100 nm (a) and 1500 nm (b), measured under excitation density of 10 μJ cm⁻². Bandpass filters were used for all transients.

Therefore, the slow power law kinetics observed at 1100 nm and 1500 nm cannot be ascribed to triplet excitons. The [60]PCBM anion was reported to absorb at 1070 nm,¹⁸ which is very close to the 1100 nm transient feature. To examine whether the 1100 nm absorption originated from [60]PCBM anions, transient absorption measurements on DT-PDPP2T-TT: [70]PCBM film was also carried out.
Figure 7.8 shows a comparison between TAS spectra for DT-PDPP2T-TT: [60]PCBM and DT-PDPP2T-TT: [70]PCBM films, both measured at 10 μJ cm⁻². In both spectra, the absorption peak at 1100 nm was observed. However for the [70]PCBM blend TA spectra the relative magnitude of the 1100 nm peak is 30 % lower than in [60]PCBM peak, suggesting possible [60]PCBM anion contribution to the 1100 nm peak observed in the DT-PDPP2T-TT: [60]PCBM TA spectra. Nonetheless, the presence of a 1100 nm peak in the [70]PCBM blend confirms the presence of a polaron species absorbing at 1100 nm. The presence of 1100 nm polaron peak, along with the 150 nm TA peak in the [70]PCBM blend, are thus attributed to DT-PDPP2T-TT polarons.

Figure 7.8 Comparison between TAS spectra of DT-PDPP2T-TT: [60]PCBM as well as DT-PDPP2T-TT: [70]PCBM films normalized to 1500 nm transient absorption signal, both excited at 650 nm under 10 μJ cm⁻² and plotted at a time delay of 500 ns. The spectra and decay transients were measured using bandpass filters.

Comparing between decay kinetics at 1100 nm and 1500 nm in the DT-PDPP2T-TT: [70]PCBM film, a larger difference in decay kinetics was observed compared to that in the [60]PCBM blend. As shown in Figure 7.9, excitation density dependence was observed at both wavelengths, where an excitation density dependent fast phase prior to 5 μs and an excitation density insensitive slow phase were present at longer timescales.
For the slow phase, the 1500 nm transient showed a faster decay with power law gradient $\alpha = 0.42$. On the other hand, the slow phase at 1100 nm showed a slower decay kinetics with $\alpha = 0.32$. As the possible contribution of [60]PCBM anions are excluded in DT-PDPP2T-TT: [70]PCBM TAS spectra, the transient decay kinetics at 1100 nm and 1500 nm shown in Figure 7.9 are solely contributed from the DT-PDPP2T-TT polarons. It should be noted that due to the limitation of material, only the DT-PDPP2T-TT: [70]PCBM kinetics was measured only once, and further repetition is required to clarify the difference between [60]PCBM and [70]PCBM blend kinetics.

It can be concluded thus far that two TA peaks at 1100 nm and 1500 nm are present for DT-PDPP2T-TT polarons. For the allocation of these absorptions there are a number of possibilities. For example, the two transient absorption features can originate from localized vs. delocalized polarons, or polarons generated in crystalline vs. amorphous domains. They could also be two electronically allowed transitions of the same polaron. As shown in Figure 7.9, different decay kinetics were observed for the 1100 nm and 1500 nm decay in DT-PDPP2T-TT: [70]PCBM. If the two transient signals are two allowed transitions for the same polaron, the decay kinetics for the two peaks are generally expected to be identical. The data presented here are thus insufficient to further ascribe the observed polaron features. To further understand the TA spectra in DT-PDPP2T-TT: PCBM, picosecond TAS was carried out.
Figure 7.9 Transient decay kinetics under a series of excitation densities at (a) 1100 nm and (b) 1500 nm in the DT-PDPP2T-TT: [70]PCBM film, excited at 650 nm. The decay transients were measured using 1100 nm and 1500 nm bandpass filters. The solid lines in figure shows fitting to power law decay and the fitted power gradients $\alpha$ are shown in figure.
7.3.3 Picosecond TAS on pristine DT-PDPP2T-TT and DT-PDPP2T-TT: [60]PCBM

In order to clarify the origin of the DT-PDPP2T-TT polaron features at 1100 nm and 1500 nm, picosecond TAS was carried out on pristine DT-PDPP2T-TT as well as DT-PDPP2T-TT: [60]PCBM blend films under the supervision of Dr Tracey Clarke. Figure 7.10 gives the picosecond transient absorption spectra and the decay kinetics at 1200 nm in pristine DT-PDPP2T-TT measured using an excitation wavelength of 650 nm. Apart from the absorption peak at 900 nm which was attributed to Stark effect as explained above, a broad absorption feature between 1100 nm and 1600 nm was observed in the pristine DT-PDPP2T-TT film, which decayed to zero in approximately 200 ps. This absorption feature was attributed to the singlet excitons and/or intramolecular CT states due to its prompt generation immediately after photoexcitation. The possibility of triplet excitons is excluded due to the short lifetime on picosecond timescale observed for the decay, see Figure 7.10b. The decay transient at 1200 nm was fitted to a double exponential decay \( \Delta OD(t) = A1exp(-t/\tau1)+A2exp(-t/\tau2)+B \), see red dash line in Figure 7.10b; no good fitting was obtained for mono-exponential decay. Two decay lifetimes of 4 ps and 46 ps were obtained from the double exponential fitting. At higher excitation densities, similar double exponential decay was observed. At higher excitation densities, the 4 ps lifetime was consistent while the longer lifetime of 46 ps showed excitation density dependence. When the excitation density increased from 1.5 \( \mu \)J cm\(^{-2}\) to 11 \( \mu \)J cm\(^{-2}\) the longer lifetime decreased from 46 ps to 40 ps. One of the possible reasons for such excitation density dependence of fitted lifetime is the singlet-singlet annihilation, which suggests that further reducing the excitation density is necessary to accurately measure the singlet decay kinetics.
Figure 7.10 (a) ps-TAS spectra of pristine DT-PDPP2T-TT film, excited at 650 nm under 11 µJ cm$^{-2}$; (b) the 1200 nm transient in the pristine DT-PDPP2T-TT film measured at 1.5 µJ cm$^{-2}$ (lowest excitation density measured), fitted to a double-exponential decay (red dash line) as well as mono-exponential decay (blue dash line). The decay time constants for the double exponential fit are listed in figure b.

The ps-TAS on DT-PDPP2T-TT: [60]PCBM blend film was also carried out, as shown in Figure 7.11. A shift of transient absorption peak from around 1200 nm to 1100 nm was observed in Figure 7.11a. As the 1200 nm peak was attributed to singlet excitons and the 1100 nm peaks was attributed to DT-PDPP2T-TT polarons (see Section 7.3.2), the shift
is a clear indication of exciton dissociation into charge carriers. It is noted that the signal above 1400 nm is noisy, making the allocation of transient absorption at longer wavelength difficult; however an increase in ΔOD was observed at wavelengths longer than 1350 nm, strongly suggesting the presence of another transient absorption feature around 1500 nm. This is in agreement with the μs-TAS shown in Figure 7.5. The normalized decay kinetics at 1100 nm and 1450 nm are plotted in Figure 7.11b. The transient decay at both wavelengths showed very similar kinetics. The rise-time of both transients is within the measurement resolution of 1 ps, which is an indication of rapid charge generation on the sub-picosecond timescale.
Figure 7.11 (a) ps-TAS spectra of DT-PDPP2T-TT: [60]PCBM film, excited at 650 nm under 11 μJ cm$^{-2}$; (b) a comparison between the 1100 nm and 1450 nm transients in the measured film at 11 μJ cm$^{-2}$.

Figure 7.12 studies the exciton decay kinetics at 1200 nm in the DT-PDPP2T-TT: PCBM blend film measured at a series of excitation densities. Biphasic kinetics was observed at all excitation densities in the DT-PDPP2T-TT: PCBM blend. The $\Delta$OD decayed to approximately 40% of the initial value at 100 ps, after which a small plateau was observed up to 1 ns, followed by a slow decay phase. For the fast phase, no excitation density dependence was observed. In the slow phase, on the other hand, excitation density dependence was observed. Comparing to 1200 nm decay obtained in pristine DT-PDPP2T-TT, the fast phase in the blend film transient showed a similar decay prior to 10 ps, whereas after 10 ps a slower decay was observed in the DT-PDPP2T-TT: [60]PCBM film (see Figure 7.12). A possible origin for the fast phase prior to 100 ps in the blend film is geminate recombination of electrons in the acceptor and holes in the donor. The excitation density dependence at the slow phase, as well as the notable change of decay kinetics beyond 100 ps suggests that these kinetics are most likely due to bimolecular recombination.
The similarity in early timescale decay kinetics at 1200 nm in DT-PDPP2T-TT: PCBM blend and pristine DT-PDPP2T-TT samples is counterintuitive, as the addition of electron acceptors is expected to quench the singlet excitons leading to much faster decay kinetics at early timescales. The fact that the DT-PDPP2T-TT: PCBM sample followed close to identical decay kinetics as the pristine polymer prior to 10 ps, particularly at high PCBM concentration, suggest that either long-lived singlets are present in the blend sample, or the transient species observed in the pristine sample has strong intramolecular CT characteristics. The possibility of unquenched singlet exciton present in blend samples is excluded due to the absence of photoluminescence signal in the blend films (see Figure A-6 in Appendix for PL spectra in PCBM blend as well as pristine DT-PDPP2T-TT films). High FF was obtained for the DT-PDPP2T-TT: PCBM devices as shown in Chapter 4, which also suggests efficient charge generation. Hence it is proposed that, the 1200 nm decay in pristine DT-PDPP2T-TT has intramolecular CT states characteristics. The decay in polymer: PCBM blend prior to 10 ps is thus attributed to intermolecular CT states, which undergo charge separation at longer timescales and lead to the bimolecular recombination kinetics observed in Figure 7.12. The presence of CT states at early timescales in the pristine DT-PDPP2T-TT further suggests efficient exciton dissociation in pristine polymer, as suggested by the Stark effect observed in Section 7.3.2. Interestingly, similar kinetics was reported very recently in an indolo-naphthyridine-6,13-dione thiophene based polymer INDT-S: PCBM (1:4 w/w) blend, where the polymer singlet exciton decay in pristine polymer and PCBM blend samples showed close to identical decay kinetics up to approximately 20 ps. It is possible that the observed decay in pristine INDT-S is not singlet decay but rather intramolecular CT state, as is proposed for pristine DT-PDPP2T-TT, which is possibly due to dielectric screening in the polymer domains.

Based on the picosecond decay kinetics obtained at 1100 nm and 1500 nm in the DT-PDPP2T-TT: [60]PCBM film, the attribution of the polaron species are further considered here. The similar signal magnitude and similar decay kinetics at 1100 nm and 1500 nm
are consistent with the μs-TAS results, which support the hypothesis that both absorption features are from two transitions of the same polaron. However, the change in decay kinetics in the μs-TAS in DT-PDPP2T-TT: [70]PCBM suggests that this might not be the case. Rather, slower decay kinetics was observed at 1100 nm in the [70]PCBM blends, suggesting the possibility that the two transient species being polarons of different physical origins. The attribution of the 1100 nm and 1500 nm polaron peaks would require further experimental as well as computational studies, such as PCBM concentration dependent TAS and DFT, are required to assign these polaron peaks. Nonetheless, in this section it is clearly demonstrated that the 1100 nm and 1500 nm TA features observed in DT-PDPP2T-TT: PCBM samples arise predominantly from DT-PDPP2T-TT polarons. The established polaron signals thus provide a baseline for following studies in ternary blend films.

7.3.4 Microsecond TAS on ternary blend films based on PCPDTBT: DT-PDPP2T-TT: PCBM system

To study the charge transfer mechanism in PCPDTBT: DT-PDPP2TPTT: PCBM ternary blend, TAS was carried out in ternary PCPDTBT: DT-PDPP2TPTT: PCBM blends with DT-PDPP2TPTT to total polymer weight ratio of 20 % and 57 %, as well as 90 %. The binary PCPDTBT: PCBM film was also measured for comparison. Figure 7.13 shows the μs-TAS for the PCPDTBT: PCBM binary blend film excited at 640 nm and Figure 7.14 shows three ternary blends excited at 500 nm. By photoexciting at 500 nm where DT-PDPP2T-TT and PCPDTBT have comparable absorption coefficient (see Figure 7.4 and Table 7.1), the 57 % DT-PDPP2T-TT ternary blend allows comparable absorption in PCPDTBT and DT-PDPP2T-TT. Therefore, if hole transfer is absent in this blend, then polaron signals for both polymers will be observed in the TAS spectrum. It should be noted that a different DT-PDPP2T-TT batch was used in the ternary blends from the μs-TAS studies. Both polymer batches used have high Mw above 60 kg mol⁻¹, and no difference in μs-TAS spectra was observed between the measured batches, see Figure A-7 in Appendix.

In PCPDTBT: PCBM film, a transient absorption peak around 1300 nm was observed in Figure 7.13. A second absorption feature around 1500 nm was also observed, which showed a much weaker ΔOD than the 1300 nm peak. These spectrum features were in
agreement with literature, where the 1300 nm peak was attributed to the absorption of free polarons and the 1500 nm peak to localized polarons.\textsuperscript{[21]}

In the ternary blend with 90 \% DT-PDPP2T-TT, a single transient absorption peak at 1300 nm was observed (Figure 7.14a), which is attributed to the PCPDTBT polarons. Comparing transient absorption at 1100 nm and 1500 nm, similar ΔOD values were observed at 200 ns while at longer times of 500 ns and 1 μs faster decay was observed at 1500 nm, giving lower ΔOD values compared to 1100 nm. In binary DT-PDPP2T-TT: [60]PCBM blend both 1100 nm and 1500 nm polaron features showed similar magnitude and close to identical decay kinetics, whereas in binary PCPDTBT: PCBM the 1500 nm TA signal showed higher magnitude compared to 1100 nm. Therefore the larger ΔOD at 1100 nm compared to that at 1500 nm at timescales longer than 500 ns in the 90 \% ternary blend cannot be explained by a simple overlay of polaron responses in PCPDTBT and DT-PDPP2T-TT. The lower ΔOD at 1500 nm compared to 1100 nm in the 90 \% DT-PDPP2T-TT ternary blend suggests that the population of DT-PDPP2T-TT polarons at 1500 nm decreased upon forming a ternary blend. A possible explanation is hole transfer
from DT-PDPP2T-TT to PCPDTBT, leading to a reduced population in DT-PDPP2T-TT polaron species. As shown in Table 7.1, in the 90 % ternary blend approximately 47 % of light was absorbed by DT-PDPP2T-TT in the film, whereas only 4 % of excitation pulse was absorbed by PCPDTBT and 49 % was absorbed by PCBM. If hole transfer between DT-PDPP2T-TT and PCPDTBT was absent, then at least 47 % of overall generated holes would locate in the DT-PDPP2T-TT domains, even if all holes generated in PCBM were transferred to PCPDTBT. The notably larger ΔOD at the PCPDTBT polaron absorption wavelength of 1300 nm compared to 1100 nm and 1500 nm is thus an indication of efficient hole transfer from DT-PDPP2T-TT to PCPDTBT. Other possibilities exist as well, such as the formation of new excited states species at the DT-PDPP2T-TT PCPDTBT interface giving rise to TA signal around 1100 nm – 1200 nm. The presence of TA feature at 1100 nm but not 1500 nm in the 90 % blend suggests that the DT-PDP2PT-TT polarons at 1100 nm and 1500 nm are likely to have different origins. It is noted that the possible influence of [60]PCBM cations is excluded, as the [60]PCBM cations has been reported to absorb around 900 nm.[22]

In the ternary blend with 57 % DT-PDPP2T-TT (Figure 7.14b), a spectral shape similar to that with PCPDTBT: PCBM was observed. The absorption peak red-shifted to around 1350 nm compared to the PCPDTBT: PCBM binary blend. The 1100 nm and 1500 nm TA signal in the 57 % blend were slightly lower than that in PCPDTBT: PCBM TA spectra. No TA feature at 1100 nm or 1500 nm was observed in the 57 % ternary blend, suggesting very low population of DT-PDPP2T-TT polarons. As demonstrated in Table 7.1, the absorption of excitation pump in DT-PDPP2T-TT was estimated to be 31 %, however no DT-PDPP2T-TT polaron feature was observed in the 57 % ternary blend. Again, the absence of DT-PDPP2T-TT polaron features could be the result of hole transfer from DT-PDPP2T-TT to PCPDTBT.
(a) 90% DT-PDPP2T-TT
PCPDTBT: PCBM
DT-PDPP2T-TT: PCBM

(b) 57% DT-PDPP2T-TT
PCPDTBT: PCBM
DT-PDPP2T-TT: PCBM

(c) 20% DT-PDPP2T-TT
PCPDTBT: PCBM
DT-PDPP2T-TT: PCBM
Further decreasing the DT-PDPP2T-TT content to 20%, spectral shape in the ternary blend was notably different from that in both binary blends. A TA absorption peak between 1300 nm and 1500 nm was observed (Figure 7.14c), and a strong absorption feature between 1050 nm and 1100 nm was also observed. The TA spectrum shape of the 20 % DT-PDPP2T-TT sample was different from that in 90 % and 57 % DT-PDPP2T-TT ternary TAS, as the strong TA feature around 1050 nm in the 20 % ternary blend was not present in ternary blends with higher DT-PDPP2T-TT ratio. This is counterintuitive considering the low DT-PDPP2T-TT concentration in the 20 % blend. The TA spectrum was thus repeated on a nominally identical sample with 20 % DT-PDPP2T-TT (all materials used were the same batch as in Figure 7.14) to check the reproducibility of the spectrum. As shown in Figure 7.15, the repeated spectrum showed different shape compared to that in Figure 7.14c, where no strong feature around 1050 nm was observed in the repeated spectrum, and the strongest TA absorption peak in the repeated spectrum was observed at a shorter wavelength around 1250 nm compared to that in Figure 7.14c. The TA feature around 1050 nm in Figure 7.14c suggests the presence of high DT-PDPP2T-TT polaron concentration in the 20 % ternary blend, whereas the TA spectrum in the repeated sample showed a similar spectrum shape to the PCPDTBT: PCBM binary blend, suggesting a low DT-PDPP2T-TT polaron concentration. One of the possible reasons for the stark difference observed in the two ternary blend TA spectra with 20 % DT-PDPP2T-TT is the sensitiveness of TA spectra to film morphology at low DT-PDPP2T-TT concentration. As DT-PDPP2T-TT has high solubility in chloroform while PCPDTBT is more soluble in dichlorobenzene, during the spin-coating process the crystallization of DT-PDPP2T-TT and PCPDTBT domains could be taking place at different times, leading to a segregated morphology. The phase segregation, if present, will influence charge separation and transport, producing different TA spectra and device performances. Due to the limitation of PhD timeframe, the ternary blend TA spectrum with 20 % DT-PDPP2T-TT was not further repeated, and the 20 % spectrum will not be
used in the following discussion regarding hole transfer mechanism in PCPDTBT: DT-PDPP2T-TT: PCBM ternary blend.

Figure 7.15 Normalized TA spectra of ternary blend with 20% DT-PDPP2T-TT, compared between spectrum shown in Figure 7.14c and the repeated spectrum.

Comparing between the TA spectra with 90 % and 57 % DT-PDPP2T-TT, three observations can be made:

1) In both ternary blends, the strongest transient absorption peak was between 1300 nm and 1400 nm;

2) No clear absorption feature at 1500 nm was observed in either ternary blend film;

3) No clear TA feature around 1100 nm was observed in the 57 % ternary blend film, whereas a 1100 nm feature was observed in the 90 % ternary blend.

7.3.5 Is there hole transfer between PCPDTBT and DT-PDPP2T-TT?

Based on above results, the hole transfer mechanism in ternary PCPDTBT: DT-PDPP2T-TT: PCBM blend is discussed. In the studied ternary blends photoexcited at 500 nm, there are three possible hole transfer pathways: from PCBM to DT-PDPP2T-TT; from PCBM
to PCPDTBT and from DT-PDPP2T-TT to PCPDTBT. As the PCBM was photoexcited at 500 nm, hole transfer from PCBM to both polymers is expected to take place depending on blending ratio and film morphology. In other words, in ternary blend with 90% DT-PDPP2T-TT more PCBM: DT-PDPP2T-TT interfaces will be present compared to the PCBM: PCPDTBT interfaces, suggesting higher possibility for hole transfer from PCBM to DT-PDPP2T-TT to occur compared to hole transfer from PCBM to PCPDTBT. In ternary blend with 57% DT-PDPP2T-TT, the hole transfer pathways has a larger dependence on film morphology, where the majority of holes in PCBM can transfer to PCPDTBT or DT-PDPP2T-TT, or approximately equal to both polymers.

As explained in Section 7.1, hole carriers in PCPDTBT and DT-PDPP2T-TT can either recombine with electrons in PCBM without hole transfer, or hole transfer from DT-PDPP2T-TT to PCPDTBT can take place. If hole transfer between polymers is absent, the TA spectra in ternary blends will be similar to the combination of TA spectra in PCPDTBT: PCBM and DT-PDP2PT-TT: PCBM. This is clearly not the case, as shown in Figure 7.14. The large magnitude of PCPDTBT polaron peaks in all measured ternary blend films suggests a dominating population of holes within the PCPDTBT domains in all ternary blends, regardless of the blending ratio. This indicates hole transfer from DT-PDPP2T-TT to PCPDTBT in the ternary system. The presence of a weak absorption feature at 1100 nm in the ternary blend with 90% DT-PDPP2T-TT could be the contributed from a small population of polaron species at 1100 nm which are not transferred to PCPDTBT, or from a different energetic state formed in the ternary blend. In either case, the absence of 1500 nm absorption feature in the ternary blends is a clear indication of hole transfer from DT-PDPP2T-TT domains to PCPDTBT domains, where the 1500 nm polaron can be attributed to a more mobile species or species situated at the PCPDTBT: DT-PDPP2T-TT intermixing phase. The possibility of the 1100 nm feature in the ternary blend with 90% DT-PDPP2T-TT being the [60]PCBM anion can be excluded because the total polymer to PCBM ratio was kept constant for all ternary blends, thus the magnitude of the [60]PCBM anion should be relatively constant in all ternary blends. Further decreasing DT-PDPP2T-TT ratio to 57% in the ternary blend, the 1100 nm TA signal showed a decrease in relative magnitude compared to the 90% blend. This suggests that further hole transfer from DT-PDPP2T-TT polaron species at 1100 nm to PCPDTBT is present when increasing PCPDTBT ratio.
To examine whether hole transfer was present for the 1100 nm DT-PDPP2T-TT polaron species, the transient decay kinetics at 1100 nm in the ternary blend with 57 % and 90 % DT-PDPP2T-TT were compared to that in binary PCPDTBT: PCBM and DT-PDPP2T-TT: PCBM, and the normalized transients are shown in Figure 7.1. It is observed that for the 1100 nm decay both ternary blends showed very similar kinetics, which is similar to that in PCPDTBT: PCBM, whereas DT-PDPP2T-TT: PCBM showed a much slower decay at 1100 nm. This could be because in the ternary blends at 1100 nm, the decay kinetics is not dominated by DT-PDPP2T-TT polarons and thus only PCPDTBT decay kinetics were measured; or that the decay kinetics of the 1100 nm DT-PDPP2T-TT polaron feature has changed due to the presence of PCPDTBT domains.

Figure 7.16 Comparison between the normalized decay transients at probe wavelength of 1100 nm for the ternary blend samples with 57 % and 90 % DT-PDPP2T-TT, as well as PCPDTBT: PCBM and DT-PDPP2T-TT: PCBM binary blends. Solid lines mark the power law fitting for each transient.

As the polaron features at 1100 nm and 1500 nm in DT-PDPP2T-TT: PCBM binary blend are not clearly ascribed, further analysis on hole transfer efficiency in PCPDTBT: DT-PDPP2T-TT: PCBM ternary blends is difficult. However, the large magnitude of ΔOD at
PCPDTBT polaron absorption wavelength and the absence of DT-PDPP2T-TT polaron features in the 90 % and 57 % DT-PDPP2T-TT ternary blends suggest hole transfer from DT-PDPP2T-TT to PCPDTBT in the ternary PCPDTBT: DT-PDPP2T-TT: PCBM blends. Therefore, it is concluded that the PCPDTBT: DT-PDPP2T-TT: PCBM ternary blend fulfils the requirement of cascade charge transfer raised in Section 7.1.1 and is suitable for further bimolecular recombination studies on the influence of dielectric screening.

### 7.4 Dielectric constant in ternary blends

The dielectric constant values in ternary blend devices with DT-PDPP2T-TT to total polymer weight ratio of 20 %, 40 %, 60 % and 80 % are characterized using bias dependent impedance measurements at frequencies between 1 kHz and 1 MHz. The calculated dielectric constant \( \varepsilon_r \) values of ternary blend devices as well as binary blends PCPDTBT: PCBM and DT-PDPP2T-TT: PCBM are shown in Figure 7.17. The device capacitance, film thicknesses and calculated \( \varepsilon_r \) values at 10 kHz are listed in Table 7.2. Highest \( \varepsilon_r \) was observed in DT-PDPP2T-TT: PCBM across all measured frequencies. PCPDTBT: PCBM binary device, as well as ternary devices with 20 % and 60 % DT, showed similar low \( \varepsilon_r \) values, while the 40 % and 80 % DT showed \( \varepsilon_r \) intermediate between DT-PDPP2T-TT: PCBM and PCPDTBT: PCBM. Strong frequency dependence of \( \varepsilon_r \) was observed in DT-PDPP2T-TT: PCBM at frequencies below 5 kHz and above 500 kHz, which was absent in the pristine DT-PDPP2T-TT device. This could be caused by thickness variation or the effect of ionic polarization at low frequency, as mentioned in Chapter 5. To exclude possible effects of low frequency polarization processes in DT-PDPP2T-TT: PCBM, the \( \varepsilon_r \) values at 10 kHz were used for further calculations. Also, using the pristine polymer dielectric constant value of 7.7 measured in Chapter 5 and \( \varepsilon_r \) of 3.9 for PCBM, the binary DT-PDPP2T-TT: PCBM dielectric constant is estimated by calculating the weighted averaging, giving \( \varepsilon_r = 4.85 \), which is close to the experimentally obtained \( \varepsilon_r \) of 4.47 at 10 kHz.
Figure 7.17 Dielectric constant values in ternary blends with 20 %, 40 %, 60 % and 80 % DT-PDPP2T-TT, characterized using bias-dependent impedance measurements at the frequency range between 1 kHz and 1 MHz. The frequency dependent dielectric constant in PCPDTBT: PCBM and DT-PDPP2T-TT: PCBM are also shown in comparison.

Table 7.2 List of geometric capacitance and calculated $\varepsilon_r$ obtained using bias-dependent impedance measurements at 10 kHz.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>C (nF)</th>
<th>$\varepsilon_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCPDTBT: PCBM</td>
<td>96 ± 8</td>
<td>1.7 ± 0.1</td>
</tr>
<tr>
<td>20 % DT-PDPP2T-TT</td>
<td>126 ± 15</td>
<td>1.3 ± 0.2</td>
</tr>
<tr>
<td>40 % DT-PDPP2T-TT</td>
<td>151 ± 13</td>
<td>1.4 ± 0.1</td>
</tr>
<tr>
<td>60 % DT-PDPP2T-TT</td>
<td>150 ± 8</td>
<td>1.1 ± 0.1</td>
</tr>
<tr>
<td>80 % DT-PDPP2T-TT</td>
<td>160 ± 14</td>
<td>1.3 ± 0.1</td>
</tr>
<tr>
<td>DT-PDPP2T-TT: PCBM</td>
<td>215 ± 25</td>
<td>1.0 ± 0.1</td>
</tr>
</tbody>
</table>
The $\varepsilon_r$ values at 10 kHz were plotted as a function of ternary blending ratio, shown in Figure 7.18. While highest $\varepsilon_r$ value was observed in DT-PDPP2T-TT: PCBM binary device, no clear trend in ternary blend dielectric constant was observed. The $\varepsilon_r$ values in ternary devices showed a fluctuation around 3.5, however the reason for observed fluctuation is unclear. No scaling of dielectric constant in ternary blends with DT-PDPP2T-TT ratio was observed. This suggests that unlike expected, introducing DT-PDPP2T-TT into the PCPDTBT: PCBM system does not increase the dielectric constant. The reason for this remains unclear, while one of the possibilities is the change in film morphology and domain size, which has been shown to affect low frequency dielectric constant. It has been shown that when DIO concentration was increased from 0 to 3 %, an increase in low-frequency dielectric constant from 4 to 4.65 was observed in PTB7: [70]PCBM devices.\cite{26} This was explained by the significantly decreased domain size, which facilitates polymer-fullerene interaction thus increasing dipolar polarization. As the majority of the DT-PDPP2T-TT batch P80 was used for the pristine dielectric constant studies carried out in Chapter 5, no sufficient material was left to reproduce the ternary blend dielectric constant results. One of the important future works is to select another polymer batch with high dielectric constant to repeat and further investigate the dielectric constant values in DT-PDPP2T-TT based ternary blends.
7.5 Device optimization

Due to the different solubility of PCPDTBT and DT-PDPP2T-TT in chloroform (CF) and chlorobenzene (CB), device optimization was first carried out using ternary blends with 50% DT-PDPP2T-TT (i.e. PCPDTBT: DT-PDPP2T-TT: PCBM = 0.5: 0.5: 3 by weight). As PCPDTBT has high solubility in CB and dichlorobenzene (o-DCB) while DT-PDPP2T-TT has high solubility in CF, a mixture of solvents were used to fabricate ternary devices, and the averaged device performance parameters are listed in Table 7.3. When mixing solvents at 1:1 ratio, poor DT-PDPP2T-TT solubility was found. Higher $J_{SC}$ and $FF$ was achieved using CF + o-DCB 1:1 mixture solvent compared to CF + CB 1:1 mixture solvent, leading to a higher overall efficiency. Further improved performance was achieved by reducing the o-DCB ratio, where a mixed solvent with 8.3 vol% o-DCB was used. Better DT-PDPP2T-TT solubility was observed. High $V_{OC}$ of 0.67 V was obtained using the CF + 8.3 vol% o-DCB mixture solvent. Further improvement on device performance was not achieved by altering solvent blending ratio. For devices used in other sections of this chapter, the CF with 8.3 vol% o-DCB solvent blend was used.

Table 7.3 List of device performance in ternary blend devices with PCPDTBT: DT-PDPP2T-TT ratio of 1:1 w/w and total polymer to PCBM ratio of 1:3 w/w. The listed performance parameters are averaged from a minimum of four devices.

<table>
<thead>
<tr>
<th>Solvent Blend</th>
<th>Thickness (nm)</th>
<th>$J_{SC}$ (Ma cm$^{-2}$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF + o-DCB 1:1</td>
<td>100 ± 8</td>
<td>5.04 ± 0.26</td>
<td>0.65 ± 0.01</td>
<td>0.35 ± 0.02</td>
<td>1.15 ± 0.11</td>
</tr>
<tr>
<td>CF + CB 1:1</td>
<td>100 ± 6</td>
<td>4.73 ± 0.19</td>
<td>0.67 ± 0.01</td>
<td>0.33 ± 0.02</td>
<td>1.04 ± 0.05</td>
</tr>
<tr>
<td>CF + 8.3 vol% o-DCB</td>
<td>150 ± 10</td>
<td>4.70 ± 0.03</td>
<td>0.67 ± 0.01</td>
<td>0.35 ± 0.02</td>
<td>1.07 ± 0.08</td>
</tr>
</tbody>
</table>
The performance of ternary blend PCPDTBT: DT-PDPP2T-TT: PCBM devices with total polymer to fullerene ratio of 1:3 using a mixture solvent of CF + 8.3 vol% o-DCB were characterized using current-voltage measurements. The devices measured here were the same as those used for dielectric constant characterizations. The current density-voltage characterizations of fabricated ternary blend devices are shown in Figure 7.19 which are the same devices as those characterized in Section 7.4. The performance parameters are listed in Table 7.4, where four devices fabricated from the same batch were used to calculate the average parameter values, while the parameters of highest performing devices are shown in parentheses. In the ternary devices, the Voc showed a relatively constant value around 0.67 V with DT-PDPP2T-TT ratio between 20 % and 80 % (Figure 7.19a), while higher Voc value of 0.71 V was observed in binary DT-PDPP2T-TT: PCBM systems and the lowest Voc of 0.60 V was observed in PCPDTBT: PCBM binary device. The Voc value for PCPDTBT: PCBM binary device obtained here is found lower than that in literature, which showed a Voc of 0.67 V.[27] The Voc in ternary blend devices showed a relatively constant value between 0.65 and 0.68 V. The lower Voc values in ternary blends compared to that in binary DT-PDPP2T-TT: PCBM suggests that charge transfer is present in PCPDTBT: DT-PDPP2T-TT: PCBM system, where a hole transfer from DT-PDPP2T-TT to PCPDTBT is likely taking place. This is also supported by the transient absorption study shown in Section 7.3. If this is indeed the case, poor hole transport within ternary blends is expected due to the low carrier mobility in PCPDTBT: PCBM binary system (see Chapter 6).

All ternary devices showed Jsc around 5 mA cm⁻², lower than that in either binary device. FF values between 0.35 and 0.38 were observed for all ternary devices whereas higher FF around 0.5 was observed in the binary devices. As shown in Figure 7.19b the Jsc and FF values in ternary blend devices are notably lower than either binary device. As Jsc is directly related to charge generation, the low Jsc in ternary blend devices indicate poor charge generation efficiency, which can also lead to low FF in the device. The voltage dependence of current density at large reverse bias also suggests lower extraction efficiency. The relatively constant Jsc value independent of blending ratio suggests that charge generation among these ternary devices is relatively constant. The relatively constant Jsc values can come from undesired film morphology where polymer domains
cannot form an interconnecting network, resulting in failure of photo-generated excitons to separate into free carriers. As a result of low $J_{sc}$ and $FF$, the ternary device efficiency was also low, giving PCE around 1 % for the ternary devices.

Figure 7.19 Current density-voltage curves characterized under AM1.5 and in the dark in ternary PCPDTBT: DT-PDPP2T-TT: PCBM devices with DT-PDPP2T-TT ratio of 20 %, 40 %, 60 % and 80 %, along with binary PCPDTBT: PCBM and DT-PDPP2T-TT: PCBM devices.
Figure 7.20 (a) open circuit voltage $V_{OC}$ values at AM1.5 plotted as a function of DT-PDPP2T-TT blending ratio; (b) $J_{SC}$ and $FF$ values at AM1.5 plotted as a function of DT-PDPP2T-TT blending ratio.

Table 7.4 Device performance parameters obtained from $J-V$ characterization. The values shown in brackets are the parameters for the best performing device at each ratio, same as shown in Figure 7.18.
<table>
<thead>
<tr>
<th>DT wt%</th>
<th>Thickness (nm)</th>
<th>Voc (V)</th>
<th>Jsc (mA cm(^{-2}))</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>96</td>
<td>0.596 ± 0.005</td>
<td>9.1 ± 0.5 (8.6)</td>
<td>0.48 ± 0.02 (0.50)</td>
<td>2.58 ± 0.04 (2.61)</td>
</tr>
<tr>
<td>20</td>
<td>126</td>
<td>0.685 ± 0.004</td>
<td>4.4 ± 0.2 (4.6)</td>
<td>0.38 ± 0.01 (0.37)</td>
<td>1.0 ± 0.2 (1.2)</td>
</tr>
<tr>
<td>40</td>
<td>151</td>
<td>0.677 ± 0.006</td>
<td>4.70 ± 0.03 (4.70)</td>
<td>0.35 ± 0.01 (0.36)</td>
<td>1.13 ± 0.03 (1.16)</td>
</tr>
<tr>
<td>60</td>
<td>150</td>
<td>0.660 ± 0.002</td>
<td>4.7 ± 0.3 (4.8)</td>
<td>0.35 ± 0.02 (0.37)</td>
<td>1.1 ± 0.1 (1.2)</td>
</tr>
<tr>
<td>80</td>
<td>160</td>
<td>0.642 ± 0.004</td>
<td>5.9 ± 0.3 (5.9)</td>
<td>0.36 ± 0.02 (0.38)</td>
<td>1.4 ± 0.1 (1.5)</td>
</tr>
<tr>
<td>100</td>
<td>215</td>
<td>0.712 ± 0.005</td>
<td>10.5 ± 0.3 (10.5)</td>
<td>0.47 ± 0.04 (0.51)</td>
<td>3.6 ± 0.2 (3.8)</td>
</tr>
</tbody>
</table>

### 7.7 Carrier mobility in ternary blends

Charge carrier mobility in ternary blend devices with 20 %, 40 %, 60 % and 80 % DT-PDPP2T-TT as shown in Section 7.4 are characterized using photo-CELIV and the obtained photo-CELIV transients at increasing delay times are shown in Figure 7.21. The extraction maxima time \( t_{\text{max}} \) showed no significant delay time dependence in ternary devices, which corresponds to constant carrier mobility at increasing delay times. This is in agreement with the lack of delay time dependence of mobility in PCPDTBT: PCBM and DT-PDPP2T-TT: PCBM binary devices, and is a clear indication of diffusion dominated recombination. The carrier mobility was calculated from recorded photo-CELIV transients using Equation 3.5, and the obtained mobility are listed in Table 7.5 along with PCPDTBT: PCBM and DT-PDPP2T-TT: PCBM devices fabricated in the same batch. Charge mobility \( \mu \) in the range of \( 3.78 \times 10^{-4} \sim 5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) was observed in all ternary devices, which is slightly higher than that in binary PCPDTBT: PCBM (\( 1.32 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \)). The binary DT-PDPP2T-TT: PCBM device showed an order of magnitude higher mobility of \( 2.39 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \). Using the obtained mobility and \( \varepsilon_r \), the Langevin recombination coefficient \( \beta_L \) is also calculated, as listed in Table 7.5. Similar \( \beta_L \) values around \( 2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \) was observed for all ternary blends, while
PCPDTBT: PCBM devices showed the lowest $\beta_L$ value as a result of low mobility and DT-PDPP2T-TT: PCBM showed the largest $\beta_L$.

The higher charge mobility in ternary blends compared to PCPDTBT: PCBM indicates that a small fraction of high mobility DT-PDPP2T-TT domains also participated in hole transport in ternary blends. However, as the ternary blend mobility is much closer to mobility in PCPDTBT: PCBM, the low mobility PCPDTBT domains are likely to dominate hole transport in PCPDTBT: DT-PDPP2T-TT: PCBM blends. This observation further confirms that hole transport in PCPDTBT: DT-PDPP2T-TT: PCBM ternary blend is mainly carried out through the low mobility PCPDTBT domains, which is in agreement with results shown above. The low mobility in ternary blends with high DT-PDPP2T-TT ratio further suggest that charge transfer from DT-PDPP2T-TT to PCPDTBT is highly likely in the PCPDTBT: DT-PDPP2T-TT: PCBM ternary blend and charge transport is mainly carried out through PCPDTBT domains regardless of the blending ratio.
Figure 7.21 photo-CELIV transients obtained in ternary PCPDTBT: DT-PDPP2T-TT: PCBM devices with DT-PDPP2T-TT ratio of 20 % (a), 40 % (b), 60 % (c) and 80 % (d), as well as binary DT-PDPP2T-TT: PCBM (e) and PCPDTBT: PCBM (f) measured under excitation density of 10 µJ cm\(^{-2}\) at increasing delay times.
Table 7.5 List of charge mobility obtained from photo-CELIV, dielectric constant values at 10 kHz, and calculated Langevin recombination coefficient $\beta_L$ in ternary and binary devices.

<table>
<thead>
<tr>
<th></th>
<th>Mobility (cm$^2$V$^{-1}$s$^{-1}$)</th>
<th>$\varepsilon_r$</th>
<th>$\beta_L$ (cm$^3$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCPDTBT: PCBM</td>
<td>1.32 ± 0.38 × 10$^{-4}$</td>
<td>3.14</td>
<td>7.6 × 10$^{-11}$</td>
</tr>
<tr>
<td>20 % DT-PDPP2T-TT</td>
<td>4.66 ± 1.11 × 10$^{-4}$</td>
<td>3.06</td>
<td>2.8 × 10$^{-10}$</td>
</tr>
<tr>
<td>40 % DT-PDPP2T-TT</td>
<td>5.02 ± 0.57 × 10$^{-4}$</td>
<td>3.88</td>
<td>2.3 × 10$^{-10}$</td>
</tr>
<tr>
<td>60 % DT-PDPP2T-TT</td>
<td>3.78 ± 0.71 × 10$^{-4}$</td>
<td>3.20</td>
<td>2.1 × 10$^{-10}$</td>
</tr>
<tr>
<td>80 % DT-PDPP2T-TT</td>
<td>4.89 ± 0.89 × 10$^{-4}$</td>
<td>3.80</td>
<td>2.3 × 10$^{-10}$</td>
</tr>
<tr>
<td>DT-PDPP2T-TT: PCBM</td>
<td>2.39 ± 0.42 × 10$^{-3}$</td>
<td>4.47</td>
<td>9.7 × 10$^{-10}$</td>
</tr>
</tbody>
</table>

7.8 Charge density decay kinetics in ternary blends

TRCE was carried out on PCPDTBT: DT-PDPP2T-TT: PCBM ternary blend devices studied in previous sections of this chapter. Figure 7.22 shows the charge density decay of ternary blend devices characterized above with DT-PDPP2T-TT ratio between 20 % and 80 %, as well as binary PCPDTBT: PCBM and DT-PDPP2T-TT: PCBM devices, measured at excitation density of 10 µJ cm$^{-2}$, at which all devices showed signal saturation. Biphasic characteristics were observed in the charge density decay in both measured ternary blends, where a fast phase prior to 5 µs and a slow phase following power law decay at longer times were observed. A power law gradient around 0.13 was observed in the slow phase for all ternary blends. Comparing charge density decay kinetics in ternary and binary blends, the biphasic kinetics in ternary blend are similar to that in PCPDTBT: PCBM, where a change in kinetics at approximately 5 µs was also observed. The power law gradient in the ternary devices is similar to that in binary blend (0.17 and 0.19 for PCPDTBT: PCBM and DT-PDPP2T-TT: PCBM, respectively, see Chapter 6). The smaller power law gradient in ternary devices indicates deeper traps in ternary blends. This is likely caused by the increase of isolated DT-PDPP2T-TT domains in ternary blends as a result of polymer blending.
Figure 7.22 Charge density decay in ternary devices with 20%, 40%, 60% and 80% DT-PDPP2T-TT, as well as binary PCPDTBT: PCBM and DT-PDPP2T-TT: PCBM devices obtained from TRCE at 10 µJ cm⁻².

7.9 Comparing recombination coefficient $\beta$

It was previously observed in Chapter 6 that very similar $\beta$ values around $2.5 \times 10^{-11}$ cm³ s⁻¹ were observed at early timescales in PCPDTBT: PCBM and DT-PDPP2T-TT: PCBM binary blends, therefore close to identical $\beta$ in ternary devices at early timescale in ternary blends is expected. This was indeed observed, and for better comparison between the devices $\beta/\mu$ was compared here instead. The bimolecular recombination coefficient $\beta$ was calculated from Figure 7.22 using Eq 3.10, and the obtained $\beta$ values normalized to charge mobility were plotted as a function of time in Figure 7.23. At short delay time of 500 ns, the lowest $\beta/\mu$ value of $7 \times 10^{-9}$ cm³ s⁻¹/cm² V⁻¹ s⁻¹ was observed in DT-PDPP2T-TT: PCBM, consistent with its stronger dielectric screening. All ternary devices showed similar $\beta/\mu$ values around $5 \times 10^{-8}$ cm³ s⁻¹/cm² V⁻¹ s⁻¹, and the largest $\beta/\mu$ of $2 \times 10^{-7}$ cm³ s⁻¹/cm² V⁻¹ s⁻¹ at 500 ns was observed in PCPDTBT: PCBM device. At times longer than 20 µs, close to identical $\beta/\mu$ values were observed for all ternary devices, approximately three times lower than that in binary PCPDTBT: PCBM.
Comparing the $\beta/\mu$ values in ternary blends and binary blend devices, lower $\beta/\mu$ values in ternary devices than that in PCPDTBT: PCBM were observed. The lower $\beta/\mu$ indicates reduced recombination in ternary blends when the difference in charge mobility is considered. Considering the low dielectric constant in ternary devices, the lower $\beta/\mu$ values in ternary devices is unlikely the result of increased dielectric screening, thus a separate mechanism must be present causing the reduced recombination in ternary blends. This will be discussed in further detail below.

Figure 7.23 Bimolecular recombination coefficient $\beta$ normalized to charge mobility $\mu$, plotted as a function of time.

7.10 How does adding DT-PDPP2T-TT affect recombination kinetics in ternary blends?

The dielectric constant, carrier mobility, $\beta_L$ values as well as $\beta$ values at 500 ns obtained from TRCE are listed in Table 7.6 for the measured devices, along with calculated $\beta/\mu$ values. The dielectric constant showed no blending ratio dependence, which was unexpected. As the dielectric screening is an environmental effect, intuitively speaking the presence of a high dielectric material should increase the dielectric screening in the
media regardless of the morphology. While the exact reason for low dielectric constant in all ternary blends, even at high DT-PDPP2T-TT concentration, is unclear, a possible explanation is the change in film morphology and domain size upon blending with DT-PDPP2T-TT. Another possible reason is the influence of ambient atmosphere during sample preparation. As shown in Chapter 5, the exposure to ambient air significantly reduces the measured dielectric constant in pristine DT-PDPP2T-TT, which could also be the case for ternary blends containing DT-PDPP2T-TT. To examine whether this is the case for ternary PCPDTBT: DT-PDPP2T-TT: PCBM blends, further studies on ternary blend dielectric constant under inert conditions and film morphology will be carried out in the future.

Table 7.6 List of $\beta$ obtained from TRCE at 500 ns, and $\beta/\mu$ at 500 ns.

<table>
<thead>
<tr>
<th>Blend</th>
<th>$\beta_{500\text{ns}}$ (cm$^3$/s)</th>
<th>$\beta_{500\text{ns}}/\mu$ (cm$^3$/s/cm$^2$V$^{-1}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCPDTBT: PCBM</td>
<td>$2.8 \times 10^{-11}$</td>
<td>$2.1 \times 10^{-7}$</td>
</tr>
<tr>
<td>20 % DT-PDPP2T-TT</td>
<td>$1.1 \times 10^{-11}$</td>
<td>$2.4 \times 10^{-8}$</td>
</tr>
<tr>
<td>40 % DT-PDPP2T-TT</td>
<td>$2.1 \times 10^{-11}$</td>
<td>$4.2 \times 10^{-8}$</td>
</tr>
<tr>
<td>60 % DT-PDPP2T-TT</td>
<td>$1.6 \times 10^{-11}$</td>
<td>$4.2 \times 10^{-8}$</td>
</tr>
<tr>
<td>80 % DT-PDPP2T-TT</td>
<td>$3.5 \times 10^{-11}$</td>
<td>$7.2 \times 10^{-8}$</td>
</tr>
<tr>
<td>DT-PDPP2T-TT: PCBM</td>
<td>$2.8 \times 10^{-11}$</td>
<td>$1.2 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

The blending ratio-independent mobility in ternary blends suggests that hole transfer from DT-PDPP2T-TT to PCPDTBT is highly likely which is also supported by transient absorption spectroscopy results. Hole transport is thus dominated by PCPDTBT domains while only a small fraction of DT-PDPP2T-TT participates in hole transport. This is in agreement with earlier predictions based on HOMO levels of PCPDTBT and DT-PDPP2T-TT and relatively constant $V_{OC}$ values in ternary blend devices. Since the dielectric constant is low and charge transport is dominated by PCPDTBT domains, fast charge recombination similar to that in PCPDTBT: PCBM is expected for ternary blends. However, the charge recombination kinetics in ternary blends suggests otherwise. While strong biphasic kinetic characteristics of PCPDTBT: PCBM were indeed observed in the ternary devices, lower $\beta/\mu$ values were observed in ternary devices compared to PCPDTBT: PCBM, suggesting reduced recombination in ternary devices. No $t_{\text{max}}$
dependence on delay time was observed in the photo-CELIV transients of the ternary blend devices, and $Q_e \approx C U_0$ was observed for all ternary devices, therefore the possibility of non-Langevin recombination in the ternary blends is excluded. Since no significant increase in ternary blend dielectric constant was observed compared to PCPDTBT: PCBM binary blends, the reduced recombination cannot be attributed to enhanced dielectric screening.

One of the possible explanations for this is the presence of DT-PDPP2T-TT as an energetic barrier between the PCPDTBT and PCBM interfaces. As observed in the ternary blend TAS spectra, hole transfer from DT-PDPP2T-TT to PCPDTBT is present in ternary blends with 90% and 57% DT-PDPP2T-TT, evidenced by the absence of DT-PDPP2T-TT polaron features in the ternary spectra. Such efficient hole transfer requires the DT-PDPP2T-TT domains to be situated close to the PCPDTBT domains. Based on this assumption, it is proposed that the reduced recombination in ternary blend devices is possibly due to the presence of a DT-PDPP2T-TT layer between PCPDTBT: PCBM interfaces, as illustrated in Figure 7.24. When DT-PDPP2T-TT domains are located on the surface of the PCPDTBT domains, the preferred hole transfer from DT-PDPP2T-TT to PCPDTBT will block recombination between PCPDTBT and PCBM. The DT-PDPP2T-TT domains could also be surrounding PCPDTBT, creating PCPDTBT energy sinks in the blend. In such case, as the majority of hole carriers are in the PCPDTBT domains, the hole depleted DT-PDPP2T-TT domains act as a spatial barrier which prohibits charge recombination from taking place. This hypothesis provides an alternative approach for reducing bimolecular recombination which does not require the discovery of a new non-Langevin material or by incorporating a non-Langevin material.[24-25] This hypothesis is particularly interesting in that, it does not involve a non-Langevin polymer. Rather, by carefully tailoring the morphology, theoretically the bimolecular recombination in any Langevin system can be reduced. As such, by selecting systems with suitable energetic offset and optimized morphology, reduced recombination can be achieved in a wide range of diffusion-dominated systems.
Figure 7.24 Schematic of DT-PDPP2T-TT (green) acting as an energetic barrier for charge recombination between PCPDTBT (blue) and PCBM (background).

The proposed hypothesis has several material and morphology requirements. Good compatibility must be achieved between DT-PDPP2T-TT and the host system, where the DT-PDPP2T-TT domains either situate at the D/A interfaces of the host system, or form an interpenetrating network. In this case the host system will benefit from both improved hole transport in DT-PDPP2T-TT domains and the increased dielectric screening, potentially leading to a ternary system with reduced recombination and fast charge transport. To achieve this goal, it is crucial to find the suitable host system and control the ternary film morphology. Further investigation of dielectric effect in other ternary blend devices will be carried out in the future.

7.11 Conclusion

This chapter investigates the effect of high dielectric constant DT-PDPP2T-TT on bimolecular recombination in ternary PCPDTBT: DT-PDPP2T-TT: PCBM blend devices. Transient absorption spectroscopy was carried out where some evidence was observed suggesting hole transfer from DT-PDPP2T-TT polarons to PCPDTBT free polarons. The dielectric constant \( \varepsilon_r \) in ternary blends was independent of DT-PDPP2T-TT blending ratio. The charge mobility in ternary blend devices were also found independent on DT-
PDPP2T-TT blending ratio, which suggests hole transport dominated by PCPDTBT domains. When bimolecular recombination kinetics was compared between ternary blends and the binary blend PCPDTBT: PCBM and DT-PDPP2T-TT: PCBM, a reduced recombination was observed compared to binary PCPDTBT: PCBM, evidenced by lower $\beta/\mu$ values and longer carrier lifetimes in the ternary blends. As no consistent increase in the dielectric constant was found when adding DT-PDPP2T-TT, the reduced recombination could not be attributed to enhanced dielectric screening due to the presence of DT-PDPP2T-TT. Rather, it is hypothesized that DT-PDPP2T-TT, which has intermediate energy levels between PCPDTBT and PCBM, acts as an energetic barrier at the PCPDTBT: PCBM interface, thereby blocking charge recombination.

The significance of this hypothesis is that, by selecting materials with matching energetics and carefully tailoring the film morphology, bimolecular recombination can be reduced without the development of any new material or the use of any non-Langevin polymer. Rather, the hundreds of reported semiconducting polymers can be utilized to achieve reduced recombination, which has only been observed in a limited number of systems. Once validated, this hypothesis could open a new aspect in PSC system designing to achieve reduced bimolecular recombination.

7.12 References


Chapter 8 Conclusions and Outlook
8.1 Conclusions

Bimolecular recombination is one of the limiting factors to high efficiency polymer solar cells (PSCs). One of the potential approaches to reduce bimolecular recombination is to increase the strength of dielectric screening. Therefore, this thesis aimed at understanding the dielectric effect on bimolecular recombination. The influences of dielectric screening on charge transport, bimolecular recombination kinetics and device performance in PSCs were studied. This was achieved using a high dielectric constant, low bandgap diketopyrrolopyrrole based polymer, DT-PDPP2T-TT. The work presented in this thesis can be summarized into three parts:

1. The first target for the research presented in this thesis was to accurately and reproducibly characterize the dielectric constant value in pristine semiconducting polymer thin-film devices. This was challenging because literature focusing on characterisation methods of geometric capacitance and dielectric constant for semiconducting polymers is scarce. Therefore, geometric capacitance measurements were carried out by comparing three different methods. By doing so, an experimental guideline for characterizing geometric capacitance in semiconducting polymer-based thin film devices was proposed for the first time in literature. It is suggested in this thesis that the dark CELIV transients should first be measured to check whether dark carriers or charge injection from electrodes are present; then the impedance spectrum of the device should be measured to examine whether additional capacitance contribution from electrode interfaces are present; then the geometric capacitance is obtained from measuring the bias-dependent impedance of the device at the frequency range corresponding to the geometric capacitance response, which could be obtained from the impedance spectrum.

Another challenge was the variation of dielectric constant values in different polymer batches. In order to understand the batch-to-batch variation of pristine dielectric constant, the influence of different sample processing conditions were compared. Ambient air exposure was found to significantly decrease measured dielectric constant, which was attributed to H₂O/O₂ doping. By carefully characterizing the geometric capacitance value and the film thickness values, a high dielectric constant of 16.8 was obtained in one of the DT-PDPP2T-TT batches and slightly lower dielectric constant value of 7 was
obtained for another batch. These values were the highest dielectric constant reported for semiconducting polymers to date.

The influence of sample processing conditions on dielectric constant is demonstrated, where ambient air and heating exposure showed a detrimental effect on dielectric constant. This is an important observation, which suggests that all semiconducting polymers may suffer from oxygen and water doping leading to the low dielectric constant values typically observed. While the effect of ambient conditions on charge mobility and long term stability in semiconducting polymers have been studied, this chapter shows that ambient environment affects the fundamental dielectric property of a semiconducting polymer, which will have a wide range of influences including charge generation and recombination in semiconducting polymers.

2. After establishing the dielectric constant values, the influence of dielectric screening on bimolecular recombination kinetics PSCs was studied. This was done by comparing charge carrier mobility and bimolecular recombination kinetics in four different PSC systems, namely DT-PDPP2T-TT: PCBM, P3HT: PCBM, PCPDTBT: PCBM and PTB7: PCBM with a wide range of dielectric constant values between 3 and 7. A large difference in charge mobility values was observed in these systems, where the highest measured mobility was close to two orders of magnitude higher than the lowest mobility. Such large difference in charge mobility makes direct comparison between bimolecular recombination coefficients difficult, as the recombination coefficient in systems with diffusion-dominated recombination is directly related to mobility. To solve this problem, the bimolecular recombination coefficient was normalized to charge mobility. It was found that DT-PDPP2T-TT based solar cell showed the lowest normalized recombination coefficient value among the four compared systems. As bimolecular recombination in DT-PDPP2T-TT based solar cell showed clear signatures of diffusion-controlled recombination, the small normalized recombination coefficient was thus attributed to the strong dielectric screening in DT-PDPP2T-TT, leading to weaker electron-hole binding thus reducing recombination. This was also supported by longer charge carrier lifetime in DT-PDPP2T-TT based solar cell.
3. As a proof of concept, the influence of adding high dielectric constant material in a low dielectric constant host system was further investigated, thereby forming a ternary blend. A low dielectric constant host system with low charge mobility and diffusion-controlled bimolecular recombination, PCPDTBT: PCBM, was selected as host system and DT-PDPP2T-TT was added into the host system blend by different ratios. Increased dielectric constant in ternary blend was not observed upon adding DT-PDPP2T-TT into PCPDTBT: PCBM. However, lower bimolecular recombination coefficient when normalized to mobility was observed in ternary devices compared to the host system. It was further proposed that this could either be the influence of ambient processing environment leading to a lower observed dielectric constant in the ternary blend, or caused by a back-transfer mechanism where DT-PDPP2T-TT, which has shallower HOMO, acts as an energetic barrier between the PCPDTBT which has deeper HOMO and the PCBM acceptor, leading to hindered recombination at the PCPDTBT: PCBM interface. The charge transfer between DT-PDPP2T-TT and PCPDTBT was thus examined using transient absorption spectroscopy, where a distinct change in spectra shape was observed between the binary and ternary transient absorption spectra. The change in spectra shape was evidence that hole transfer from DT-PDPP2T-TT to PCPDTBT was present.

In conclusion, this thesis shows for the first time a detailed photophysics study on the effect of enhanced dielectric screening on bimolecular recombination. The main findings of this thesis are i) high dielectric constants of 16.8 in pristine DT-PDPP2T-TT and 7 in DT-PDPP2T-TT: PCBM blend are observed and validated with accurate characterizations, which are the highest dielectric constant values for pristine semiconducting polymer and polymer: PCBM blends up to date; ii) the enhanced dielectric screening reduces bimolecular recombination and enables longer charge carrier lifetime by reducing the Coulomb interaction between electrons and holes; iii) characterization methodology for geometric capacitance in thin-film polymer devices is proposed with a detailed comparison of characterization conditions, making it applicable to the general field of capacitance measurement in polymer thin-film devices. These findings are expected to enhance our understanding on bimolecular recombination, generating new debates regarding the role of dielectric screening and the validity for
existing models developed decades ago. Some important questions, however, are left unanswered. The origin of high dielectric constant, despite the detailed and systematic effort, remains to be clarified.

8.2 Outlook

One of the key findings in this thesis is the reduced bimolecular recombination caused by increased dielectric screening. This conclusion opens up a new perspective in reducing recombination and improving performance in polymer solar cells. For example, high dielectric constant materials (both organic and inorganic semiconductors) can be added into organic photovoltaic devices to increase the dielectric screening of the medium, which can not only reduce charge recombination, but also enable larger active layer thickness and better photon harvesting. The effect of increased dielectric screening on bimolecular recombination can also be extended to recombination at the interface between the active bulk layer and the electrodes. Modifying the electrode with a thin layer of high dielectric constant semiconductor can screen the charge carriers, leading to reduced interface recombination.

High dielectric constant of 16.8 and 7 was obtained for two different batches of DT-PDPP2T-TT pristine polymer. Both values are higher than other dielectric constant values reported to date, where P61 showed a dielectric constant over two times larger than highest value reported in literature. The importance of high dielectric constant in DT-PDPP2T-TT is that, it provides opportunities to study the influence of dielectric screening on charge generation, transport and recombination processes which has been limited to theoretical analysis before. With such high dielectric constant, experimental studies on influence of dielectric screening on charge-photogeneration and recombination processes become possible for the first time, making this polymer a unique material in semiconducting polymers. For example, it would be extremely meaningful to study the charge generation and separation process using ultrafast spectroscopy. If strong dielectric screening could indeed facilitate charge separation as predicted by multiple theoretical studies, the charge separation will be much faster than in typical PSC systems. More interestingly, as the dielectric constant in DT-PDPP2T-TT has been shown to strongly depend on processing environment, direct comparison between charge generation process
on the same sample under different atmosphere environments is possible. If the theory of
dielectric screening on charge generation process is experimentally confirmed, it is even
possible to fabricate photovoltaic devices using DT-PDPP2T-TT only, which would
eventually narrow the gap between organic photovoltaic and inorganic photovoltaic
devices.

The origin of the high dielectric constant is another interesting topic to be further
investigated. As mentioned in Chapter 5, the polymer chain orientation and end group
structure could potentially be the origin of the observed high dielectric constant. To
further understand the origin of the high dielectric constant, the polymer synthesis
procedure could be controlled to produce a series of polymer batches, and the dielectric
constant in these batches could be compared to examine the key aspect during polymer
synthesis influencing dielectric constant. Advanced microscopic techniques could also be
used to reveal the influence of chemical structure on dielectric screening at the atomic
scale. For example, scanning electrochemical microscopy (SECM) could be used to study
the localized dipole moment in response to an applied field. The polymer could be
measured at room temperature or in cryostat, to examine whether high dielectric constant
is caused by delocalized polymer segments or not.

For the first time in literature, three experimental techniques for geometric capacitance
measurement are studied in detail and are compared. No such study has been carried out
in literature before, which makes the comparison between dielectric constant values
obtained from different techniques at question. In this chapter, not only were three
different characterization techniques compared, the measurement conditions at which
geometric capacitance could be accurately measured were proposed for the first time.
This chapter provides an experimental guideline for geometric capacitance
characterization in thin-film polymer devices including but not limited to semiconducting
polymers, and is thus beneficial for the field of polymer devices in a broader context. It
would be useful to characterise the dielectric constant following the suggested
experimental process in a wide range of semiconducting polymers under strictly
controlled inert environment. This will not only provide accurate dielectric constant
values for theoretical studies, but it will also reveal if the observed environment effect on
the dielectric constant of DT-PDPP2T-TT is present in other polymers. If the influence
of oxygen and moisture on dielectric constant is widely present in semiconducting
polymers, the charge recombination losses in these PSC devices could be reduced simply by controlling the material processing environment.

The back-transfer mechanism proposed in this thesis also provides a new designing concept in ternary blend PSCs. By selecting donors with cascaded HOMO levels and controlling the film morphology, reduced recombination can be achieved in a ternary blend using two materials with diffusion controlled recombination in their respective binary systems. The back-transfer mechanism not only provides an alternative mechanism explaining recombination kinetics in complex systems like ternary blend solar cells, it can also be a design strategy to reduce recombination in polymer based solar cells, which could give a promising step for performance enhancement in polymer solar cells.
APPENDIX

Figure A-1 TRCE transients in DT-PDPP2T-TT: PCBM 1:3 w/w at 100 μJ cm\(^{-2}\).

Figure A-2 The influence of epoxy and UV curing on capacitance value of the device.
Table A-1 A list of geometric capacitance values obtained from thin-film pristine devices with different thicknesses, and the calculated dielectric constant values.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>Geometric Capacitance (nF)</th>
<th>Dielectric constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>500 ± 15</td>
<td>0.662 ± 0.018</td>
<td>6.23 ± 0.17</td>
</tr>
<tr>
<td>221 ± 10</td>
<td>1.56 ± 0.1</td>
<td>6.47 ± 0.40</td>
</tr>
<tr>
<td>272 ± 7</td>
<td>1.33 ± 0.02</td>
<td>6.79 ± 0.14</td>
</tr>
<tr>
<td>630 ± 58</td>
<td>0.55 ± 0.047</td>
<td>6.53 ± 0.54</td>
</tr>
</tbody>
</table>

Figure A-3 1H-NMR data for three DT-PDPP2T-TT batches, P61, P80 and P33.
Figure A-4 Bimolecular recombination coefficient obtained from three DT-PDPP2T-TT: [60]PCBM (1: 3 w/w) devices with different active layer thicknesses, fabricated from the same polymer batch.
Figure A-5 Charge carrier lifetime plotted as a function of $V_{oc}$ for DT-PDPP2T-TT: PCBM (1:3, w/w) and P3HT: PCBM (1:1, w/w) devices with different active layer thicknesses, as listed in figure legend.
Figure A-6 Photoluminescent spectra of pristine DT-PDPP2T-TT and DT-PDP2PT-TT: PCBM blend films casted from chloroform solutions.

Figure A-7 Comparison between microsecond TA spectra obtained from two different DT-PDPP2T-TT batches.