

Strong Light-Matter Coupling in Organic Photovoltaics

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Statement of originality

This is to certify that to the best of my knowledge, the content of this thesis is my own work.

This thesis has not been submitted for any degree or other purposes.

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Abstract

Organic photovoltaic (OPV) solar cells are a promising next-generation solar harvesting technology based on organic polymers and small molecules. They can be flexible and lightweight, and their fabrication can be achieved using environmentally friendly materials with low financial and energy costs of production. They possess tunable absorption spectra, allowing for maximum energy harvesting and for the tailoring of their optical properties for particular applications such as building-integrated solar harvesting.

Perylene diimides are a promising class of electron acceptor OPV molecule due to their excellent absorption properties, low cost, ease of synthesis, stability and tunability. These can be paired with the electron donor PTB7-Th to create a suitable material system for solar energy harvesting. We show here that perylene diimide monomers (PDIs) are plagued by strong intermolecular $\pi - \pi$ interactions which inhibit their device performance, but we also show that these interactions can be partially overcome by the use of dimers having a twisted plane of conjugation (TPDIs). Intensity-dependent device measurements are used to demonstrate that TPDI dimers experience reduced recombination losses due to their more favourable morphology. The system is also seen to exhibit dual-direction energy harvesting through transient absorption spectroscopy measurements since charge transfer states are formed from excitation of both the PTB7-Th donor and the (T)PDI acceptors. We provide a method to quantify the contribution of each material to the overall charge production, and show that TPDI blend films demonstrate more balanced dual-direction energy harvesting compared to PDI blend films.

It is also possible to alter the properties of organic materials by strong light-matter coupling, where a photon in resonance with an optical cavity couples to the excitonic transition of a material, producing a new quasi-particle termed a polariton. The formation of polaritons causes splitting of the excited state energy levels such that new energy levels, termed polariton branches, are created. We fabricate and compare bare and cavity-based OPV devices and demonstrate the presence of strong coupling in cavity-based OPVs through both optical and

electrical measurements. We demonstrate improved device functioning in cavity devices once the cavity structure is accounted for. We also fabricate cavity-based devices of different thicknesses in order to control the interaction between the exciton in the material and the photon in the cavity. Through these experiments, we demonstrate that the presence of a resonant cavity within an OPV device has the ability to alter properties which are normally intrinsic to a material without changing the material itself, having profound implications for the study of device physics in OPVs.

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Preface

All PhD projects are full of challenges, and this project has been no different. It is worth noting that the work reported here was undertaken in the context of the global pandemic of COVID-19. I began my PhD in March 2020, the same month that the pandemic became a concern in Australia, leading to nationwide lockdowns. In July 2020, I switched my work to an entirely new project which was more feasible under COVID-19 imposed travel restrictions. This involved starting again from the beginning in a new scientific area: that of OPVs.

Positive outcomes and silver linings of the COVID-19 pandemic are few and far between. However, in my case I can say that it provided me with the opportunity to study the fascinating topic of OPV devices and strong light-matter coupling, and I am deeply grateful for that.

Statement of contribution

All sample fabrication, measurements and analysis presented in this thesis are my own work except where otherwise specified.

Simulations of the effect of strong light-matter coupling on the creation of polariton energy states shown in Figures 1.9 and 1.10 were performed using a Matlab app written by Julien Leoni.

PDI and TPDI materials for this project were provided by Prof. Satish Patil, Suraj Yadav and Chandrasekhar Gangadharappa from IIT Bangalore. All other materials were obtained commercially.

Cavity samples of (T)PDI dispersed in a polystyrene matrix were fabricated by Patrick Conaghan. The samples presented in Figure 6.6 were measured by Patrick whereas the sample presented in Figure 6.4 was measured by myself. Both measurements were analysed by myself.

The refractive index of PTB7-Th presented in the Appendix section B.2 was measured by Phoebe Pearce.

Authorship attribution

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I designed the study, analysed the data, performed deconvolution and modelling in consultation with A. N. Stuart and wrote the manuscript.

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I performed the relevant measurements, analysed the data, and wrote the accompanying discussion for the measurements.

I hereby certify that all work presented in this thesis is my own work except for where otherwise acknowledged. The work presented here was undertaken between July 2020 and December 2023 at the School of Chemistry, The University of Sydney or Cavendish Laboratories, The University of Cambridge.

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As supervisor for the candidature upon which this thesis is based, I can confirm that the authorship attribution and statements of contribution above are correct.

Signed:

Name:

Date:

The heavens declare the glory of God;
the skies proclaim the work of his hands.
Day after day they pour forth speech;
night after night they reveal knowledge.
They have no speech, they use no words;
no sound is heard from them.
Yet their voice goes out into all the earth,
their words to the ends of the world.

Psalm 19:1-4

List of abbreviations

AFM	Atomic force microscopy
AR	Angular reflectance
BHJ	Bulk heterojunction
CT	Charge-transfer (state)
DBR	Distributed Bragg reflector
EA	Electron affinity
EL	Electroluminescence
EQE	External quantum efficiency
ETL	Electron transport layer
FF	Fill factor
FP	Fabry-Pérot (cavity)
FRET	Förster resonant energy transfer
FWHM	Full width half maximum (linewidth)
GSB	Ground state bleach
HET	Homoelectron transfer
HOMO	Highest occupied molecular orbital
HTL	Hole transport layer
ICT	Intramolecular charge transfer (state)
IoT	Internet of things
IP	Ionisation potential

IPA	Isopropyl alcohol
IRF	Instrument response function
ITO	Indium tin oxide
J_{sc}	Short circuit current
JV	Current-voltage (measurement)
LP	Lower polariton
LUMO	Lowest unoccupied molecular orbital
MP	Middle polariton
NFA	Non-fullerene acceptor
NOPA	Non-collinear optical parametric amplifier
NREL	National Renewable Energy Laboratory
OLED	Organic light emitting diode
OPV	Organic photovoltaic (device)
P3HT	Poly(3-hexylthiophene)
PCBM	1-(3-methoxycarbonyl)propyl-1-phenyl[6,6]C61 (functionalised Buckminster fullerene)
PCE	Power conversion efficiency
PDI	Perylene diimide (monomer)
PEIE	Polyethylenimine
PES	Polyethersulfone
PHJ	Planar heterojunction
PIA	Photo-induced absorption
PL	Photoluminescence
PMMA	Polymethyl methacrylate
PS	Polystyrene
PTB7-Th	Poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b;4,5-b']dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-b]thiophene)-2-carboxylate-2,6-diyl)]

PTFE	Polytetrafluoroethylene
PV	Photovoltaic
SE	Stimulated emission
SRH	Shockley-Reid-Hall (recombination)
TA	Transient absorption (spectroscopy)
TCSPC	Time-correlated single photon counting
TPC	Transient photocurrent
TPDI	Twisted perylene diimide (dimer)
TPV	Transient photovoltage
TRES	Time-resolved emission spectra
UP	Upper polariton
V_{oc}	Open circuit voltage

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Chapter 1

Introduction

1.1 Organic Photovoltaics

Light is of fundamental importance to the way that we experience the world, far more than simply enabling us to see. Nature itself is sustained by sunlight; if it were to be removed there would be no ability for plants to photosynthesise, leading to the disappearance of critical food sources and the collapse of entire ecosystems. Sunlight has been central to human flourishing for many thousands of years, and still powers our modern sun-asynchronous lifestyles in many ways. Even fossil fuel deposits are created by long-term compression of biomass, for which sunlight was instrumental in its original production.

Solar energy is so plentiful that the amount reaching the surface of the Earth in one hour is enough to meet modern worldwide energy demands for over a year, if we are able to successfully capture and store it. Even if we only consider the amount of solar energy claimed to be easily harvestable this still far exceeds worldwide energy demand.⁴⁻⁶ Worldwide investment in renewable energy is critical for reducing the harm of climate change caused by the burning of fossil fuels, and solar energy is widely considered to be one of the key technologies able to assist with this challenge.

1.1.1 The evolution of OPVs

The history of solar energy harvesting began over a century ago when Alexandre Edmond Becquerel first observed the photovoltaic effect in 1839.⁷⁻⁹ The first modern silicon solar cell was reported by Bell Laboratories in 1954 with an efficiency of 6%.¹⁰ Since then, silicon photovoltaics have been heavily researched and optimised, such that the maximum efficiency sits at 26.8 %, ¹¹ not far below the theoretical limit originally proposed by Shockley and Quieser of $\sim 30\%$.^{12,13}



1

Organic photovoltaics (OPVs) are an emerging thin-film photovoltaic technology which make use of organic semiconductors, where the active layer is comprised of conjugated polymers and/or small molecules. OPVs are often considered a young technology, but the first OPVs containing photosynthesis-inspired porphyrins were developed in 1975.¹⁴ Major milestones in the development of OPVs include the discovery of conducting polymers, for which Heeger, MacDiarmid and Shirakawa won the 2000 Nobel Prize in Chemistry;¹⁵ the mixing of multiple semiconducting materials and the creation new heterojunction architectures;^{16–19} and improvements in solubility of fullerene derivatives.²⁰ For two decades, research focused on devices comprised of n-type fullerene-based electron acceptors paired with p-type polymer donors, and improvements in device performance originated primarily from improvements in polymer morphology, stability, processability and photophysical properties.²¹

The emergence of non-fullerene acceptors (NFAs) in the early 2010s generated a new wave of interest in OPVs, since NFAs can be synthetically altered to tune the electrical and optical properties as desired. Typical and novel OPV active layer materials are discussed in more detail in Section 1.1.6. In 2017, the efficiency of NFA-based OPVs overtook that of fullerene-based OPVs,²² signalling the beginning of a new era in OPV research. Continued research has led to continued improvements in device performance, with the highest reported efficiencies for single-junction devices sitting just under 20%.^{23–27} This is represented in context with other emerging photovoltaic technologies in the National Renewable Energy Laboratory (NREL) efficiency chart in Figure 1.1. In summary, improvements in device performance have been driven by an ever-increasing understanding of the structure-property relationships of the materials and devices they are contained within. These device structures and their implications are explored below.

1.1.2 OPV device properties

Due to the solution processability of the active components, OPVs can be fabricated via roll-to-roll fabrication methods.²⁸ This enables the production of flexible, lightweight devices that can be deployed in applications where traditional silicon solar panels are unsuitable.^{29,30} Additionally, optimised roll-to-roll fabrication processes have lower cost and energy requirements compared to the fabrication of crystalline silicon devices. The energy payback time of a renewable energy source is defined as the amount of time this technology must harness energy in order to offset the energy consumed by its production. For silicon photovoltaics this can be up to 4 years,

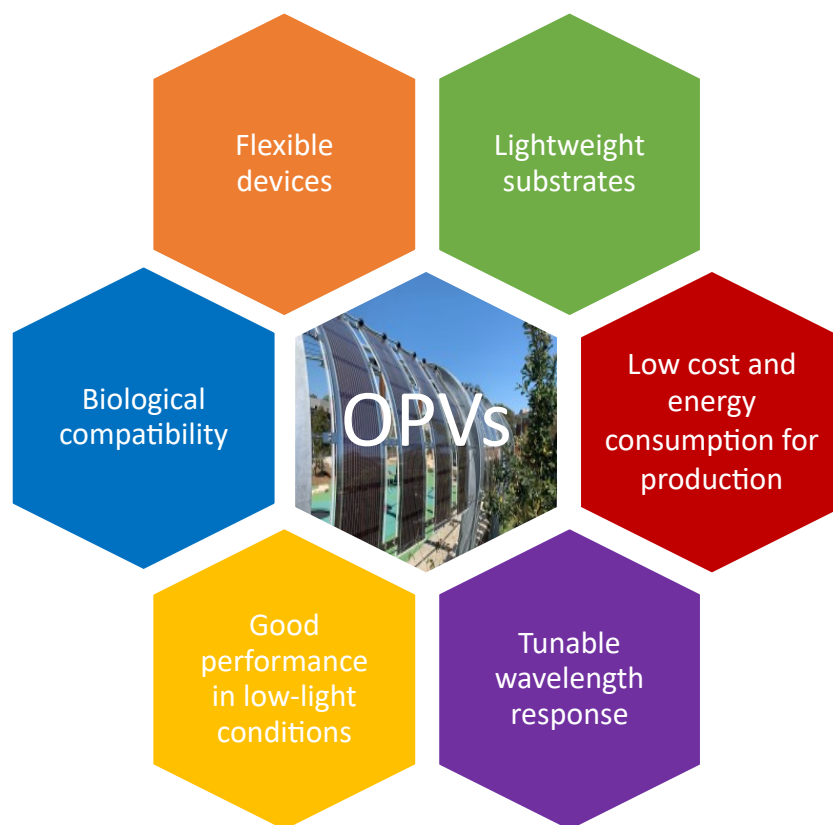


Figure 1.2: Properties of OPVs which make them useful for a variety of applications. The centre image is of a community demonstration of OPVs at The Canopy in Lane Cove, Sydney.

whereas for OPVs this can be on the order of days.^{6,31} The ease of chemical synthetic adjustment of organic molecules also allows for highly tunable macroscale properties such as the colour and transparency of the final product, making them well-suited to building-integrated photovoltaic applications.^{32,33} Semi-transparent OPVs have even been shown to outperform monocrystalline silicon modules when mounted at non-ideal angles of incident irradiation as is often the case for building-integrated photovoltaic modules.³⁴ Transparent OPVs are made possible when the absorbing molecules are tailored to absorb ultraviolet or near-infrared light, with cells able to achieve up to 80% transparency.^{35,36}

Apart from outdoor or building-integrated applications, OPVs have demonstrated more efficient light energy harvesting from indoor conditions compared to other inorganic technologies, making them an especially promising technology for indoor applications for light harvesting and for powering small internet-of-things (IoT) devices such as sensors, monitors and control systems.^{37–40} This arises in part due to their tunable bandgap, since indoor light sources often emit in a much narrower spectral range compared to the sun, and organic materials can be tailored such that their absorption spectrum matches the emission spectrum of common light

sources. The tunable light response of OPVs also makes them effective as photodiodes^{41–44} including for infrared light detection.^{45,46} This extends to photodetection in biological contexts, such as retinal prosthesis.^{47,48} The tunability of organic molecules also makes them well suited for tandem devices, where different layers in the cell are responsible for harvesting different sections of the visible spectrum.⁴⁹ OPVs have even been proposed for space applications, since their tunable bandgap makes them useful for harvesting energy from stars other than our own sun.⁵⁰

1.1.3 Charge generation

The basic function of all photovoltaic devices is to generate charges from harvested light. The absorption of a photon by a material leads to the formation of a bound electron-hole pair which is termed an exciton. In inorganic materials, the high dielectric constant due to increased electron shielding causes the formation of a Wannier-Mott exciton which is loosely bound and can often be separated at room temperature.^{51,52} In contrast, organic materials have a low dielectric constant and the Frenkel excitons formed are often highly localised on the molecule participating in absorption. The strong exciton binding energy means that it is often necessary to include a second molecule with offset energy levels in order to achieve spatial separation between the electron and hole, although there are some exceptions to this as discussed in Section 1.1.4. This leads to the concept of the electron donor and the electron acceptor, hereto referred to as the donor and acceptor, and the resulting heterojunction formed between them.

The ability of an organic molecule to accept an electron can be understood as the electron affinity (EA), whilst the ability of a molecule to be ionised is (at least to first order) the ionisation potential (IP). These values are measured from the vacuum level, corresponding to zero energy, and are defined as having a negative value. Often these terms are represented by the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) respectively.²¹ OPV material combinations are chosen such that the EA of the acceptor is greater than the EA of the donor, which leads to a deeper (lower) LUMO frontier orbital, allowing downhill electron transfer when the donor undergoes photoexcitation as shown in Figure 1.3 a). The IP of the acceptor should also be greater than the IP of the donor, leading to a deeper (lower) HOMO, allowing uphill hole transfer if the acceptor is photoexcited. In either case, this leads to the generation of a charge transfer (CT) state, where the electron is localised on the acceptor and the hole on the donor.

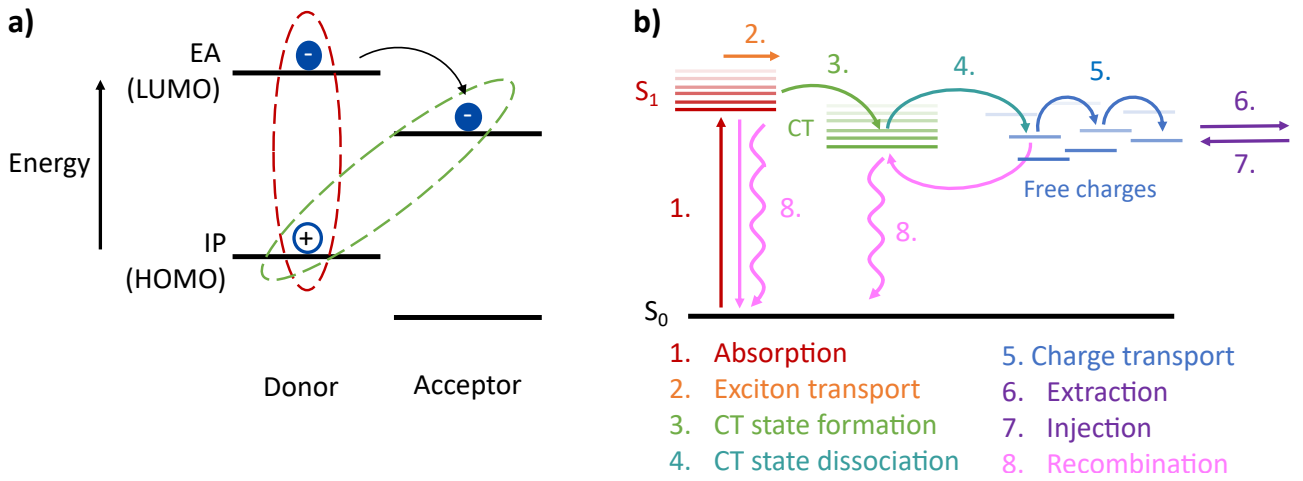


Figure 1.3: a) OPVs are usually comprised of an electron donor and an electron acceptor with offset electron affinity (EA) and ionisation potential (IP) levels to allow for downhill electron transfer from the donor to the acceptor, and uphill hole transfer from the acceptor to the donor. The singlet excited state thus turns into a charge transfer (CT) state. b) Energy level diagram demonstrating the absorption of a photon and exciton transport in the donor or acceptor material, the formation and dissociation of the CT state into free charges and subsequent charge transport, extraction and injection currents and the recombination of free charges to form a CT state and of the CT and S_1 states to the ground state. For recombination, straight arrows represent radiative decay and wavy arrows non-radiative decay.

The difference in energy E_{offset} between the optical bandgap and the CT state dictates the driving force for charge separation. Fullerene OPV blends reliably require an offset of > 0.3 eV in order to achieve charge separation, however this is not the case for non-fullerene acceptors.^{21,53} Instead, it has been demonstrated that cells can reach up to 90 % internal quantum efficiency with near zero driving energy, as was shown for a P3TEA:SF-PDI blend.⁵⁴ The lack of necessity of an offset to drive charge generation in non-fullerene acceptors is an area of hot debate, as is the necessity for considering a CT state in the first place.

Figure 1.3 b) provides a summary of the key processes that occur in OPVs to enable charge production. After the photon is absorbed to create an exciton, this must (usually) migrate to an interface. If the exciton binding energy can be overcome, exciton dissociation will occur to enable the formation of the CT state, which can then dissociate into free charges. As long as the free charges are able to be transported to the electrodes by drift or diffusion processes and undergo successful extraction, a current will be produced. Figure 1.3 b) also details the loss mechanisms of charge injection, recombination of free charges to the CT state and recombination of the CT and S_1 states to the ground state through radiative and non-radiative processes, a discussion of which is provided in Section 1.1.4.

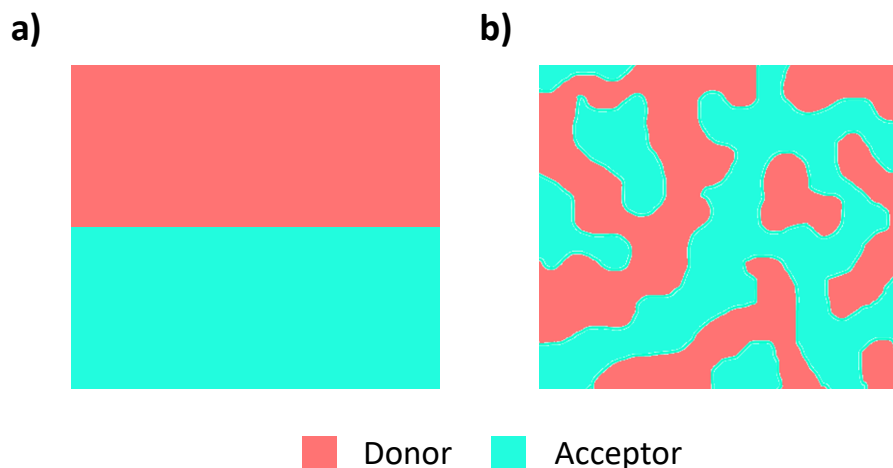


Figure 1.4: a) Planar (bilayer) and b) bulk heterojunction morphologies.

The donor and acceptor can be arranged in either a planar heterojunction (PHJ), where they exist in distinct layers,⁵⁵ or in a bulk heterojunction (BHJ), where they are mixed together,⁵⁶ or even a combination of the two.⁵⁷ Schematics of planar and bulk heterojunctions are shown in Figure 1.4. Planar heterojunctions, also termed bilayer devices, have the benefit of effective charge transport of materials through each layer, however if the dimension of the layer is larger than the exciton diffusion length the excitons may decay before reaching the interface and dissociating into free charges. Bulk heterojunctions encourage donor/acceptor blending such that the domains are broken down into dimensions smaller than the exciton diffusion length, allowing excitons to more easily reach an interface and dissociate. However, donor and acceptor domains must be arranged in an intercalating network such that a continuous path exists between the interface where free charge is generated and the electrode.

When charges reach the electrodes they are extracted and current is produced. This description assumes the complete conversion of excitons into electrical charge, however there are loss mechanisms that prevent this from occurring, which are discussed below.

1.1.4 Charge recombination

Recombination is a topical issue in the area of OPVs as it is the leading cause for the discrepancy between device performance and the theoretical maximum performance achievable as predicted by the Shockley-Queisser limit. A variety of loss mechanisms are present inside devices which prohibit the complete conversion of excitons into electrical charge, and these will be discussed below.

If CT state formation and dissociation is not competitive with exciton or CT state decay, electrons and holes can recombine before they have been spatially separated at the donor-acceptor interface. This is referred to as geminate recombination, arising from the Latin ‘gemini’ meaning twins, as the electron and hole were created by the absorption of the same photon. On the other hand, non-geminate recombination refers to the recombination of an electron and hole pair which encounter each other as free charges and thus have not arisen from the same photon absorption event. This is often referred to as bimolecular recombination due to the dependence of the rate on the concentration of both the exciton and hole populations, making it a second-order process.⁵⁸

When traps are present for one carrier species, the rate of the resulting recombination depends only on the concentration of the free (opposite sign) charges. This type of recombination is termed monomolecular recombination as the rate equation is described by a first-order process. Trap-assisted recombination is also referred to as Shockley-Reid-Hall (SRH) recombination.⁵⁹ This can exist concurrently with bimolecular recombination. In some disordered blends, it may be necessary to go beyond the classical description of SRH recombination and include a distribution of trap state energies or the inclusion of trapping and detrapping rates in a multiple trapping model.⁶⁰

Bimolecular recombination is often described by Langevin theory,⁶¹ where recombination of an electron and hole occurs when they exist at a distance less than the Coulomb radius. However, bimolecular recombination has been shown to be dependent on other factors such as mobility, temperature, internal electric field and charge carrier concentration, rendering the Langevin formalism overly simplistic. A reduction factor introduced to characterise reduced Langevin-type recombination⁶² is thus commonly used to describe bimolecular recombination. Other models such as the Onsager model⁶³ together with the additions of Braun⁶⁴ or the Arkhipov model^{65,66} have also been used to describe recombination in OPVs, but where they are used adaptations or modifications are also frequently applied, making it a complex and highly nuanced area of study.^{67,68}

Regardless of how it is modelled, the presence of radiative (photon-emitting) and non-radiative (non photon-emitting) recombination processes in devices is one of the main factors limiting OPV device efficiencies. Shockley and Quieser’s work on detailed balance suggests that non-radiative recombination must be limited in devices in order to achieve high efficiencies. Radiative recombination cannot be avoided as it is the reverse of the absorption process. Put

simply, a good OPV must also be a good organic light-emitting diode (OLED). Recombination is also the true reason that heterojunctions between donor and acceptor materials are required for high performing OPV devices. It has often been assumed that the role of the electron donor and acceptor are critical to the generation of charge transfer states, but charge generation has recently been shown for single component devices comprising the high-performing OPV acceptor Y6.⁶⁹ Here, it was shown that the presence of bimolecular recombination in the single-component devices was the limiting factor for their performance. This is discussed in further detail in Chapter 3. Thus the investigation, control, and reduction of recombination is one of the main challenges for the OPV research field today.

1.1.5 Conventional and inverted geometries

One way to influence the device performance of OPVs is to alter the device structure. OPVs are typically built with either a conventional or inverted structure as shown in Figure 1.5. In both cases, the active layer is sandwiched between two conducting electrodes, one of which must be transparent to allow light to enter the cell. In a conventional structure, electrons move to the cathode, which is usually a low work function material such as aluminium in order to ensure electron extraction. Meanwhile, holes move to the anode, often indium-tin-oxide (ITO), to be extracted. In an inverted structure, the polarity is reversed and a high work function material such as silver (Ag) is used as the top anode for hole extraction whilst the transparent electrode becomes the cathode where electron extraction takes place.

Inverted device geometries are often preferred due to their improved stability and performance.⁷⁰ The use of air-stable high work function materials as the top anode is preferable over low-work function materials as the latter are easily oxidised.^{71,72} Additionally, anode materials such as Ag are able to be deposited from colloidal nanoparticle solutions which have a higher compatibility with roll-to-roll processing compared to electrodes deposited by thermal evaporation processes.^{73,74} Finally, the use of inverted device geometries has also been linked to sustained device performance over time due to more favourable morphology and phase separation leading to lowered recombination.⁷⁵

Regardless of the conventional or inverted geometry of the cell, it is ubiquitous to use charge transport layers in between the active layer and the electrodes. The purpose of these layers is to selectively transport one charge whilst blocking the other, hence they are also termed charge-blocking layers. Specifically, the electron transport layer (ETL) enables the selective

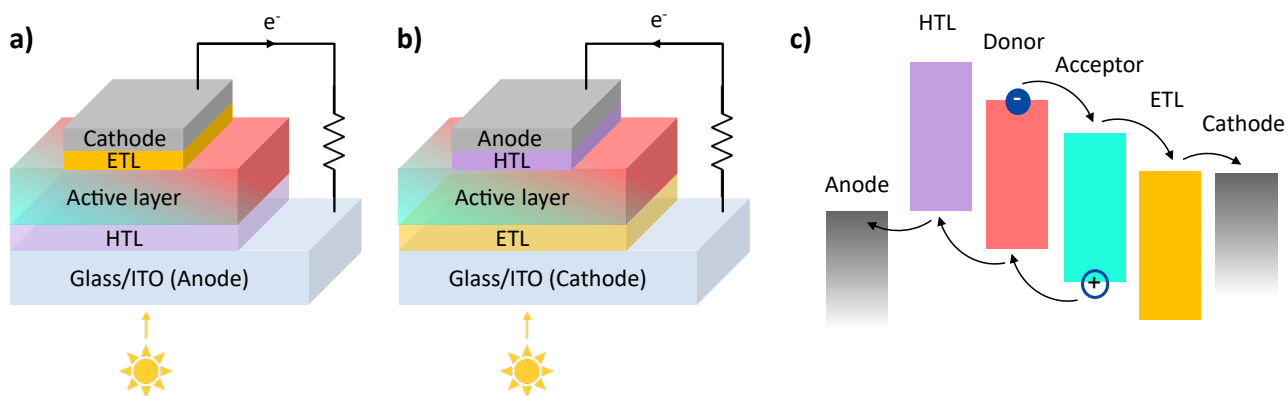


Figure 1.5: a) Conventional and b) inverted device geometries commonly used in OPVs. The active layer is sandwiched by the electron transport layer (ETL) and cathode on one side, and the hole transport layer (HTL) and anode on the other. c) Cascading energy levels for the relevant layers of the cell which enable charge generation, transport and extraction.

transport of electrons at the cathode, which is the top (reflective) electrode in a conventional device or the bottom (transparent) electrode in an inverted device as shown in Figure 1.5. Conversely, the hole transport layer (HTL) enables selective transport of holes at the anode, which is the bottom (transparent) electrode in a conventional device or the top (reflective) electrode in an inverted device. Interlayers also play other key roles in device functionality such as adjusting the energetic barrier between the electrodes and the active layer, determining the device polarity, forming a physical barrier between the active layer and the electrodes to prevent chemical reactions between them, and acting as optical spacers to ensure the electric field in the device is maximum at the location of the active layer.^{72,76} Where interlayer materials are used at the bottom (transparent) electrode, there is an additional requirement that they must be transparent at visible wavelengths to allow for transmission of light through to the active layer. Materials suitable for use at the cathode include inorganic crystalline materials such as LiF, which is commonly used for conventional geometries, or metal oxides such as ZnO or TiO_x which are commonly used for inverted geometries. Materials suitable for use at the anode include organic blends such as the PEDOT:PSS polymer blend, which is nearly exclusively used for conventional geometries, or metal oxides such as MoO₃ or V₂O₅ frequently used in inverted geometries. Much research has been performed on understanding and optimising interlayers since they are so crucial to device performance.^{77–80} However, in this thesis we use well-studied interlayers and focus purely on the properties and effects of the active layer.

1.1.6 Active layer materials

The most common way to alter device performance is to choose an alternative set of active layer materials. The most studied active layer material system for OPVs is undoubtedly that of Poly(3-hexylthiophene) (P3HT) and 1-(3-methoxycarbonyl)propyl-1-phenyl[6,6]C61 (PCBM),⁸¹ the structures of which are shown in Figure 1.6. P3HT is a p-type polymer electron donor whilst PCBM is a functionalised Buckminster fullerene and acts as a n-type electron acceptor as demonstrated in Figure 1.3. P3HT has a good absorption coefficient for light in the visible range and is also a relatively good charge conductor. PCBM is necessary to assist with charge separation at the interface, although it does not contribute as much to the absorption of incident light. P3HT:PCBM device efficiencies frequently lie between 2-4 %, which is far less than current state of the art materials as mentioned in Section 1.1.1, however it remains a (relatively) cheap, reliable, and well-studied system and thus a good choice for mass production or for benchmarking OPV fabrication techniques.

In contrast to P3HT:PCBM, current high performing devices are often made with polymers and small molecules such as non-fullerene acceptors that are both capable of strong visible absorption and charge transport. High-performing polymer-polymer⁸²⁻⁸⁵ or small molecule-small molecule systems⁸⁶⁻⁸⁸ have also been realised. Nonetheless, this thesis will focus on the use of polymer donors and small molecule acceptors.

Non-fullerene acceptors simultaneously achieve high photocurrent and low voltage losses compared to fullerenes, and do not require driving energies as fullerenes do as mentioned in Section 1.1.3. They are often tunable, since the ease of making structural changes allows chemists to create acceptor molecules with energy levels of their own choosing, allowing for the realisation of donor-acceptor systems with complementary absorption and efficient charge separation.⁵³ This provokes intriguing questions as to the role of the donor and acceptor materials and their relative contribution to charge generation, as will be discussed further in Chapters 4 and 5.

There are two main categories of non-fullerene acceptors: those based on fused aromatic diimides and those based on electron push-pull effects. In both cases, conjugated backbones are modified with π -conjugated electronegative elements such as oxygen or nitrogen, which participate in the conjugation of the backbone. This allows both for good electron-accepting abilities, as well as a low reorganisation energy making for better charge transport without electron traps.

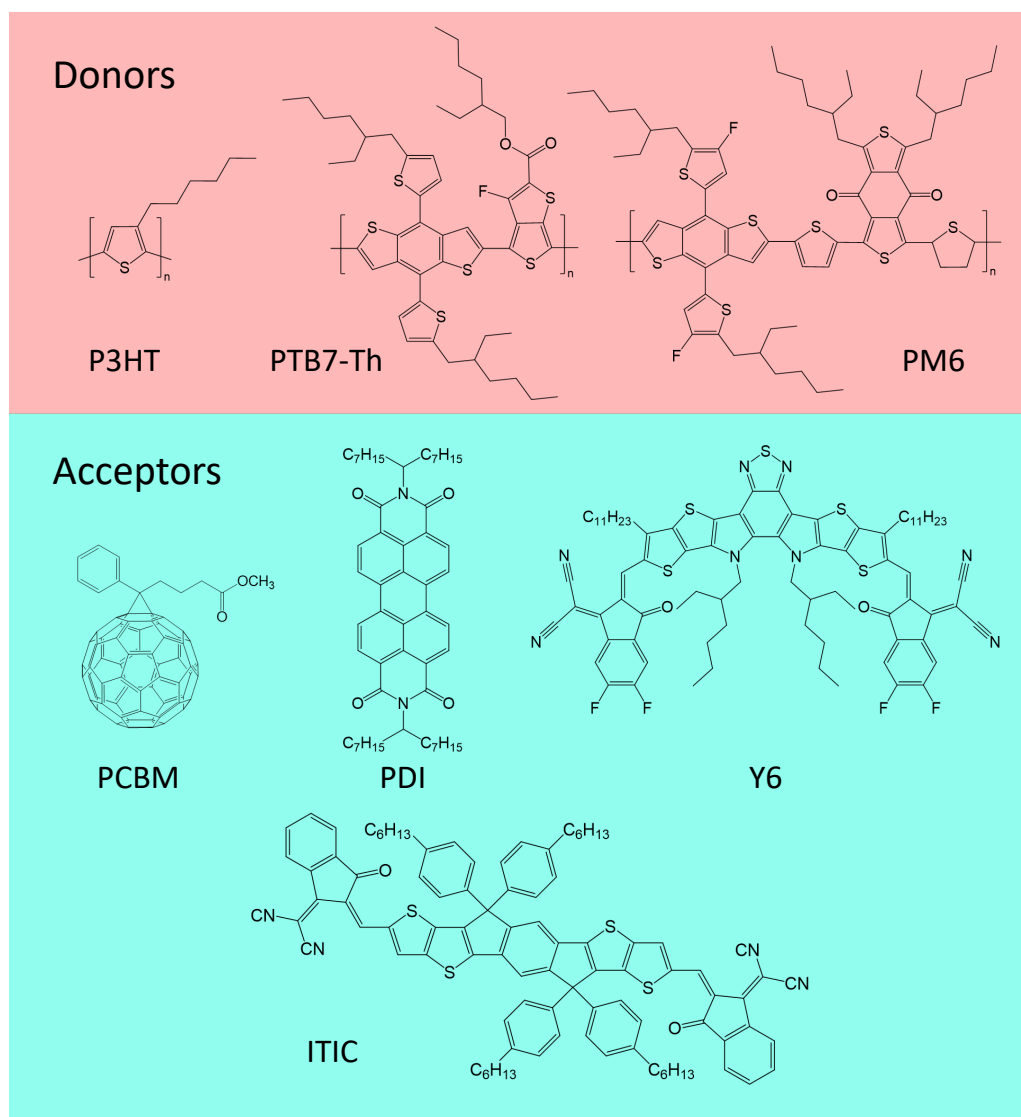


Figure 1.6: Structures of key OPV materials that function as electron donors and acceptors.

Common fused aromatic dye molecules include perylene diimide-based molecules, such as that shown in Figure 1.6, and naphthalene diimide-based molecules. These are commonly used as acceptors in OPVs due to their excellent absorption properties, thermal, chemical and photostability and their low cost of synthesis.⁸⁹ They have multiple sites for chemical modification, high electron affinities due to the electron-withdrawing imide groups, atom-economic synthetic procedures and high electron mobility due to intermolecular electronic coupling.⁹⁰ These intermolecular interactions can be problematic, causing aggregation and phase separation. However, aggregation of perylene structures can be minimised through synthetic control techniques such as the formation of perylene dimers, as will be discussed in Chapter 4.

Push-pull acceptors are effective electron acceptors due to their ability to move charge around the molecule through push-pull interactions. An example of this class of molecule is ITIC, as shown in Figure 1.6, and related derivatives. The properties of these molecules can also be easily synthetically tuned. For example, the inclusion of electron-rich end-capping units such as methyl or methoxy groups can raise the energy of the acceptor LUMO, whereas the inclusion of electron-deficient atoms such as F in the end-capping groups can lower (deepen) the LUMO energy.⁵³ Many push-pull acceptors can be described by an A-D-A, where ‘A’ represents an electron-withdrawing block and ‘D’ an electron-donating block.⁹¹ The complexity of push-pull acceptors has steadily increased, and it is common to see molecules such as those in the Y-series with an A-DA’D-A type structure^{92,93} or an A-D-D’-D-A type structure,⁹⁴ where the apostrophe represents a unique donor or acceptor unit. The most well-studied of these molecules is Y6, the structure of which is also pictured in Figure 1.6, and first enabled devices to reach efficiencies over 15 %.⁹⁵ However, these fused-ring acceptors are often highly synthetically complex, placing difficulty on the scale-up of their manufacturing and thus their availability for use in commercial OPVs.⁹⁴ Non-fused ring acceptors have been proposed and have demonstrated good progress, but still remain more complex than aromatic dye molecules.

In addition to the production of new non-fullerene acceptor molecules, much research has been performed on polymer donors, such that there is now a large range of choice for both components of the blend. It is critical that the HOMO and LUMO of the polymer appropriately match that of the acceptor to allow for downhill electron transfer to the acceptor and preferably also uphill hole transfer to the donor. Other considerations that should be included in the choice of donor is the absorption profile, which should be complementary to that of the acceptor; the minimisation of voltage losses through the reduction of the driving force, seeing as non-fullerene acceptors do not seem to require this; and morphology and miscibility control, so as to enable appropriate mixing between the donor and acceptor domains.⁹⁶ Material cost, stability and other functionality such as transparency for semi-transparent OPVs should also be considered.⁹⁷

Polymer donors are classified into four main categories: homopolymers such as the polythiophene derivative P3HT pictured in Figure 1.6, donor-acceptor co-polymers, quinoid polymers and other types.⁹⁸ Homopolymers often have large bandgaps which limits the absorption of visible light. Joining multiple chromophore units into co-polymers with electron-donating and accepting domains enables intramolecular charge transfer and delocalisation of π electrons along the conjugated backbone. The formation of quinoid polymers from two aromatic units

which are fused together leads to resonant energy stabilisation, resulting in the reduction of the bandgap of the polymer. These systems often have high HOMO levels which can be lowered in energy (made deeper) by alternating them with other prequinoid monomers such as thiophenes and fluorenes along the polymer backbone to improve their performance as measured by the open circuit voltage V_{OC} . An example of this is the polymer PTB7, which is made up of alternating electron-accepting thieno[3,4-b]thiophene units and electron-donating benzo[1,2-b:4,5-b']dithiophene units.⁹⁹ The properties of this molecule were further improved by incorporating a heterocyclic side chain to produce PTB7-Th as shown in Figure 1.6; namely, the HOMO level was deepened, the absorption range red-shifted and the hole mobility improved.¹⁰⁰ This improvement assisted OPVs in surpassing the 10 % performance benchmark, so as a result PTB7-Th is also known as PCE-10, as well as PBDTTT-EFT. PTB7-Th also matches well with various non-fullerene acceptors such as perylene diimides, due to its deep HOMO and complementary absorption profile, and thus it is the polymer donor chosen for the majority of the studies in this thesis.

Despite the development of tunable acceptors and donors enabling remarkable coverage of the AM1.5G solar spectrum, and the common ability of both material components to produce charge, little work has been done to thoroughly understand the role of dual-direction energy harvesting and the influence of morphology and chromophore packing upon it. For example, to the best of our knowledge there has been no quantification of the role of each of the domains in charge generation. In this thesis, we adress this gap by explicitly quantifying the contribution of the donor and acceptor domains to overall charge generation in OPV-like blend films.

It is also generally assumed that the only way to alter the properties of a material is to alter the structure or processing conditions of the material, however it is also possible to do so by strong light-matter coupling as explained below.

1.2 Strong coupling

An additional strategy for altering the performance of devices is to change the photophysics of the materials inside the device through strong light-matter coupling. This has great potential to unlock further levels of material tunability without requiring the substitution of the materials themselves, thus removing the need to perform extensive photophysical and morphological characterisation which exists for each new material combination. This Section (1.2) introduces the concept of strong light-matter coupling in more detail, and Section 1.3 forms links between the two concepts of OPVs and strong light-matter coupling.

1.2.1 Introduction to polaritons

The successful functioning of OPVs is not possible without the presence of light. For many centuries, light and matter were studied independently of each other, with each considered to have differing properties.¹⁰¹ Newton’s 1672 discovery of the dispersion of light through a prism¹⁰² began an inquiry into the interaction of light and matter.^{103,104} Maxwell’s description of light as a wave^{105,105} led to the development of the Lorentzian model of light interacting with classical matter particles.¹⁰⁶ In the early 20th century, Einstein proposed that light exists as quanta of energy, i.e. photons, which interact with matter.^{107,108} True unified consideration of light and matter was then made possible by the development of quantum mechanics, quantum electrodynamics and quantum optics.¹⁰⁹

As discussed above, we now understand that the absorption of light by matter leads to the formation of electron-hole quasiparticles, termed excitons, which are loosely bound in inorganic materials (Wannier-Mott type) and strongly bound in organic materials (Frenkel type). Just as these Frenkel excitons in organic materials can couple to each other to achieve resonant energy transfer, so too can either a Frenkel or a Wannier-Mott exciton couple to a photon.¹⁰¹ In this interaction, the photon is not simply a spectator but rather plays an active role in coupling to the exciton. The resulting quasiparticles, termed polaritons, have hybrid properties between that of the photon and exciton and new energy levels arising from splitting. Strong exciton-photon coupling and the accompanying splitting of energy levels was first observed in an inorganic material through the creation of surface polaritons in LiF thin films.¹¹⁰ Much research effort was subsequently dedicated to the field of exciton-photon strong coupling in inorganic materials, including quantum wells,^{111–113} surface plasmon polaritons,¹¹⁴

and Rydberg atoms.^{115–118} The importance of the field was recognised through the 2012 Nobel Prize in Physics being awarded to Serge Haroche and David J. Wineland for their work in strong light-atom coupling.

For organic materials, research on emissive, weakly coupled microcavities^{119–123} led to first the prediction¹²⁴ then the observation¹²⁵ of strong exciton-photon coupling. Coupling can be achieved at room temperature in organic materials due to the tightly bound nature of Frenkel excitons and their large transition dipole moments.¹²⁶ In contrast, polaritons in inorganic materials can only be studied at cold temperatures. Since polaritons are bosonic particles, it is possible to achieve Bose-Einstein condensation and lasing without population inversion in polaritonic systems. Condensation, lasing and fluidity have been demonstrated in a large range of organic materials including single crystals,¹²⁷ thin polymer films,¹²⁸ molecular dyes^{129–132} and proteins.^{133,134}

Aside from lasing, the coherence of polaritons can result in dramatic modification of material properties and excited state processes. Properties that are usually considered intrinsic to a material such as its reactivity and excited state dynamics are able to be altered. Strong coupling has been used as a kind of catalyst in photochemical and photophysical reactions^{135–139} and to alter excited state transformations between singlet and triplet states.^{140–149} Strong coupling also has dramatic implications for non-linear phenomena.^{150–152} Therefore, strong coupling has been proven to be a powerful tool for manipulating a vast array of material properties.

In order to achieve strong coupling, the rate of energy exchange between the exciton in the material and the photon or optical field inside the cavity must exceed the rate at which energy is dissipated through losses. Cavities that are fabricated with either metallic reflective surfaces or distributed Bragg reflectors (DBRs) composed of alternating layers of high and low refractive index materials are classified as Fabry-Pérot cavities, and an example is shown in Figure 1.7 a). Strong coupling also occurs in other geometries, for example in 1D waveguides such as nanowires¹⁵³ and in open cavities where excitons couple to surface plasmon modes to form surface plasmon polaritons.^{154–156} Excitons in organic materials deposited on top of DBRs have been shown to couple to Bloch surface waves,^{157,158} leading to fast and long-range transport for distances over 100 μm and with speeds up to 150 $\mu\text{m/s}$. Polaritons have even been observed within organic materials in the absence of any kind of dedicated cavity structure.^{159–162} In the following discussion, we focus on planar, Fabry-Pérot (FP) microcavities.

Figure 1.7 a) shows an example of a FP cavity formed by two reflective Ag mirrors separated by a volume of solid organic material. The thickness d of the FP cavity determines the energy of the photon that can be resonantly sustained in the cavity, known as the cavity photon. When the thickness of the FP cavity is equal to an integer multiple of half the wavelength of the cavity photon λ , constructive interference allows the photon to exist in resonance with the cavity. All other photons experience destructive interference in the FP cavity. The mode m

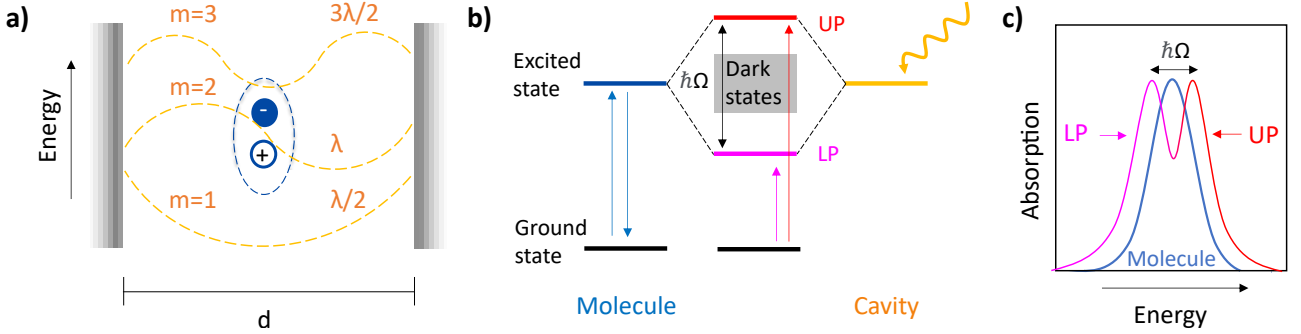


Figure 1.7: a) Schematic of a Fabry-Pèrot (FP) cavity showing the condition for resonance, being that the cavity thickness d must be equal to an integer m multiple of half the resonant photon wavelength $\lambda/2$. b) Energy level splitting is caused by strong coupling between matter (excitons) and light (cavity photons) when these exist in resonance to form new energy states termed polaritons. These are referred to as the upper (UP) and lower (LP) polariton states and are separated by an energy of $\hbar\Omega$, also known as the Rabi splitting. Dark states remain at the energy of the exciton. c) Energy level splitting causes the appearance of new features in the absorption spectra of strongly coupled systems.

of the cavity photon represents the integer multiplier for a set of resonant photons to exist in a particular FP cavity, as shown in Figure 1.7 a), with $m = 1$ corresponding to the lowest energy mode. The effective refractive index of the material in the FP cavity n_{eff} must also be considered. These concepts are summarised in Equation 1.1 below which gives the resonance condition for a FP cavity:¹⁶³

$$n_{\text{eff}}d = m\frac{\lambda}{2} \quad (1.1)$$

If the energy of the cavity photon is sufficiently close to the energy of the exciton, peak splitting will occur as shown in Figure 1.7 b). This leads to the creation of two new excited states, termed the upper (UP) and lower (LP) polariton branches. These are separated in energy by the Rabi splitting $\hbar\Omega$, where $\hbar$ is the reduced Planck's constant and Ω the Rabi oscillation frequency for energy exchange between the photon and exciton. For N coupled oscillators,

there will be $N - 1$ dark states at the energy of the exciton which form a collective reservoir with no photonic component.^{163–165} The transition between these states and the ground state is forbidden, thus rendering them ‘dark’. These are also referred to as the exciton reservoir, exciton bath or incoherent excited states, but are distinct from uncoupled molecules.^{166–168}

1.2.2 Photon modes supported in an optical cavity

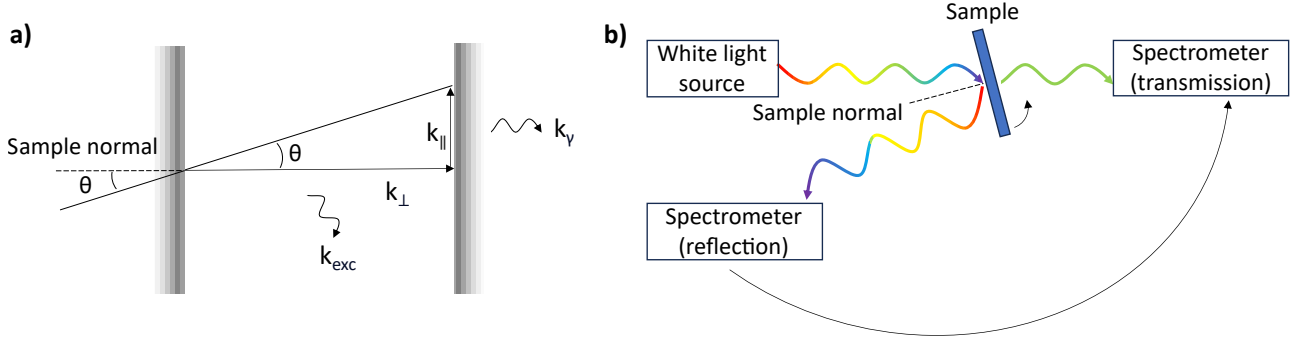


Figure 1.8: a) Schematic of light incident on a FP cavity with angle θ to the sample normal. The parallel ($k_{||}$) and perpendicular ($k_{\perp}$) components of the photon wave vector and the exciton k_{ex} and photon k_{γ} decay rates are marked. b) For angular reflectometry, the sample is rotated through angles 0-80° and the reflected or transmitted light measured with a mobile spectrometer.

FP cavity modes are dispersive, i.e. the energy of the resonant photon increases with the angle of measurement as shown in Figure 1.8 a). This arises from the photon wave vector components $k_{\perp}$ and $k_{||}$ and their contribution to the resonant FP cavity energy $E_{ph}(k_{||})$ as given by:

$$E_{ph}(k_{||}) = \frac{\hbar c}{n_{eff}} \sqrt{k_{\perp}^2 + k_{||}^2} \quad (1.2)$$

where c is the speed of light in a vacuum, and $k_{||}$ and $k_{\perp}$ the components of the photon wavevector in the direction parallel to and perpendicular to the plane of the FP cavity respectively. $k_{\perp}$ is determined by the thickness of the FP cavity d and the resulting constructive photon interference:

$$|k_{\perp}^{\rightarrow}| = n_{eff} \frac{m\pi}{\lambda} = \frac{m\pi}{d} \quad (1.3)$$

$k_{\parallel}$ describes the in-plane momentum through the following relation:

$$|\vec{k}_{\parallel}| = \frac{2\pi}{\lambda} \sin\theta \quad (1.4)$$

where θ is the angle of incidence of the wavevector as it enters the FP cavity. At 0° incidence, the parallel wavevector vanishes and only the perpendicular wavevector $k_{\perp}$ contributes to the cavity mode energy. At increasing angles, since $k_{\parallel}$ is a function of angle but $k_{\perp}$ is not, the angle-dependence of the cavity mode energy arises from the parallel wavevector $k_{\parallel}$.

1.2.3 Coupled oscillator model

When a material with an optical transition of wavelength λ is placed inside a cavity in resonance with this transition, the strength of the interaction can be characterised by the coupling constant g_0 according to:¹⁶⁹

$$g_0 = \sqrt{N} \left(\frac{\pi \mu^2 c}{n_{\text{eff}}^2 \lambda \epsilon_0 \hbar V} \right)^{\frac{1}{2}} \quad (1.5)$$

where N is the number of oscillators, μ the dipole moment of the exciton, ϵ_0 the vacuum permittivity and V the volume of the cavity, termed the mode volume.

The dissipation of the exciton by processes such as non-radiative decay and emission in a direction exiting the cavity is captured by the exciton decay rate k_{ex} , and the cavity photon decay rate by k_{γ} . When exciton and cavity decay occur faster than the coupling exchange rate, i.e. $g_0 < k_{\text{ex}}, k_{\gamma}$, the system is in the weak coupling regime and the system can be considered a perturbation of the uncoupled exciton. When the coupling exchange rate is faster than the exciton and cavity decay rates, i.e. $g_0 > k_{\text{ex}}, k_{\gamma}$, the system is in the strong coupling regime. The cavity photon and material exciton then exchange energy with a rate of $\Omega = 2g_0$, where Ω is the Rabi frequency. A simplistic picture is that the cavity photon is absorbed by the material to form an exciton, then the exciton relaxes and causes the emission of a photon, which is then absorbed again, and so on with a frequency characterised by Ω . In reality, the polariton is a quantum superposition of both the exciton and the photon, with energy exchange oscillations occurring at the Rabi frequency.

The cavity photon and exciton are considered coupled oscillators, much like two masses on a spring in the study of classical mechanics.¹⁰¹ The Hamiltonian describing this system takes the form of a 2×2 matrix system:

$$\begin{pmatrix} E_{\text{ph}}(\theta) & \hbar\Omega/2 \\ \hbar\Omega/2 & E_{\text{ex}} \end{pmatrix} \begin{pmatrix} \alpha(\theta) \\ \beta(\theta) \end{pmatrix} = E_{\text{pol}} \begin{pmatrix} \alpha(\theta) \\ \beta(\theta) \end{pmatrix} \quad (1.6)$$

where $E_{\text{ph}}(\theta)$ is the angle-dependent cavity photon energy, E_{ex} is the (angle-independent) energy of the exciton and E_{pol} the energy of the polariton created by their mixing. The components of the eigenvector, $\alpha(\theta)$ and $\beta(\theta)$, are mixing coefficients termed Hopfield coefficients and describe the extent of the photonic or excitonic character of the polariton as a function of angle. For materials with more than one exciton transition, the coupled oscillator Hamiltonian takes the form of a $(n+1) \times (n+1)$ matrix for n exciton transitions.

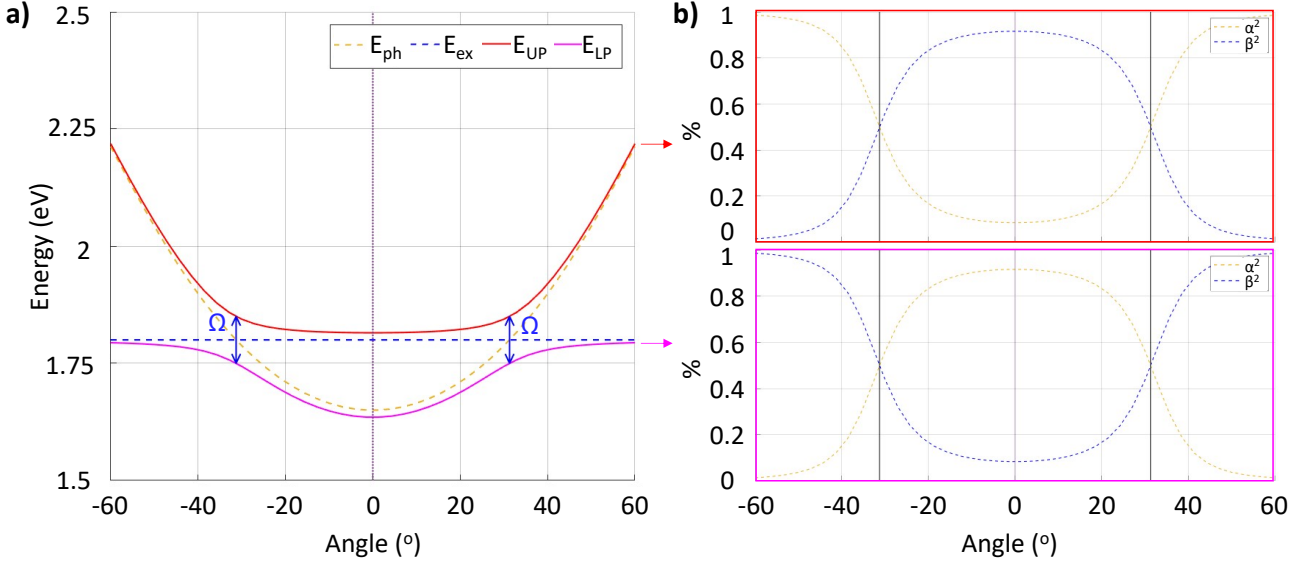


Figure 1.9: a) Dispersion graph for a two-branch coupled oscillator model. When the angle-dependent cavity mode couples to the angle-independent exciton resonance, two new angle-dependent branches are formed termed the upper (UP) and lower polariton (LP) branches. These are separated by an energy equal to their Rabi splitting Ω at the point of anti-crossing. b) Hopfield coefficients for the branches plotted in a). The top box demonstrates the photonic (α) and excitonic (β) character of the upper polariton branch, and the bottom box the same for the lower polariton branch.

The eigenvalues of the Hamiltonian system are the polariton energies E_{pol} . Diagonalization of the Hamiltonian leads to two solutions for a coupled system involving one cavity photon and one exciton transition:

$$E_{\text{pol}} = \frac{E_{\text{ph}}^2 + E_{\text{ex}}^2}{2} \pm \frac{1}{2} \sqrt{(E_{\text{ph}} - E_{\text{ex}})^2 + (\hbar\Omega)^2} \quad (1.7)$$

which correspond to the upper and lower polariton branches respectively. The Hopfield coefficients comprising the eigenvector of the Hamiltonian system can also be determined according to:

$$\alpha^2 = \frac{E_{\text{ph}} - E_{\text{pol}}}{E_{\text{ph}} + E_{\text{ex}} - 2E_{\text{pol}}} \quad \beta^2 = 1 - \alpha^2 \quad (1.8)$$

Since the square of the Hopfield coefficients must add to 1, it is possible to use this reciprocal relationship to calculate one coefficient when the other is known.

The polariton branches are often represented as single energy levels on a state diagram as shown in Figure 1.7 b), but are in fact angle-dependent (dispersive) due to the dispersivity of the cavity photon as shown in Figure 1.9. At the point where the cavity photon mode energy intersects with the exciton energy, the two polariton branches show avoided crossing behaviour

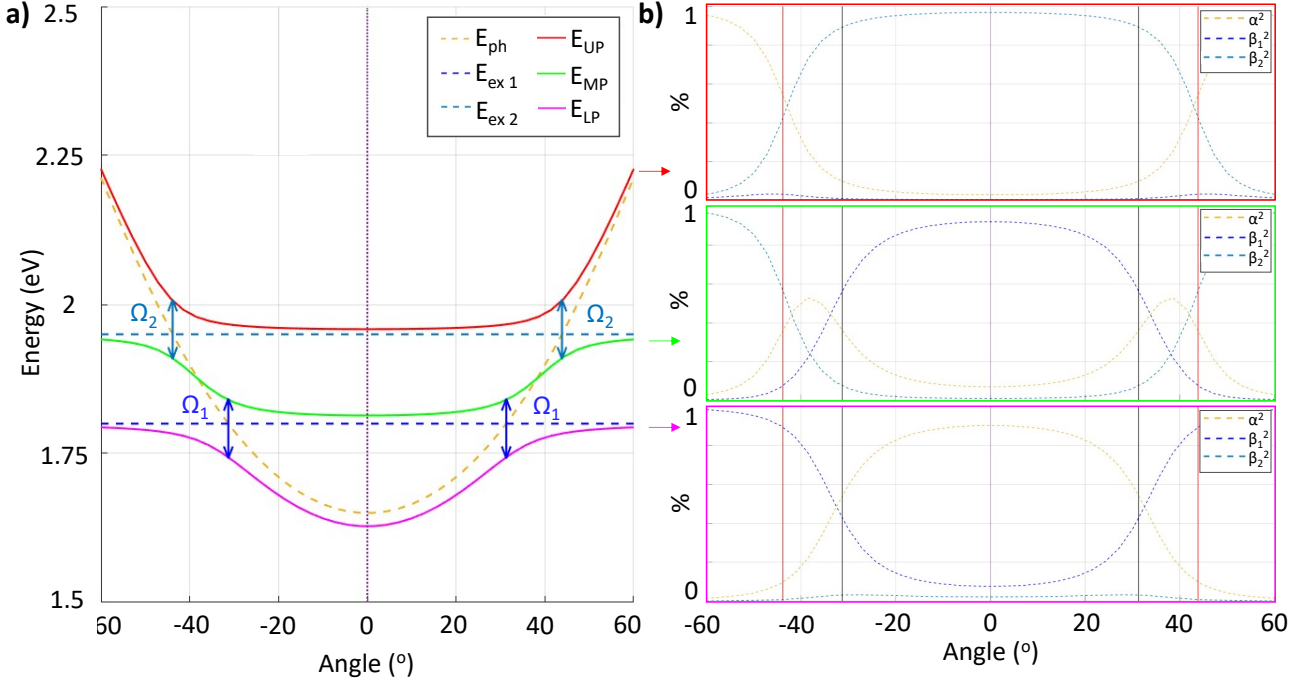


Figure 1.10: a) Dispersion graph for a three-branch coupled oscillator model. The cavity mode can couple to two exciton resonances to form three polariton branches separated by two Rabi splitting energies. These are now termed the upper (UP), middle (MP) and lower polariton (LP) branches. b) Hopfield coefficients for the branches plotted in a) demonstrating mixing between the cavity mode and the two exciton resonances.

known as anti-crossing which is characteristic of coupled systems. This is also the point where the dominant photonic or excitonic character of the branches switches, as shown in Figure 1.9 b).

An example of a three-branch coupled oscillator model is also shown in Figure 1.10. In this case, two exciton resonances couple to the cavity mode to produce three polariton branches, termed the upper (UP), middle (MP) and lower (LP) polariton branches. This gives rise to two Rabi splitting values for the energy difference between each set of adjacent branches. The Hopfield coefficients are calculated the same way, however there are now three components for each branch arising from the photonic (α) character as well as the character of the first (β_1) and second (β_2) polariton branches.

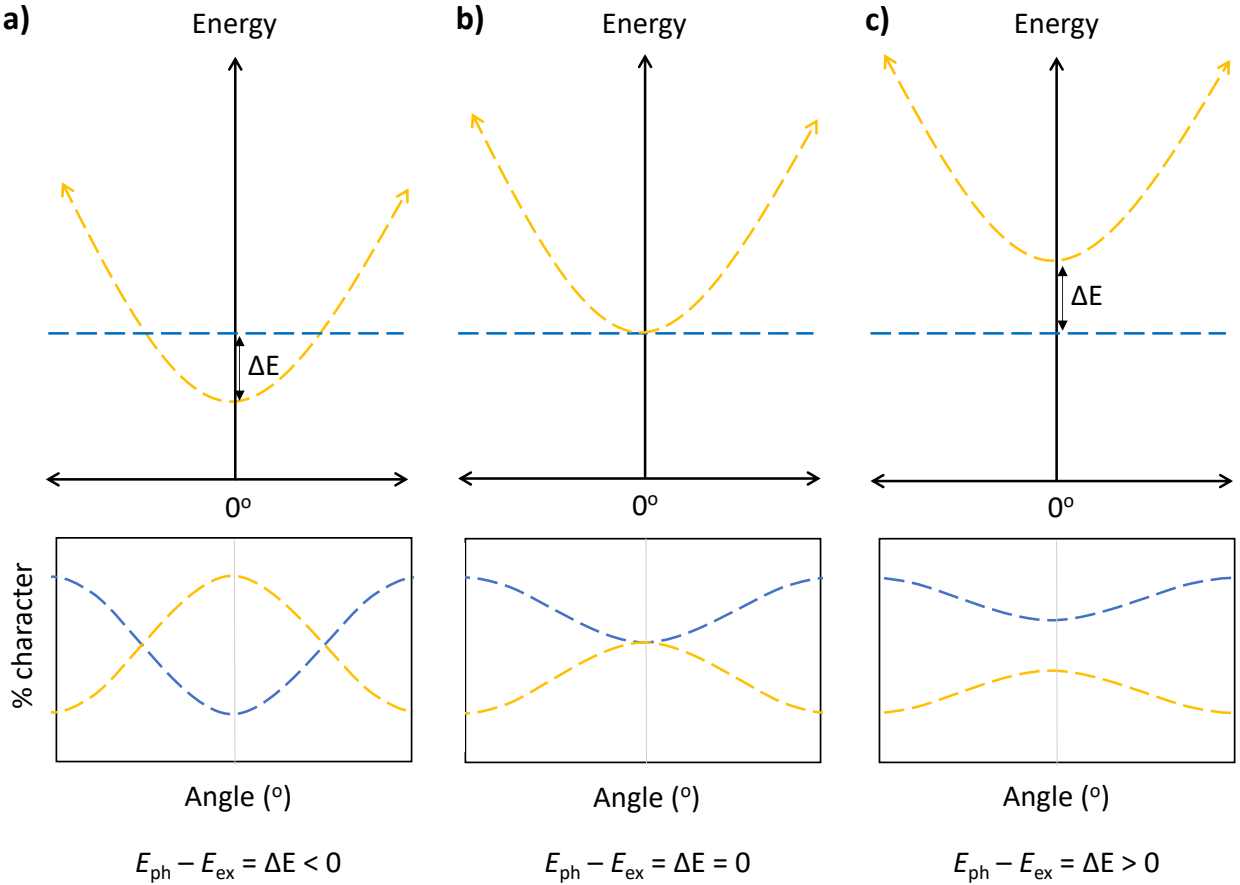


Figure 1.11: Different regimes of detuning and the corresponding lower polariton Hopfield coefficients. a) Negative detuning, where the cavity mode at 0° E_{ph} sits below that of the exciton resonance E_{ex} . The lower polariton has photonic character at small angles and excitonic character at large angles, with maximum mixing where E_{ph} and E_{ex} intersect. b) Zero detuning where $E_{ph} = E_{ex}$. The lower polariton is mostly excitonic in character, with maximum mixing again occurring at the point of intersection between E_{ph} and E_{ex} . c) Positive detuning where $E_{ph} > E_{ex}$. The lower polariton remains primarily excitonic for all angles of incident light.

In the two examples shown here, since the energy of the cavity mode E_{ph} at 0° sits below the energy of the (lowest) exciton E_{ex} , these samples are classified as negatively detuned. This results in maximum mixing between the photon and exciton. In the opposite case, where $E_{\text{ph}} > E_{\text{ex}}$, this sample would be positively detuned, and the Hopfield coefficients would not show switching but rather would retain a dominant excitonic or photonic character across all angles; for example, the lower polariton would possess excitonic character. It is also possible to have a sample of zero detuning if $E_{\text{ph}} = E_{\text{ex}}$, in which case the photonic and excitonic character would be equal at 0° incidence but would be otherwise dominant as per the case of positive detuning. These three detuning regimes are demonstrated in the schematic in Figure 1.11 alongside a schematic of the expected lower polariton Hopfield coefficients.

Since the cavity detuning dictates the degree of mixing of the exciton and the polariton, it has important implications for the photophysical behaviour of the coupled system. For example, more negatively detuned cavities have shown more efficient energy transfer between dyes^{170,171} and enhanced triplet yield from singlet fission.¹⁴¹ Controlling the cavity detuning has also been shown to alter relaxation pathways between polariton branches,¹⁷² control the population of molecular trap states¹⁷³ and to alter rates of reverse intersystem crossing.^{146,174}

1.2.4 Polaritons in perylenes and polymers

Since the first demonstration of strong light-matter coupling in organic materials,¹²⁵ many classes of organic material have been coupled to optical cavities. Of particular interest are perylene diimides, due to their high oscillator strength, fluorescence quantum yield, and tunable chemical properties allowing for solution-processable fabrication and aggregation control.^{129,175,176} Polariton lasing has been demonstrated with both imide-functionalised perylene diimides,^{130,177,178} bay-substituted perylene diimides^{179,180} and both imide- and bay-substituted perylene diimides.¹⁸¹

Strong exciton-photon coupling has also been achieved previously in polymers, being demonstrated for the ladder-type polymer MeLPPP,¹²⁸ polyphenylenevinylene,^{122,182} polydioctylfluorene,^{183,184} pentafluorene¹⁸⁵ and liquid crystalline conjugated polymers.¹⁸⁶ Of most relevance to this work, strong exciton-photon coupling has also been demonstrated in the organic photovoltaic donor material P3HT.^{139,187} We discuss the properties of strongly coupled materials within the context of OPV devices below in Section 1.3.

1.3 Strong coupling in OPV devices

Organic photovoltaic devices are multi-layered as described in Section 1.1.5, often having active layers of ~ 100 nm. At least one electrode is usually transparent to allow for light to successfully penetrate into the cell, however refractive index mismatches can still cause cavity effects within the cell due to constructive and destructive interference of the cavity photon.¹⁸⁸ Thus, all organic photovoltaic samples can be thought of as weakly coupled cavities with the correct thickness to couple to visible light.

In order to convert a weakly coupled OPV into a strongly coupled OPV, an additional reflective layer must be added to increase the reflectivity of the cavity mirrors. This leads to increased absorption of the light available inside the cavity.^{189–191} Much study has been dedicated to understanding the optical field effects of photonic crystals in the context of OPV devices, however little work has been done to understand the effect of light-matter coupling.

Since polaritons are hybrid particles having properties of both the exciton and the photon, this allows for excitons to assume photonic character (and vice versa) which can have dramatic implications for material properties. The increased photonic character of the exciton causes their wavefunction to extend over large distances resulting in long-range “ballistic” energy transfer up to several microns and speeds up to two-thirds of the speed of light.^{192–196} The delocalisation of charge can also result in enhancements in carrier mobility of up to an order of magnitude.^{154,187} These observations have the potential to incite significant changes to the photophysics of devices and may provide avenues for the avoidance of issues that plague OPV devices. In simulations of bare devices, even a small amount of delocalisation has been shown to improve exciton and charge mobilities^{197,198} and charge generation and separation efficiencies.^{199,200} Polariton formation has the capacity to take these improvements to their most extreme limit of delocalisation across the entire cavity volume. Fast exciton-polariton transport through OPV materials boosts the competitiveness of this pathway as compared to decay pathways, which can be expected to reduce geminate recombination in OPV devices. The high exciton binding energy which makes charge generation problematic in OPVs and necessitates donor/acceptor architectures is also the very feature that enables strong coupling to occur, and the potential for it to improve device performance has only been explored in a few isolated cases.

The first demonstration of a strongly coupled OPV device was performed by Nikolis et al. in 2018, where the transparent ITO electrode was substituted for a reflective Ag electrode

in SubNc:Cl₆-PhOSubPc based devices.²⁰¹ Strong exciton-photon coupling was observed both optically through angular reflectometry as well as electronically through external quantum efficiency (EQE) measurements. Due to coupling-induced peak splitting, the absorption edge of the lower polariton was steepened and the energy losses reduced compared to bare devices.

The polariton-induced delocalisation of donor and acceptor states over the whole cavity region is a particularly useful property for bilayer cells where the donor and acceptor are spatially separated. Wang et al. demonstrated that ‘optical mixing’ of the donor and acceptor exciton states in a DPA:PTCDA bilayer system with the cavity vacuum field was just as efficient as physical mixing of the donor and acceptor in a BHJ blend morphology for enabling fast energy transfer.²⁰² This is ascribed to three effects: a longer exciton diffusion length, faster hole transfer from the PTCDA electron acceptor to the DPA electron donor, and faster energy transfer all enabled as a result of the formation of delocalised polaritonic states.¹⁴⁰ For BHJs, the rate of energy transfer from the donor to the acceptor was doubled due to energy transfer mediation by the middle polariton branch. However, the efficiency of the devices studied was low, having < 0.05% EQE.

DelPo et al. also studied the effects of strong coupling on P3HT:PCBM solar cells where the P3HT was strongly coupled to the cavity mode.²⁰³ Transient reflection spectra revealed that an additional decay pathway is present in coupled bilayer devices where the C₆₀ acceptor is present due to charge transfer from the LP which is competitive with charge transfer from uncoupled molecules. In contrast, in a BHJ system the uncoupled molecules were still primarily responsible for charge transfer state formation due to the smaller distances between donor and acceptor domains in this geometry. A similar conclusion was reached by Brigeman,²⁰⁴ who also suggested that strong coupling in OPVs forms an interesting system in which to study nonlinear effects in materials, such as the enhancement of third-order susceptibility. However, the effect of strong light-matter coupling on charge transport and extraction from OPV devices has not yet been studied.

Strong light-matter coupling in OPVs is not limited to organic materials: most recently, it has also been demonstrated in perovskite-based photovoltaics where a ~100% increase in EQE was demonstrated for a section of the absorption spectrum.²⁰⁵ This curiosity of physics of the synergy between photovoltaic function and strong light-matter coupling is a phenomenon with the potential to affect a broad variety of materials, making it a noteworthy phenomenon to study. Since the properties of materials are altered in such dramatic ways as mentioned above,

this field requires careful and dedicated study to firstly observe and secondly work towards understanding the potential of strong coupling to significantly alter material properties and thus device performance for OPVs and beyond.

1.4 Aims and outline

Despite much research into charge-generating non-fullerene acceptors, there have been no studies quantifying the contribution of the donor and acceptor domains to the overall production of charge and the impact of blend film morphology upon this. Also, previous studies of strongly coupled OPV devices have focused on the role of strong coupling in improving energy transfer and exciton transport, yet none have examined the role of strong coupling on charge transport. Thus the aims of this thesis are as follows:

1. Examine the role of dual-direction energy harvesting in OPV devices, and quantify the contribution of the donor and acceptor to charge generation
2. Investigate the impact of strong light-matter coupling on device physics, particularly charge generation and transport

Specifically, this thesis explores the effects of molecular structure on blend film and device photophysics through the comparison of a perylene non-fullerene acceptor monomer and dimer paired sequentially with the polymer donor PTB7-Th. Since these materials are also capable of coupling to cavity photons, we also explore the possibility to alter the material properties through strong light-matter coupling both in and outside of OPV devices. We hypothesise that strong coupling in the OPV devices will lead to changed device behaviour, such as reduced recombination due to the delocalisation of the wavefunction of the exciton upon coupling to the cavity photon.

The thesis is laid out as follows. Chapter 2 first describes the methods used for the investigations in the thesis, including sample preparation, measurement and analysis techniques. Chapter 3 then provides a detailed description of OPV device measurements such as current-voltage curves in the context of benchmarking work undertaken to ensure the trustworthiness of the following measurements.

Chapter 4 introduces in detail the materials which remain the focus for the rest of the thesis, namely the perylene monomer (PDI), dimer (TPDI) and PTB7-Th. Optical properties

of thin PDI:PTB7-Th and TPDI:PTB7-Th blend films are reported as well as the results of devices based on these blends. We demonstrate dual-direction energy harvesting from both donor and acceptor domains, and demonstrate that TPDI-based devices outperform PDI-based devices due to their favourable morphological packing.

The nature of this dual-direction energy harvesting is investigated in further detail in Chapter 5 through picosecond transient absorption measurements. We directly visualise fast donor-to-acceptor electron transfer, as well as acceptor-to-donor hole transfer. We characterise these processes in detail, and show through modelling that hole transfer is indistinguishable from energy transfer plus back electron transfer. We also use the decay profiles to quantify the contribution of electron and hole transfer to overall charge generation, and demonstrate that TPDI-based blends are able to achieve more balanced dual-direction energy harvesting due to their favourable morphology. To the best of our knowledge, this is the first work of quantification of donor and acceptor contributions to charge generation. Thus together in Chapters 4 and 5 we answer the first section of the aim through the extensive characterisation of photophysical behaviour of these PTB7-Th:(T)PDI blend films.

In Chapter 6, we discuss relevant strong-coupling experiments. We first investigate the properties of the photon mode and the effect of changing the thickness, mode, angle of incidence, refractive index and Q-factor of cavities. We then investigate the ability of PDI, TPDI and PTB7-Th to achieve strong light-matter. Even when dispersed in polymer matrices, the intermolecular interactions in (T)PDI materials prohibit coupling from reaching the strong coupling regime. Neat PTB7-Th also suffers from intermolecular interactions that prohibit its demonstration of strong light-matter coupling, however this can be overcome for films dispersed in polymer matrix. Blend films of PTB7-Th:(T)PDI are able to demonstrate coupling around any of PTB7-Th, PDI or TPDI resonances due to the ability to tune the cavity mode by tuning cavity thickness. For (T)PDI resonances, the TPDI-based blend film exhibits much stronger coupling. Thus the prerequisite strong coupling behaviour is demonstrated in preparation for the fabrication of strongly coupled OPV devices.

Chapter 7 demonstrates the fabrication and characterisation of strongly-coupled PTB7-Th:TPDI OPV devices. These devices are compared to non-cavity (bare) OPV devices to elucidate the effects of strong coupling. Coupled devices are shown to have better diode behaviour and reduced recombination compared to bare devices. The coupled devices are also fabricated with varying cavity thicknesses to investigate the role of positive or negative detuning

on device performance. This demonstrates the ability to alter the properties of a material in a device through strong coupling without changing the material itself.

Finally, in Chapter 8, we present simulations of bare and cavity PTB7-Th:TPDI OPV devices with the aim to deepen the understanding of device performance gained in Chapter 7. We reproduce experimental JV curves through fitting and investigate the role of the Langevin recombination factor as well as the density of chargeable sites.

Chapter 9 then summarises the results across the entire thesis and presents a number of suggestions for future work.

Overall, we perform an extensive investigation into the material properties of the PTB7-Th:(T)PDI system and demonstrate that it is possible to change the material properties through strong coupling. This suggests device properties can be customised through the advanced management of light inside OPV devices to achieve strong light-matter coupling.

Chapter 2

Methods

This chapter outlines the experimental methods used for the preparation and characterisation of all samples included in this thesis, as well as simulation details.

2.1 Samples

All chemicals and reagents were used as received from commercial sources without any further purification. The PDI and TPDI were synthesised by following previously reported procedures.² P3HT and PCBM was obtained from Lumtec. PTB7-Th and ITIC were obtained from 1-material. Y6 was obtained as part of a collaboration.⁶⁹

2.1.1 Thin films

This section includes sample preparation details for experiments reported in Chapters 4-5.

Thin films of (T)PDI and PTB7-Th were prepared by spin coating 18 mg/mL solutions from chlorobenzene at 1500 rpm for 60 seconds followed by 4000 rpm for 10 seconds onto microscope glass slides cleaned by 5 minutes of sonication in acetone followed by isopropyl alcohol (IPA). Blend films were prepared by combining the 18 mg/mL solutions in a 1:1 weight ratio and spun using the same spin conditions.

Films for AFM were prepared by spin coating 20 mg/mL solutions of (T)PDI and PTB7-Th from chlorobenzene at 1500 rpm for 60 seconds followed by 4000 rpm for 10 seconds onto microscope glass slides cleaned by 10 minutes sonication in acetone followed by IPA. Blend films were prepared by combining 20 mg/mL solutions in a 1:1 weight ratio and spun using the same spin conditions.

2.1.2 Fabry-Pérot cavities

The following section includes sample preparation details for experiments reported in Chapter 6. All thicknesses refer to the thickness of the organic layer only (excluding the thickness of the Ag reflective layers). Except where mentioned, glass slides were cleaned by 5 minutes of sonication in acetone then IPA, then 25 nm of Ag was deposited by thermal evaporation with a rate of 1 Å/s at a pressure of $\sim 2 \times 10^{-6}$ mbar. After spincoating the organic layer, the top layer of Ag was then deposited by thermal evaporation using the same parameters as for the bottom layer to a final thickness of 25 nm.

A summary of the sample codes for the Fabry-Pérot (FP) cavity samples and their descriptions is provided in Table 2.1.

Table 2.1: Description of FP samples

Sample code	Description
L1, L2, L3, L4, L5	PMMA blank cavity
R7, S1, S2, S3, S4,	PS blank cavity
(T)PDI in PS	PDI or TPDI dispersed in PS
N1, N2, N4, N5, N9	PTB7-Th neat films
S7, S8	PTB7-Th dispersed in PS
J4, M1, M2, M3, M4	PTB7-Th:PDI blend
K3, K4, K5	PTB7-Th:PDI blend (cavity mode in region of PTB7-Th resonance)
L9	PTB7-Th:PDI blend (cavity mode in region of PDI resonance)
K7, K9, K10	PTB7-Th:TPDI blend (cavity mode in region of PTB7-Th resonance)
L8	PTB7-Th:TPDI blend (cavity mode in region of TPDI resonance)

PMMA and PS controls

For polymethyl methacrylate (PMMA) control cavities (experiment L), PMMA (Sigma Aldrich, average $M_w \sim 350,000$) was dissolved in chlorobenzene (Sigma Aldrich) at a concentration of 40 mg/mL and stirred at 50°C overnight. Dilutions in chlorobenzene were performed to prepare

solutions of appropriate concentrations according to Table 2.2 which were then spin-coated at 2000 rpm for 60 seconds followed by 1000 rpm for 10 seconds.

Table 2.2: PMMA concentrations used for sample preparation in Experiment L

Sample	PMMA concentration (mg/mL)	Thickness (nm)
L1	40	277
L2	35	218
L3	30	165
L4	25	128
L5	20	90

For polystyrene (PS) control cavities, PS (Sigma Aldrich, average $M_W \sim 192,000$) was dissolved in chlorobenzene (Sigma Aldrich) and was spincoated at 2000 rpm for 60 seconds followed by 4000 rpm for 10 seconds. For experiment S, solutions of 70 mg/mL were stirred for 75 minutes at 50°C before being diluted to the appropriate concentration according to Table 2.3. Film R7 was spun from a 30 mg/mL solution.

Table 2.3: PS concentrations used for sample preparation for Experiment S

Sample	PS concentration (mg/mL)	Thickness (nm)
S1	35	147
S2	40	158
S3	45	184
S4	50	214

PDI and TPDI in PS

For the active layer, solutions of (T)PDI dissolved in 35 mg/mL chlorobenzene were spincoated at 2000 rpm to give cavities with a volume concentration of 120 mM (T)PDI dispersed in the PS matrix. Samples were prepared with either 28 nm thick or 50 nm thick top and bottom Ag mirrors.

PTB7-Th cavities

For experiment N, a 12 mg/mL solution of PTB7-Th (1-material) was prepared in chlorobenzene and this was spincoated onto the slides at the speeds listed below to form neat PTB7-Th cavity samples.

For experiment S, cavity films PTB7-Th dispersed in PS were prepared. PTB7-Th (20 mg/mL) and polystyrene (140 mg/mL) solutions were prepared in chlorobenzene and were

Table 2.4: Spin speeds used for preparation of neat PTB7-Th films used in Experiment N

Sample	Spin speed (rpm)	Thickness (nm)
N1	500	243
N2	1000	148
N4	1500	112
N5	2000	100
N9	3000	79

stirred for 24 hours and 1 hour respectively at 50° prior to being combined. Sample S7 is made with a 40 g/mL solution of PS and % w/w loading of 20% PTB7-Th, whilst Sample S8 is made with a 35 mg/mL solution of PS and a loading of 40% PTB7-Th. Both films were deposited by spincoating at 2000 rpm.

Blend films

Glass slides are cleaned by 5 minutes sonication in acetone then IPA. 50 nm of Ag was deposited by thermal evaporation with a rate of 1 Å/s at a pressure of $\sim 2 \times 10^{-6}$ mbar. For experiment M, PTB7-Th and PDI were dissolved in chlorobenzene and stirred at 50° for 2 hours before being combined to give the concentrations in Table 2.5. These were spincoated onto glass slides at varying spin speeds before the final deposition of 50 nm of Ag by thermal evaporation with the same conditions as the bottom layer.

Table 2.5: Conditions used for preparation of blend PTB7-Th:PDI films used in Experiment M

Sample	Solution concentration (mg/mL)	Spin speed (rpm)	Thickness (nm)
M1	22	1500	163
M2	22	3000	98
M3	22	5000	76
M4	20	2000	76

For experiment J, the sample was prepared much the same way as for experiment M using the same 20 mg/mL solution of PTB7-Th:PDI and a new 20 mg/mL solution of PTB7-Th:TPDI, with 50 nm thick Ag top and bottom layers. The spin speed used for the relevant device is shown in Table 2.6.

Table 2.6: Spin speed for preparation of blend PTB7-Th:(T)PDI film used in Experiment J

Sample	Material blend	Spin speed (rpm)	Thickness (nm)
J4	PTB7-Th:PDI	1000	136

For experiment K and L, samples were prepared much the same way as for experiment M and

J, however with 25 nm Ag layers. For the active layer, the blend film solution prepared with 20 mg/mL concentration was spincoated at varying speeds as listed in Table 2.7 below.

Table 2.7: Spin speeds for preparation of blend PTB7-Th:(T)PDI films used in Experiment K and L

Sample	Material blend	Spin speed (rpm)	Thickness (nm)
K3	PTB7-Th:PDI	1000	163
K4	PTB7-Th:PDI	1250	135
K5	PTB7-Th:PDI	1500	124
L9	PTB7-Th:PDI	3000	90
K7	PTB7-Th:TPDI	1000	185
K9	PTB7-Th:TPDI	1250	163
K10	PTB7-Th:TPDI	1500	155
L8	PTB7-Th:TPDI	3500	92

2.1.3 OPV samples

P3HT:PCBM devices

The conventional P3HT:PCBM device discussed in Chapter 3 had the structure of ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al and was prepared using the following method. ITO-coated glass slides were cleaned by sonication for 10 minutes in acetone then IPA followed by 10 minutes in a UV-ozone cleaner (Ossila, L2002A2). Approximately 200 μL of PEDOT:PSS (Ossila, Al4083) filtered through a 0.22 μm polyethersulfone (PES) hydrophilic filter was deposited onto the slides via static deposition spincoating for 60 seconds at 4000 rpm with an acceleration of 1000. Substrates were then baked on a hotplate at 110°C for 15 minutes to remove any excess moisture before being immediately transferred to a nitrogen glovebox. Meanwhile, 20 mg/mL solutions of P3HT and PCBM were prepared in chlorobenzene in a nitrogen glovebox and left to stir on a hotplate set to 50° for 5 hours before being combined in a 1:1 ratio. Active layer deposition was performed in the nitrogen glovebox by dynamic spincoating at 1500 rpm for 60 seconds followed by 4000 rpm for 10 seconds. 1 nm of LiF was deposited by thermal evaporation at a pressure of 1×10^{-6} mbar and a rate of 0.1 Å/s, followed by 80 nm of Ag evaporated at a pressure of 9×10^{-6} mbar and a rate of 1 Å/s. The device was annealed at 130°C for 1 minute and left on the cooling hot plate for 30 minutes to slowly cool.

The inverted device was made with the structure of ITO/ZnO/P3HT:PCBM/MoO₃/Ag. Glassware was cleaned by sonication for 10 minutes in acetone then IPA, then 10 minutes of UV-ozone cleaning. A solution of ZnO nanoparticles dissolved in IPA (Sigma Aldrich) was filtered using a 0.45 μm polytetrafluoroethylene (PTFE) filter. The ZnO was then spincoated via static deposition onto the cleaned glass/ITO slides at 4000 rpm for 60 seconds followed by baking on the hotplate for 110°C for 15 minutes to remove any excess moisture. A solution of P3HT:PCBM was prepared using the same procedure as that for the conventional device, but stirred on the hotplate for only 1 hour. Active layer solutions were spincoated by dynamic deposition onto the substrates at 1500 rpm for 60 seconds followed by 10 seconds at 4000 rpm. 5 nm of MoO₃ was deposited by thermal evaporation at a rate of 0.2 Å/s followed by 100 nm of Ag at a rate of 1 Å/s, both at a pressure of 1.3×10^{-6} mbar. Devices were annealed at 100°C for 1 minute followed by a slow cool for 30 minutes.

PTB7-Th:ITIC device

The PTB7-Th:ITIC device discussed in Chapter 3 was fabricated in the conventional structure of ITO/PEDOT:PSS/PTB7-Th:ITIC/LiF/Al following a similar recipe to that presented in Section 2.1.3. Glassware was cleaned by 10 minutes sonication in acetone then IPA, followed by 10 minutes of UV-ozone cleaning. PEDOT:PSS was filtered using a 0.22 μm PES filter before being deposited by static deposition spincoating at 1500 rpm for 60 seconds. Substrates were baked at 110°C for 15 minutes before being transferred to the glovebox. Solutions of PTB7-Th and ITIC were prepared in chlorobenzene with a concentration of 25 mg/mL each and stirred at 50°C for 6 hours before being combined to make a 1:1.5 weight ratio solution, which was chosen due to the success of this ratio in previously published ratio optimisation results.²⁰⁶ The active layer was deposited by dynamic spincoating at 1500 rpm for 60 seconds followed by 4000 rpm for 10 seconds. 1 nm of LiF was deposited at a pressure of 1×10^{-6} mbar and a rate of 0.2 Å/s followed by 100 nm of Al at a pressure of 4×10^{-5} mbar and a rate of 1 Å/s. No annealing was performed for this sample.

Y6 device

Single component Y6 devices discussed in Chapter 3 were fabricated in the conventional structure of ITO/PEDOT:PSS/Y6/LiF/Al using the following procedure. Glass/ITO substrates were cleaned by 10 minutes of sonication in acetone then IPA, followed by 10 minutes of UV ozone-

cleaning. PEDOT:PSS was filtered using a 0.22 μm PES filter prior to spincoating with static deposition and rotation at 4000 rpm for 60 seconds with an acceleration of 1000. Substrates were baked at 110°C for 15 minutes. A 5 mg/mL solution of Y6 dissolved in chloroform was prepared and spincoated at 1500 rpm for 60 seconds followed by 4000 rpm for 10 seconds. 1 nm of LiF was evaporated by thermal evaporation at a pressure of 1.3×10^{-6} mbar and a rate of 0.1 Å/s followed by 100 nm of Al at a pressure of 1×10^{-5} and a rate of 1 Å/s. No annealing was performed.

PTB7-Th:(T)PDI devices

The following section includes sample preparation details for experiments reported in Chapter 4. Inverted OPV devices were prepared for each material combination of PTB7-Th:PDI and PTB7-Th:TPDI, having the following structure: ITO/ZnO/PTB7-Th:(T)PDI/MoO₃/Ag. The glass/ITO slides were cleaned by sonication in acetone then IPA for 10 minutes each, followed by 10 minutes of ozone cleaning using a UV ozone cleaner. The ZnO solution was filtered through a 0.45 μm PTFE filter before being spincoated onto the glass/ITO slides at 4000 rpm with an acceleration of 1000 rpm for 60 seconds. The substrates were then dried at 110 °C for 15 minutes before being transferred to a nitrogen glovebox. Active layer solutions were prepared by dissolving (T)PDI and PTB7-Th in chlorobenzene at 50 °C for approximately 6 hours to form 20 mg/mL solutions before combining these in a 1:1 ratio. PTB7-Th:(T)PDI solutions were spun onto the substrates by dynamic deposition at 1500 rpm for 60 seconds followed by 4000 rpm for 10 seconds. MoO₃ (10nm) and Ag (100 nm) electrodes were deposited by thermal evaporation at 0.5 Å/s and 1.1 Å/s respectively under a vacuum of 2.7×10^{-6} mbar. No annealing was performed in order to simplify the variables considered, since it is possible that annealing could further increase the domain sizes, exacerbating phase separation and related recombination processes.

Cavity devices (PTB7-Th:TPDI)

The following section includes sample preparation details for experiments reported in Chapter 7. The same procedure was followed as described in Section 2.1.3 for PTB7-Th:(T)PDI bare devices except for the following changes: the addition of a semi-transparent Ag layer at the cathode, a layer of polyethylenimine (PEIE) between the ZnO and the active layer, and UV illumination during preparation to minimise defects at the ZnO interface. These process alterations were

also performed for the control bare device discussed in Chapter 7 except for the additional Ag layer.

Polyethylenimine 80 % ethoxylated (Sigma Aldrich) was diluted in IPA to form a 0.1 wt % solution. After deposition and baking of the ZnO, 200-250 μL of the PEIE was spincoated by static deposition at 5000 rpm and an acceleration of 5000 rpm/s for 45 seconds before being baked on a hotplate for 2 minutes at 120° to remove excess solvent. The devices were transferred to the glovebox and illuminated by the solar simulator (including UV wavelengths) for 2 minutes before and after being left overnight to outgas any remaining oxygen adsorbed on the ZnO/PEIE layer. The devices were ‘activated’ pre-measurement by 2 minutes exposure to the solar simulator, then were transferred to the Paios system and immediately measured in order to minimise the time the devices were exposed to oxygen. The same procedure was used for EQE measurements. The spin speeds used for active layer deposition are reported in Table 2.8.

Table 2.8: Active layer spin speed and thicknesses for cavity devices and associated bare control device

Sample type	Spin speed (rpm)	Thickness (nm)
Cavity	2000	116
Cavity	2500	100
Cavity	3000	91
Cavity	3500	84
Cavity	5000	74
Bare	2500	111

2.2 Spectroscopy and device characterisation

2.2.1 Steady-state film measurements

UV-vis measurements were taken using a Cary-60 UV-vis spectrometer in dual-beam mode. Atomic Force Microscopy (AFM) images were taken on a Bruker Icon Atomic Force Microscope operating in tapping mode using an FMV-A tip, having a tip radius of 8 nm. Sample film thickness measurements were performed using a Dektak surface profilometer.

2.2.2 TCSPC

Time-correlated single photon counting (TCSPC) data was taken using a HORIBA Scientific Deltaflex Modular Fluorescence Lifetime system. Laser excitation was provided through an NKT Photonics EXU-6 SuperK extreme high-power supercontinuum with a repetition rate of 2.29 MHz, an excitation wavelength 533 nm for PTB7-Th:PDI films and 544 nm for PTB7-Th:TPDI films, and a bandwidth of 16 nm. Photon emission was detected in a perpendicular geometry compared to the excitation beam. Time-resolved emission spectroscopy (TRES) measurements were taken using excitation at 505 nm and a bandwidth of 8 nm. The width of the instrument response function (IRF) is typically 180-300 ps depending on the wavelength of excitation.

2.2.3 Angular reflectance and PL

Angular reflectance was performed using a SuperK Compact white light source (NKT Photonics) and a Flame visible spectrometer (Ocean Optics). Transmission measurements were made in a linear geometry, with the light being collected by an integrating sphere before being coupled to an optical fibre and transmitted to the spectrometer. Reflectance measurements were performed in a similar fashion but with the integrating sphere placed in the path of reflectance. The sample was mounted on a rotating stage and rotated through angles of incidence ranging from 10-80°. Photoluminescence (PL) measurements were made using excitation from the same SuperK laser as for TCSPC with emission collected by a lens pair and measured by the same Flame spectrometer. Coupled oscillator fitting including the calculation of Hopfield coefficients was performed using a custom Matlab code.

2.2.4 OPV device measurements

OPV bare devices were tested under illumination from a solar simulator (Oriel LCS-100 94011A) set to AM1.5G illumination as determined by a silicon reference cell (Oriel 91150V). JV curves were measured using a Keithley 2450 SourceMeter. Intensity-dependent JV measurements were made by using neutral density filters and adjusting the height of the solar simulator to achieve different levels of illumination intensity. EQE measurements were performed on an IQE instrument (Newport, IQE 200B). The device area was 6 mm^2 for bare devices and 9 mm^2 for cavity devices, defined as the overlap of top and bottom electrodes. Analysis of measurements was performed using a custom Matlab code.

Measurements of the cavity devices were performed using a Paios all-in-one measurement system (Fluxim). JV measurements are performed using illumination provided by a white LED at varying levels of intensity measured as a percentage of the maximum intensity. Transient photocurrent (TPC) and photovoltage (TPV) measurements were performed using 500 μs pulse lengths and 10 ms perturbation pulse lengths respectively at varying illumination intensities and applied bias values. Charge carrier lifetimes as a function of carrier density were found by comparing the charge carrier lifetime as a function of light intensity from TPV measurements with the charge carrier densities found from tail-integration of TPC measurements. Electroluminescence (EL) measurements were performed at 2 V applied bias. Analysis of cavity device performance was performed using custom Python code.

2.2.5 Transient absorption spectroscopy

Broadband pump-probe transient absorption experiments were performed using a Yb:KGW laser (1030 nm, 38 kHz, 15W, Pharos, Light Conversion) and an associated home-built optical setup. The pump pulse was created with a non-collinear optical parametric amplifier (NOPA) using a 1030 nm seed and wavelength selector attachments and had an average duration of 150 fs. The probe pulse was also generated from the same source, where a YAG crystal was used to produce a chirped white light continuum from 500 to 950 nm. The average spot size (full-width half maximum, FWHM) was $300 \text{ }\mu\text{m}$.

2.3 Setfos simulations

Simulations were performed for samples with configurations shown in Figure 8.1 a) for bare devices and b) for cavity devices respectively. Material files already loaded into the Setfos software were used for all layers except the active layer. n and k constants for the PTB7-Th:TPDI active layer were imported into the software from ellipsometry data. All other parameters used in the simulations are listed below and are used for all simulations unless otherwise specified.

Table 2.9: Parameters used in Setfos simulations

Parameter	Description	Value
ϕ (ZnO)	ZnO workfunction	5.1 eV (Ohmic)
ϕ (MoO ₃)	MoO ₃ workfunction	4.2 eV (Ohmic)
HOMO	Energy of highest occupied molecular orbital (HOMO) of blend material	5.2 eV
LUMO	Energy of lowest unoccupied molecular orbital (LUMO) of blend material	4.1 eV
N ₀ -H	Density of states (HOMO)	10^{26} m^{-3}
N ₀ -L	Density of states (LUMO)	10^{26} m^{-3}
ϵ_r	dielectric constant	3.5
G	Optical generation efficiency	0.7
μ_{*n}	Electron mobility	1.4×10^{-4}
μ_{*p}	Hole mobility	2.74×10^{-4}

Chapter 3

OPV device characterisation and benchmarking

A significant part of this project was to set up device fabrication and characterisation instrumentation. Before novel work on perylenes was undertaken, it was necessary to build these pieces of instrumentation and understand their functionality. It was also critical to benchmark results from initial experiments against results reported in the literature to ensure the reliability of the fabrication and characterisation protocols developed.

This chapter presents a selection of results demonstrating successful fabrication of OPVs using the three OPV material systems of P3HT:PCBM, PTB7-Th:ITIC and Y6. P3HT:PCBM is prepared in both a conventional and inverted geometry, whereas PTB7-Th:ITIC and Y6 are prepared in a conventional geometry. A description of the standard testing procedures and fundamental device physics of OPV devices is provided alongside the results.

3.1 P3HT:PCBM devices

The most historically studied material system for OPV devices is that of P3HT:PCBM, the structures of which are shown in Figure 1.6. P3HT is a p-type polymer electron donor and PCBM a functionalised Buckminster fullerene n-type electron acceptor. These materials are relatively cheap due to their lower synthetic complexity compared to higher performing materials, and make for a good material system on which to study device fabrication and characterisation.

3.1.1 JV curves

The ability of a sample to function as a photovoltaic device can be investigated through an electrical measurement termed a current-voltage (JV) measurement. Here, the device is swept across different applied bias voltages, and the current produced at each voltage is measured both in the presence and absence of illumination. In the dark, an ideal device will act as a rectifier, that is to say it will pass current only in one direction when the applied bias is sufficient to overcome the rectification ability of the device. This operating condition is termed forward bias. In reverse bias, when the voltage bias is applied in reverse (i.e. with opposite sign), an ideal device will block the current. This behaviour can be seen in the dark measurement (dashed line) in Figure 3.1.

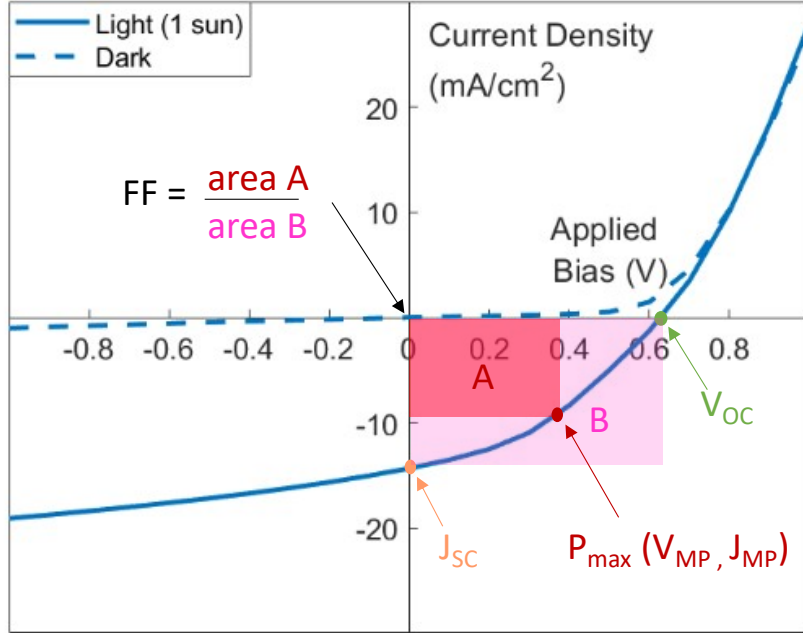


Figure 3.1: JV measurement of a conventional P3HT:PCBM device. Key features are marked as described in the text.

Illumination is provided by a solar simulator at 1 sun intensity unless otherwise specified. Under illumination, the device produces a photocurrent I_{ph} . This adds an additional term to the diode equation which is otherwise followed by the device in the dark, such that the equation for device performance under illumination becomes:

$$I = I_0 \left(e^{\frac{qV}{nkT}} - 1 \right) - I_{ph} \quad (3.1)$$

where I is the measured current output of the cell, I_0 the dark saturation current, i.e. the leakage current of the device at reverse bias in the dark, q the charge of an electron, V the applied voltage across the device, n a factor to account for non-ideal diodes, k Boltzmann's constant and T the temperature (K).²⁰⁷ The presence of photocurrent has the effect of shifting the JV curve down into the negative region.

Since the measured current I depends on the area A of the device, current measurements are often reported as a current density taking into account the device area. The current density is given by:

$$J(\text{mA}/\text{cm}^2) = I/A \quad (3.2)$$

At reverse bias, the high internal field assists with charge movement through the device, such that the current is dominated by drift current. The current density measured with 0 V applied bias is known as the short circuit current (J_{SC}) and is defined by the y-axis intercept as shown in Figure 3.1. The J_{SC} of a cell depends on a number of factors, such as the area of the device as mentioned above, the incident light intensity, the spectrum of incident light, the optical properties (such as absorption and reflection) of the cell and the charge carrier lifetimes.

When the device is held at increasingly positive forward bias voltages, the charge production capability of the solar cell competes with the externally applied bias, and the internal electric field is reduced. Under these conditions, the charges are driven to the electrodes increasingly by diffusion rather than drift. At the point where the internally produced current of the cell is exactly opposed by the externally applied bias voltage, no current will flow. This is termed the open circuit voltage (V_{OC}). The V_{OC} can be found by setting the net current in the device to zero such that:

$$V_{\text{OC}} = \frac{nkT}{q} \ln \left(\frac{I_{\text{ph}}}{I_0} + 1 \right) \quad (3.3)$$

Graphically, this is defined by the x-axis intercept as shown in Figure 3.1. The V_{OC} also depends on many factors, such as the illumination intensity, the temperature of the cell, its behaviour as an ideal or non-ideal device, the work function of the electrodes and a variety of material properties.^{208–210}

The power generated is defined as the current multiplied by the voltage:

$$P = VI \quad (3.4)$$

A device held at either open or close circuit will not generate power, since one of the two values in the above equation is set to zero. Instead, maximum power (P_{MP}) is generated at the maximum power point somewhere in between these two conditions, which is defined by the voltage at maximum power (V_{MP}) and the current at maximum power (I_{MP}) as shown in Figure 3.1. The more ‘square’ the JV curve appears, the higher the power will be.

The measure of the ‘squareness’ of the JV curve is termed the fill factor (FF) and is calculated by the following equation:

$$FF = \frac{P_{MP}}{V_{OC} \times I_{CS}} = \frac{V_{MP} \times I_{MP}}{V_{OC} \times I_{CS}} \quad (3.5)$$

The FF can be understood graphically as the ratio between area A defined by the J_{MP} and V_{MP} at the maximum power point and area B defined by the J_{SC} and V_{OC} as shown in Figure 3.1.

The efficiency of a solar cell is defined by the ratio of power generated (P_{MP}) to the power of light incident on the cell (P_{in}) and is reported as a percentage of 100%. The power conversion efficiency (PCE) can be calculated by the following equation:

$$PCE = \frac{P_{MP}}{P_{in}} = \frac{V_{OC} \times I_{CS} \times FF}{P_{in}} \quad (3.6)$$

It is important to remember that the maximum power that can be generated from a single-junction cell due to detailed balance is approximately 30%.¹²

Other important insights into device functioning provided by a JV curve include the presence of series or shunt resistances. An ideal device should have a low series resistance and a high parallel or shunt resistance. If the series resistance is too high, the slope of the curve at the point of V_{OC} will decrease. If the shunt resistance is too low, the slope of the curve at the point of J_{SC} will increase. In both cases, the fill factor will be reduced, causing a reduction to the PCE of the device. In extreme cases, the value of the J_{SC} and the V_{OC} will also be affected.

The JV curve presented in Figure 3.1 is a conventional P3HT:PCBM device with the structure ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al, and represents the best performing device measured during P3HT:PCBM investigations. Key performance parameters are listed in Table 3.1. A wide variety of PCEs is reported in the literature for the P3HT:PCBM system.

Most reports published between 2002 and 2010 report PCEs of 3-4 %, ⁸¹ and this result sits comfortably in that range. Thus we conclude that we can have confidence in the fabrication and characterisation protocols for the devices made in this lab going forward.

Table 3.1: Performance metrics for the conventional P3HT:PCBM device shown in Figure 3.1

J_{SC} (mA/cm ²)	V_{OC} (V)	FF	PCE (%)
14.3	0.63	0.37	3.34

3.1.2 Intensity-dependent measurements

Intensity-dependent JV curves reveal information about loss mechanisms in an OPV device. Figure 3.2 plots the JV curve as a function of incident light intensity for the same device as that reported in Section 3.1.1. The most obvious difference is the higher current produced for higher illumination intensities due to the increased absorption of photons and subsequent charge generation occurring in the device.

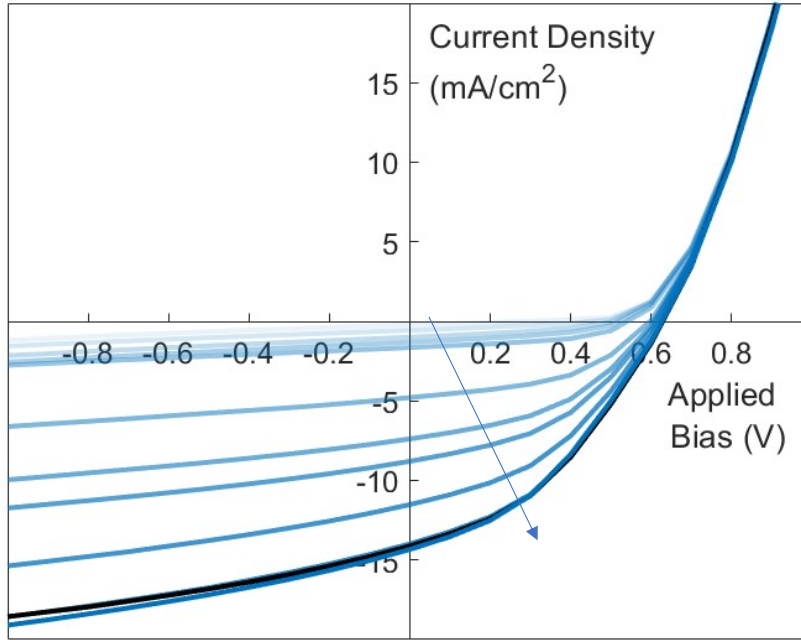


Figure 3.2: Intensity-dependent JV curves for the P3HT:PCBM device reported in Section 3.1.1. The arrow shows the influence of increasing illumination intensity, and the same JV curve from Figure 3.1 is reproduced in black for comparison.

Analysing the J_{SC} as a function of incident light intensity reveals information about recombination mechanisms caused by charge carrier drift at high internal fields. An ideal solar cell will show power law dependence of J_{SC} on illumination intensity: ^{211,212}

$$J_{SC} \propto I^\alpha \quad (3.7)$$

with $\alpha = 1$. When $\alpha < 1$, this indicates non-ideal device behaviour arising from increased bimolecular recombination or the build up of space-charge.^{213,214}

Figure 3.3 a) displays the intensity-dependent J_{SC} for the highest performing P3HT:PCBM device plotted on a log-log scale. A linear fit is performed on the data which yields a slope (and hence an alpha value) within error of 1. This demonstrates that the device does not suffer from bimolecular recombination at short circuit conditions within the intensity range studied.

The V_{OC} can also be studied as a function of light intensity and follows a linear trend when plotted against the natural log of illumination intensity. The slope of such a graph can be used to calculate the diode ideality factor η according to:^{58,215}

$$V_{OC} = \frac{1}{e} (IP_D - EA_A) - \frac{\eta kT}{e} \ln \left(\frac{J_{BI}}{J_{SC}} \right) \quad (3.8)$$

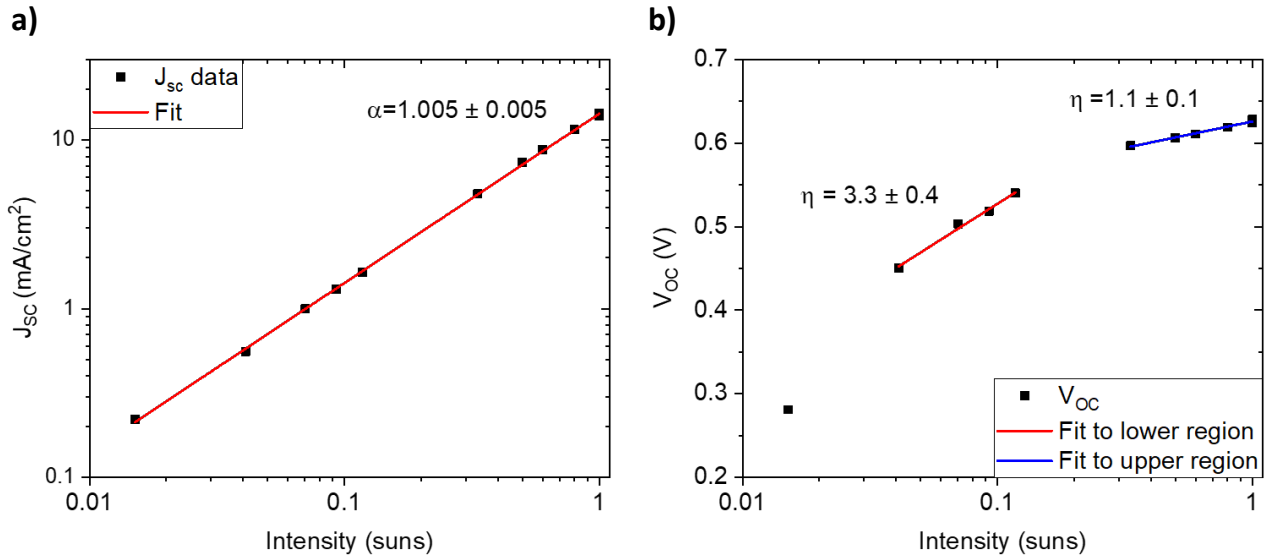


Figure 3.3: a) Intensity-dependent J_{SC} demonstrates a linear trend on a log-log graph which can be fit to reveal an alpha value of 1, demonstrating ideal device behaviour at short circuit conditions. b) Intensity-dependent V_{OC} which can be fit to find an ideality factor of $\eta = 3.3$ for low intensity measurements and $\eta = 1.1$ for high intensity measurements, demonstrating extraction issues at low intensities which are not present at high intensities of illumination.

where IP_D and EA_A are the ionisation potential of the donor and electron affinity of the acceptor respectively, J_{BI} is the bimolecular recombination current, J_{SC} is the short circuit current, and kT the Boltzmann-temperature product. Thus, the slope of the V_{OC} plotted as a function of light intensity is equal to $\eta kT/e$, from which the ideality factor η can be found. It should be noted that open circuit conditions refer to low internal electric fields, where current is produced by diffusion only; and the definition of open circuit voltage maintains that all photogenerated charges must recombine (none can be extracted). An ideal cell containing only bimolecular recombination will have an ideality factor of $\eta = 1$ but a cell suffering from trap-assisted (monomolecular) recombination will have an ideality factor of $\eta = 2$.

Figure 3.3 b) plots the intensity-dependent V_{OC} . Two distinct regimes are seen for this device, suggesting that it exhibits different behaviour for low and high illumination intensities. The ideality factor for each region was calculated according to Equation 3.8 and these were found to be $\eta = 3.3$ and $\eta = 1.1$ for the low and high intensity regions respectively. This suggests that there is significant trap-assisted or extraction issues in the device at low intensities and open circuit conditions, but at intensities near 1 sun the device behaves more satisfactorily with primarily bimolecular recombination and some trap-assisted recombination.

3.1.3 External quantum efficiency measurements

EQE measurements provide wavelength-resolved insight into charge generation in a device. The device is measured at short circuit with monochromatic pulsed illumination, with the electrical output of the cell detected through a lock-in amplifier mechanism to reduce noise.

An EQE measurement is performed on the device reported in Sections 3.1.1 and 3.1.2, and the result is shown in Figure 3.4 a). The device is most efficient at producing charge from 500 nm illumination, where the EQE reaches 50%.

Figure 3.4 b) displays a measurement of the absorption spectra of film materials corresponding to the device. The normalised absorption is shown for both a neat P3HT film and a neat PCBM film as well as for a 1:1 blend film replicating that in the device. Peaks in the EQE spectrum correspond to peaks in the absorption spectra as the production of charge is more efficient at wavelengths of increased absorption in the device. This EQE spectrum also matches well with those found in the literature.^{216–220}

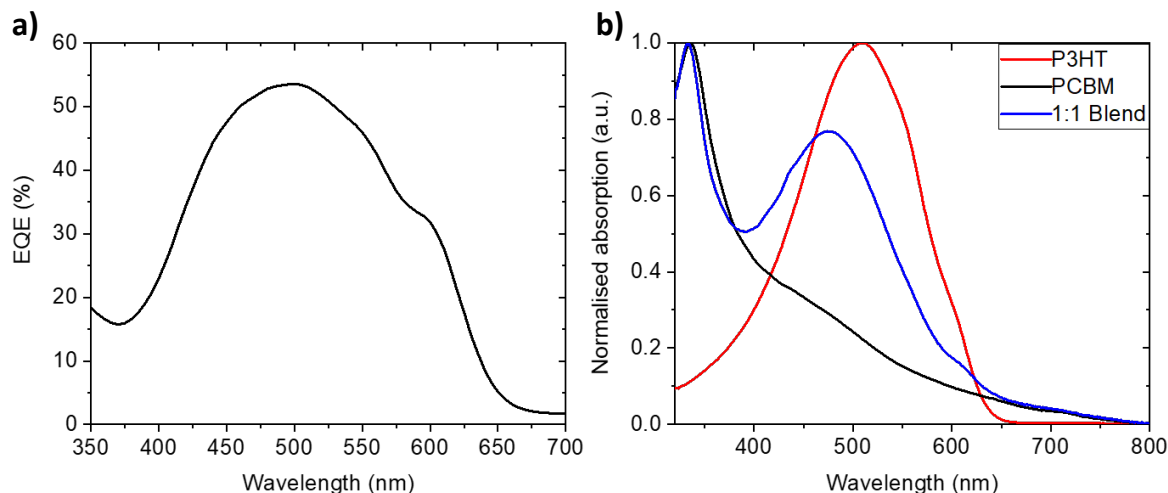


Figure 3.4: a) EQE of a P3HT:PCBM device and b) normalised film absorption spectra for a similar blend film and neat films for each blend component.

3.1.4 Inverted device

As described in Section 1.1.5, there are two structure types commonly used for OPVs, being conventional and inverted geometries. In a conventional structure, the anode is deposited first and forms the semi-transparent electrode through which illumination occurs as well as the extraction of holes, with electrons extracted at the cathode. In an inverted structure, this is reversed such that the cathode is deposited first and forms the semi-transparent electrode through which illumination occurs as well as the extraction of electrons, with holes extracted at the anode. A schematic of current flow is provided in Figure 1.5.

Inverted devices are often preferred due to their inclusion of high work function metals as functioning anodes, which have a lower tendency to oxidise and thus a greater stability than those used for conventional devices.^{71,72} For P3HT:PCBM, inverted devices have been shown to exhibit more favourable morphology of the active layer due to partial vertical phase segregation between the P3HT and PCBM components. PCBM-rich layers have been observed near the bottom cathode and P3HT-rich layers near the top anode, creating self-assembled electron and hole blocking layers which contribute to device function in inverted devices but hinder the functioning of conventional devices.^{221–223} Increased device performance due to avoidance of acidic PEDOT:PSS,²²⁴ improved charge mobilities,²²⁵ increased absorption arising from a more transparent charge collecting layer,²²⁶ improved optical field effects (especially for thin active layers)²²⁷ and slower degradation due to charge transport layer deterioration effects⁷⁵ have also

been reported for inverted P3HT:PCBM devices.

An inverted device was prepared with the configuration ITO/ZnO/P3HT:PCBM/MoO₃/Ag in order to confirm the capability of the lab instrumentation to fabricate inverted devices. The JV curve is reported in Figure 3.5 and the performance parameters in Table 3.2. The PCE obtained is 2.0%, which is in the range of commonly reported values.⁸¹ Thus we confirm the success of these device fabrication and testing protocols for P3HT:PCBM devices in both conventional and inverted geometries, and move on to other material systems.

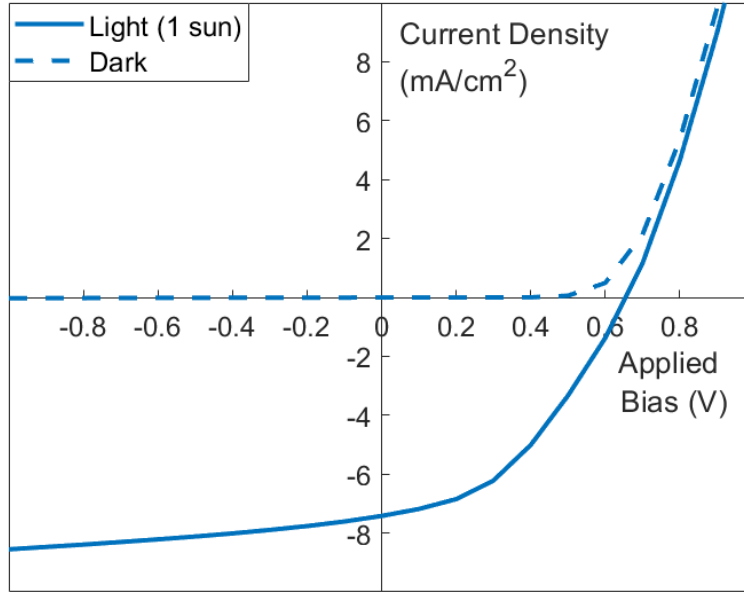


Figure 3.5: JV measurement of an inverted P3HT:PCBM solar cell.

Table 3.2: Performance metrics for the inverted P3HT:PCBM device shown in Figure 3.5

J_{SC} (mA/cm ²)	V_{OC} (V)	FF	PCE (%)
7.42	0.65	0.41	2.00

3.2 PTB7-Th:ITIC device

A higher performing material system consisting of the polymer donor PTB7-Th (also known as PCE10 or PBDTT-FTTE) and the non-fullerene acceptor ITIC was also studied as part of the benchmarking procedure. The synthesis and performance of ITIC as a non-fullerene acceptor was first reported in 2016 by Lin et al.²²⁸ ITIC has an extended absorption range and a

push-pull structure which supports intramolecular charge transfer. It has low lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) energies, good electron transport properties and good miscibility with polymer donors such as PTB7-Th.

In this experiment, the fabrication procedure reported by Yin et al.²⁰⁶ was followed using a device structure of ITO/PEDOT:PSS/PTB7-Th:ITIC/LiF/Al with a 1:1.5 PTB7-Th:ITIC ratio as this was reported to give the best device performance. The JV curve for the best performing device is shown in Figure 3.6 and the performance parameters are given in Table 3.3. The PCE of the device compares favourably with those reported in the literature, even exceeding those reported by Yin et al. It is possible to achieve higher PCEs for PTB7-Th:ITIC devices through solvent vapour annealing,²²⁹ fabrication in an inverted structure²³⁰ or the use of additives,²³¹ although the use of additives can also decrease the PCE of some cells.²³²

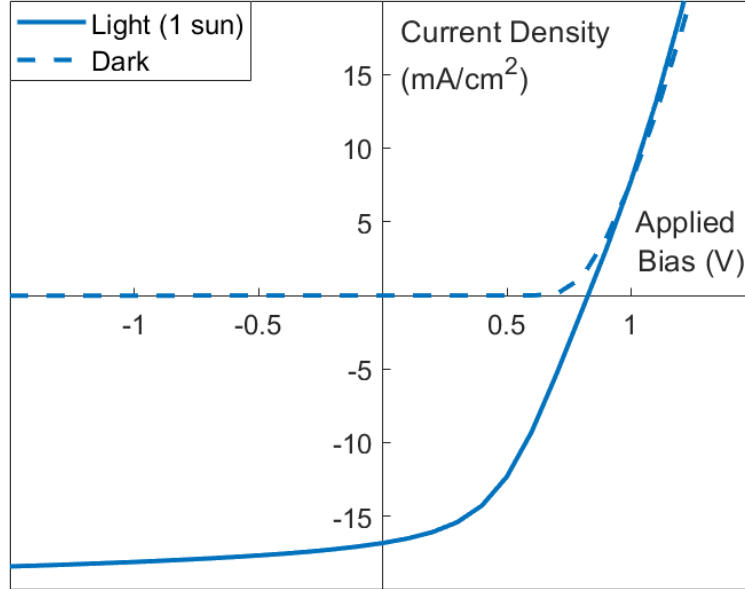


Figure 3.6: JV measurement of a conventional PTB7-Th:ITIC device.

Table 3.3: Performance metrics for the conventional PTB7-Th:ITIC device shown in Figure 3.6

J_{SC} (mA/cm ²)	V_{OC} (V)	FF	PCE (%)
16.8	0.83	0.44	6.16

3.3 Y6 device

One of the highest performing non-fullerene acceptors available is Y6, first reported in early 2019 by Yuan et al.⁹⁵ This molecular has attracted great interest, with over 100 publications in the two years alone after it was first reported.²³³ Y6 displays extended absorption into the NIR, as well as low radiative and nonradiative losses totalling below 0.6 eV.²³⁴ The exciton binding energy of Y6 is known to be low, measuring 100-250 meV, much lower than other materials such as P3HT which was estimated as 700 meV.⁶⁹ As an implication of this, it is reasonable to expect that a large fraction of charges are generated intrinsically in Y6, without the need for the presence of an electron donor.

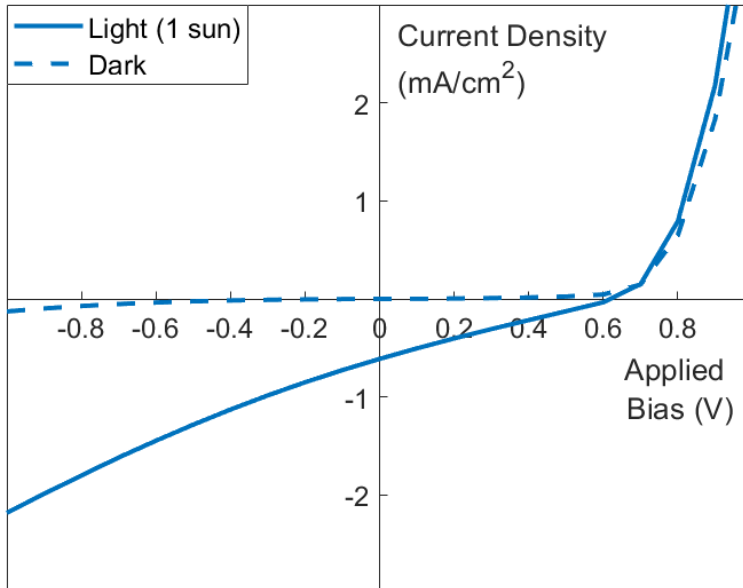


Figure 3.7: JV curve for a Y6 single component device.

Table 3.4: Performance metrics for the single component Y6 device shown in Figure 3.7

J_{SC} (mA/cm ²)	V_{OC} (V)	FF	PCE (%)
0.61	0.62	0.24	0.09

The work presented in this section appears in the following publication: Price, M. B.; Hume, P. A.; Ilina, A.; Wagner, I.; Tamming, R. R.; Thorn, K. E.; Jiao, W.; **Goldingay, A.**; Conaghan, P. J.; Lakhwani, G.; Davis, N. J. L. K.; Wang, Y.; Xue, P.; Lu, H.; Chen, K.; Zhan, X.; Hodgkiss, J. Free charge photogeneration in a single component high photovoltaic efficiency organic semiconductor. *Nature Communications*, **2022**, 13, 2827. DOI: 10.1038/s41467-022-30127-8

Single component Y6 devices with the structure ITO/PEDOT:PSS/Y6/LiF/Al were fabricated to investigate the possibility of free charge generation. The JV curve for the best performing device is shown in Figure 3.7 a). The dark curve shows the device behaves as a rectifying diode. Under illumination, some charge is produced, although much of it recombines leading to the appearance of non-ideal device behaviour especially at reverse bias. The device performance parameters are listed in Table 3.4.

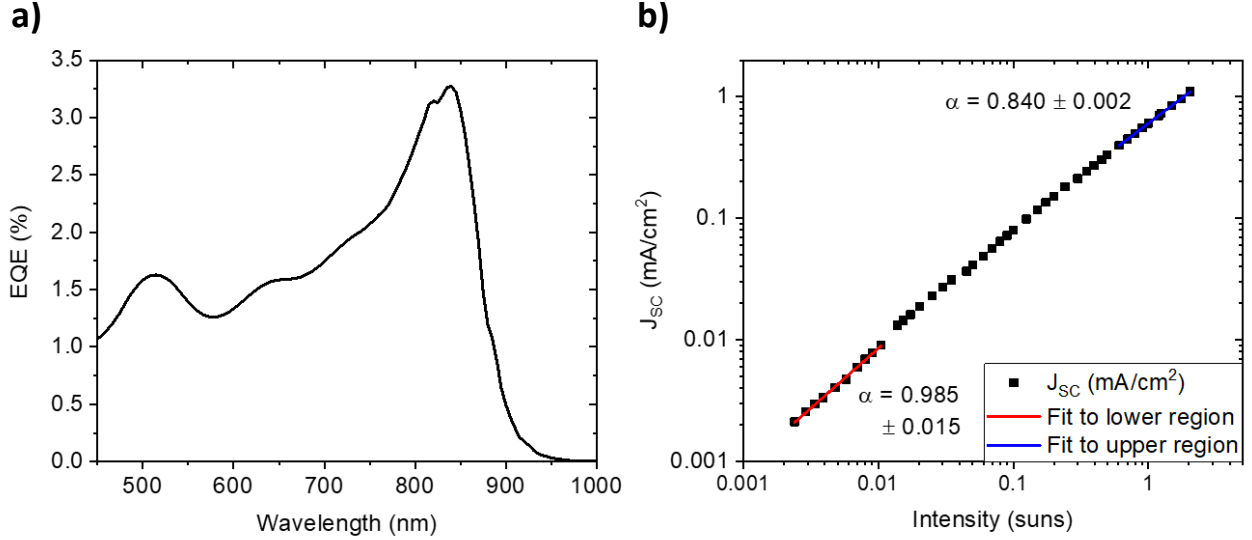


Figure 3.8: a) EQE and b) intensity-dependent J_{SC} measurements of the single component Y6 device. Fits to the low and high intensity regions provide insight into recombination behaviour occurring in each illumination regime.

Figure 3.8 a) shows the EQE measurement for this device. Albeit small, the EQE is non-zero and matches the absorption spectrum of neat Y6 reported in literature,^{235–237} demonstrating the ability of Y6 to produce charges without any donor material present. The intensity-dependent J_{SC} is reported in Figure 3.8 b). The low illumination intensity data is fit to produce a value of $\alpha = 0.985$ as shown in the figure, whereas the fit to the high intensity data produces a value of $\alpha = 0.84$. This indicates the presence of recombination losses at high intensities which are not present at low intensities. Alpha values of less than 1 indicate the presence of either bimolecular recombination or space-charge limited current caused by a significant difference in electron and hole mobilities. Y6 is known to display ambipolar charge transport, with electron and hole mobilities of 1.8×10^{-4} and 5.6×10^{-4} cm²V⁻¹s⁻¹ respectively,²³⁸ making it more likely that the device suffers from bimolecular recombination. This aligns with other observations such as intensity-dependent photoluminescence measurements.⁶⁹ Thus we see that bimolecular recombination is the limiting factor for Y6 single component devices. To overcome this, a donor

material must be included. Even a very small percentage of donor (such as 1% by weight) can drastically improve device functionality. Therefore, whilst two materials are not always necessary for charge generation as is often reported, some donor content is necessary to enable proper device functioning.

3.4 Conclusions

In conclusion, we have shown a selection of results demonstrating the successful fabrication and characterisation of various OPV devices. Section 3.1.1 reports the characterisation of a P3HT:PCBM device in detail. A JV curve is reported and extensively analysed to provide a demonstration of the key features of these measurements. The performance compares favourably to that reported in the literature, demonstrating appropriate benchmarking of the experimental protocols. An EQE and intensity-dependent measurement is also reported. Overall, the success of the device fabrication and characterisation procedure is confirmed. Section 3.2 reports the fabrication and characterisation of a device comprised of the higher-performing material blend of PTB7-Th:ITIC, which again compares favourably with values found in the literature. Section 3.3 reports the fabrication of a single component Y6 device. This experiment demonstrates the possibility for free charge generation from Y6 single component devices, however confirms the practical necessity of the donor in order to minimise bimolecular recombination. Thus, all future experiments reported in subsequent chapters are performed with two component material systems.

Chapter 4

PDI- and TPDI-based OPV devices

4.1 Introduction

As described in Chapter 1, the field of OPVs has experienced immense growth since the introduction of non-fullerene acceptor molecules, with recent breakthroughs enabling efficiencies to climb to over 19%.^{23–25} In addition to the efficiency of non-fullerene devices overtaking that of fullerenes, these new materials also offer lower synthetic complexity and electronic tunability due to their ease of chemical modification.^{21,239} Perylene diimides are particularly promising non-fullerene acceptors possessing excellent stability and structural and electronic tunability,^{90,240} making them good candidates for low-cost, stable and reliable OPVs.

Much research has been dedicated to optimising spectral overlap between the absorption of OPV material blends and the AM1.5G solar spectrum. In many cases, this has been achieved by adding additional components to the OPV material blend to form ternary^{241–243} or even quaternary^{244,245} heterojunctions, or tandem architectures.^{246,247} However, this can complicate device morphology, energetics, and photophysics. A more straightforward strategy is to choose donor and acceptor materials with complementary absorption profiles, ensuring maximum spectral overlap of the blend with the solar spectrum whilst retaining the simplicity of the binary bulk heterojunction. In these systems, excitations in both the donor and acceptor materials undergo energy transfer to reach the donor-acceptor interface where they subsequently undergo charge transfer in order to contribute to the formation of free charges in the device.²⁴⁸

Whilst a good choice for maximising spectral overlap, the performance of monomeric perylene diimides as non-fullerene acceptors is limited by their crystallisation, with the highest

The work presented in this chapter appears in the following publication: **Goldingay, A.**; Stuart, A. N.; Ghosh, P.; Yadav, S.; Gangadharappa, C.; Patil, S.; Rao, A.; Lakhwani, G. Quantifying dual-direction energy harvesting in twisted perylene non-fullerene acceptor organic photovoltaics. *The Journal of Physical Chemistry C*, **2023**, *127*, 51, 24598–24607. DOI: doi/10.1021/acs.jpcc.3c05050

PCE of monomeric perylene diimides sitting at just over 5%.^{249,250} This is due to their propensity to undergo π - π stacking which causes the acceptor domains in the blend to grow larger than the exciton diffusion length.^{251,252} Several strategies have been proposed to disrupt perylene crystallisation including the addition of bulky substituents,^{253,254} and the linkage of monomers to form dimers,^{2,255–257} trimers,²⁵⁸ tetramers,^{259,260} oligomers,^{261,262} macromolecules²⁶³ and even star-shaped structures.^{264–266}

Improvements in device efficiency in perylene diimide dimers have been ascribed to increased short circuit current (J_{SC}), which arises from the improved morphology and reduced recombination losses attainable upon dimerisation.² Twisted perylene dimer molecules are capable of achieving a desirable balance between the formation of clusters and the disruption of long-range ordering,²⁶⁷ and at the same time benefit from improved oscillator strengths and exciton diffusion lengths due to J-like aggregate behaviour.²⁶⁸ When paired with polymer donors, these dimers have proven to be especially promising materials for non-fullerene OPVs due to efficient charge generation arising from excitation of both the donor and acceptor domains.²⁵⁷ Thus TPDI dimers experience many of the benefits of PDI monomers such as their stability, tunability, ease of synthesis and solution processability whilst avoiding excessive π - π stacking.

PDI monomers and dimers are excellent molecular choices for which to investigate and compare not just the presence but the role of dual-direction energy harvesting, and the effect that altering chromophore packing and morphology has on it. Whilst the performance of PDI- and TPDI-based devices is lower than many state-of-the-art organic systems,^{23–25} the use of a simple device material system allows for a thorough comparison of the device photophysics and origins of charge generation between the two device types. Many high-performing acceptors have complicated photophysics, such as Y6, which has been predicted to undergo several types of photophysical pathways such as intersystem crossing,²⁶⁹ singlet fission,²⁷⁰ and free polaron formation without a donor material.⁶⁹ The more straightforward photophysics of PDI and TPDI allow us to directly compare the charge generation, and thus more clearly determine the effects of morphology and packing on the dual direction energy harvesting. The use of a simple architecture and device preparation procedure also allows for direct probing of the natural morphological differences between the monomer and the dimer without additional complication.

In this chapter, we focus on understanding the origin of improved device performance in TPDI dimer-based devices as compared to PDI monomer-based devices. We report the fabrication and characterisation of solar cells and blend films comprised of PTB7-Th paired

in turn with a perylene monomer (PDI) and twisted dimer (TPDI) linked through the imide position as shown in Figure 4.1 a). By directly comparing the optoelectronic performance of PTB7-Th:PDI devices with those of PTB7-Th:TPDI devices, we show that dimerisation of the perylene produces a three-fold increase in the device PCE due to nanoscale morphological improvement. We observe increased non-geminate recombination in PDI-based devices compared to TPDI-based devices, which we attribute to differences in nanoscale morphology. Overall, we find the role of morphology in blend films to have a crucial influence on the photophysics of these OPV devices.

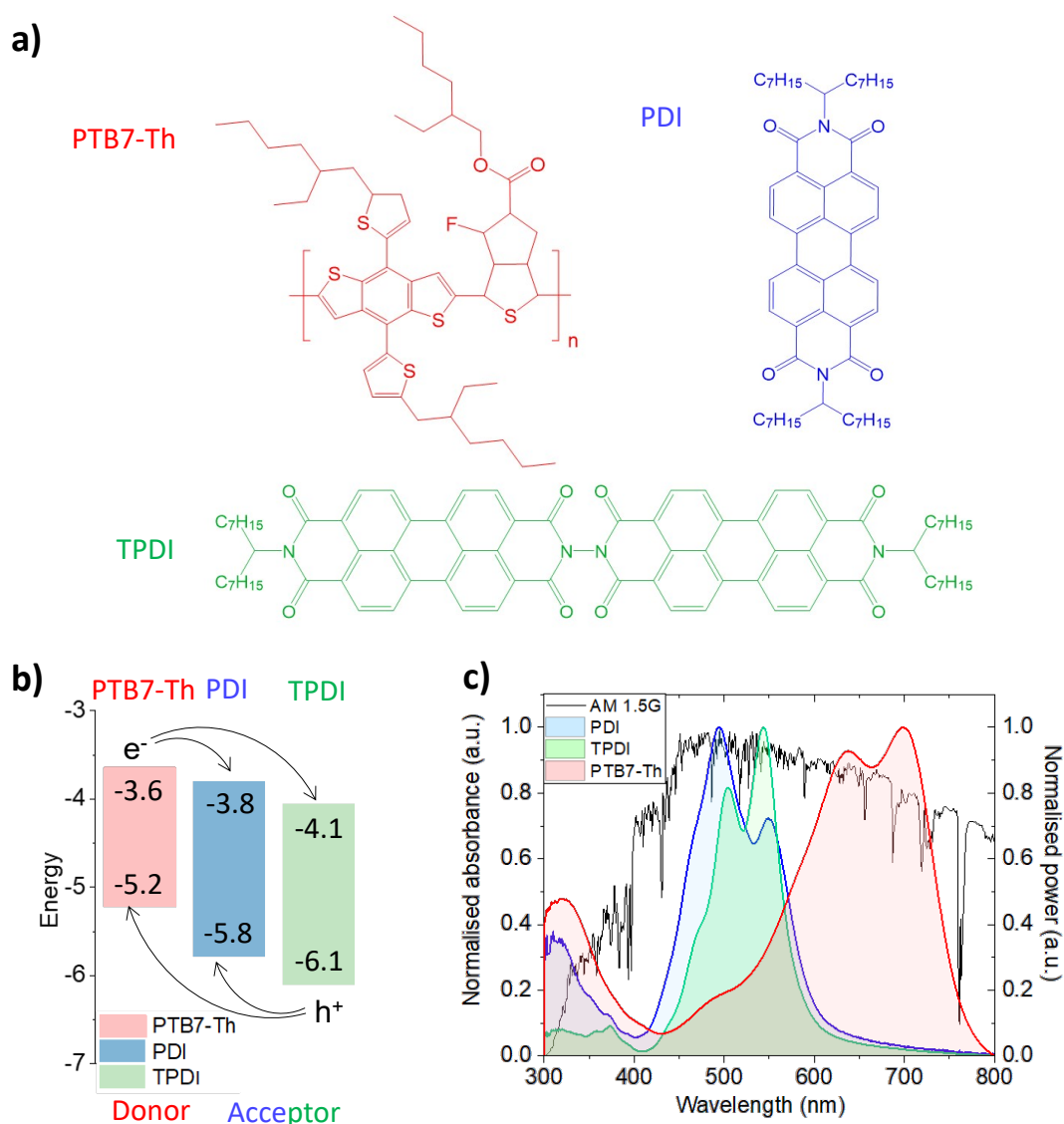


Figure 4.1: a) Chemical structures and b) energy levels for the three materials used in this study. PTB7-Th is an electron donor while PDI and TPDI are electron acceptors. Energy levels are taken from literature.^{2,3} c) Film absorption profiles of the three neat materials, demonstrating their complementary coverage of the AM1.5G solar spectrum.

4.2 Material properties

The chemical structures of the three materials used for this investigation are shown in Figure 4.1 a). Figure 4.1 b) shows the ionisation potentials and electron affinities of the materials, often referred to as the HOMO and the LUMO respectively, approximated from the literature.^{2,3} The cascading energy levels demonstrate the ability of this system to undergo downhill electron transfer from the LUMO of the PTB7-Th donor to the LUMO of the (T)PDI electron acceptor as well as uphill hole transfer from the HOMO of the (T)PDI acceptor to the HOMO of the PTB7-Th donor. Figure 4.1 c) shows the complementary absorption profile of PTB7-Th and (T)PDI neat films, and the resulting coverage of the AM1.5G solar spectrum which allows for dual direction energy harvesting. The ability of an OPV donor to undergo electron transfer to the acceptor is not unusual; rather it is considered fundamental to the function of OPV devices. However, the ability of an electron acceptor to be photoexcited in a complementary spectral region and donate a hole to the electron donor has arisen due to the electrical tunability of non-fullerene acceptors and is key to unlocking dual-direction energy harvesting.^{21,271}

Time-resolved emission spectroscopy (TRES) of blend films shown in Figure 4.2 reveals the effective quenching of (T)PDI emission in the presence of PTB7-Th, which can be explained by charge generation due to hole transfer from (T)PDI to PTB7-Th. However, since the optical bandgap of (T)PDI is higher than that of PTB7-Th, and the fluorescence profile of the former overlaps the absorption of the latter, it is possible that the fluorescence quenching of (T)PDI could also be attributed to energy transfer.

4.3 Device measurements

OPV bulk heterojunction devices were prepared in an inverted structure as shown in Figure 4.3 a) inset with seven devices fabricated for each material combination. Representative JV curves are shown in Figure 4.3 a) and the corresponding device parameters are shown in the table in 4.3 c). The TPDI-based devices performed over three times as well in PCE as PDI-based devices, due to a three-fold improvement in J_{SC} as well as an improved fill factor. Since TPDI consists of two chromophores instead of one, it is essential to distinguish whether the improved device performance of TPDI blends is simply due to increased charge generation occurring due to increased photon absorption, or whether there is a difference in device physics. The

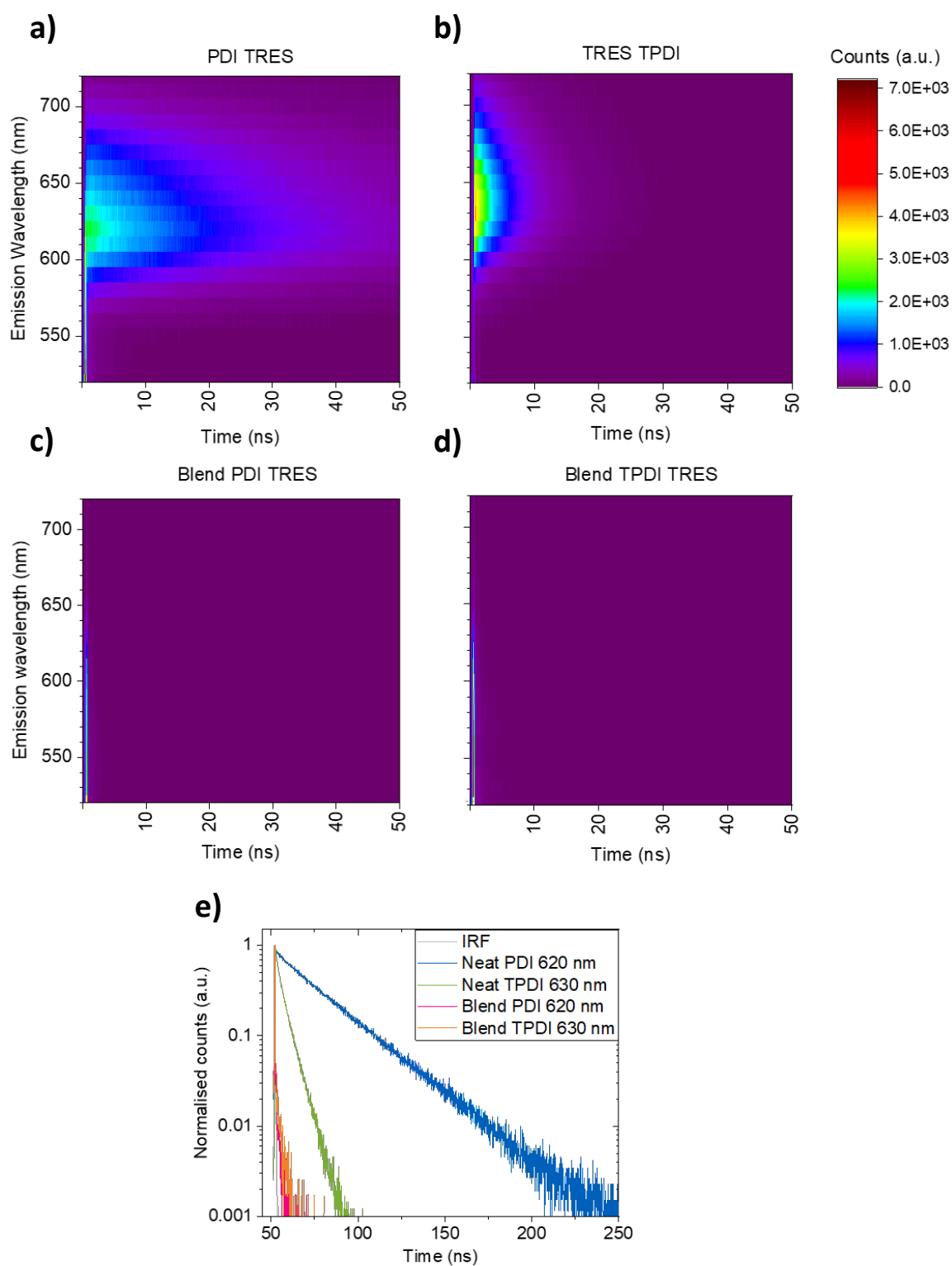


Figure 4.2: Time-resolved emission spectra (TRES) for a) neat PDI, b) neat TPDI, c) PTB7-Th:PDI blend and d) PTB7-Th:TPDI blend films demonstrating the effective quenching of (T)PDI emission in the presence of PTB7-Th. Line cuts and the instrument response function (IRF) are also shown in e) for the wavelengths of maximum emission in neat films.

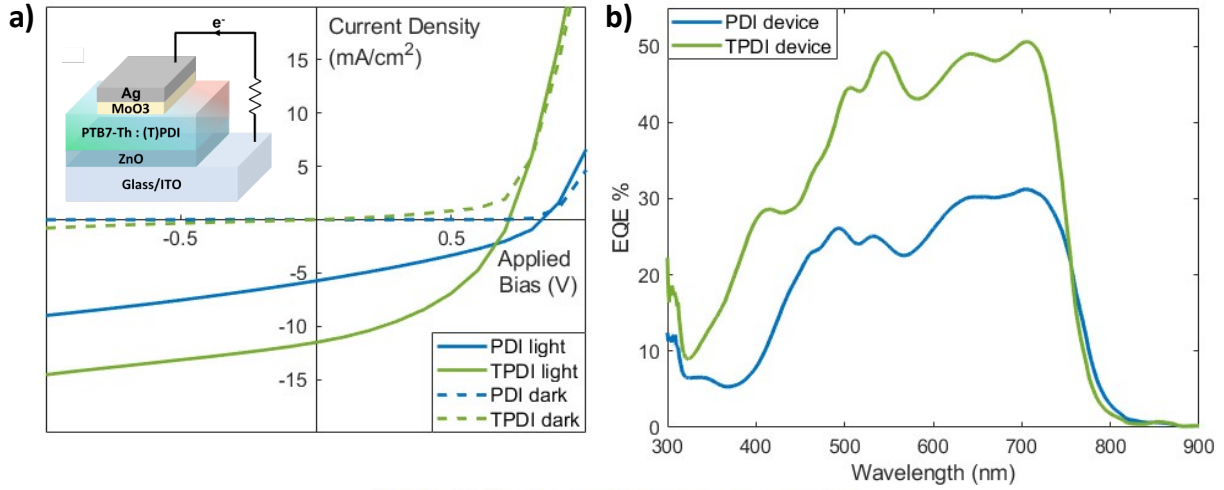


Table 1: Device performance parameters

c)

Blend material	$J_{SC}(mA/cm^2)$	$V_{OC}(V)$	FF	$PCE(\%)$
PTB7-Th:PDI	4.8 ± 0.5	0.80 ± 0.02	0.33 ± 0.01	1.3 ± 0.2 (champion 1.68)
PTB7-Th:TPDI	14.3 ± 1.5	0.74 ± 0.02	0.40 ± 0.01	4.15 ± 0.76 (champion 5.30)

Figure 4.3: a) Representative JV curves for PTB7-Th:PDI and PTB7-Th:TPDI devices, with the inverted device architecture shown in the inset. Dark curves and photocurrent curves are shown in Figure 4.4. b) EQE measurements show broad absorption for both devices, with a two-fold increase in performance in TPDI-based devices. c) Device performance parameters, showing the three-fold improvement in PCE for TPDI devices.

blends were prepared in a 1:1 weight ratio with PTB7-Th which equates to only a 1.35 increase in chromophores per mole for TPDI compared to PDI, which is much less than the ratio of improvement seen in the J_{SC} and the PCE. The photocurrent shown in Figure 4.4 b) also demonstrates the superior current generation in TPDI devices. The open circuit voltage (V_{OC}) is smaller in TPDI than PDI, however this is more than accounted for by the difference in the electron affinities of the two materials (often referred to as ΔE_{LUMO}) since $\Delta V_{OC} < \frac{\Delta E_{LUMO}}{q}$ where q is the charge on an electron.

The dual-direction energy harvesting of this system is confirmed through wavelength-resolved EQE measurements shown in Figure 4.3 b). Photons absorbed across the energy spectrum are successfully converted into charges at both the PTB7-Th absorption peak wavelengths ($\sim 640, 700$ nm) and the (T)PDI absorption peak wavelengths ($\sim 495, 550$ nm for PDI and $\sim 505, 545$ nm for TPDI). The PTB7-Th:TPDI device again clearly outperforms the PTB7-Th:PDI device, exhibiting a two-fold improvement in EQE at all wavelengths, which is also much higher than the PDI:TPDI chromophore ratio.

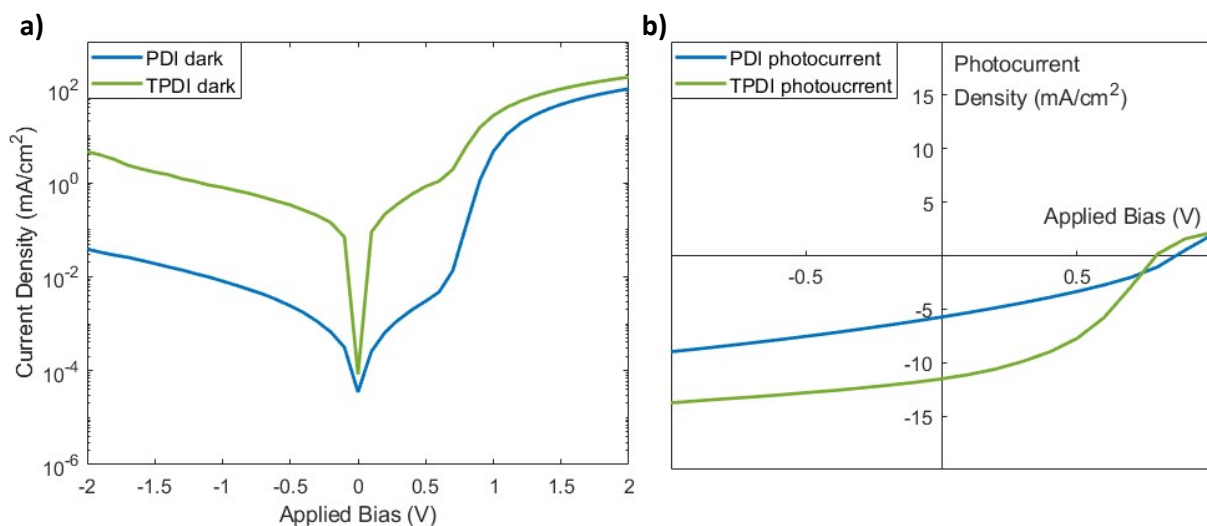


Figure 4.4: a) Dark JV curves for PTB7-Th:PDI and PTB7-Th:TPDI devices. b) Photocurrent in the same devices, calculated as $J_{ph} = J_L - J_D$.

4.4 Morphology studies

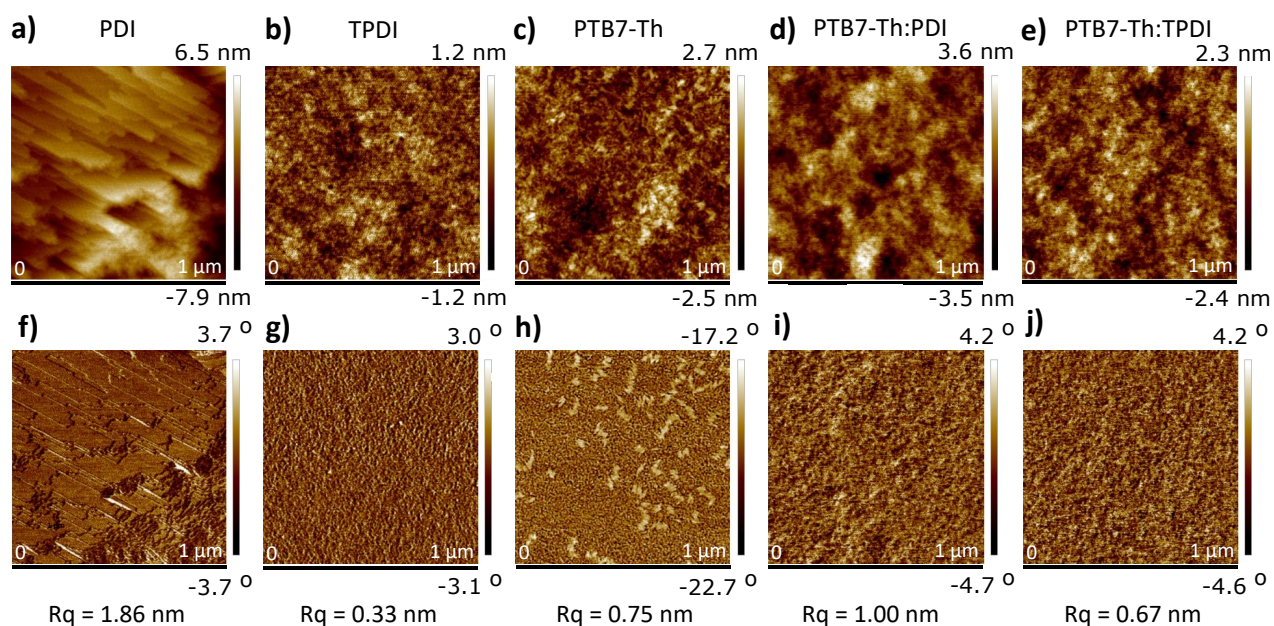


Figure 4.5: Atomic Force Microscopy (AFM) images of neat and blend films showing that dimerisation of PDI prevents the formation of microstructures seen in PDI films and causes finer mixing in blend films. a) Height and f) phase images of neat PDI, b) height and g) phase images of neat TPDI, c) height and h) phase images of neat PTB7-Th, d) height and i) phase images of the PTB7-Th:PDI blend film, e) height and j) phase images of the PTB7-Th:TPDI blend film, all with root-mean-squared roughness values displayed underneath.

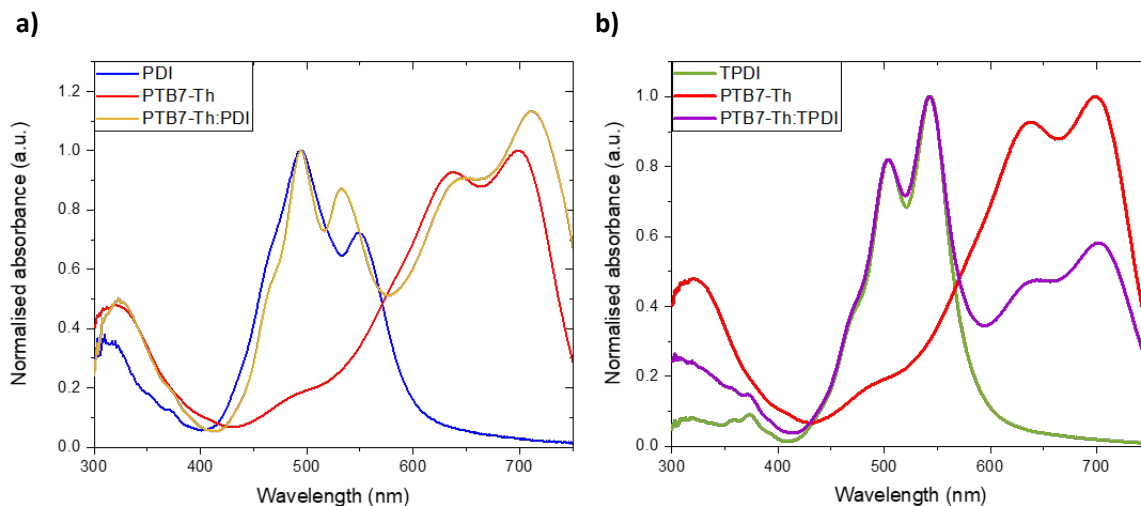


Figure 4.6: Film absorption spectra for the a) PDI material system and b) TPDI material system. Line broadening in PDI thin films caused by aggregation of PDI monomers is lessened in the blend with PTB7-Th, however there is no change in linewidth between the TPDI neat and blend films since the degree of aggregation is lower for TPDI dimers.

To determine the role of morphology in the improved performance of TPDI-based devices, thin films of the neat materials and their blends were studied through Atomic Force Microscopy (AFM) enabling visualisation of the nanoscale morphology of the films. As shown in Figure 4.5 a) and f), PDI appears to form large, ordered structures due to strong interfacial π - π bonding. In contrast, TPDI forms significantly smaller structures as shown in Figure 4.5 b) and g) due to its interrupted planarity arising from the twisted dimer configuration. Whilst we are unable to observe bulk structures, the measured root-mean-square roughness (R_q) of the images demonstrates the smoothness of the films, which is taken as indicative of the degree of mixing in the blend films. R_q is reduced from 1.86 nm to 0.33 nm when comparing the monomer to the dimer, revealing a reduction in surface roughness as would be expected from a reduction in π - π stacking. The ordered structures in PDI are successfully broken into smaller structures upon addition of PTB7-Th. Blend films showed a reduction in surface roughness from 1.00 nm to 0.67 nm for PDI blends compared to TPDI blends, suggesting that the disruption of long-range ordering results in the formation of smaller surface structures due to finer blend mixing, ultimately leading to improved device performance for PTB7-Th:TPDI devices. Other factors such as differences in energetic disorder, charge transport, and delocalisation may also influence the device performances, however it has been shown that these can also be closely related to the morphology of the films.^{272,273} Increased aggregation in PDI films compared to

TPDI films is also shown by line broadening in UV-visible absorption spectra presented in Figure 4.6.

4.5 Intensity-dependent device measurements

In order to understand the processes underpinning the increased performance of the PDI-based devices, JV measurements of the best performing devices were again made for varying levels of illumination intensity as shown in Figure 4.7.

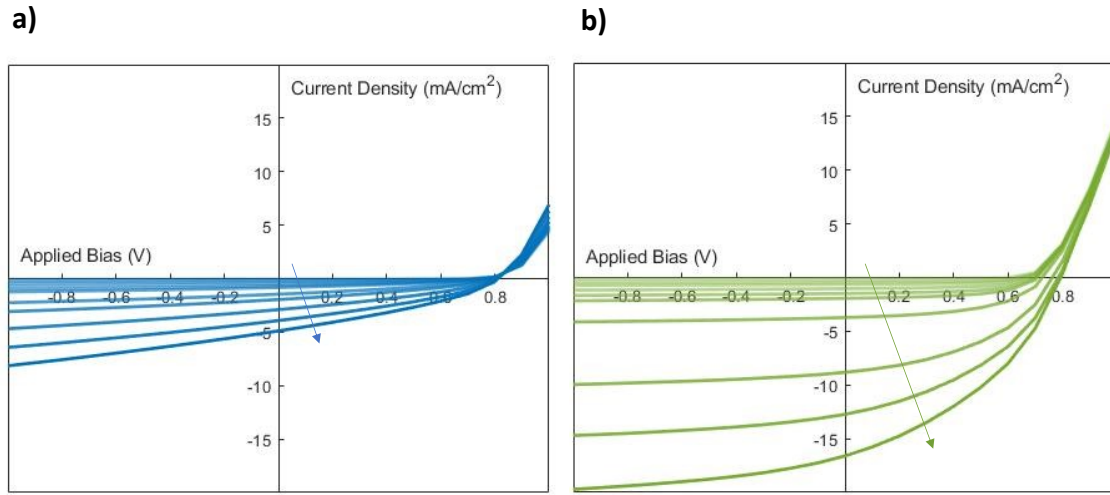


Figure 4.7: Intensity-dependent JV curves for the best performing a) PTB7-Th:PDI device and b) PTB7-Th:TPDI device measured at varying levels of illumination. The arrows show the direction of increasing illumination intensity.

Intensity-dependent J_{SC} plots reveal information about recombination mechanisms as described in Chapter 3. Ideal devices will show a power law exponent of $\alpha = 1$, and any values less than this indicate the presence of bimolecular recombination or the build-up of space charge.^{213,214} The intensity-dependent J_{SC} is shown for both the PDI and TPDI-based devices in Figure 4.8 a). Using the method described in Chapter 3, the best performing PDI-based device is found to have a value of $\alpha = 0.80$ whereas the best performing TPDI-based device has a value of $\alpha = 0.93$. This indicates that the PDI-based device suffers from increased non-geminate recombination compared to the TPDI-based device at short circuit.

The V_{OC} was also studied as a function of incident light intensity and followed a linear trend for both devices when plotted against $\ln(I)$ as shown in Figure 4.8 b). The ideality factor was found as per the method described in Chapter 3. Ideality factors were found to be $\eta = 1.1$

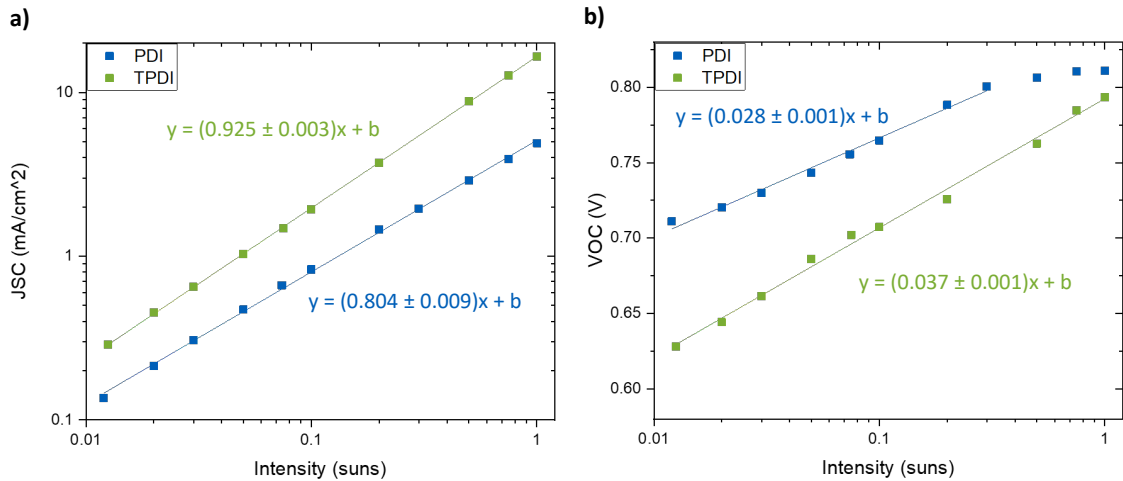


Figure 4.8: a) Intensity-dependent J_{SC} for both devices. The slope of the J_{SC} plot is fit to give alpha values of $\alpha = 0.804 \pm 0.009$ and $\alpha = 0.925 \pm 0.003$ for PDI- and TPDI-based devices respectively. b) Intensity-dependent V_{OC} for both devices. The slope of the V_{OC} plots are fit and shown on the graph, which give ideality factors of $\eta = 1.1$ and $\eta = 1.4$ respectively for PDI- and TPDI-based devices.

and $\eta = 1.4$ for PDI- and TPDI-based devices respectively. The V_{OC} of the PDI device also reaches a plateau at high intensities, demonstrating the presence of illumination-induced losses. This reveals a saturation of charge carrier density in the device²⁷⁴ and further supports the claim that PDI devices suffer from bimolecular recombination at intensities near 1 sun. Thus we demonstrate that TPDI-based devices have reduced non-geminate recombination compared to PDI-based devices. In future it would be insightful to perform a similar study with devices in bilayer configurations, resulting in the PDI and TPDI domain being of similar sizes to each other, and to see if bimolecular recombination is indeed the same in both devices.

4.6 Conclusions

In conclusion, we have comprehensively studied the device performance of a perylene monomer and dimer each blended with PTB7-Th. Both PTB7-Th:PDI and PTB7-Th:TPDI blends have broad absorption spectra capable of covering a significant portion of the AM1.5G spectrum due to the complementary absorption profiles of the materials. Time-resolved emission spectra reveal efficient quenching of the (T)PDI fluorescence in the presence of PTB7-Th, indicating the presence of hole or energy transfer from (T)PDI to PTB7-Th. This exists in addition to the primary charge generation mechanism in OPV devices of electron transfer from the

donor to the acceptor. The dual-direction energy harvesting mechanism in both device blends is confirmed due to charge generation from broad spectrum illumination as seen through wavelength-dependent EQE measurements.

PTB7-Th:TPDI devices are seen to outperform PTB7-Th:PDI devices due to their improved J_{SC} and FF, which arise from their improved diode behaviour. They also exhibit approximately twice the EQE of PDI-based devices. Intensity-dependent J_{SC} and V_{OC} measurements demonstrate reduced bimolecular recombination in TPDI-based devices, suggesting that the improved device performance arises from reduced recombination losses.

Morphology studies indicate that neat PDI suffers from aggregation on a scale visible by AFM, whereas neat TPDI does not. Upon the addition of PTB7-Th to PDI and TPDI neat films, smoother surfaces are formed for TPDI-based blends, suggesting increased domain mixing. Steady-state UV absorption measurements also indicate changes in the morphology of the PDI film upon the addition of PTB7-Th, suggesting that the neat film suffers from aggregation. No such change is suggested for the TPDI neat and blend film. Combined, the morphology studies indicate that PDI forms crystalline domains which acts to the detriment of the device performance. In contrast, this crystallisation is broken up in TPDI domains due to the twisted structure of the dimer which reduces the amount of $\pi - \pi$ stacking occurring in the film.

Thus we have demonstrated the critical importance of active layer morphology for device performance. The simple structural change of linking two perylene monomer units to form a twisted dimer has been shown to drastically improve the device performance. In Chapter 5, we delve deeper into the effects of morphology on the charge generation mechanisms of these devices, and show that more balanced dual-direction energy harvesting is achieved by TPDI-based devices.

Chapter 5

Time-resolved studies of PDI- and TPDI-based blend films

5.1 Introduction

In Chapter 4, we studied both material properties and device photophysics of PTB7-Th:(T)PDI neat films and blends. We saw that the morphology is critically important to device functionality, namely that the morphology differences created by the dimerisation of the perylene acceptor allow for a three-fold improvement in device performance. We also saw through EQE measurements that both material blends have the capability to harvest energy across a significant portion of the AM1.5G spectrum due to the complementary absorption profiles of the donor and acceptor materials, however this is more efficient for TPDI-based devices.

Despite significant research into dual-direction energy harvesting in donor-acceptor blends, to the best of our knowledge no comprehensive study has been performed to compare and quantify charge generation. The quantification of the contribution of the donor and acceptor components in an OPV blend to the overall generation of charge is thus a novel and effective approach to understanding the role of the morphology of the two blend components. The distinction between charge and energy transfer in systems where both are possible is also not often considered in the literature.

In this chapter, we study the same film samples from Chapter 4 using transient absorption (TA) spectroscopy. We again provide direct observation of dual-direction energy harvesting, thus confirming the ability of this system to form charge transfer states when both domains are

The work presented in this chapter appears in the following publication: **Goldingay, A.**; Stuart, A. N.; Ghosh, P.; Yadav, S.; Gangadharappa, C.; Patil, S.; Rao, A.; Lakhwani, G. Quantifying dual-direction energy harvesting in twisted perylene non-fullerene acceptor organic photovoltaics. *The Journal of Physical Chemistry C*, **2023**, *127*, 51, 24598–24607. DOI: doi/10.1021/acs.jpcc.3c05050

excited by broad bandwidth excitation such as the solar spectrum. We determine the rates and efficiencies of the electron and energy or hole transfer processes through spectral deconvolution and modelling of the TA data. We show that hole transfer is indistinguishable from energy transfer and electron back transfer in these and possibly other material systems. We find that the TPDI blend film achieves balanced dual-direction energy harvesting since PTB7-Th and TPDI excitation contribute equally to charge generation. In contrast, excitons in the larger, more crystalline PDI domains decay before they reach an interface, thus the PTB7-Th:PDI blend relies twice as heavily on electron transfer for charge generation. Overall, we again find the role of morphology in blend films to have a crucial influence on the mechanisms of charge generation in OPV devices. This work demonstrates a thorough investigation into the photophysics of the two material systems presented, and introduces an approach to quantification of charge generation that can be applied to other material systems in the future.

5.2 Transient absorption spectroscopy

5.2.1 The technique of transient absorption spectroscopy

TA spectroscopy is a powerful technique allowing insight into the time-resolved and wavelength-resolved response of a material to excitation provided by a pulsed light. TA is typically performed with a monochromatic pump pulse followed by a broadband probe pulse operating at twice the frequency of the pump. The time delay between the pump and the probe is altered to allow for the measurement of the transmission through the sample as a function of time after the pump pulse. The probe is also used to measure the ground state transmission in between pump pulses to provide a reference signal from which the change in transmission ΔT is calculated. In this way, the technique is similar to UV-visible absorption spectroscopy, but performed in the excited state, and in a time-resolved manner. This provides insight into which species are created following pump excitation and how these decay as a function of time on the nano-, pico- or femto-second timescale as dictated by instrument resolution.

There are three signatures that comprise a TA spectrum which are shown in the schematic in Figure 5.1. When a molecule is pumped into the excited state, ground state absorption will no longer occur and thus the wavelength corresponding to the ground state absorption will be transmitted through the sample to a greater degree than when the pump is off. This is termed a ground state bleach (GSB) and is positive in nature for a $\Delta T/T$ measurement as shown in

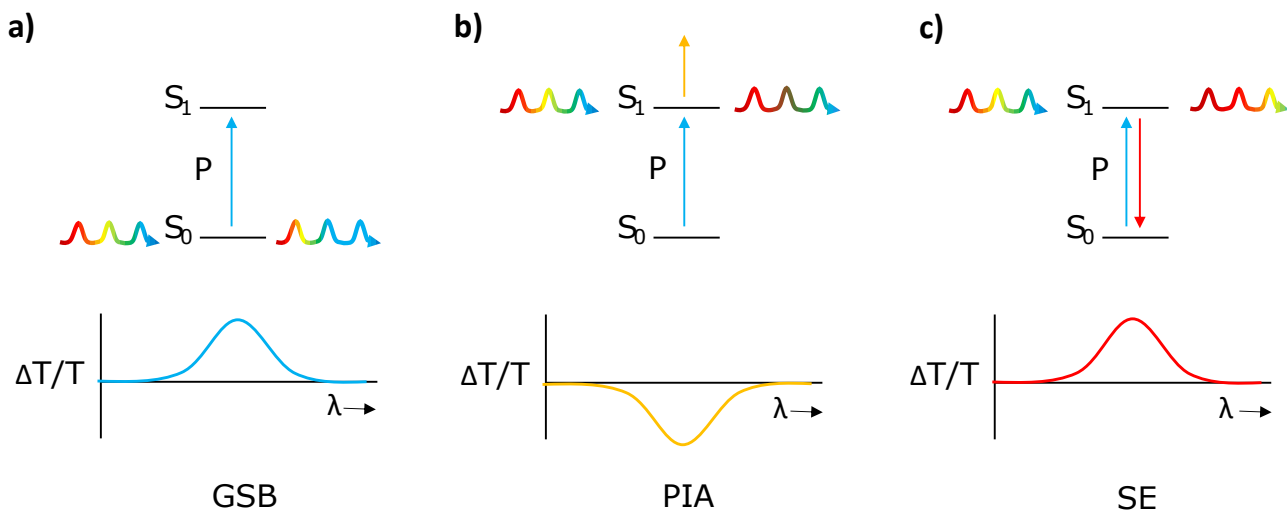


Figure 5.1: Three features of TA spectra: a) ground state bleach (GSB), b) photoinduced absorption (PIA) and c) stimulated emission (SE).

Figure 5.1 a). Excited state absorption results in a negative signature termed photoinduced absorption (PIA) as shown in Figure 5.1 b). Finally, emission from the excited state can be stimulated by the probe beam causing stimulated emission (SE) which results in a positive signature as shown in Figure 5.1 c). Once these features have been identified for a sample, they can be tracked as a function of time to provide information about the decay of excited state species, as is done below.

5.2.2 Transient absorption on neat films

Picosecond TA spectroscopy was performed on neat films of PDI, TPDI and PTB7-Th to investigate the spectral and kinetic features of the materials in isolation from each other.

The TA spectrum of a neat PDI film is shown in Figure 5.2 a) for five different time periods after excitation by a 540 nm laser pulse. This excitation wavelength was chosen as it is near the peak of absorption of PDI, as can be seen in Figure 4.1. The positive feature at 560 nm is assigned to a GSB, as it is also near to the known PDI absorption peak measured by steady-state experiments. This feature arises due to the transmission of the probe pulse at the wavelength that would otherwise be absorbed by molecules in the ground state. Hence, the GSB feature is reduced as the excited state population generated by the pump pulse decays back to the ground state. The broad negative feature from 600-1000 nm is ascribed to a PIA, where already excited molecules are able to absorb this section of the probe to be promoted into a higher-energy excited state. Figure 5.2 b) shows the kinetics, i.e. the time-resolved

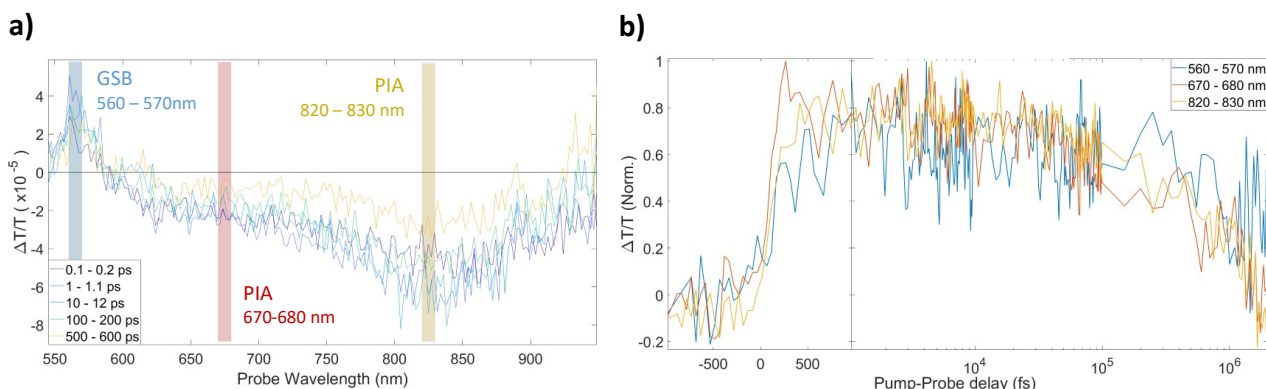


Figure 5.2: TA a) spectra and b) kinetics of a neat PDI film excited at 540 nm and 2.2 uJ/cm^2 . The positive peak at 565 nm is attributed to the GSB of PDI whilst the broad feature from 600–1000 nm is attributed to a PIA. Kinetic traces of these features show that they decay with the same kinetics.

decay profile, of the three wavelength regions selected with coloured bars on Figure 5.2 a). The kinetics are normalised by setting value of the initial peak to 1. The decay curves show that all three regions of interest decay with the same kinetic profile.

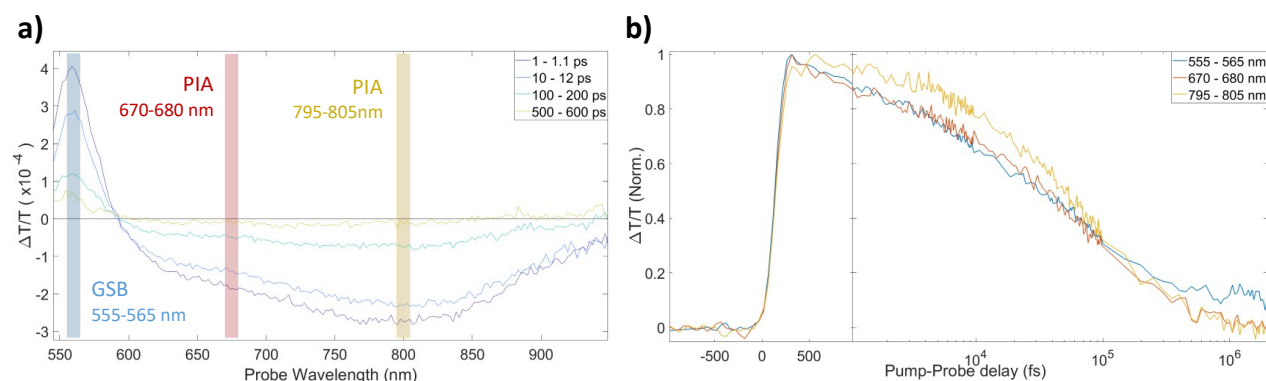


Figure 5.3: TA a) spectra and b) kinetics of a neat TPDI film excited at 540 nm and 2.2 uJ/cm^2 . The positive peak at 560 nm is attributed to the GSB of TPDI whilst the broad feature from 600–1000 nm is attributed to PIA. The central wavelength kinetic trace appears to have a similar decay to the GSB at early times and then a similar decay to the peak of the PIA at later times, indicating that there may be an additional species present.

The same procedure is performed for a TPDI neat film excited at 540 nm as shown in Figure 5.3. The data appears less noisy as there was a greater signal-to-noise ratio during measurement arising from the increased absorption of TPDI compared to PDI. A similar set of features is seen, namely a GSB at 560 nm and a broad PIA from 600-1000 nm. The kinetic traces in Figure 5.3 b) demonstrate that the central region of interest appears to have a similar decay profile to the GSB at early times ($< 100 \text{ ps}$) and a similar decay to the peak of the PIA

at later times. Since these two features (the GSB and the PIA) have different kinetic decays, there must be an additional species present such that the decay profiles cannot be described by a simple two-level decay system.

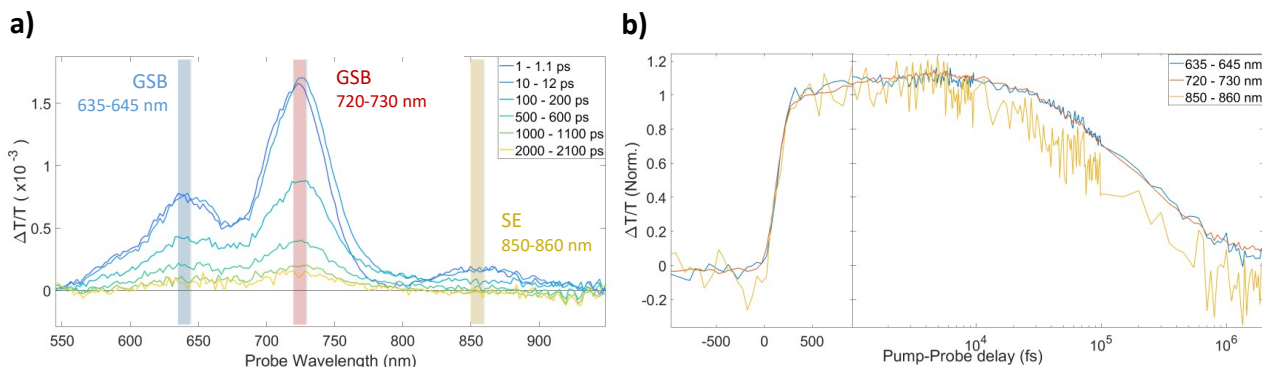


Figure 5.4: TA a) spectra and b) kinetics of a neat PTB7-Th film excited at 540 nm and 1.8 uJ/cm². The positive peaks at 635 and 725 nm are attributed to GSB features of PTB7-Th whilst the peak at 855 nm is attributed to SE of PTB7-Th which is quenched by the presence of (T)PDI in blend films. The GSB and SE kinetics decay with a similar profile at early times (< 10 ps) but diverge at later times.

Selected time slices of the TA spectrum for a neat film of PTB7-Th are shown in Figure 5.4 a). The two vibronic peaks of the PTB7-Th absorption from Figure 4.1 are clearly visible, and these features are assigned as GSB features. The positive feature at 850 nm is assigned to an SE feature, since this appears at a higher wavelength than any steady-state absorption feature and thus cannot be a GSB feature. This SE appears only in the absence of (T)PDI, since it is quenched in blend films as shown in Figures 5.8 and 5.9. We also expect the presence of an underlying PIA at near-infrared wavelengths (> 950 nm) due to charge separation occurring within the PTB7-Th copolymer backbone due to its push-pull architecture as has been seen previously.^{275,276} The kinetic traces show similar decay behaviour between the GSB and the SE at early times (< 10 ps), however at later times the SE signal decays more quickly than the GSB, likely due to the underlying PIA.

Studying the kinetics of each of the films as a function of fluence provides insight into the presence of annihilation losses in the films. The fluence dependent kinetics for the PDI neat film are shown in Figure 5.5 for four fluences at the three wavelengths of interest from Figure 5.2. The normalisation of the initial peak to 1 is adjusted to account for the noise in the measurement. The kinetic traces reveal fluence-dependent decay behaviour, which signifies the presence of decay processes such as singlet exciton-exciton annihilation.

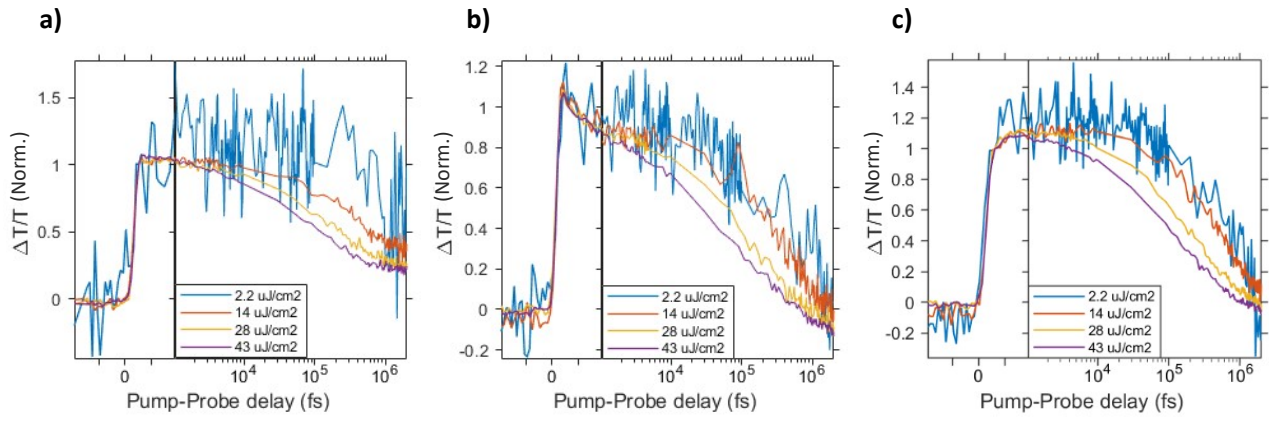


Figure 5.5: Fluence dependent TA kinetic traces for neat PDI films at a) 560–570 nm (GSB), b) 670–680 nm and c) 820–830 nm (PIA). There is a clear dependence of the decay constant on the pump fluence, revealing the presence of decay processes such as singlet exciton-exciton annihilation.

The same procedure is performed for TPDI neat films as shown in Figure 5.6. In this case, there appears to be threshold-dependent behaviour, since there is a significant change in the kinetic behaviour between the 2.2 $\mu\text{J}/\text{cm}^2$ and the 14 $\mu\text{J}/\text{cm}^2$ measurements.

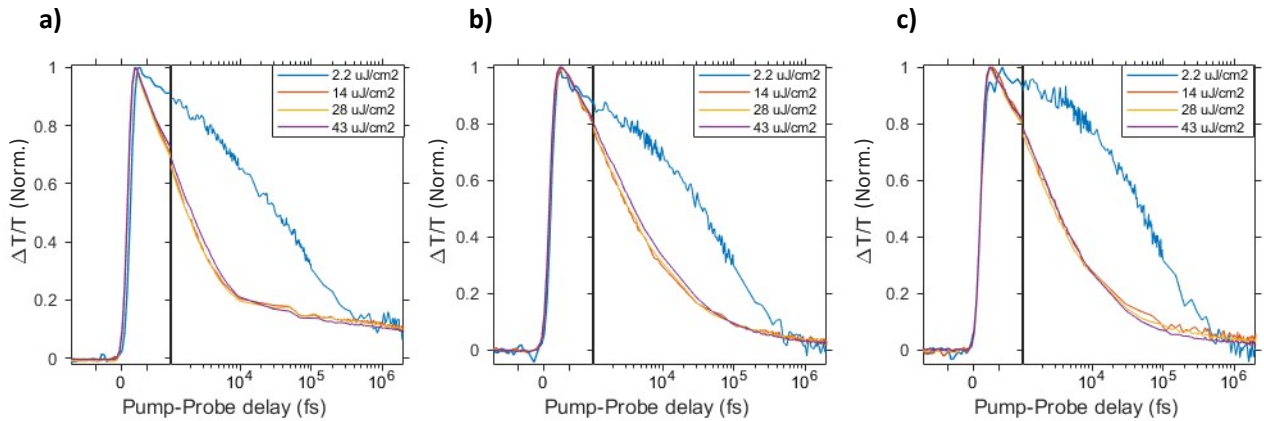


Figure 5.6: Fluence dependent TA kinetic traces for neat TPDI films at a) 555–565 nm (GSB), b) 670–680 nm and c) 795–805 nm (PIA). In contrast to Figure 5.5, there is a threshold for intensity-dependent behaviour and exciton-exciton annihilation processes which lies between 2.2 and 50 $\mu\text{J}/\text{cm}^2$.

Finally, the fluence-dependent kinetics are shown for PTB7-Th neat films in Figure 5.7. Intensity-dependent behaviour is also seen here, again demonstrating the presence of exciton-exciton annihilation.

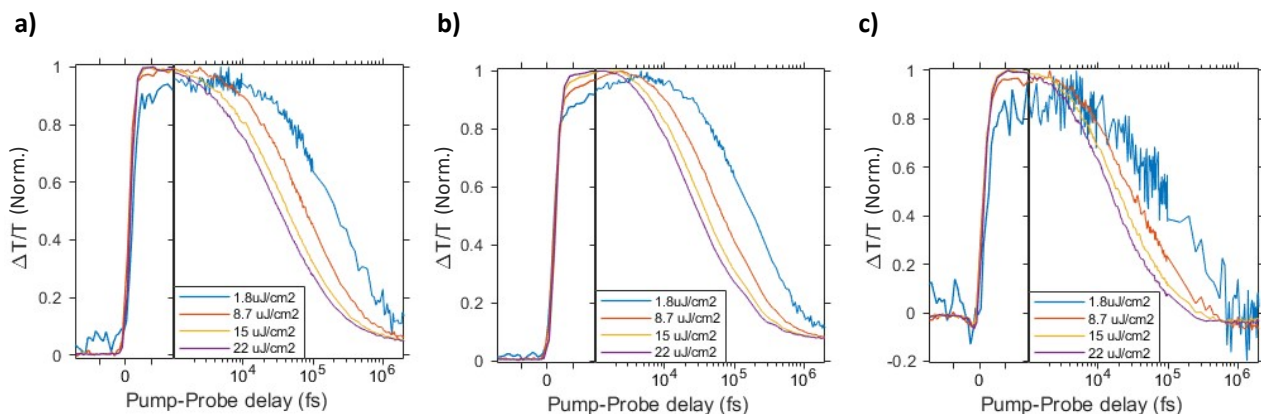


Figure 5.7: Fluence dependent TA kinetic traces for neat PTB7-Th films at a) 635–645 nm (GSB), b) 720–730 nm (GSB) and c) 850–860 nm (SE). Exciton-exciton annihilation is present at high illumination intensities leading to intensity-dependent behaviour.

5.2.3 Transient absorption on blend films

TA spectroscopy was then performed on blend films in order to probe their ability to produce charge transfer states away from an electric field. By selectively exciting the blend films and comparing the resulting features to those observed in neat films, we observed CT state formation from both excitation of the PTB7-Th domains and the (T)PDI domains, further demonstrating the ability of these material systems to undergo dual-direction energy harvesting.

When PTB7-Th:(T)PDI blend films were excited at 700 nm, achieving selective excitation of PTB7-Th as seen in the absorption spectrum of Figure 4.1 c), electron transfer occurred over a timescale of hundreds of femtoseconds as shown in Figure 5.8. The positive peaks at 640 and 725 nm are attributed to the GSB of PTB7-Th in the film as seen in Figure 5.4. The feature at 825 nm is attributed to SE in PTB7-Th which is quenched over a few hundred femtoseconds by the (T)PDI and transforms into a negative PIA belonging to the CT state. The PIA appears flat across the long wavelength region and is long-lived, supporting its assignment as CT state PIA. The PTB7-Th GSB at 640 & 725 nm decays much more slowly than in the neat film, revealing the presence of a long-lived charge/CT state. There are no (T)PDI S_1 features seen as they are not directly excited.

TA spectra were also taken of the two blend films when excited at 540 nm, the region of maximum absorption of (T)PDI, as shown in Figure 5.9. PTB7-Th also absorbs at this wavelength, so it is not a perfectly selective excitation, however it predominantly involves excitation of (T)PDI. When excited at 540 nm, blend films show the GSB of (T)PDI at 555 nm

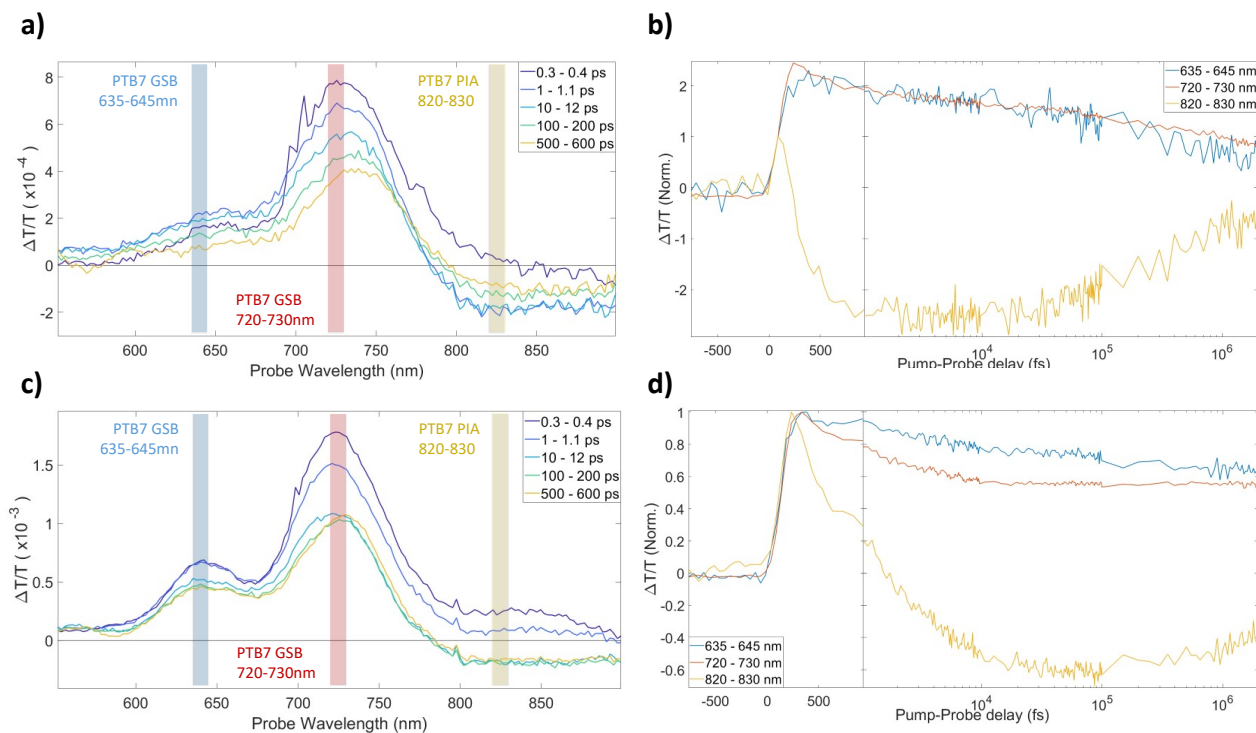


Figure 5.8: TA a) spectrum and b) kinetics of PTB7-Th:PDI blend film and c) spectrum and d) kinetics of PTB7-Th:TPDI blend film, all with selective excitation of the PTB7-Th at 700 nm. The stimulated emission of PTB7-Th appears briefly before being quenched by electron transfer to the (T)PDI, indicating that the timescale for electron transfer is on the order of a few hundred femtoseconds. The kinetics are normalised to the maximum of the signal at 825 nm.

in addition to PTB7-Th GSB peaks at 635 and 725 nm and the CT PIA at wavelengths >800 nm. In both blend films it is possible to see the rise of the PTB7-Th GSB and CT PIA coinciding with the decay of the (T)PDI GSB. Note that the traces are normalised by setting their maximum value to 1.

The ability of non-fullerene acceptors to contribute to CT state generation in addition to the donor contribution is well-known, such that the two competing processes have been termed the two “channels” of CT state formation.^{248,277} Specifically, channel I refers to electron transfer from the electron donor to the electron acceptor, whereas channel II refers to hole transfer in the opposite direction. It is assumed that channel I and II mechanisms lead to the production of the same CT state. However, since the bandgap of (T)PDI is larger than that of PTB7-Th, and the emission of (T)PDI significantly overlaps with the absorption of PTB7-Th, it is possible that energy could be transferred from the (T)PDI acceptor to the PTB7-Th donor through Förster Resonant Energy Transfer (FRET) followed by back transfer of an electron. In a system such as this, FRET followed by channel I electron transfer can exist instead of, in competition

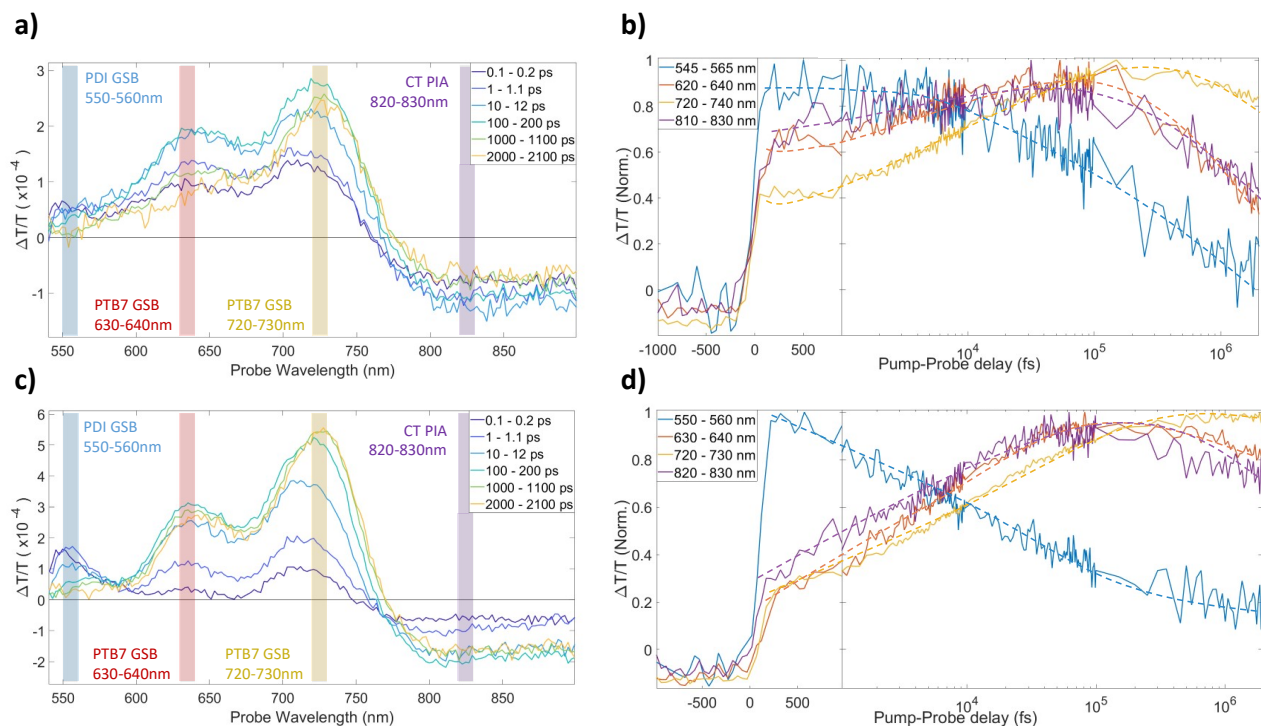


Figure 5.9: TA a) spectrum and b) kinetics of PTB7-Th:PDI blend film and c) spectrum and d) kinetics of PTB7-Th:TPDI blend film, all with partially selective excitation of the (T)PDI at 540 nm. The (T)PDI GSB can now be seen at 555 nm in addition to PTB7-Th GSB and the CT PIA, all of which grow as hole transfer progresses. Dashed lines are provided as a guide to the eye.

with, or simultaneously with channel II hole transfer.^{248,278}

As demonstrated in Figure 5.8, the rate of CT state formation through channel I generation from selective excitation of PTB7-Th at 700 nm is on the order of a few picoseconds, which is consistent with previous reports.²⁵⁷ Interestingly, this rate is faster in the PDI blend than the TPDI blend. This is despite a greater electron affinity offset in the latter, which could be expected to provide a greater driving force. We propose that the increased π - π stacking in PDI domains of blend films leads to a nanoscale morphology characterised by large PDI domains and small PTB7-Th domains. The faster channel I electron transfer in PDI blend films compared to TPDI blend films is consistent with this picture, as there is a smaller distance through PTB7-Th domains that excitons must travel to reach the interface.

When blend films are excited at 540 nm, as in Figure 5.9, the formation of the CT state as demonstrated by the rise of the feature at >800 nm can be explained either by channel II hole transfer or FRET and channel I electron transfer processes, or a combination of the two.

Fluence dependence of the neat films, shown in Figures 5.5, 5.6 and 5.7, demonstrates

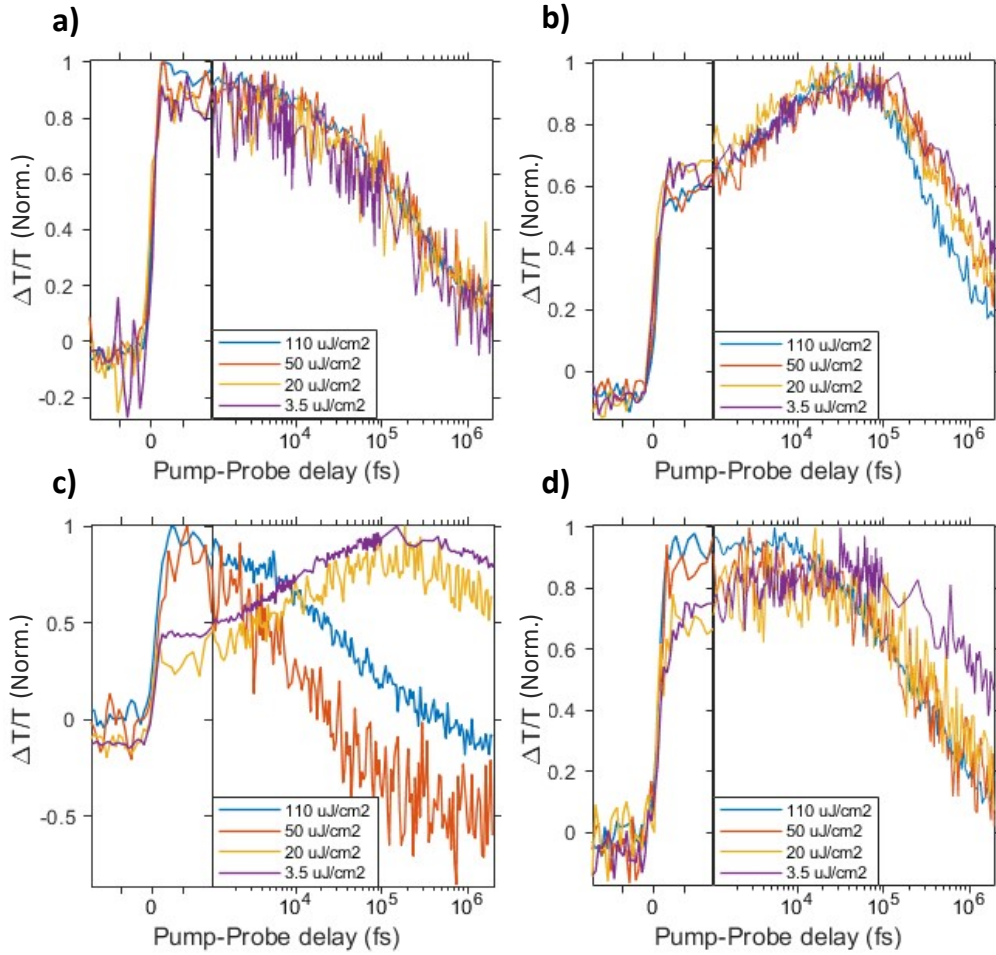


Figure 5.10: Fluence dependent TA kinetic traces for PTB7-Th:PDI blend films excited at 540 nm and measured at a) 550–560 nm (PDI GSB), b) and c) 630–640 and 720–730 nm respectively (PTB7-Th GSB) and d) 820–830 nm (CT PIA). Differences in kinetics at 720–730 nm indicate that there is spectral shift at this wavelength which appears as fluence is increased, indicating the presence of non-linear processes such as singlet exciton or charge annihilation.

that all three films suffer from exciton-exciton annihilation. The PDI-based blend film also demonstrates significant fluence dependence as seen in Figure 5.10. Differences in the kinetics at 720–730 nm indicate that there is spectral shift at this wavelength which appears as fluence is increased. We attribute this to singlet exciton annihilation at early times ($< \sim 500$ ps) and charge annihilation or recombination at later times.

The fluence dependence of TPDI blend films is shown in Figure 5.11. In contrast to the other films, no fluence dependence is seen. This demonstrates the presence of annihilation losses in PDI blend films which are absent in TPDI blend films. Combining this with insights from device studies in Chapter 4, it is clear that PDI blends are much more prone to bimolecular recombination than TPDI blends. This is due to the fact that more crystalline materials such

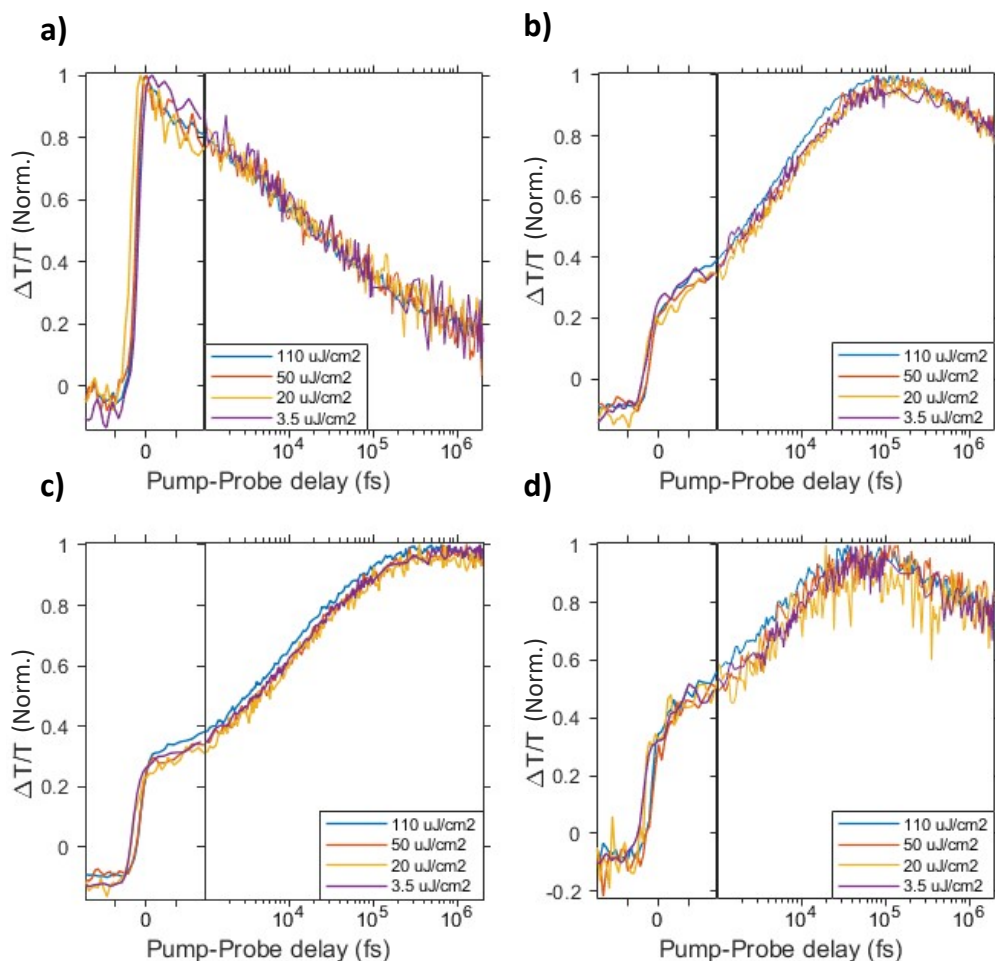


Figure 5.11: Fluence dependent TA kinetic traces for PTB7-Th:TPDI blend films excited at 540 nm and measured at a) 550–560 nm (TPDI GSB), b) and c) 630–640 and 720–730 nm respectively (PTB7-Th GSB) and c) 820–830 nm (CT PIA). There is no fluence dependence observed, indicating significantly less bimolecular recombination than in PDI blends, consistent with the intensity-dependent device characterisation.

as PDI can be expected to have higher charge transport properties, leading to a greater number of electron-hole encounters and resulting bimolecular recombination.

5.3 Deconvolution and modelling

To determine the rates and relative contributions of electron transfer and hole transfer processes in PDI and TPDI blends, the TA spectra of neat and blend films were deconvoluted and fit to a system of coupled differential equations as described below.

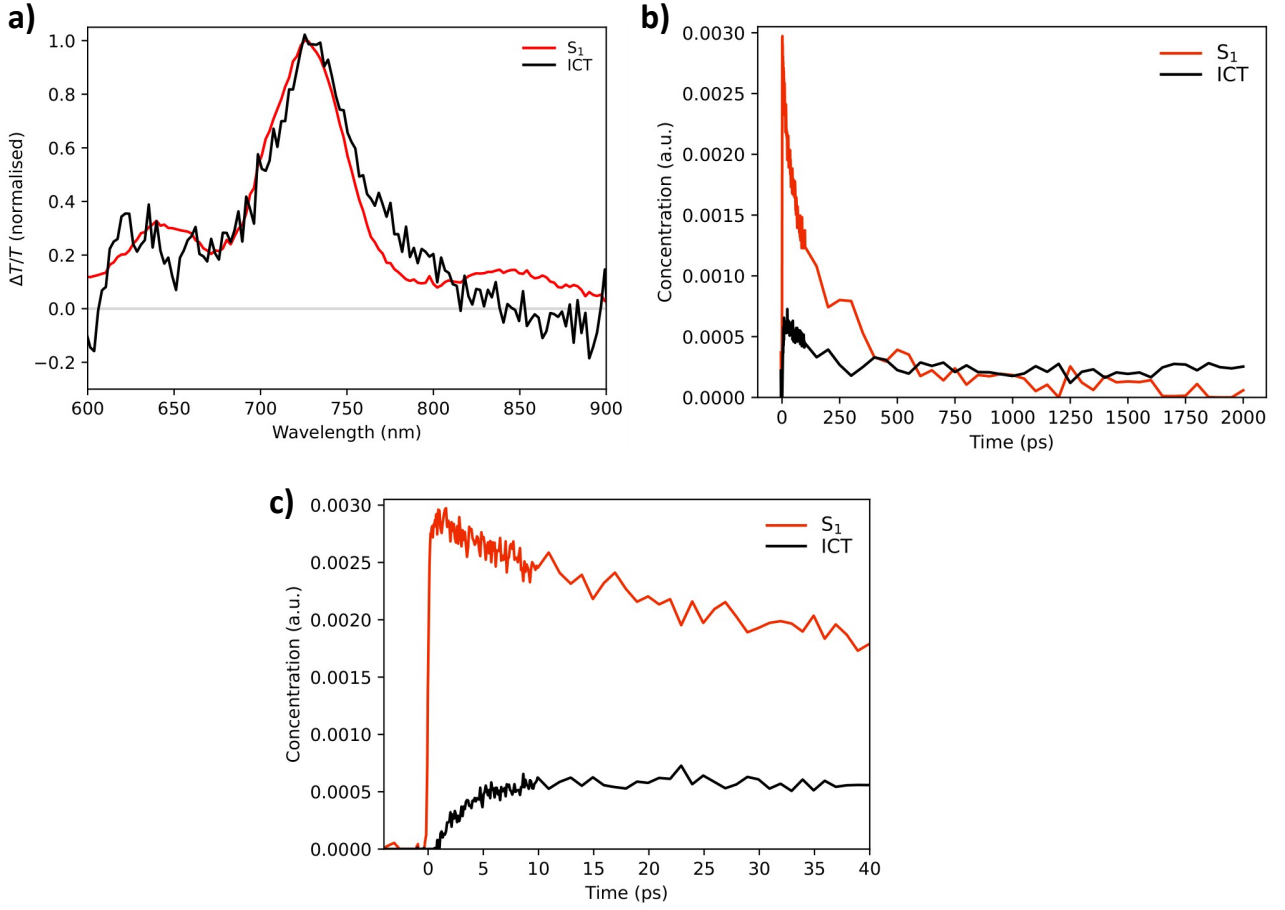


Figure 5.12: a) TA basis spectra of neat PTB7-Th film excited at 700 nm and 0.04 uJ/cm². b) Deconvoluted concentrations of PTB7-Th S₁ and ICT states over 2 ns. c) S₁ and ICT concentrations over 40 ps. Note the concentrations are in arbitrary units, and are not necessarily to scale.

5.3.1 Deconvolution

The TA spectra were first deconvoluted into their respective component basis spectra, being PTB7-Th S₁, (T)PDI S₁ and CT states. The basis spectra were determined for each sample individually. The blend TA spectra were then fit to a linear combination of the basis spectra at each time point t according to:

$$\Delta T/T = \epsilon_{\text{PTB7-Th},S_1}(\lambda)[\text{PTB7-Th}, S_1(t)] + \epsilon_{(\text{T})\text{PDI},S_1}(\lambda)[(\text{T})\text{PDI}, S_1(t)] + \epsilon_{\text{CT}}(\lambda)[\text{CT}(t)] \quad (5.1)$$

where $[\text{PTB7-Th}, S_1(t)]$, $[(\text{T})\text{PDI}, S_1(t)]$, and $[\text{CT}(t)]$ are the concentrations of PTB7-Th S₁, (T)PDI S₁, and CT states, respectively, and $\epsilon_{\text{PTB7-Th},S_1}(\lambda)$, $\epsilon_{(\text{T})\text{PDI},S_1}(\lambda)$ and $\epsilon_{\text{CT}}(\lambda)$ are the respective coefficients of the linear combination of concentration terms. The deconvolution

process fits each time point individually and does not assume a model. Note that only the shape of the basis spectra are calculated and not their magnitudes, hence the concentration of the basis spectra are in arbitrary units and are not necessarily comparable in magnitude between samples.

The deconvolution procedure for the neat PTB7-Th film is reported here as an example, and the deconvolution procedures for blend films are discussed in Appendix section A.1. No deconvolution is necessary for neat PDI and TPDI as only one species is present. In contrast, as neat PTB7-Th has the ability to form charges without the presence of a heterojunction, we consider the formation of intermolecular and intramolecular charge transfer states within the neat film which form a second basis spectrum in addition to the S_1 spectrum.^{275,276} We term this process homoelectron transfer (as distinct from electron transfer between the donor and acceptor materials). Since both intramolecular and intermolecular charge transfer are possible, we term the resulting state the inter/intramolecular charge transfer (ICT) state (as distinct from the formation of a CT state across a heterointerface).

To fit the neat PTB7-Th film, we isolated both a PTB7-Th S_1 component and an ICT state component, as shown in Figure 5.12. The S_1 component was taken from the spectra at 1 ps, before significant spectral evolution occurs and therefore when there is minimal ICT state present. The ICT state was extracted from the TA spectra at 2000 ps. TCSPC shows less than 1% of the emission remains at 2000 ps, indicating 2000 ps can be treated as a ‘pure’ ICT spectra. The resulting fits are shown in Figures 5.13 and 5.14. The basis spectra are able to reproduce the experimental spectra extremely well at early times and late times. There are some small discrepancies at intermediate times (50–200 ps), potentially arising from a spectral shift in the ICT ESA as the delocalisation of the states change.²⁷⁶

5.3.2 Modelling

Once the basis spectra were found for the components of each blend film and excitation condition, these were used to model the charge and energy processes taking place in the films using systems of coupled differential equations. An example of this process is included below for the neat PTB7-Th film; the same is shown for blend films excited at both 700 nm and 540 nm in Appendix section A.2.

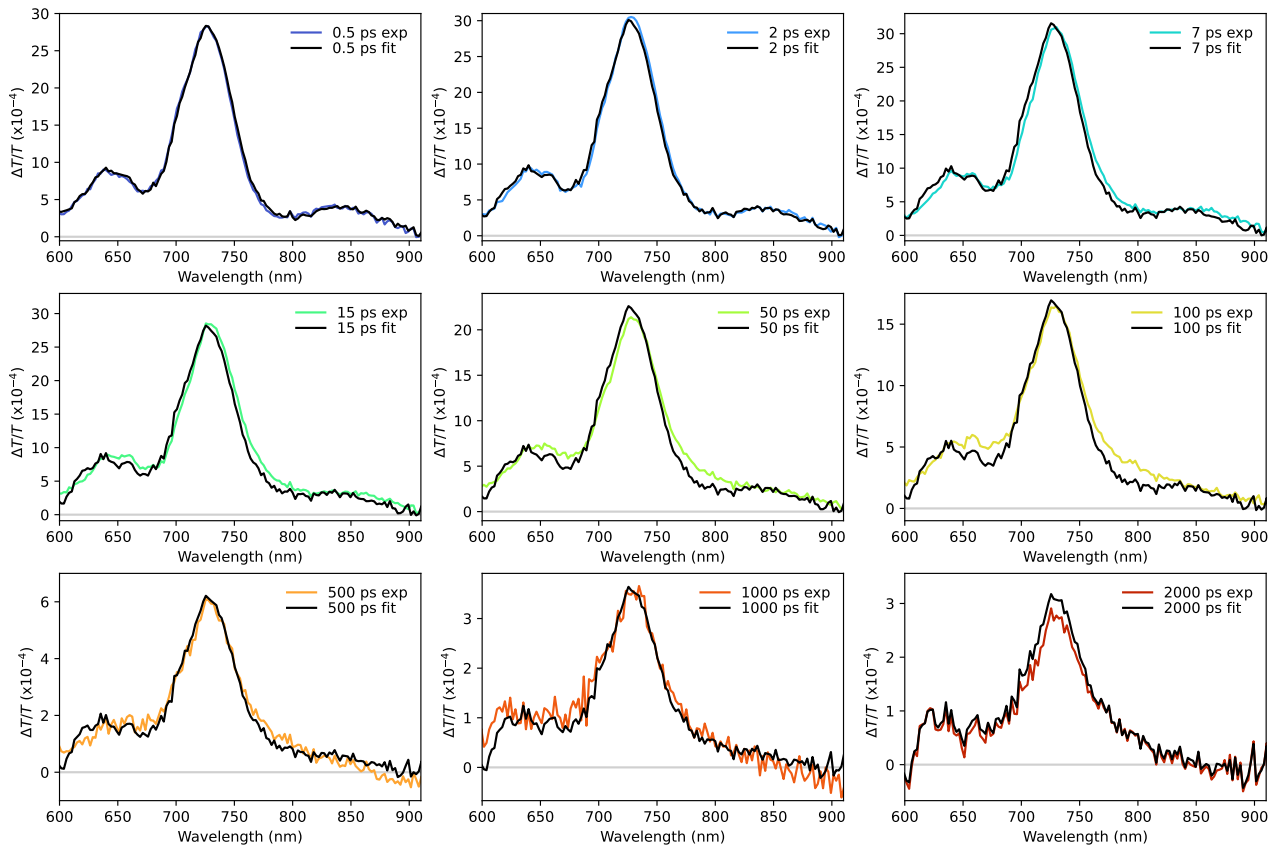


Figure 5.13: Deconvolution fit of neat PTB7-Th film excited at 700 nm and 0.04 uJ/cm^2 at different delay times. Corresponding basis spectra and concentrations are in Figure 5.12.

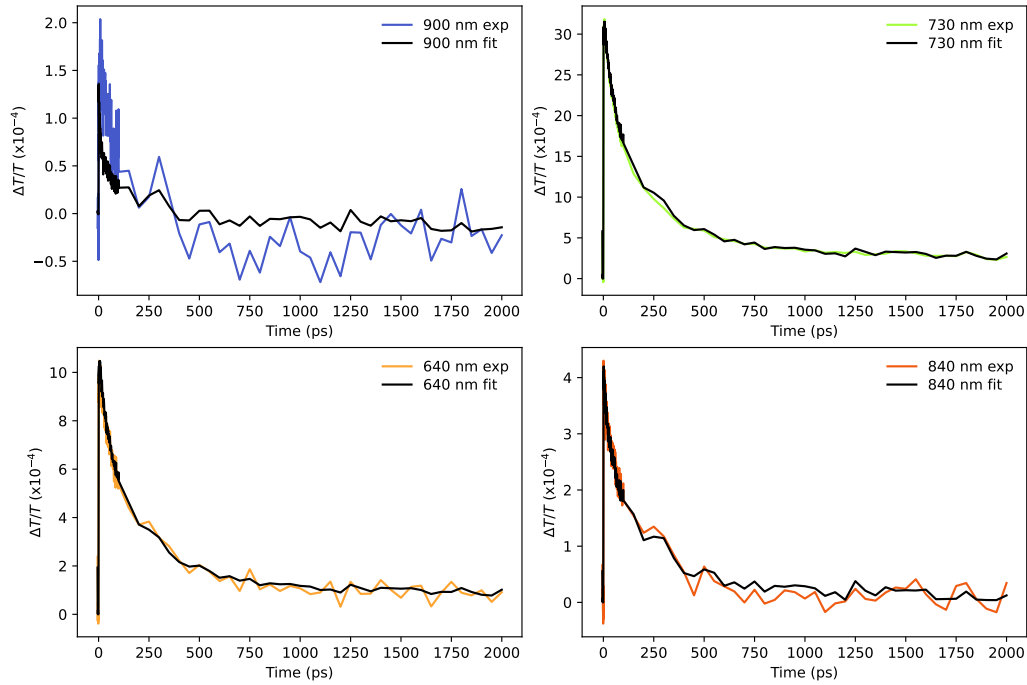


Figure 5.14: Deconvolution fit of neat PTB7-Th film excited at 700 nm and 0.04 uJ/cm^2 at different wavelengths. Corresponding basis spectra and concentrations are in Figure 5.12.

The deconvoluted kinetics of a neat PTB7-Th film excited at 700 nm and 0.04 uJ/cm² were fit to the following set of coupled differential equations:

$$\begin{aligned}
\frac{d[\text{PTB7-Th } S_1]}{dt} &= -k_{\text{PTB7-Th } S_1}[\text{PTB7-Th } S_1] - k_{\text{HET}}[\text{PTB7-Th } S_1] \\
\frac{d[\text{PTB7-Th } S_1 - \text{trap}]}{dt} &= -k_{\text{PTB7-Th } S_1}[\text{PTB7-Th } S_1 - \text{trap}] \\
\frac{d[\text{ICT}]}{dt} &= k_{\text{HET}}[\text{PTB7-Th } S_1] - k_{\text{ICT}}[\text{ICT}]
\end{aligned} \tag{5.2}$$

where $[\text{PTB7-Th } S_1]$ is the concentration of PTB7-Th S_1 excitons and $k_{\text{PTB7-Th } S_1}$ is the rate constant associated with their decay. It is known that PTB7-Th can undergo homoelectron transfer (HET) to create spatially separated hole and electron signatures^{275,276} as already mentioned above, so we include a term for HET taking place with a rate constant of k_{HET} . The population of the ICT state decays with rate constant k_{ICT} and its repopulation via homoelectron transfer as given by k_{HET} . To fit the deconvoluted data it was necessary to include a population of morphologically trapped excitons $[\text{PTB7-Th } S_1 - \text{trap}]$ which do not undergo homoelectron transfer, corresponding to excitons located at geometries that are not favourable for charge transfer. This is achieved by modelling the PTB7-Th excitations using two populations: one that is able to undergo HET to form the ICT state, and another that is not, labelled $[\text{PTB7-Th } S_1 - \text{trap}]$. Figure 5.15 summarises this information with a flow chart representing the coupled differential equations above.

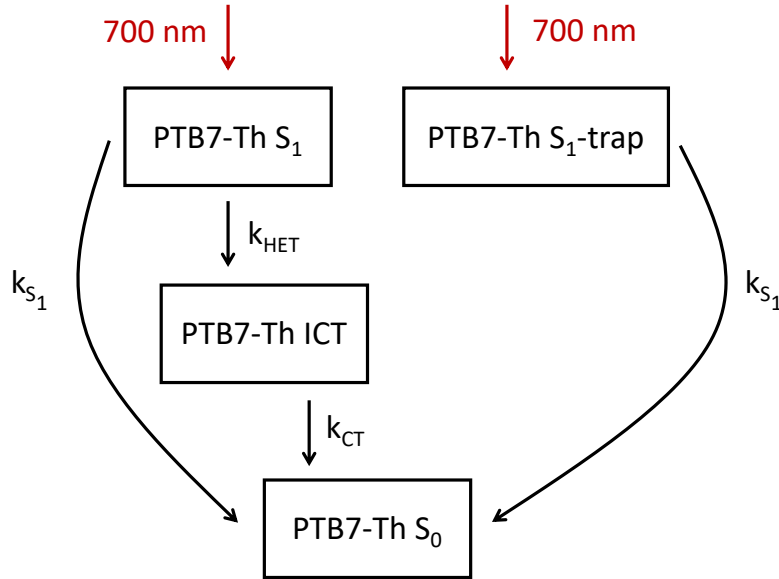


Figure 5.15: Flow diagram representing the coupled differential equations described in Equation 5.2 used to model the neat PTB7-Th TA data.

The decay curves and the fit to [PTB7-Th S_1] and k_{ICT} are shown in Figure 5.16. The fitted time constants for the PTB7-Th singlet exciton, the ICT state and the homoelectron transfer are given below in Table 5.1 alongside a 90% confidence interval. The lifetime of the ICT state is consistent with past investigation.²⁷⁵ The difference between the deconvoluted S_1 kinetics and the fit at 100–1000 ps is likely due to exciton annihilation, which is not explicitly described here. Importantly, the fit is able to describe the rise of the ICT state well. This is the result that informs subsequent modelling of blend films as presented in Appendix section A.2.

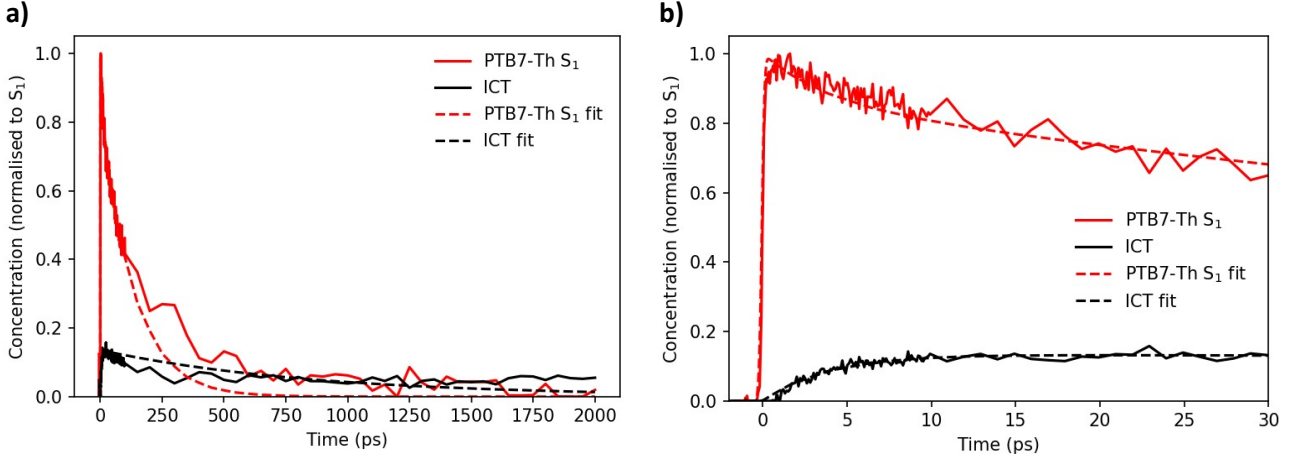


Figure 5.16: a) PTB7-Th S_1 and ICT basis spectra decay from excitation at 700 nm and 0.04 uJ/cm² over a) 2 ns and b) 30 ps, fit to the coupled differential equations given in Equation 5.2.

Table 5.1: Time constants for neat PTB7-Th film (excitation at 700 nm)

Homoelectron transfer: $1/k_{HET}$ (ps)	3.9 ± 0.2
ICT decay: $1/k_{ICT}$ (ps)	860 ± 60
PTB7-Th S_1 decay: $1/k_{PTB7-Th S_1}$ (ps)	128 ± 11
Trapped S_1 (%)	86 ± 2

Blend films excited at 700 nm were modelled using channel I electron transfer from PTB7-Th to (T)PDI. Blend films excited at 540 nm were modelled using channel II hole transfer from (T)PDI to PTB7-Th and FRET followed by channel I back electron transfer. In the 540 nm excitation case, it was necessary to also include a population of trapped or isolated (T)PDI excitons that decay before they are able to reach an interface with PTB7-Th. These traps could be energetic (i.e. excimers) or morphological in nature.

Since channel I electron transfer from PTB7-Th to (T)PDI is a fast process, particularly for the PDI blend, the PTB7-Th excited state decays before it is able to be resolved. Figures

5.17 and 5.18 show that charge generation from hole transfer is indistinguishable from FRET followed by Channel 1 back electron transfer. This arises from the fast nature of electron transfer, which renders the S_1 excited state in PTB7-Th unobservable as it is converted to CT states before any observable population of S_1 can build up. Thus, we now refer to channel II charge generation as inclusive of hole transfer from (T)PDI to PTB7-Th and FRET plus back electron transfer.

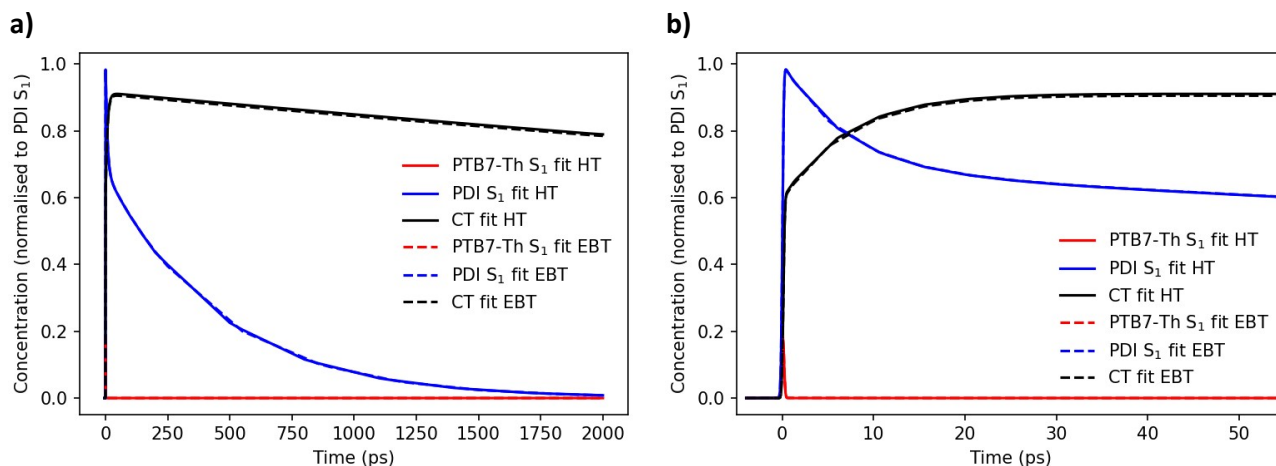


Figure 5.17: a) Comparison between modelling results for hole transfer and energy transfer plus electron back transfer mechanisms for CT state formation in PTB7-Th:PDI films excited at 540 nm. b) Modelling results over 55 ps.

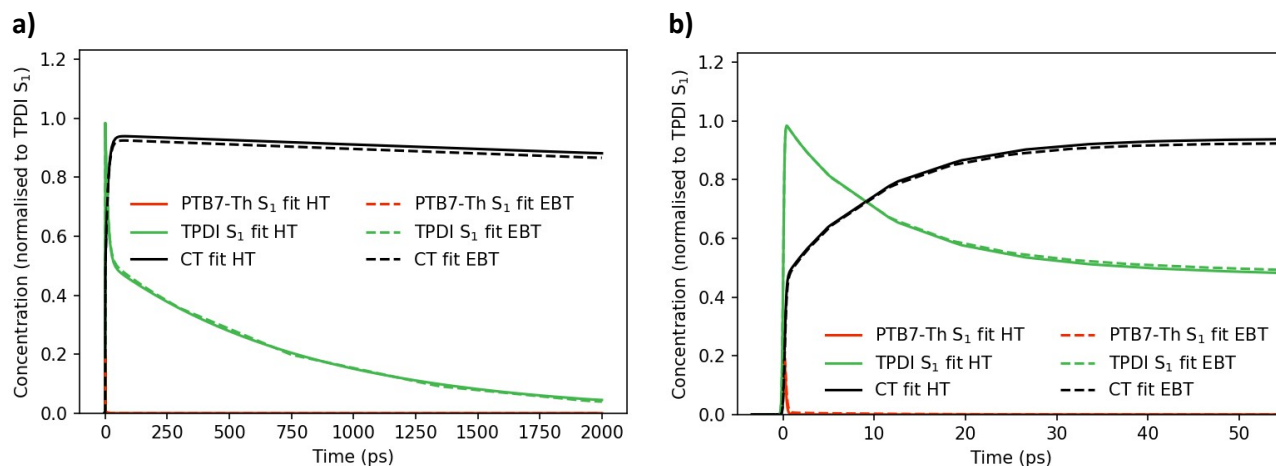


Figure 5.18: a) Comparison between modelling results for hole transfer and energy transfer plus electron back transfer mechanisms for CT state formation in PTB7-Th:TPDI films excited at 540 nm. b) Modelling results over 55 ps.

5.3.3 Comparison between PDI and TPDI blends

A comparison between PDI and TPDI blend kinetics as determined by deconvoluted basis spectra with excitation at 700 nm is shown below in Figure 5.19.

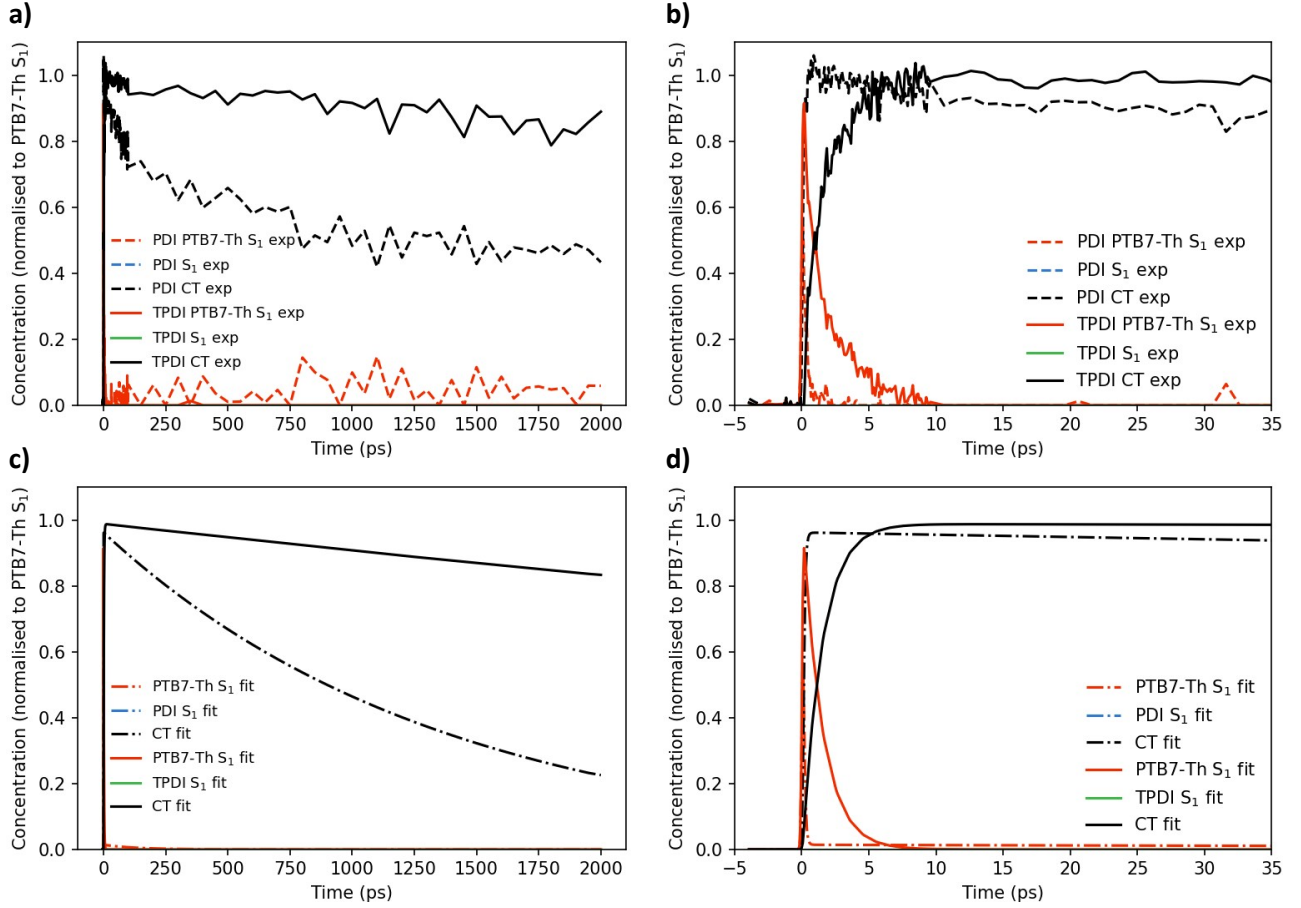


Figure 5.19: Comparison of the experimental PTB7-Th S_1 and CT state decays using deconvoluted basis spectra in PDI and TPDI blend films excited at 700 nm over a) 2000 and b) 35 ps. c) Comparison of the model PTB7-Th S_1 and CT state decays in films excited at 700 nm. d) Modelled PTB7-Th S_1 and CT state rise and decay over 35 ps.

The PTB7-Th S_1 state is short-lived in the PDI blend compared to TPDI due to faster electron transfer (0.02 compared to 0.14 ps). This causes a slower rise of the CT state in the TPDI blend, however the resulting CT state lives longer in TPDI which provides greater opportunity for the dissociation of the CT into free charges inside the device.

A comparison between PDI and TPDI blend kinetics as determined by deconvoluted basis spectra with excitation at 540 nm is shown below in Figure 5.20. The (T)PDI S_1 concentration is noisy due to the low magnitude of this signal as seen at ~ 550 nm in Figure 5.9. The CT state concentration has a lower noise level due to the increased number of CT states in the blend film,

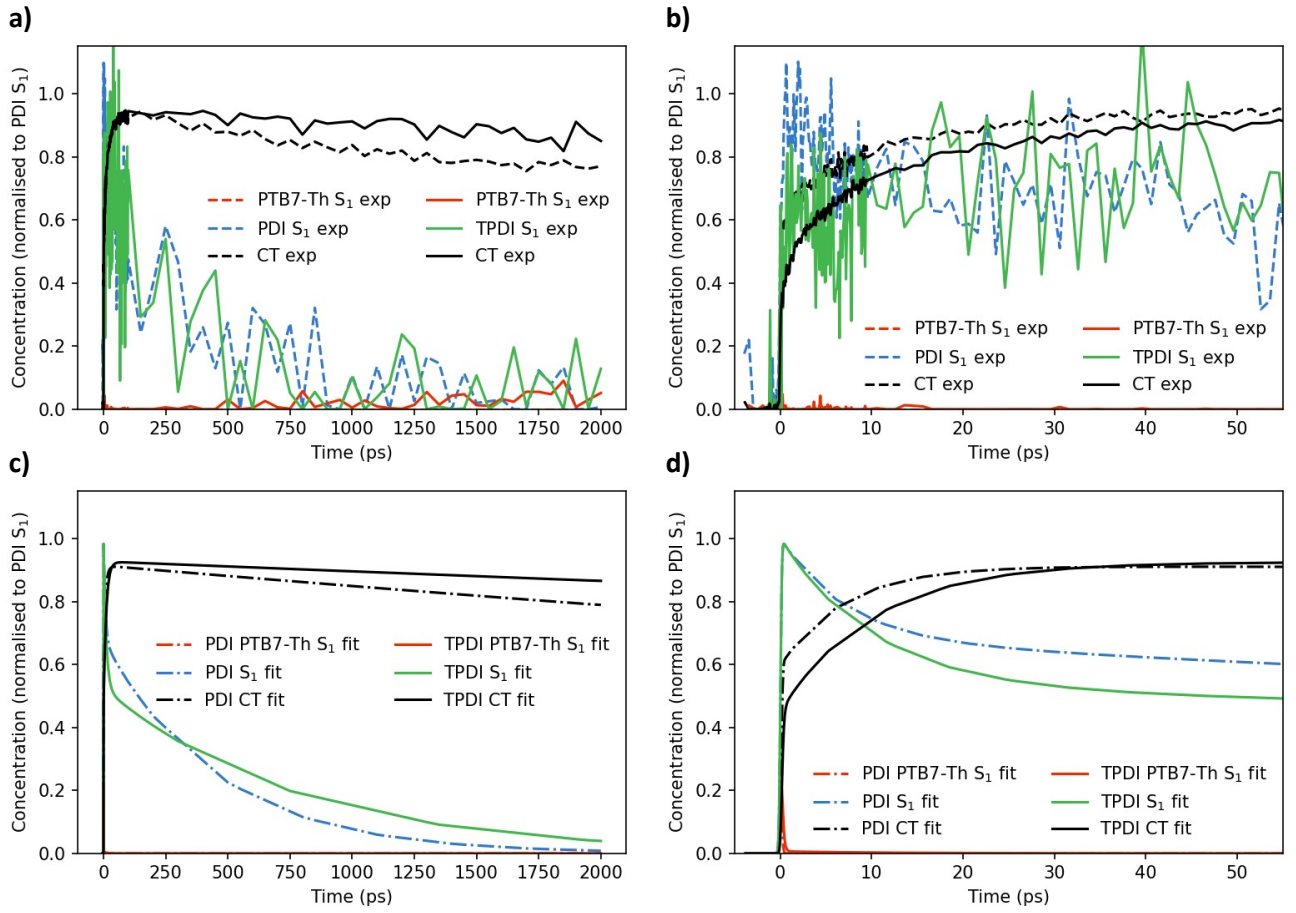


Figure 5.20: a) Comparison of the experimental PTB7-Th S_1 , (T)PDI S_1 and CT state decays using deconvoluted basis spectra in PDI and TPDI blend films excited at 540 nm. b) Experimental PTB7-Th S_1 and (T)PDI S_1 decay and CT rise and decay over 55 ps. c) Comparison of the model of PTB7-Th S_1 , (T)PDI S_1 and CT state decays in films excited at 540 nm. d) Modelled PTB7-Th S_1 and (T)PDI S_1 decay and CT rise and decay over 55 ps.

which arises from their longevity in contrast to the (T)PDI S_1 states. Due to the lower noise level of the CT state concentration, this is used preferentially for fitting, with a weighting factor of four times that of the (T)PDI S_1 state. In both the experimental and modelled kinetics, faster electron and hole transfer in PDI films causes a faster rise in the CT state, however the greater proportion of untrapped excitons in TPDI films means that the yield of the CT state is fit as approximately the same in both films. The CT state also lives longer in the TPDI film, again providing a greater opportunity for dissociation of the CT state into free charges inside the device.

5.3.4 Quantifying channel I and II contributions

We next compare the percentage contribution of channel I electron transfer and channel II hole transfer or energy transfer and electron back transfer charge generation mechanisms in the two blend films. Since hole transfer and energy transfer plus electron back transfer are indistinguishable, we use the terminology of channel II charge generation to refer to both processes. A summary of the two channels of charge generation are represented along with the timescales of these processes in Figure 5.21 a).

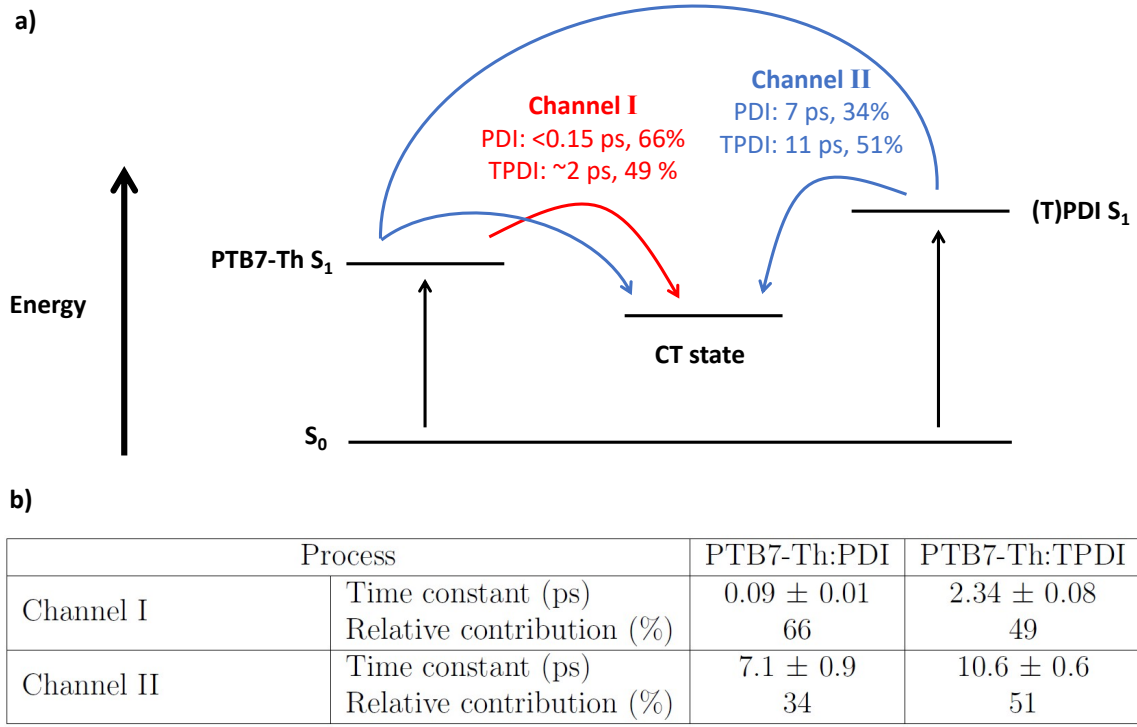


Figure 5.21: a) Schematic and b) summary table showing the timescales and relative contributions of channel I and II charge generation processes for 540 nm excitation of PDI and TPDI blend films.

Excitation at 700 nm causes charge generation solely from electron transfer. Due to the rate of electron transfer being much faster than that of PTB7-Th S_1 decay, we assume that all excitations in the PTB7-Th population lead to CT state formation by electron transfer.

For excitation at 540 nm, rate competition between channel I charge generation and PTB7-Th S_1 decay is used to determine the efficiency of this charge generation process according to:

$$\text{Channel I efficiency} = \frac{k_{\text{channel I}}}{k_{\text{channel I}} + k_{\text{PTB7-Th } S_1}} \quad (5.3)$$

This produces an estimate of 100% efficiency for channel I charge generation in both PDI and TPDI films due to fast electron transfer as compared to PTB7-Th S_1 decay.

For channel II, rate competition between channel II charge generation and (T)PDI S_1 decay as well as the population of trapped (T)PDI excitons is used to determine the efficiency this charge generation process according to:

$$\text{Channel II efficiency} = \frac{k_{\text{channel II}}}{k_{\text{channel II}} + k_{(\text{T})\text{PDI } S_1}} \times (1 - \text{proportion of trapped excitons}) \quad (5.4)$$

This produces an estimate of 32% and 48% efficiency for channel II charge generation in PDI and TPDI blend films respectively.

In order to determine the total contribution of each generation mechanism, we must take into account the ratio of photons absorbed by the PTB7-Th domain as compared to the (T)PDI domain during 540 nm excitation. Setting the relative absorption in (T)PDI domains to 1, the fit suggests an absorption value of 0.6 in PTB7-Th domains in the PDI blend film and a value of 0.46 in PTB7-Th domains in the TPDI blend film. We then compute the relative number of electron and hole transfer events by taking into account the relative absorption and the efficiency of charge transfer according to Equation 5.5:

$$\begin{aligned} \text{Relative number Channel I events} &= \frac{E_{\text{ET}} \times P_{\text{PTB7-Th}}}{E_{\text{ET}} \times P_{\text{PTB7-Th}} + E_{\text{HT}} \times P_{(\text{T})\text{PDI}}} \\ \text{Relative number Channel II events} &= \frac{E_{\text{HT}} \times P_{(\text{T})\text{PDI}}}{E_{\text{ET}} \times P_{\text{PTB7-Th}} + E_{\text{HT}} \times P_{(\text{T})\text{PDI}}} \end{aligned} \quad (5.5)$$

where E_{ET} is the efficiency of electron transfer, E_{HT} the efficiency of hole transfer, $P_{\text{PTB7-Th}}$ the proportion of PTB7-Th excitons and $P_{(\text{T})\text{PDI}}$ the proportion of (T)PDI excitons in the blend film.

We then compare the relative frequency of the electron and hole transfer events in order to determine the overall contribution of each pathway to charge generation. Channel I electron transfer occurs with a time constant of 2.3 ps in the TPDI blend film, consistent with previous reports,²⁵⁷ while in the PDI blend film it occurs within the duration of the pump pulse (< 150 fs). This result agrees with the proposition that the formation of large PDI domains reduces the distance that the exciton must diffuse through PTB7-Th in order to reach an interface, enabling fast electron transfer compared to TPDI blend films. Channel II generation is also more

competitive in PDI blend films, having a time constant of 7 ps compared to 11 ps in the TPDI blend film, which could be explained by faster exciton transport in the PDI crystalline domains. However, the S_1 state of TPDI in blend films also decays more slowly than that of PDI, living nearly twice as long, which provides more opportunity for the CT state to form and then dissociate into free charges. Additionally, the model suggests that a more significant percentage of the excitons generated in the PDI film are trapped or isolated from the interface, and therefore unable to form charge transfer states, compared to TPDI films (68% compared to 51%).

Finally, we quantify the contribution of each charge generation channel in each blend film by analysing the competition between the decay rates of CT state formation and geminate decay. When excited at 700 nm, 100% of CT states in both blend films are generated by channel I electron transfer as (T)PDI does not absorb at this wavelength. When excited at 540 nm, channel I accounts for 66% of CT generation in the PDI blend film compared to 49% in the TPDI blend film, with the remaining 34% and 51% respectively of CT generation coming from channel II charge generation. Therefore, we see that while there is a slower rate of CT generation by channel II in TPDI than PDI, there are also less trapped or isolated excitons that do not contribute to CT generation, which leads to an overall greater contribution of channel II hole transfer in the TPDI blend film. The timescales and relative contributions of channel I and II charge generation processes from excitation at 540 nm are summarised in Figure 5.21 b). Notably, in both 540 nm and 700 nm excitations, CT states decay significantly faster in PDI blends than in TPDI blends, consistent with faster non-geminate recombination. This is compatible with the hypothesis that PDI has larger domain sizes compared to TPDI, as also suggested by AFM in Chapter 4 and supported by faster electron transfer in PDI blends.

5.4 Conclusions

In conclusion, we have comprehensively studied the charge generation properties of a perylene monomer and dimer each blended with PTB7-Th using TA spectroscopy. This revealed fast electron transfer in PDI films, which we attribute to the hypothesised smaller distances that excitons must travel in small PTB7-Th domains to reach an interface and dissociate. The ability of photoexcited (T)PDI domains to produce CT states can arise from hole transfer from (T)PDI to PTB7-Th or from FRET to PTB7-Th and back electron transfer which are shown to be

indistinguishable. CT lifetimes and fluence dependence measured through TA also show more significant bimolecular recombination of CT states in PDI blends than TPDI blends, consistent with device measurements. Modelling suggests that electron transfer from PTB7-Th to PDI is responsible for the majority (66%) of charge production in PDI blend films even when excited at the PDI absorption peak, whereas the TPDI blend film had a more even contribution (49%) from electron transfer compared to hole transfer, demonstrating its superior ability to achieve balanced dual-direction energy harvesting. Thus we demonstrate that detailed morphological consideration is necessary in order to make further improvements to device performance and advance the field of OPVs. The approach we have taken to determining the contribution of each blend component to charge generation could also be translated to high performing systems such as PM6:Y6 in the future. In the next chapter, we will investigate a new method to alter the properties of materials through strong light-matter coupling.

Chapter 6

Strong exciton-photon coupling in (T)PDI and PTB7-Th Fabry-Pérot thin films

6.1 Introduction

When a photon of light is confined in a microcavity containing a material with significant oscillator strength at the resonant energy of the microcavity, the photon can couple to the exciton transition(s) of the material to produce a new quasi-particle termed a polariton, as explained in Chapter 1. This intriguing phenomenon enables the alteration of the very properties of a material simply by placing it in a resonant optical cavity, termed a Fabry-Pérot (FP) cavity.

In the previous chapter, we have studied (T)PDI and PTB7-Th materials in the context of organic photovoltaic devices as well as investigating the charge and energy transfer processes that underpin device functionality. In this chapter, we investigate how the properties of thin films of these materials can be modified by placing them in optical cavities by coupling the exciton transitions in the material to optical cavity photons. We first start by investigating the features of the photonic mode in a cavity with a transmissive polymer, including studying the effects of changing the cavity thickness, angle of incidence of light into the cavity, the cavity mode, and the refractive index of the material contained in the cavity. Excimer formation in PDI and TPDI molecules dispersed in a polymer matrix are seen to outcompete polariton formation, leading to only weak coupling being achieved in these films, despite increasing the Q-factor of these cavities through more reflective mirror surfaces. In contrast, strong coupling was achieved in PTB7-Th films, but only when PTB7-Th aggregation was broken up by the presence of another polymer matrix to solubilise it. We also demonstrate coupling in blend films, where changing the thickness of the cavity allows for coupling primarily to one or another

of the blend components. We thus demonstrate that it is possible to couple the cavity photon to exciton resonances in both the PTB7-Th and (T)PDI domains in blend films, particularly in films based on TPDI for the (T)PDI resonance. This is a critical result to achieve before these films are incorporated into cavity OPV devices in Chapter 7.

6.2 Photon modes supported in an optical cavity

The confinement of a photon to a microcavity or optical resonator results in the formation of a photon mode due to constructive and destructive interference of photons in the FP cavity as explained in Section 1.2.1. Polymethyl methacrylate (PMMA) and polystyrene (PS) FP samples of varying thicknesses were prepared to study the features of the cavity mode separately from those caused by strong exciton-photon coupling. The effects of changing the cavity thickness d , mode m , angle of incident light θ and refractive index n_{eff} on PMMA and PS cavities are discussed below.

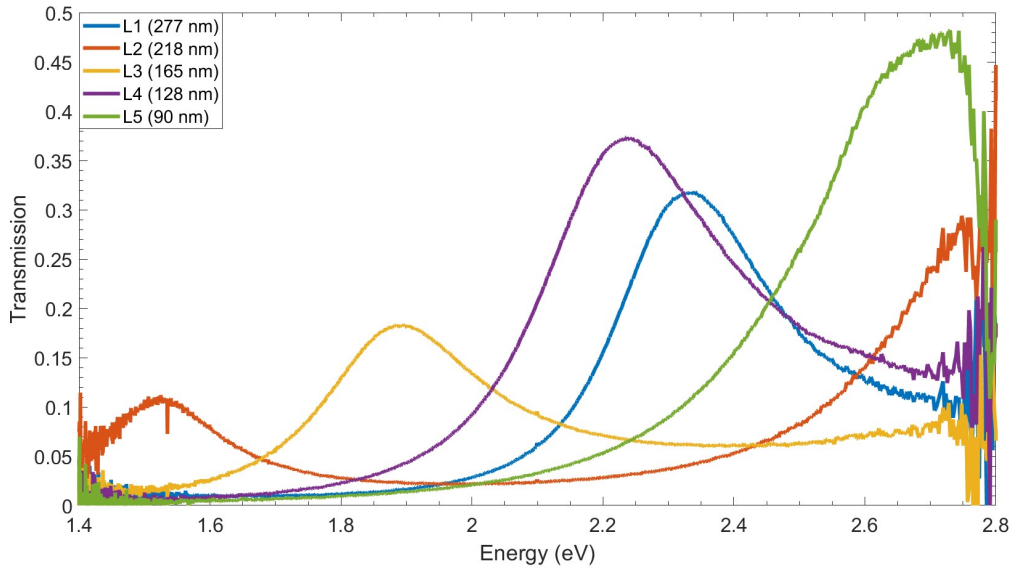


Figure 6.1: Transmission of five FP cavity samples of architecture Ag/PMMA/Ag with varying PMMA thickness.

Effect of cavity thickness

To study the effect of changing the FP cavity thickness d on the features of the photon mode, transparent PMMA films sandwiched between two 25 nm semi-transparent silver (Ag) mirrors were prepared. The transmission curves are shown in Figure 6.1. As the thickness of the PMMA

layer is decreased, the resonance energy of the FP cavity at zero degrees is also increased as predicted by Equation 1.2.

Effect of cavity mode

It is possible to calculate the order of the mode sustained in each of these cavities by considering the relationship between the wavelength of the cavity photon λ and the FP cavity length d at 0° incidence as given by Equation 1.1. Using a refractive index of 1.5 for PMMA²⁷⁹ and thicknesses measured by surface profilometry, the mode m can be calculated for each 0° degree transmission peak wavelength λ as shown in Table 6.1. Thicknesses are measured with a Dektak surface profilometer which has an uncertainty of $\sim \pm 2$ nm. The spectra are measured with a Flame spectrometer which has a pitch of 0.5 nm, corresponding to 0.003 eV at 450 nm and 0.008 eV at 900 nm. Note that the cavity mode is reported as the nearest rounded integer. Note also that since the wavefunction of the cavity photon bleeds into the Ag electrodes, the thickness of the two electrodes must also be included in the mode calculation.

Table 6.1: Mode calculation for PMMA FP cavity samples

Sample	PMMA thickness (nm)	Transmission peak (eV) (calculated from Figure 6.1)	Cavity mode m
L1	277	2.34	2
L2	218	1.53	1
L3	165	1.88	1
L4	128	2.24	1
L5	90	2.71	1

Within the range of visible wavelengths studied in this investigation, samples L2-L4 sustain a 1st order cavity mode, whereas sample L1 is thick enough to sustain a second-order cavity mode.

Effect of angle of incidence of light

We now consider the angular dependence of the cavity mode energy by studying angular reflectance. Figure 6.2 demonstrates the shifting of this cavity mode to higher energies as the angle of incidence of light increases for two of the above samples. Since angular reflectance measures the light reflected out of the FP cavity, and the wavelengths which constructively interfere are sustained by and transmitted through the FP cavity, these resonant wavelengths are missing from the spectrum of reflected light. In order to see these resonant wavelengths

clearly we calculate and plot $1 - \text{reflectance}$, turning any dips in reflectance into peaks in the resulting $1 - \text{reflectance}$ graph which are easier to analyse.

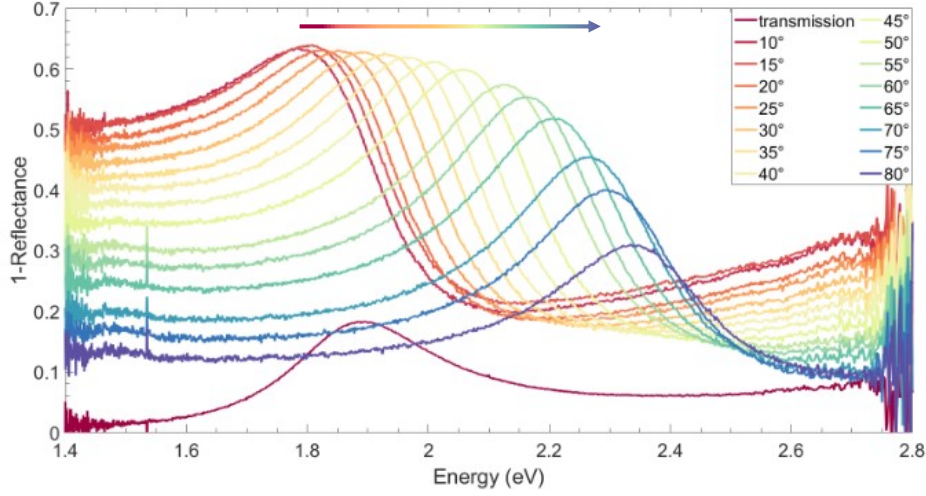


Figure 6.2: Angular reflectance of a 128 nm thick PMMA FP cavity sample (L3).

Effect of refractive index of cavity material

In addition to PMMA, PS is a good choice for fabricating non-coupled cavities as it is also transparent for visible wavelengths. PS has a higher refractive index compared to PMMA, being 1.6^{280} compared to 1.5, and thus it also provides an appropriate choice of material for studying the effect of changing the refractive index of material inside a cavity on the features produced.

Table 6.2: Mode calculation for PS FP samples

Sample	PS thickness (nm)	Transmission peak (eV) (calculated from Figure 6.3 and B.1)	Cavity mode m
S1	147	1.92	1
S2	158	1.84	1
S3	184	1.64	1
S4	214	1.50	1

The relationship between the energy of the photonic mode measured in reflectance and the angle of incidence of light is demonstrated for PS FP cavities prepared with a similar procedure as for PMMA cavities. Figure 6.3 shows the angular reflectometry of a PS FP cavity (S1), and more examples are shown in Appendix section B.1. The transmission feature in Figure 6.3 corresponds to the first mode as reported in Table 6.2. The mode calculation was performed on three cavities of other thicknesses in the same way as for PMMA cavities using Equation 1.1, and the film thicknesses and transmission peaks are reported in Table 6.2.

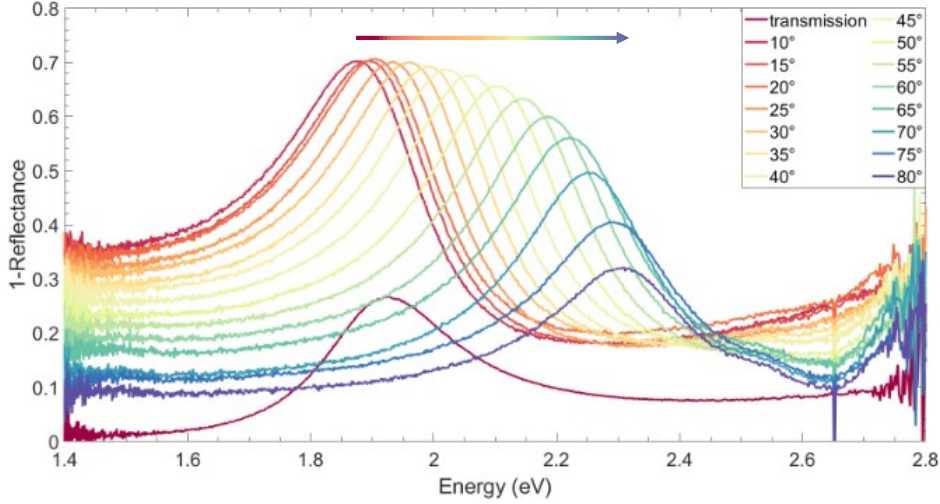


Figure 6.3: Angular reflectance of a 147 nm thick PS FP cavity sample (S1). More examples of PS FP cavities are shown in Section B.1.

In summary, we see that cavity modes appear wherever integer multiples of half the photon wavelength can be sustained within the FP cavity. This is affected by both the refractive index of the material and the thickness of the FP cavity. The lowest mode is determined by the longest wavelength resonant with the cavity, and higher modes are possible for integer multiples of the lowest photon energy. Increasing the angle of incident light on the cavity causes the photon mode feature to shift to higher energies. It is critical to gain an understanding of these effects before a material that can strongly couple to the cavity photon mode is placed into a cavity.

6.3 PDI and TPDI in optical cavities

When an active material with an exciton transition equal in energy to the cavity mode is placed into the FP cavity, strong exciton-photon coupling can occur. As explained in Section 1.2.1, for this to happen materials must have a large oscillator strength, narrow absorption linewidth(s), a small Stokes shift, and a high doping concentration since the Rabi splitting increases with the number of oscillators N according to $\sqrt{N}$.¹²⁹ Perylene diimide monomers (PDI) and twisted dimers (TPDI) fulfill these requirements, and due to their solubility in common organic solvents they can also be solution-processed to create thin films with ease. Perylene diimide dyes have already been shown to produce high Rabi splittings in optical cavities when dissolved in a polymer matrix,^{129,130} hence they make an excellent candidate material for the present study.

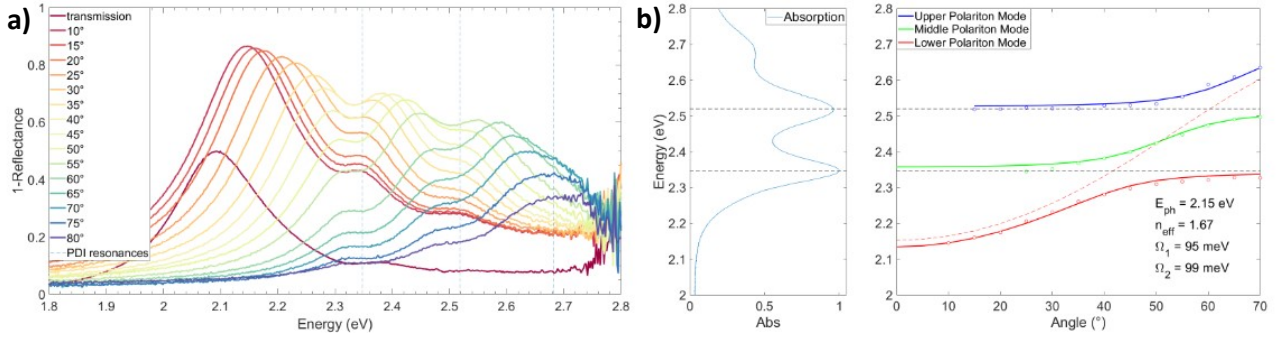


Figure 6.4: a) Angular reflectance and b) Rabi splitting of a thin film comprising PDI molecules dispersed in a polystyrene (PS) matrix at a concentration of 120 mM with two 28 nm thick Ag mirrors. The peak positions from a) are plotted as data points in b), which are then fit to a three-branch coupled oscillator model as described in Section 1.2.3 from which the Rabi splitting is calculated.

Figure 6.4 a) displays the angular reflectance of a thin film of PDI monomers dispersed in a PS matrix at 120 mM concentration with two 28 nm Ag mirrors. As the angle of incidence is increased, the energy of the 1 – reflectance peaks also increases. This result clearly differs from Figures 6.2 and 6.3 which only contain the cavity mode, since now the exciton transitions (shown with dotted lines) play an important role in the sample’s optical response. Peak splitting around the resonance energies of the PDI excitons is apparent in Figure 6.4 a), especially for angles $\sim 40^\circ$ for the lowest energy resonance and $\sim 50^\circ$ for the upper resonance. These features are a direct result of the anti-crossing behaviour common to polaritonic materials as shown in Figures 1.9 and 1.10.

If strong coupling did not play a role in the optical response of the film, the 1 – reflectance graph would demonstrate absorption features arising from the film and the cavity mode only. This effect is shown in Figure 6.5, where the absorption of the PDI film in Figure 6.5 a) is multiplied by the cavity mode of a blank PS FP cavity of similar dimension to the PDI FP cavity (R7) shown in Figure 6.5 c), to give the resulting spectrum in Figure 6.5 d). Some peak shifting is visible due to the dispersivity of the cavity mode, however peak splitting is not present in this case. The same calculation is performed for the absorption of the TPDI film shown in Figure 6.5 b) to give the resulting spectrum in Figure 6.5 e). Peak splitting and associated anti-crossing behaviour is therefore a defining feature of the presence of strong exciton-photon coupling.

The locations of the peaks in the 1 – reflectance graph are extracted and plotted as the data points (open circles) in Figure 6.4 b). The exciton transitions are again shown with dashed

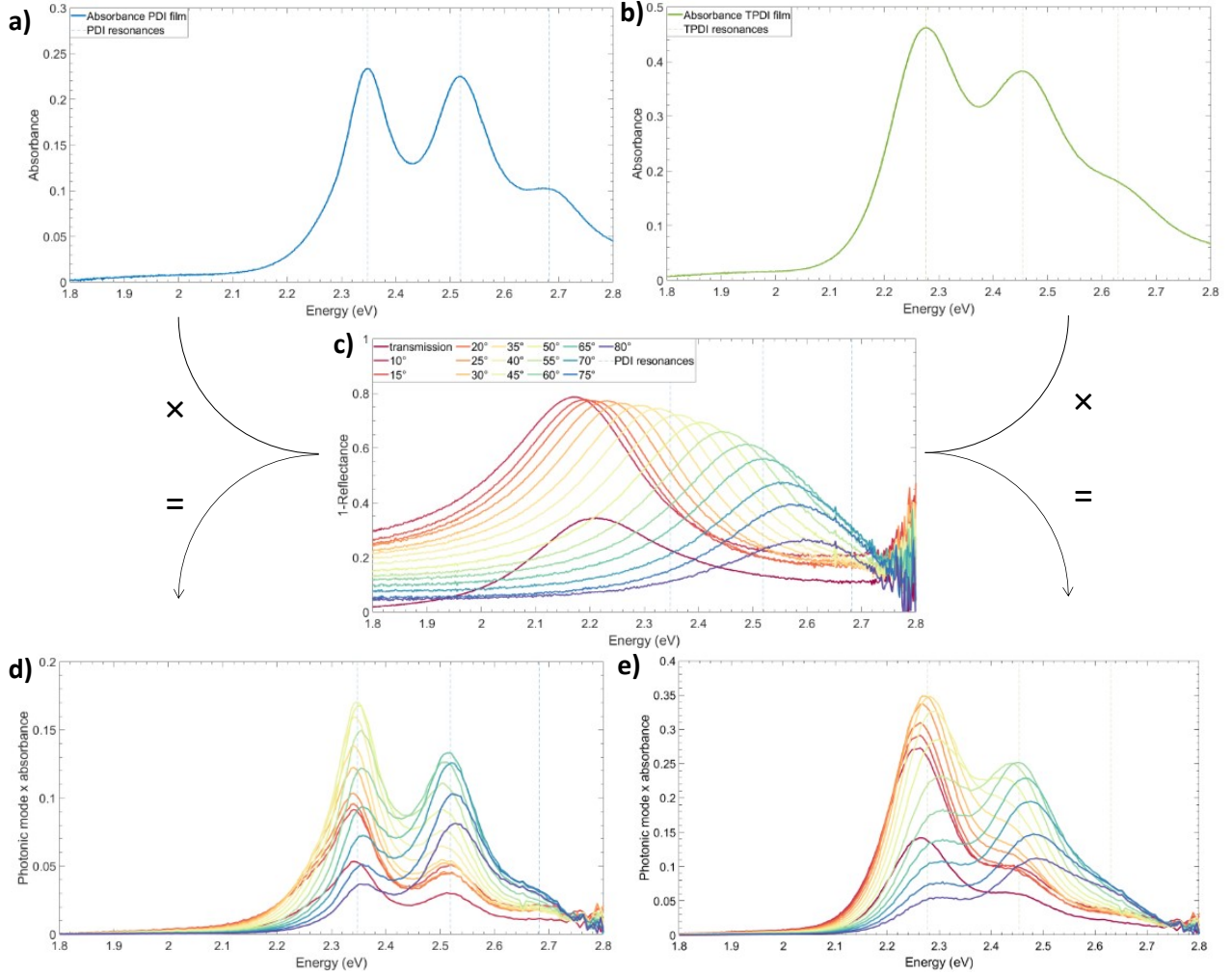


Figure 6.5: Calculations demonstrating the features of the photon mode as distinct from the features of strong coupling. a) PDI film absorption, b) TPDI film absorption and c) R7 blank PS FP cavity mode. d) The result of multiplying a) by c) and e) the result of multiplying b) by c). Some peak shifting is observed, however peak splitting is not observed since coupling is not present. (Common legend for c), d) and e).)

lines in the main panel and are also overlaid in the left panel displaying the absorption spectrum for a bare film of this material. There is no angular dependence of the exciton resonances since these transitions in the material are not sensitive to the angle of the incident light. However, the cavity mode, also represented as a dotted line in the main panel, is highly dispersive, as discussed above. The peaks from Figure 6.4 a) form three new features in Figure 6.4 b) which are termed the lower (LP), middle (MP) and upper polariton (UP) branches, each having a combination of photonic and excitonic character. As discussed earlier in Section 1.2.3, these branches are the eigenvector solutions to the coupled oscillator Hamiltonian. Thus they are fit to a three-branch coupled oscillator model, and the results are also shown in Figure 6.4 b).

Anti-crossing behaviour can be observed at approximately 40° between the LP and MP branches and at 50° between the MP and UP branches, as is suggested by the peak splitting in Figure 6.4 a). The fit also produces a value for the cavity photon energy E_{ph} , here defined as the energy of the cavity mode at 0° incidence, and the effective refractive index n_{eff} , both of which are written on Figure 6.4 b). Since the cavity photon energy at 0° (E_{ph}) lies ~ 200 meV below the energy of the first exciton resonance, this sample is significantly negatively detuned, as is also the case in Figures 1.9 and 1.10.

The strength of the coupling is measured by comparing the Rabi splitting to the linewidths of the cavity mode and the exciton transition. Strong coupling is generally defined as the regime where the Rabi splitting is comparable to or greater than the cavity and exciton linewidths, although this is not always the case since organic molecules can have broad absorption spectra and still exhibit coupling.¹⁵⁶ Here, the Rabi splitting values of $\Omega_1 = 95$ eV and $\Omega_2 = 99$ eV are significantly smaller than the cavity linewidth of 180 meV as determined by the full-width half maximum (FWHM) of the transmission measurement. The exciton linewidths determined by the FWHM of the first and second vibronic peaks are also larger than the Rabi splitting values, being 112 meV and 174 meV respectively. Thus we conclude that the reflectivity of the Ag mirrors is not high enough to form strong coupling in this sample since the transmission mode and exciton linewidths are broader than the energy of the Rabi splitting.

6.3.1 Effect of the Q-factor on coupling strength

The Rabi splitting is directly related to the Rabi oscillation frequency by a factor of 2, since oscillations between the excitonic and photonic state occur according to $\sin^2 \frac{\Omega t}{2}$.²⁸¹ Therefore, the energy of the split peaks is inextricably linked to this frequency of oscillation. As long as this oscillation occurs with a faster timescale than the energy dissipation due to absorption, scattering or leakage of light through the cavity mirrors, then the film is in the strong coupling regime. The energy dissipation is characterised by the quality factor (Q-factor):¹⁰¹

$$Q = \frac{\omega_r}{\Delta\omega_c} \quad (6.1)$$

where ω_r is the resonant frequency of the cavity mode and $\Delta\omega_c$ the linewidth of the cavity mode as given by the FWHM. The Q-factor should be high to minimise the amount of light leaked from the cavity, however must also be balanced to allow for sufficient transmission of light into

and out of the cavity such that its optical properties can be measured. The reflectivity of the material forming the reflective surfaces defines the Q-factor of the cavity. Highly reflective DBRs made of alternative high and low refractive index materials are able to form cavities of high Q-factors on the order of $10^3 - 10^6$. In contrast, metallic mirrors give rise to Q-factors on the order of $10 - 100$.¹⁶³ Despite their low Q-factors, all-metallic mirrors are often sufficiently reflective to achieve strong coupling due to the reduced optical path length inside the cavity, leading to an increased optical field inside all-metallic cavities compared to DBR cavities.²⁸² Silver is an excellent choice of material for cavity mirrors since it is a highly reflective substance, being more reflective at visible wavelengths than gold and aluminium for example.²⁸³ Silver is also highly conductive, allowing it to be used as an electrode as well as a reflective mirror, as will be seen in Chapter 7.

Samples of (T)PDI dispersed in a PS matrix with 50 nm Ag mirrors were made to compare to the above sample prepared with 28 nm mirrors and study the effect of the improved Q-factor on the Rabi splitting observed. The Q-factor and relevant calculation data for the FP cavity presented in Figure 6.4 is reported in Table 6.3 alongside the two FP cavities with Ag thicknesses of 50 nm. It was seen that using thicker Ag mirrors doubled the Q-factor for the TPDI film and tripled it for the PDI film due to the significantly reduced cavity linewidths as reported in Table 6.3.

Table 6.3: Q-factor calculation for (T)PDI in PS cavities

Sample	Ag thickness (nm)	Transmission peak (eV)	Transmission FWHM (eV)	Q-factor
PDI	28	2.09	0.18	12
PDI	50	2.19	0.07	31
TPDI	50	2.21	0.11	20

Figure 6.6 a) displays the angular reflectance of this thin film of PDI monomers prepared with two 50 nm Ag mirrors. Peak splitting around the resonance energies of the PDI excitons is again apparent in Figure 6.6 a), especially for angles between 30° and 45° for the lowest energy resonance and 50° and 60° for the upper resonance. The fits to the coupled oscillator model shown in Figure 6.6 b) produce an E_{ph} value of 2.18, making this cavity also negatively detuned by 160 meV. The Rabi splitting values of $\Omega_1 = 75$ eV and $\Omega_2 = 73$ eV are now both larger than the cavity linewidth of 66 meV, but are still less than the exciton linewidths of 112 and 174 meV, indicating that the light-matter coupling is still not considered to be strong.

Angularly-resolved photoluminescence (PL) is also measured for this film and is plotted in

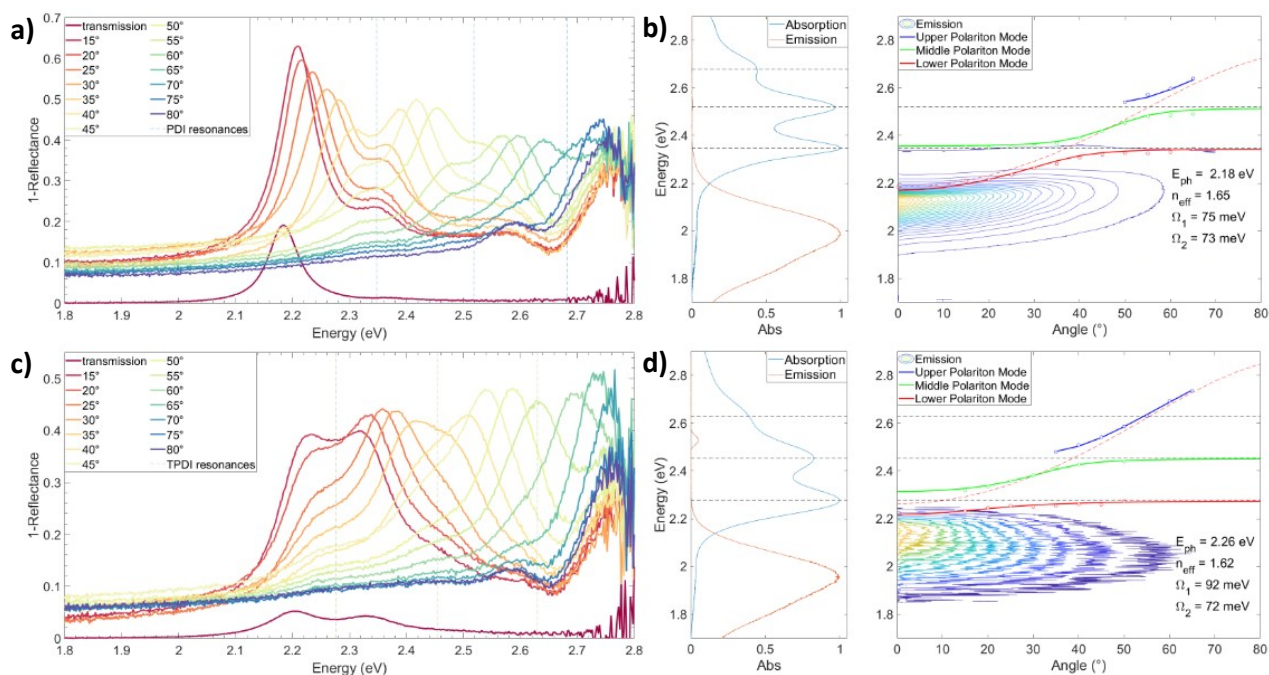


Figure 6.6: a) Angular reflectance and b) Rabi splitting of a thin film comprising PDI molecules dispersed in a PS matrix at a concentration of 120 mM with 50 nm thick Ag mirrors. c), d) The same for a TPDI thin film prepared with the same conditions.

Figure 6.6 b) alongside the angular reflection. The maximum of PL occurs ~ 0.05 - 0.1 eV below the energy of the lower polariton and is only mildly dispersive, which demonstrates that PL does not originate primarily from the lower polariton states. Instead, the PL arises primarily from a lower-energy state due to aggregation. The tendency for PDIs to form excimers is well known,^{284–286} and aggregation is known to lower both the PLQY and increase the absorption linewidth in molecular dyes.¹²⁹ Due to the low dispersivity of the PL in this sample, we conclude that aggregation-induced excimer emission is responsible for the PL emission here as opposed to polariton emission. This indicates that energy transfer from the exciton to the excimer state is dominant and likely outcompetes the exchange coupling between the exciton and the photon which is necessary to sustain strong light-matter coupling. There is still some dispersivity in the shape of the PL emission indicating that some level of coupling is taking place, but this is only weak coupling.

The same reflectance measurement is performed for a thin film of TPDI dimers with two 50 nm Ag mirrors as shown in Figure 6.6 c) and d). Figure 6.6 c) demonstrates the shifting and splitting of the 1–reflectance peaks, which are then plotted and fit to a coupled oscillator model in Figure 6.6 d). Anticrossing is observable between the LP and MP branches at approximately

15° and between the MP and UP branches at approximately 35°. The fit produces a cavity photon energy E_{ph} sitting only 14 meV below the first exciton resonance, thus this FP cavity is close to zero detuning. The Rabi splittings of $\Omega_1 = 92$ meV and $\Omega_2 = 72$ meV are larger than those of the PDI film, which is expected since TPDI is known to experience less aggregation as shown in Chapter 4. However, they are still lower than the cavity linewidth of 114 meV as well as the exciton linewidths of 154 and ~ 280 meV. We also see here that the PL is non-dispersive, indicating that aggregation-induced excimer emission is present as is also seen for the PDI film in Figure 6.6. Unfortunately, peak splitting was not observed in the 1 – reflectance graphs for samples prepared with a lower (T)PDI concentration. Thus we see that the tendency for PDI and TPDI molecules to form excimers prohibits them from achieving strong coupling when dispersed in polymer matrices. It would be insightful to study the suppression of excimer emission as a function of cavity detuning, as shown by Mony et al.¹⁷³ If the lower polariton branch is lowered to an energy below that of the excimer state, aggregation-induced emission would be expected to decrease and instead emission from the lower polariton branch should become more prominent.

6.4 PTB7-Th cavities

6.4.1 Neat PTB7-Th films

Next, we investigate the potential of PTB7-Th to couple to optical cavities. Figure 6.7 shows the cavity mode sustained by five cavities comprising a neat PTB7-Th polymer film sandwiched by two Ag mirrors of thickness 25 nm (Experiment N). The cavity mode that these peaks correspond to is calculated using the same method as for the PMMA and PS cavities using Equation 1.1 described in Section 6.2 and is reported in Table 6.4. The refractive index of PTB7-Th is highly wavelength-dependent as shown in Appendix section B.2, thus the index value at the energy of the transmission peak is used.

Sample N2-9 have a first-order cavity mode falling within the visible range detected by the spectrometer, but sample N1 is thick enough that the second-order mode is visible in transmission. Interestingly, because of the large variation in the PTB7-Th refractive index, it is possible to see a second appearance of the first-order cavity mode in N2 and N4 samples occurring around 2.4 eV, where the refractive index is much lower. Taking the second-order mode for N1 and the lowest energy modes for all other samples, these occur below the first

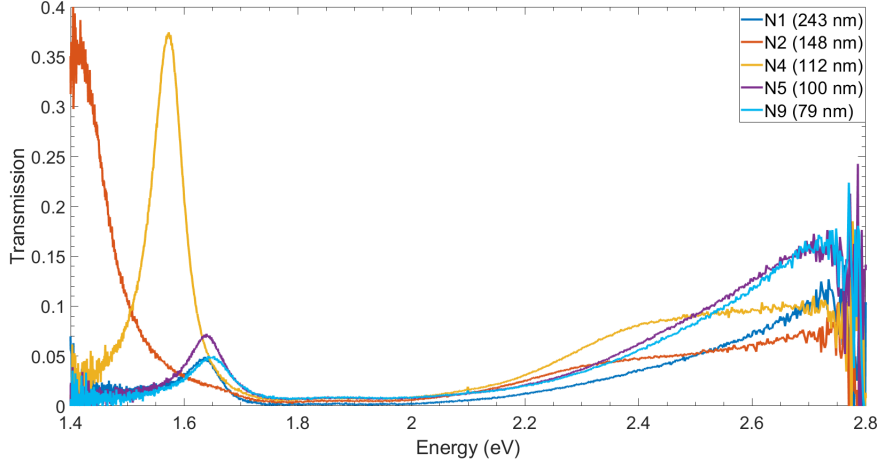


Figure 6.7: Transmission spectra of five samples of architecture Ag/PTB7-Th/Ag with varying PTB7-Th thickness.

Table 6.4: Mode calculation for PTB7-Th cavities

Sample	PTB7-Th Thickness (nm)	Transmission peak (eV) (calculated from Figure 6.7)	Effective refractive index n_{eff} (calculated from Figure B.2)	Cavity mode m
N1	243	1.64	2.66	2
N2	148	1.41	2.41	1
N4	112	1.57	2.65	1
N5	100	1.64	2.65	1
N9	79	1.65	2.60	1

exciton resonance of PTB7-Th at 1.76 eV, classifying the cavities as negatively detuned cavities ($E_{\text{ph}} < E_{\text{ex}}$) as explained in Section 1.2.3.

Figure 6.8 displays the angular reflectance of one of these samples (N5). The full sample set is shown in Appendix section B.2. As expected, there is a shift of the 1 – reflectance peaks to higher energies as the angle of incidence increases. An additional higher-energy peak is also visible, which could correspond to either the second mode or a second peak correlating to the first mode due to the highly wavelength-dependent refractive index. Despite the faint presence of a peak between the two PTB7-Th resonance energies, it is not possible to clearly observe a set of angle-dependent 1 – reflectance peaks distinct from the cavity mode(s). It may be possible that this sample shows some coupling behaviour since the high energy peak appears at a different energy from the underlying cavity mode as revealed by the transmission curve, however this is not clear.

In order to achieve strong coupling, the rate of the exchange between the photon and

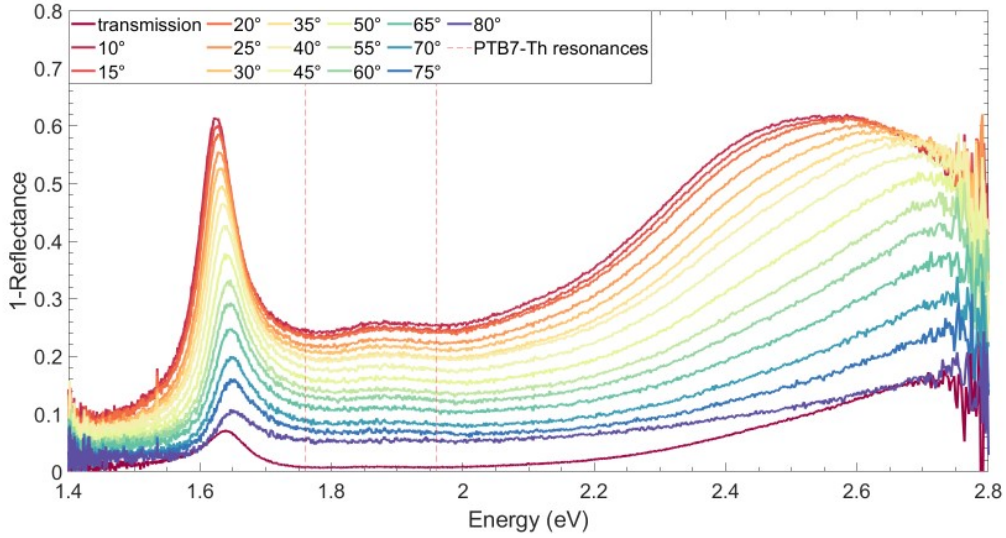


Figure 6.8: Angular reflectance of a neat PTB7-Th film with a thickness of 100 nm (N5).

the exciton must be faster than the rate of thermalisation losses and exciton decay. Since the cavities have the correct thickness to couple but no coupling is observed, we conclude that the rate of thermalisation is faster in this system, prohibiting strong coupling from occurring. Aggregation and resulting intermolecular interactions between PTB7-Th molecules are likely to be the source of this thermalisation process. If this is the case, breaking up the domains of PTB7-Th by the presence of other molecules should enable strong coupling to occur, as smaller PTB7-Th domains would lead to less thermalisation losses in the cavity that compete with strong coupling.

6.4.2 PTB7-Th in PS

In order to test the above hypothesis, PTB7-Th cavities were prepared with different loading ratios in polymer matrices. The solubility of PTB7-Th in PMMA was found to be insufficient for this investigation, causing the formation of macroscale features as seen by evaporated Ag mirrors appearing to scatter rather than reflect light. However, this was improved by the use of PS as a matrix for the dispersion of PTB7-Th. The angular reflectance of two coupled samples are shown below in Figure 6.9 a) and c), prepared at 20% (S7) and 40% (S8) weight percentage of PTB7-Th in PS. Peak splitting is observed for both films around the lower-energy PTB7-Th resonance. Again, an additional higher-energy peak is visible which corresponds to either the second mode or a second peak from the first mode due to the wavelength-dependent refractive index.

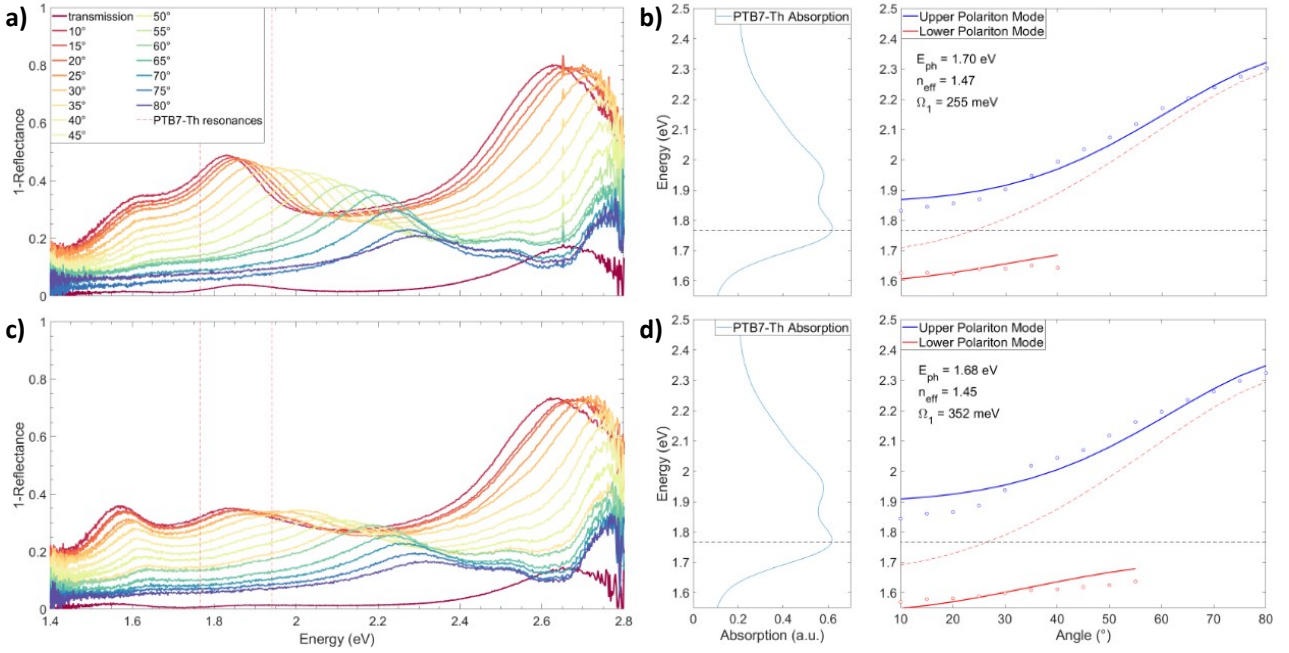


Figure 6.9: a) Angular reflectance and b) Rabi splitting for thin film samples of PTB7-Th dispersed in a PS matrix at 20% w/w loading (S7). c) Angular reflectance and d) Rabi splitting for a similar sample with 40% w/w loading (S8). (Common legend for a) and c).)

We see that when PTB7-Th neat films are broken up by the presence of another material, in this instance PS, it is possible to achieve coupling. The 1 – reflectance peaks are fit to a two-branch coupled oscillator model in Figure 6.9 b) and d) for 20% (S7) and 40% w/w (S8) loading ratios of PTB7-Th in PS. Both cavities are seen to be ~ 70 meV negatively detuned with respect to the lowest PTB7-Th resonance. The Rabi splitting in the 20% loading sample is $\Omega = 255$ meV whereas the Rabi splitting in the 40% sample is $\Omega = 352$ meV. These values are significantly larger than the absorption linewidth of PTB7-Th of 180 meV and even larger than that of a similar PS FP cavity (S2) of 220 meV. It is known that Rabi splitting scales as the square root of the number of oscillators according to $\Omega \propto \sqrt{N}$ with this square root dependence being proof that the coupled oscillators are in the strong coupling regime.¹⁶³ Since this ratio is upheld between these two samples, we confirm that strong coupling is achieved for PTB7-Th when it is blended with PS. This supports the above hypothesis that PTB7-Th aggregates must be broken into smaller domains in order to allow the exciton-photon exchange coupling to be competitive with aggregation-induced energy transfer or dissipation. Hence, we then move on to attempts to couple blend films of PTB7-Th:(T)PDI.

6.5 Blend film cavities

The aim of this section was to observe strong coupling in blend PTB7-Th:(T)PDI films such that the blend films could then be reproduced inside an organic photovoltaic device. Blend films are prepared in a 1:1 ratio as this is suitable for incorporation into devices.

Before strong coupling could be observed in these blend films, first the correct sample preparation protocol needed to be found, in particular the spin speed which results in a cavity thickness such that the photon mode is close in energy to the exciton resonances. Instead of PTB7-Th being dissolved in PS, we now dissolve (T)PDI in a PTB7-Th matrix. The film thickness is seen to change even with the same sample preparation variables as for PS:PTB7-Th films such as the concentration of the materials in solution and the spin coating speed. Additionally, the ideal thickness of the film that can sustain a cavity mode close to the exciton resonances of the (T)PDI or PTB7-Th materials will also be different due to the different effective refractive index of the blend material system.

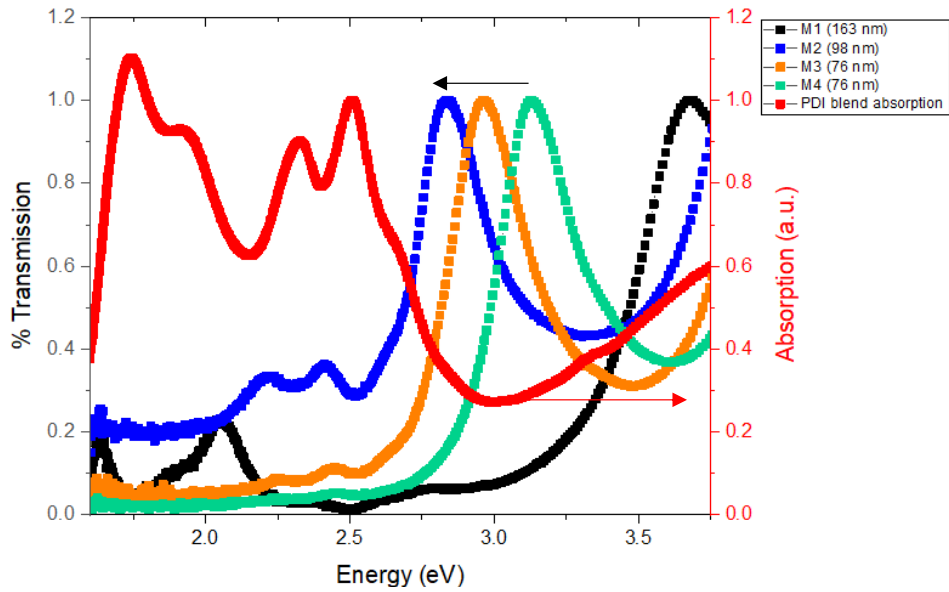


Figure 6.10: Example UV-visible transmission measurements for a thickness tuning experiment, plotted alongside PDI blend film absorption.

PTB7-Th:PDI FP cavities of different thicknesses were fabricated using 50 nm Ag mirrors to find the sample preparation conditions that would result in a cavity mode of appropriate energy to match the exciton resonances. These were studied through both angular reflectometry and UV-visible transmission measurements, since the compact white light source on the angular reflectometry does not contain wavelengths lower than 450 nm and thus does not allow for the

measurement of high energy cavity modes. In contrast, the Xenon flash lamp in the UV-visible setup permits the measurement of transmission for higher energies up to and beyond the onset of absorption of glass (~ 300 nm), and has a better signal-to-noise ratio. An example of a UV-visible transmission measurement is shown in Figure 6.10, which also includes the PDI blend film absorption for comparison.

It is clear to see that as the thickness of the blend film inside the FP cavity increases, the transmission peak shifts lower in energy, in this case towards the absorption peaks of the bare blend film. The thickest of the samples shown here (M1, 163 nm) exhibits a second-order peak at high energies as well as a first-order peak in between the absorption maxima of the PTB7-Th and PDI components of the blend film. For the other three samples, as the transmission peak approaches the bare film absorption peak, splitting appears at ~ 2.2 and ~ 2.4 eV, and these features also grow in magnitude.

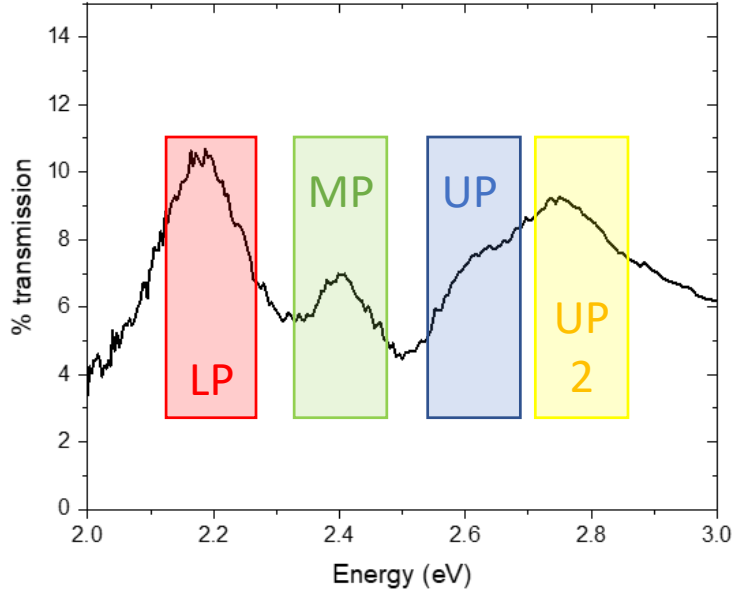


Figure 6.11: UV-visible transmission measurement of a coupled PTB7-Th:PDI blend film (J4) demonstrating the presence of a fourth high energy transmission peak. This appears at a high enough energy that it is not visible with angular reflectometry, therefore we simply refer to the lower three peaks as the LP, MP and UP branches.

It should also be noted that for the three exciton resonances for (T)PDI, one might expect to see four polariton branches. It is difficult to resolve the presence or absence of a fourth branch due to the noise level of the angular reflectance spectra above ~ 2.7 eV. The UV-visible transmission measurement of another PDI blend film (J4) shown in Figure 6.11 suggests that a fourth polariton branch is present at ~ 2.75 eV, which is above the highest-energy vibronic

peak of PDI and thus exists approximately where we would expect to find it. This is just out of range of the angular reflectance spectra, since the signal-to-noise ratio becomes insufficient at energies above 2.7 eV. Since only three branches are visible by angular reflectometry, we retain our nomenclature of naming the three peaks visible in the angular reflectance spectra as the LP, MP and UP branches.

Despite having a better Q-factor than 25 nm cavities, the angular reflectance on 50 nm cavities is low in signal and also rather noisy due to the lower transmission of light into the cavity. Thus all further experiments were performed with 25 nm Ag mirrors.

6.5.1 Films coupled to PTB7-Th resonances

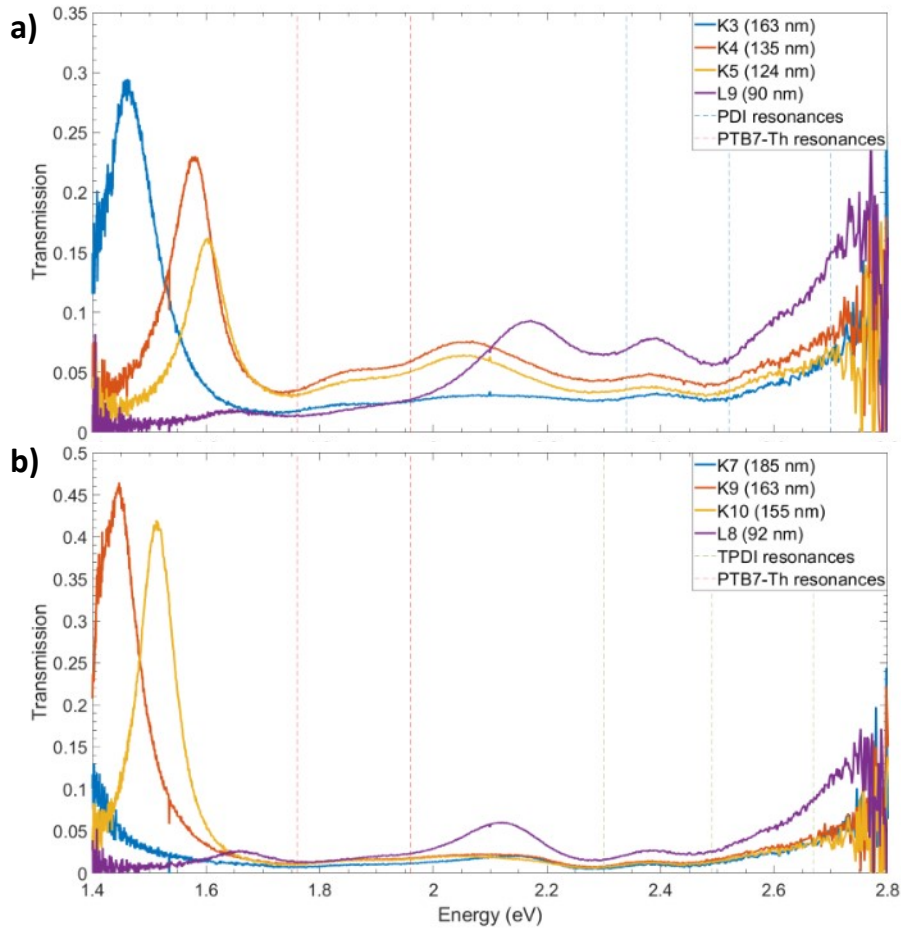


Figure 6.12: Transmission of a) PDI and b) TPDI blend films with architecture Ag/PTB7-Th:(T)PDI/Ag demonstrating the shifting of the cavity mode to higher energies as thickness decreases, causing peak splitting around the PTB7-Th and then (T)PDI resonances.

Transmission measurements are shown for a selection of blend films in between 25 nm Ag mirrors for PTB7-Th:PDI films in Figure 6.12 a) and for PTB7-Th:TPDI films in Figure 6.12 b).

As spin speed is increased and thickness is decreased, the position of the cavity mode peak shifts to a higher energy, and the peak splitting becomes more apparent for energies around the higher-energy (T)PDI resonances compared to the lower-energy PTB7-Th resonances.

Figure 6.13 a) shows the angular reflectance of a PTB7-Th:PDI blend film (K5) coupled to the PTB7-Th exciton resonances. In this case, there appear to be three branches, especially at low angles of incidence into the cavity before the middle polariton peak becomes too difficult to distinguish at higher angles. This contrasts with Figure 6.9 where we see only two polariton branches for coupled PTB7-Th films. It is possible that the peak at ~ 2 eV corresponds to coupling with the PDI domains only in the blend film. However, it is also known that strong coupling can cause exciton mixing¹²⁴ leading to energy transfer between materials^{170,193,287} or even hybridisation between two organic materials^{288–290} and thus it is more likely that this peak arises because of exciton mixing and hybridisation between the excitonic transitions in the PTB7-Th and (T)PDI materials. For simplicity, and since it appears in a similar wavelength region to the upper polariton peak in Figure 6.9 a), we treat it here in context with the PTB7-Th resonances and thus label it as an UP peak with reference to PTB7-Th.

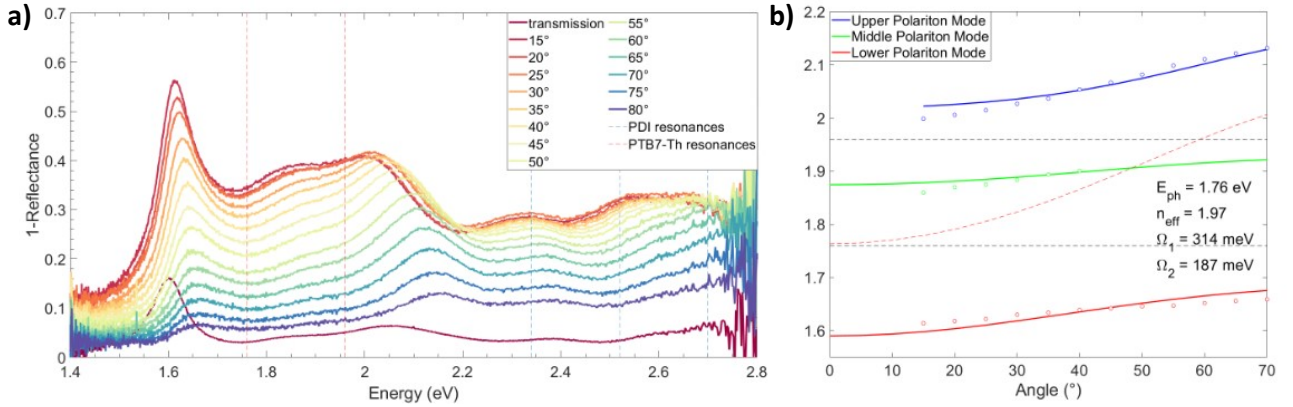


Figure 6.13: a) Angular reflectance and b) Rabi splitting for a PDI blend film sample in a FP cavity (K5) coupled to the PTB7-Th resonances.

The angle-resolved polariton branches and the fits to the three-branch coupled oscillator model are shown in Figure 6.13 b). Coupled oscillator model fitting suggests the cavity is positively detuned by only 36 meV, making it very close to a zero-detuned cavity. The Rabi splitting values are found to be $\Omega = 314$ and 187 meV for the lower-middle and middle-upper polariton branch coupling respectively. The first vibronic resonance of PTB7-Th has a FWHM of 234 meV as measured from Figure 4.6 a) in Chapter 4, whilst the cavity linewidth for this

sample measures 88 meV. Since Ω_1 is significantly greater than both of these values, this film is classified as strongly coupled.

6.5.2 Films coupled to (T)PDI resonances

By changing the thickness of the film, it is possible to shift the cavity mode to higher energies such that it primarily interacts with the (T)PDI resonances. Figure 6.14 a) and c) show the angular reflectance of a PDI (L9) and TPDI (L8) blend film respectively where the cavity photon is resonant with the (T)PDI resonance. Figure 6.14 b) and d) show the corresponding three-branch oscillator model fits to the angular reflectance. The PDI blend FP cavity is negatively detuned, whilst the TPDI blend is positively detuned. Both films have significant Ω_1 Rabi splitting values of $\Omega_1 = 198$ and $\Omega_1 = 314$ for the PDI and TPDI blend respectively. In both cases the fit produces a value for Ω_2 as well, however this value is less trustworthy as there are only a small number of data points for the coupled oscillator model to fit, and as such the fit does not extend to the region where anticrossing would be expected to occur. The linewidth of the first vibronic peak of the PDI absorption in the blend film as shown in Figure 4.6 a) cannot be measured due to the presence of PTB7-Th peaks, but is known to be > 310 meV. In contrast, the linewidth of the first vibronic peak of TPDI absorption in the blend film as shown in Figure 4.6 b) is easier to determine and measures 262 meV. The cavity linewidths are 254 meV for the PDI blend film and 168 meV for the TPDI blend film. For the PDI blend film, despite being large, the Ω_1 value does not exceed the linewidth of absorption or of the cavity photon, so the film is coupled to some extent but not strongly so. However, for the TPDI blend film, given that the first Rabi splitting value of Ω_1 is significantly greater than the absorption and cavity linewidths this film is considered strongly coupled. This is a critical result to achieve before coupled blend films are incorporated into OPV devices, since it is important to first measure their coupling in a Fabry-Pérot device, as has been done here.

Future work could include using a five-branched coupled oscillator model to determine the Rabi splitting of all the branches visible in PTB7-Th:(T)PDI blend films. Whilst mathematically complex, this would provide a more complete picture of coupling by accounting for the relationship between the polariton branches located near the PTB7-Th resonances and the (T)PDI resonances at the same time. Calculating Hopfield coefficients for fitting performed with a five-branch coupled oscillator would also allow for numerical quantification of the relative contributions of the PTB7-Th and (T)PDI resonances to the various polariton branches, as a

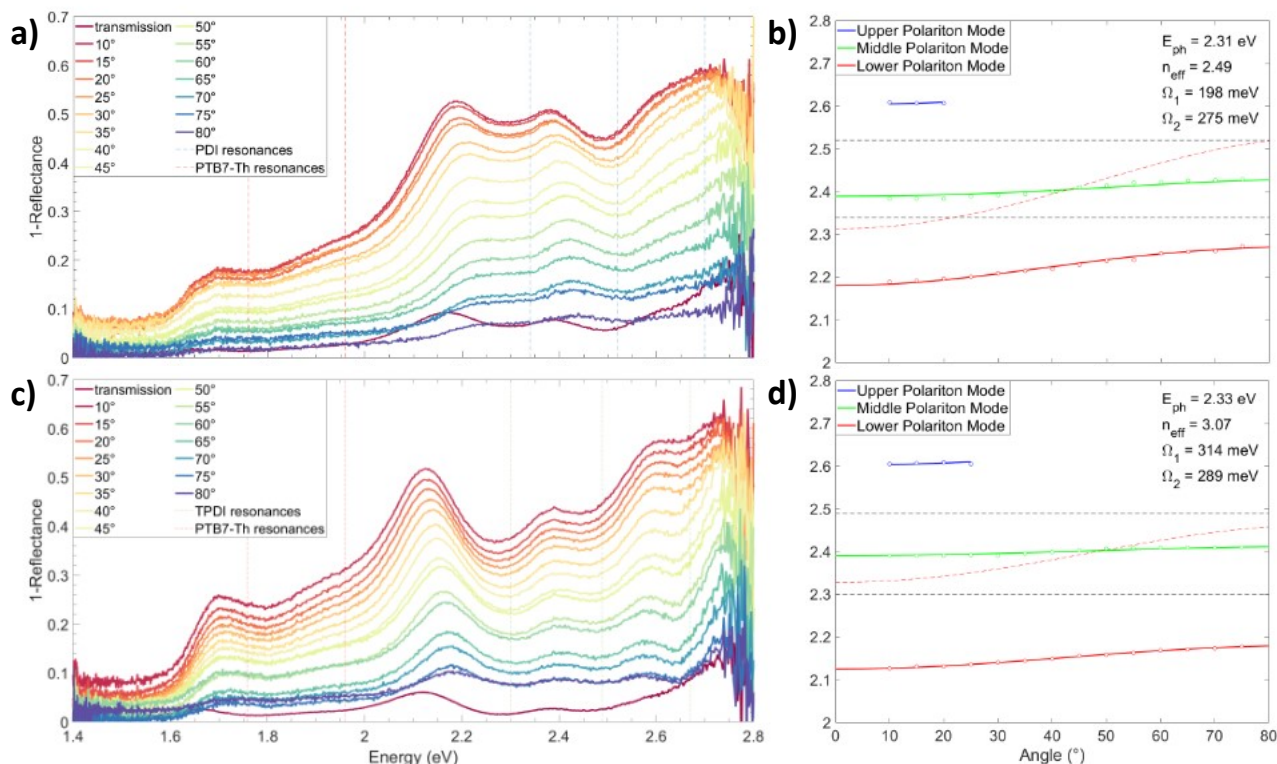


Figure 6.14: a) Angular reflectance and b) Rabi splitting of a blend film of PTB7-Th:PDI (L9) coupled to the PDI resonances. c) Angular reflectance and d) Rabi splitting of a similar blend film of PTB7-Th TPDI (L8) coupled to the TPDI resonances.

function of incident angle. This would allow for the quantification of the overall percentage contribution of PTB7-Th vs (T)PDI domains to the effect of strong coupling.

It would also be insightful to study PDI trimers and tetramers in this context and investigate the relationship between the number of chromophores in a molecule and its ability to achieve strong coupling. For monomers and dimers, we have seen that strong coupling was outcompeted by excimer formation, despite the reduced crystallinity of the TPDI film morphology. It would be insightful to see if further structural changes to the perylene molecules such as the creation of trimers or tetramers could reduce excimer formation to the point at which strong coupling becomes competitive for films of chromophores dispersed in PS as has been seen previously.^{129,130} Changing the FP cavity detuning may also enable strong coupling if the lower polariton becomes lower in energy than the excimer state, thus enabling relaxation from the excimer state to the lower polariton. Finally, adding bulky constituents to the perylene molecules may also decrease molecular aggregation and lead to strong coupling, as has been shown previously for other perylene monomers.¹²⁹

6.6 Time-resolved measurements

When a photon is placed inside a resonant cavity, the resulting change in the density of states of the electromagnetic field causes a change in the spontaneous emission rate of a material coupled to that cavity. This phenomenon was first proposed by Purcell, and thus the effect is known as the Purcell effect, whereby the rate of spontaneous emission of a material is enhanced when it is coupled to a resonant cavity.²⁹¹ PDI and TPDI films and blends were studied by Time-Correlated Single Photon Counting (TCSPC) in and out of cavities in order to see the effects of the cavity on the lifetime of the material.

For PDI, the TCSPC decay of a neat bare film is compared to the coupled cavity in Figure 6.4 where PDI is dispersed in a PS matrix with 28 nm Ag mirrors, with the results shown in Figure 6.15. The long lifetime of the bare neat film is likely due to excimer formation as discussed above in Section 6.3.1. In the cavity sample, whilst excimers are still present as already discussed, it is possible to observe the Purcell effect since the initial decay of the cavity sample is faster than that of the bare neat film. Since the Purcell enhancement of emission rate is observed for this sample, and the PL of a similar sample in Figure 6.6 a) still exhibits a small amount of angular dependence, we reiterate that this film exhibits some coupling, albeit in the weak coupling regime. For samples that are not coupled at the conditions (angle) of measurement, no Purcell decay rate enhancement is seen, as shown in Appendix section B.3.

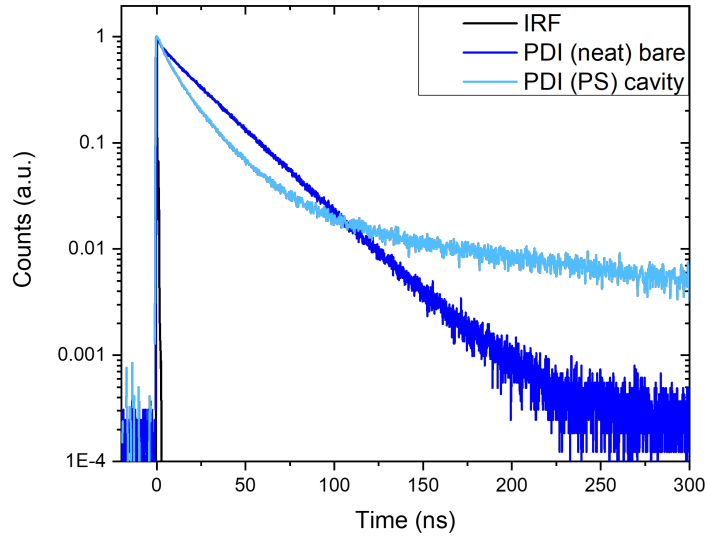


Figure 6.15: Observation of the Purcell effect in a PDI-based cavity compared to a bare film.

6.7 Conclusions

In conclusion, we have studied the features of the photon mode, as well as the presence of strong light-matter coupling in neat and blend films of PTB7-Th and (T)PDI. In Section 6.2, we demonstrated the features of the cavity mode in PMMA and PS FP cavities, and studied the effect of changing the cavity thickness, mode, angle of incidence and refractive index on these features. In Section 6.3, we explored the effect of Ag reflectivity on the Q-factor of the cavity using (T)PDI dispersed in PS. Despite studying higher Q-factor cavities, the (T)PDI molecules demonstrated a tendency to form excimers which outcompeted interactions between the photon and exciton and prohibited strong coupling from occurring in these samples. In Section 6.4, we demonstrate strong coupling for PTB7-Th films. However, we saw that it was necessary to break up the domains of PTB7-Th with another material, namely PS, in order to achieve this strong coupling.

Turning to blend films, we demonstrate that by changing the thickness of the blend film inside the FP cavity, the photon mode can be shifted such that it can be made to couple primarily to one or the other of the blend film components in a controlled and selected way. A blend PDI film is shown to have significant strong coupling to the PTB7-Th resonances. When films are prepared to couple to the (T)PDI resonances, some coupling is achieved for the PDI blend film, but strong coupling is achieved for the TPDI blend film.

This is an important set of foundational experiments upon which to build a coupled organic photovoltaic device. We have demonstrated that it is feasible to fabricate coupled FP samples of blend PTB7-Th:(T)PDI films and control the domain which is primarily coupled through controlling the active layer thickness. For coupled OPV devices, the active layers are prepared the same way as these blend films but additional layers must be included to ensure sufficient charge extraction at the electrodes. Namely, to make inverted coupled OPV devices, ZnO must be added as an electron transport layer at the cathode and MoO₃ as a hole transport layer at the electrode, similarly as was seen for non-cavity (bare) devices in Chapter 4. We focus on TPDI-based blend films for the investigation of coupled OPV devices, since these outperform PDI-based devices as also shown in Chapter 4 and also demonstrate stronger coupling in the blend film as shown in Figure 6.14. These coupled PTB7-Th:TPDI devices will be explored next in Chapter 7.

Chapter 7

PTB7-Th:TPDI OPV devices in Fabry-Pérot optical cavities

7.1 Introduction

In Chapter 4, we studied both PTB7-Th:PDI and PTB7-Th:TPDI devices, and saw that TPDI-based devices significantly outperformed the PDI-based devices due to differences in packing morphology arising from the twist in the dimer structure. In Chapter 5, we used transient absorption and associated modelling to determine that there is more balanced dual-direction energy harvesting in TPDI-based devices compared to PDI, since the excitation of TPDI contributes more significantly to overall charge generation than for PDI excitation. In Chapter 6, we saw that both of these materials are able to couple to optical cavities, and that by changing the size of the optical cavity the photonic mode could be controlled and shifted towards either (T)PDI or PTB7-Th absorption resonances. Significantly stronger coupling was achieved for the TPDI-based film than for PDI when coupled to the (T)PDI resonances. Since the TPDI-based devices were seen to perform better and have stronger coupling, this material system is chosen for investigations into strongly coupled OPV devices.

Strong coupling causes energy level splitting in cavity devices as shown in Figure 7.1. Where energy levels change, we expect that the rates of processes occurring inside OPVs such as CT state formation or dissociation at the interface will also change, leading to differences in device performance. Strong coupling has been studied in OPVs on only a few occasions. It has been shown to achieve optical mixing of the donor and acceptor where these remain separated in space;²⁰² it has been shown to present an additional pathway for charge transfer and the creation of CT states;²⁰³ and it has been shown to steepen the absorption edge and

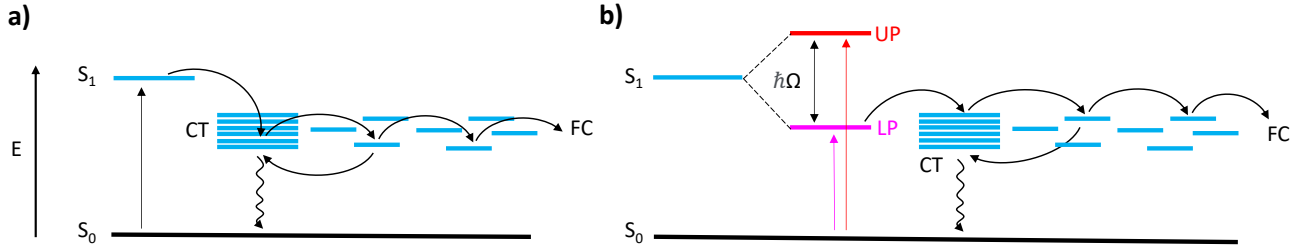


Figure 7.1: Approximate energy levels for a) a bare device and b) a cavity device demonstrating the splitting of energy levels. CT = charge transfer state, FC = free charge, LP = lower polariton and UP = upper polariton. The Rabi splitting $\hbar\Omega$ for the coupled device is also shown.

reduce energy losses compared to bare devices.²⁰¹ However, much remains to be discovered in this area, such as the role of coupling on charge generation and transport. Also, the effect of cavity detuning remains largely unexplored. It follows that the more negative the detuning of the devices, the higher the photonic character of the polariton, and thus the more drastic any strong coupling-induced changes to device performance will be.

In this chapter, the knowledge from the previous three chapters is combined in order to design, fabricate and test organic photovoltaic devices where the active layer is strongly coupled to the optical cavity it resides within. Cavity and bare devices are compared to find the effect of coupling on device performance. Cavity devices are shown to have a higher effective J_{SC} and FF than bare devices. Devices with different detuning achieved through altering the active layer thickness are also compared. More positive detuning gives rise to higher energy polariton features detected both optically and electrically, which leads to decreased bimolecular recombination and a longer lifetime of charge in the cavity.

7.2 Impact of the cavity on device performance

We focus here on TPDI-based devices since these outperform PDI-based ones and show stronger coupling in the blend film. In order to create an optical cavity within a device, an additional Ag layer is added into the device layer stack as shown in the inset of Figure 7.2 b). This layer must be partially transmissive in order to allow light into the cavity, yet also reflective enough to form a low-loss cavity with a sufficiently high Q-factor. In this project, 25 nm of Ag is chosen as an appropriate thickness to balance these two requirements. This layer is in contact with the conductive ITO, and thus only needs to transport charges to the ITO and not laterally within

the device. The top electrode is maintained at 100 nm thick to allow for sufficient conductivity of charge to the point of electrical connection during testing.

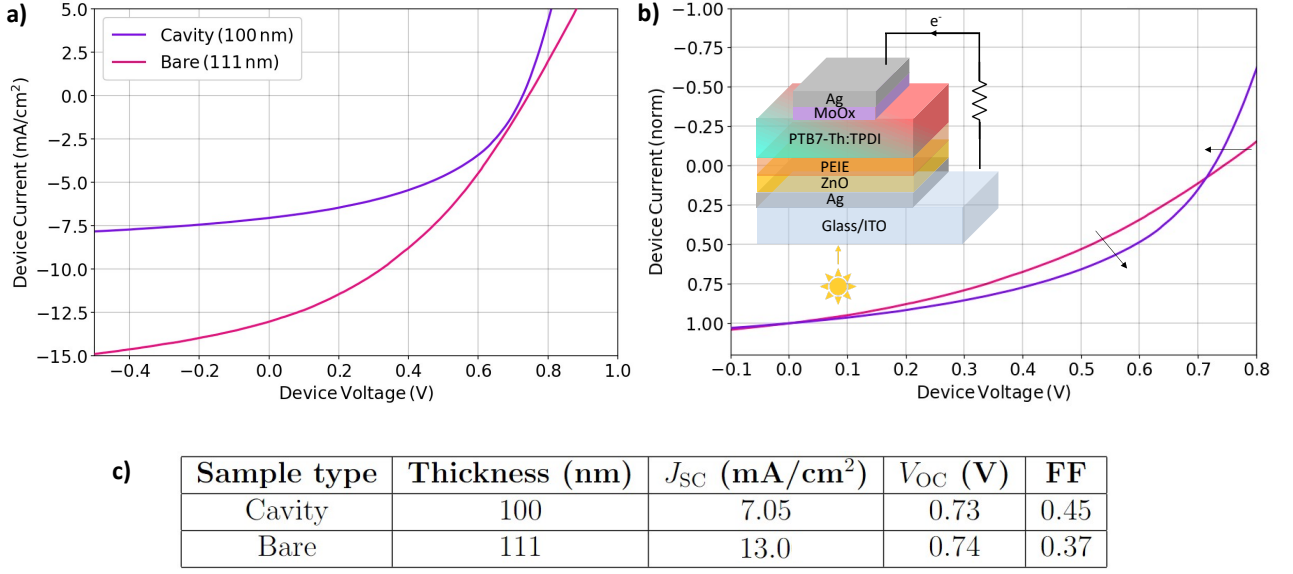


Figure 7.2: a) JV light and dark curves demonstrating the effect of the additional Ag layer on the device performance for a cavity OPV as compared to a bare device. Most notably there is a decrease in J_{SC} leading to a reduced PCE. b) JV curves normalised to the J_{SC} demonstrating the improved fill factor of the cavity device. Inset: cavity device structure with additional Ag layer at the cathode. (Common legend) c) Device performance parameters for the bare and cavity device.

A cavity device and a bare device prepared using the same processing conditions are compared in Figure 7.2. Note that all thicknesses reported in this chapter correspond to that of the active layer only, as is also the case in Chapter 6. There is a significant reduction in the J_{SC} for the cavity device as shown in Figure 7.2 a). This is due to the reduced level of illumination reaching the active layer as a result of the partially transmissive Ag layer blocking some of the incident light, and leads to a reduction in the PCE. However, modelling presented in Figure 8.5 in Chapter 8 suggests that the additional 25 nm Ag mirror should reduce the J_{SC} threefold between the bare and cavity device with thickness 105 nm, when in reality the cavity device measures over half the J_{SC} of the bare device. This means the effective J_{SC} , taking into account the reduced incident light, is higher for the cavity device. There is little change in the V_{OC} between the two sets of devices.

Interestingly, there appears to be an appreciable difference in the fill factor between the two device batches, with the fill factor improving for cavity-based devices. Figure 7.2 b) shows normalised JV curves for the bare and cavity devices. A differing fill factor often demonstrates

that there is a difference in the photophysics between two devices, such as differing recombination mechanisms. The series resistance is lower for the cavity device leading to a better diode shape in the vicinity of the V_{OC} , however we are able to reproduce this improved fill factor for a number of cavity devices with less drastic differences in series resistance as shown in Figure C.1 in the Appendix, so we rule this out as a reason for the improved diode behaviour.

EQE measurements are useful for understanding the wavelength-resolved charge production abilities of a particular OPV sample. For cavity OPVs, EQE measurements are particularly insightful since they are capable of demonstrating peak splitting as can be seen in angular reflectometry measurements.

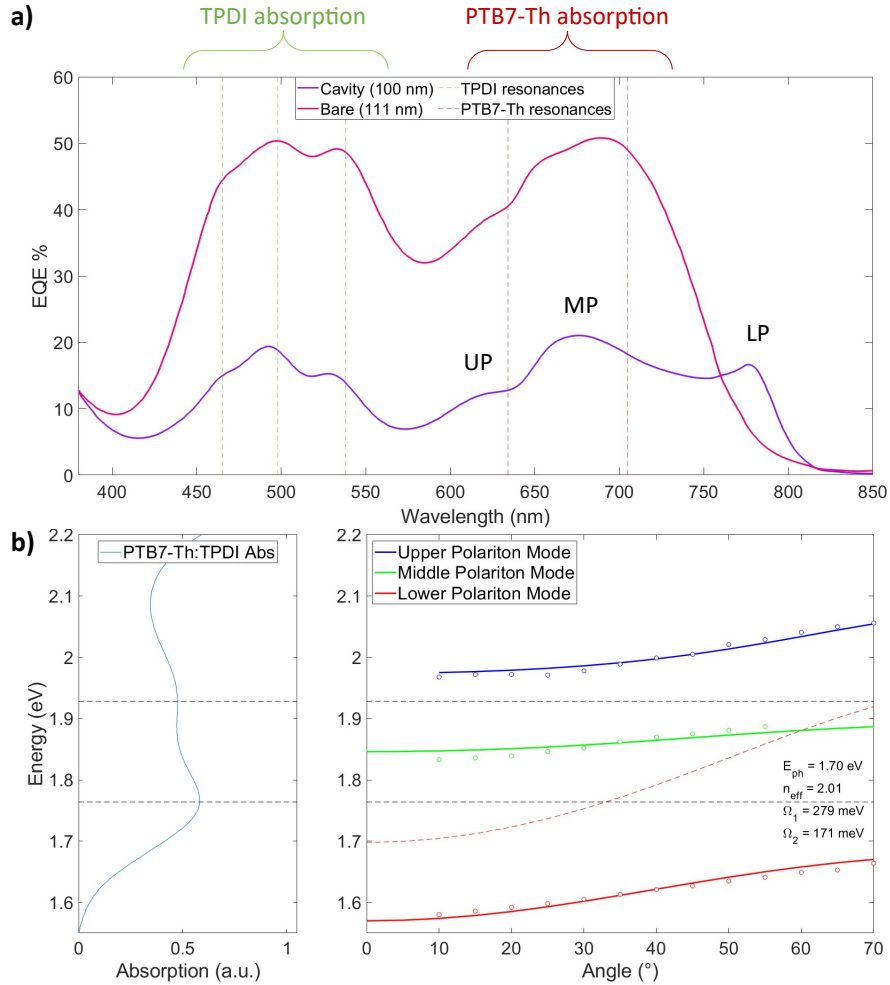


Figure 7.3: a) EQE measurements of the bare and cavity devices, demonstrating electrical detection of energy level splitting around the wavelengths of PTB7-Th absorption and the creation of polariton branches. b) Angular reflectometry Rabi splitting graph demonstrating optical detection of energy level splitting around the PTB7-Th absorption wavelengths. Coupled oscillator model fits to the lowest three branches are shown. The sample is negatively detuned (66 meV) with respect to the lowest vibrational resonance of PTB7-Th.

Figure 7.3 a) compares the EQE of the bare device to that of the cavity device. Dotted lines indicate the peak wavelengths for PTB7-Th and TPDI absorption features in a blend film studied outside the devices. For the cavity device, peak splitting is visible around the PTB7-Th resonances, as has been seen previously in angular reflectometry measurements in Chapter 6. The three peaks around the PTB7-Th resonances can therefore be understood as the LP, MP and UP polariton peaks. There is some ambiguity with the UP as there is also a feature in the bare device EQE at ~ 620 nm, where the UP occurs for the cavity device. However, we still assign this as the UP as it is a dispersive feature as shown through angular reflectometry.

Figure 7.3 b) demonstrates optically detected peak splitting through angular reflectance for the cavity device. Just as in Chapter 6, the $1 - \text{reflectance}$ peaks are represented as data points on the Rabi splitting plot. The adjacent graph displays the film absorption spectrum of PTB7-Th with both the first and second vibronic peaks marked. We focus here on splitting around the PTB7-Th resonance energies, treating these three branches as the lower, middle and upper polariton branches with respect to the PTB7-Th resonances, as is supported by peak splitting in the EQE measurement around the PTB7-Th resonances. The LP-MP Rabi splitting is calculated as 279 meV, which exceeds the exciton linewidth of PTB7-Th in blend films of 217 meV as calculated from Figure 4.6 b), placing this sample in the strong coupling regime. Due to the presence of the opaque top Ag layer, it is not possible to perform transmission measurements on these samples to determine the cavity linewidth. Since the energy of the cavity photon E_{ph} lies beneath the E_{0-0} PTB7-Th transition, this sample is negatively detuned by 66 meV. The full Rabi splitting data is shown in Figure C.3 in the Appendix.

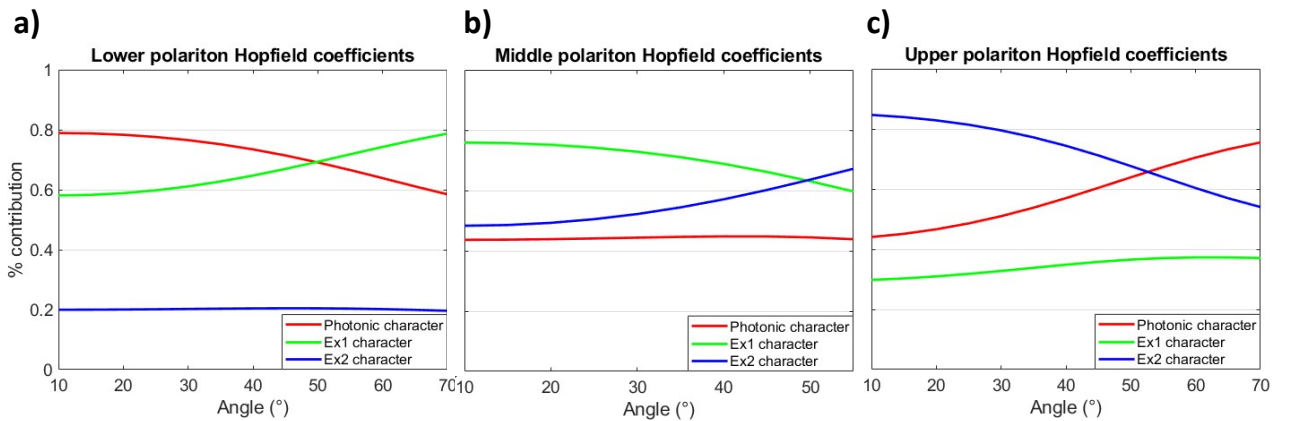


Figure 7.4: Hopfield coefficients for the a) lower, b) middle and c) upper polariton branches determined by coupled oscillator fits shown in Figure 7.3 b) conveying the photonic and excitonic character of the branches.

Next we calculate the Hopfield coefficients, i.e. the mixing fractions of the photon and the excitons for each polariton branch, as shown in Figure 7.4 using the coupled oscillator fits in Figure 7.3 b). Since the sample is negatively detuned, the lower polariton takes on primarily photonic character at lower angles of incidence. At higher angles of incidence the lower polariton transitions to having higher excitonic character from the lowest vibrational peak. The second vibrational peak provides a steady contribution to state mixing of around 20%. The middle polariton takes on primarily the character of the first exciton resonance, with significant contribution from the second exciton especially at higher angles, and the upper polariton takes on primarily the character of the second exciton before transitioning to having primarily photonic character at higher angles.

In order to understand what loss mechanisms might be present in the bare and cavity devices, and how strong coupling might affect them, intensity-dependent JV measurements were performed as shown in Figure 7.5. The fits to the intensity-dependent J_{SC} demonstrate high alpha values close to unity, indicating that there are minimal losses due to bimolecular recombination or space charge limited effects as previously outlined in Chapter 4. The alpha values are within error of each other, suggesting comparable bimolecular recombination for the two devices.

The intensity-dependent V_{OC} shown in Figure 7.5 b) demonstrates complex behaviour that requires two different fitting regions. Ideality factors can be extracted from the slope of intensity-dependent voltage fits as described in Chapter 4. These values are expected to lie in

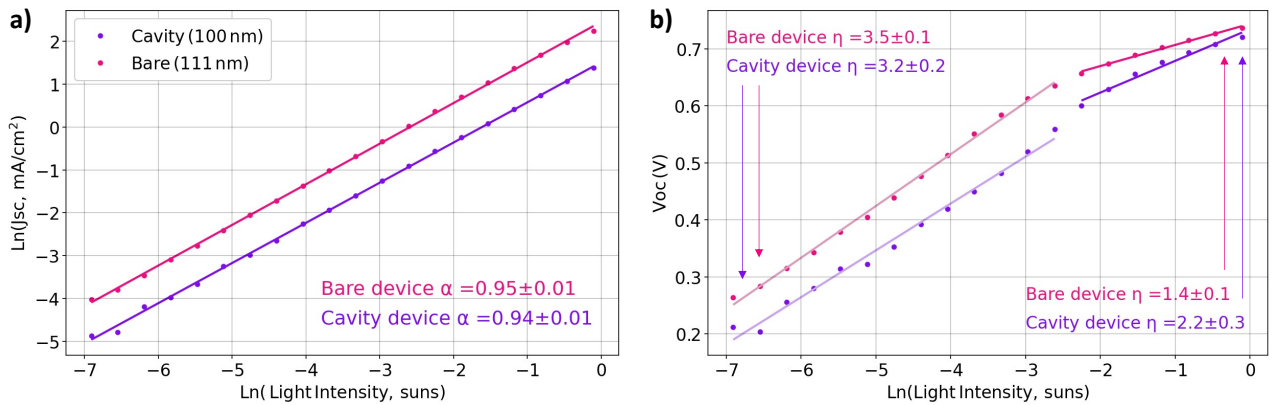


Figure 7.5: a) Intensity-dependent J_{SC} of a bare and cavity device. The data is fit according to Equation 3.7 to yield the alpha values written on the graph. b) Intensity-dependent V_{OC} for the same. The data is fit in two different regions according to Equation 3.8 to yield the ideality factors written on the graph. (Common legend)

the range between $\eta = 1$ for bimolecular recombination and $\eta = 2$ for monomolecular (trap-assisted) recombination, however in this case ideality factors as high as 3.5 are seen especially for low light intensity measurements. This demonstrates the presence of trap-assisted recombination or extraction issues at the electrodes which are particularly problematic for low light intensities. These issues appear to be more detrimental to the performance of the cavity device than the bare device.

Transient photocurrent (TPC) and transient photovoltage (TPV) measurements provide information on charge carrier densities, charge lifetimes, and the kinetics of charge generation, recombination and extraction in devices.^{292–297} TPC is performed at short circuit using a step-function voltage provided to an external light source, in this instance a white LED; whilst TPV is performed at open circuit with a small perturbation to a constant illumination intensity in order to mimic the operating conditions of the device. For TPC measurements, the rise time of the current in response to the turn-on of an illumination source reports the time to establish charge equilibrium inside a device, and the fall time after turn-off reports the time for residual charge to be extracted. The charge carrier density for a particular level of illumination can be found by integrating the tail of current extraction after turn-off. For TPV, the perturbation in illumination intensity produces a perturbation in the measured signal, the decay of which provides the lifetime of the charges inside the device for a particular level of illumination.

TPC and TPV measurements were performed on the bare and cavity device in order to reveal more information about the presence of recombination and the timescale of its occurrence.

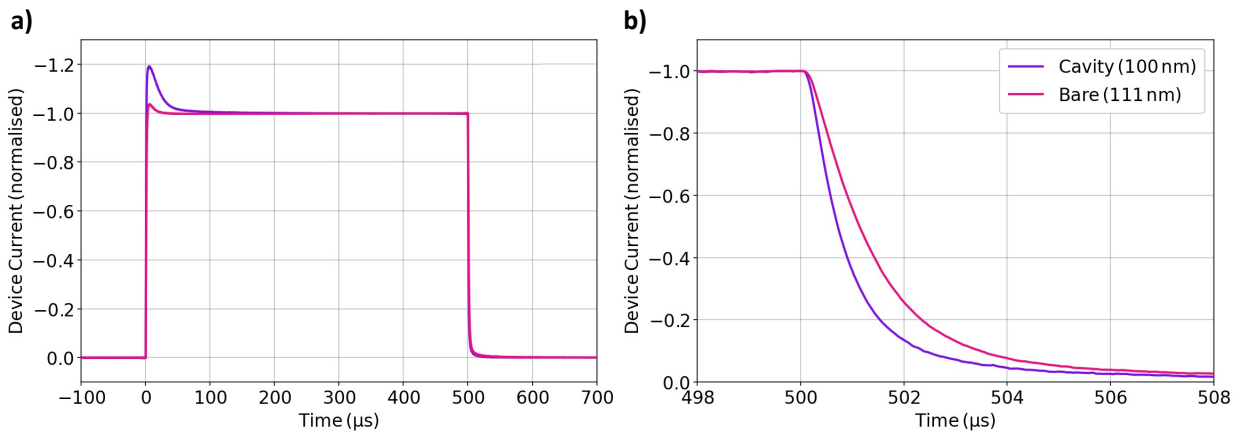


Figure 7.6: TPC response for the bare and cavity device measured at short circuit and 90% light intensity, normalised to the value of the plateau. There is a clear overshoot for both samples due to charge trapping and/or extraction issues in the devices. b) A close-up section of the photocurrent response showing the fall times of the devices. (Common legend)

The complete set of bias voltage and intensity-dependent TPC measurements are shown in Appendix section C.3. Figure 7.6 shows TPC traces for the bare and cavity device normalised to the plateau value for 0 V bias (short circuit) at 90 % light intensity. Both devices show an overshoot where there is a larger amount of current initially extracted before this is reduced to the plateau value. Similar features have been attributed to charge trapping in the literature since trapping reduces the current that can be extracted to the plateau value.^{298–300} The timescale of the fall of the peak to the plateau value is indicative of the timescale of trapping, and the fall of the plateau value is indicative of detrapping. Charge extraction issues due to imperfect electrodes can have the same effect, as they also reduce the current that can be extracted to the value of the plateau.

Comparing the bare and cavity devices, we see a higher peak value for the cavity device, indicating greater charge-trapping and/or extraction issues. This is contrary to what we expect to see for the cavity device, since the formation of a delocalised polariton could be reasonably expected to overcome shallow trap states and lead to a lower current overshoot. The additional Ag layer should not limit the conductivity of the electrode but rather improve it, being the highest conducting metal and having a resistance two orders of magnitude lower than the ITO-only electrode in the bare device.³⁰¹ The additional Ag layer for cavity devices also has not caused extraction issues for previously studied fullerene cavity devices.³⁰² It may instead be the case that the current overshoot is caused by trapping or extraction issues to do with the charge transport layers or interfaces at the electrodes. This matter is also re-addressed in Section 7.5 and also in Chapter 8.

Studying the fall of the TPC provides an interesting insight into the effect of the cavity. If the height of the peak with respect to the plateau demonstrates the extent of charge trapping, it would be logical to expect the detrapping to be slower for samples exhibiting a higher overshoot. However, the cavity device exhibits a faster extraction time despite the presence of a higher overshoot compared to the bare device. The enhancement of the spontaneous emission of materials in metallic cavities is known as the Purcell effect and is explained in Section 6.6. The measurement presented here does not concern radiative decay, concerning rather the recombination and extraction of charges, but it may have similar origins to the Purcell effect.

In order to make a fair comparison of the charge lifetimes, it is necessary to account for the different charge densities in the devices. This can be done by comparing charge densities

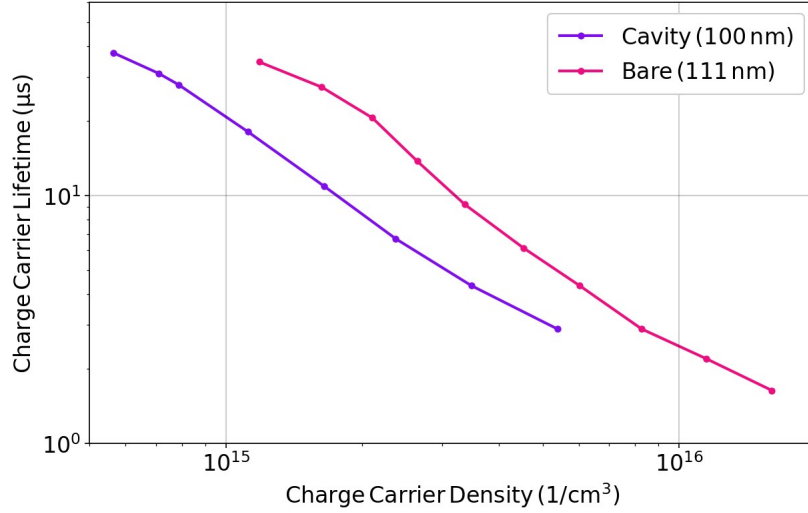


Figure 7.7: Charge carrier lifetime as a function of charge carrier density for the bare and cavity devices, extracted from transient TPC and TPV measurements.

measured from TPC with charge lifetimes measured from TPV for the same illumination intensity. The charge lifetimes measured as a function of density are shown in Figure 7.7. Comparing the bare and cavity devices, we see that charges live longer in the bare device as is also suggested by the longer fall time shown in Figure 7.6 b). This is an unexpected result, as we would have expected that the formation of delocalised polariton states in the cavity device would have reduced the recombination rate leading to a longer charge lifetime, as has been reported previously.³⁰²

It is also possible to study the energetics of the system through the electrical measurements of EQE and electroluminescence (EL) by following the method proposed by Vandewal et al.³⁰³ The distance between vibrational modes in organic materials is often less than the thermal energy, such that optical transitions between electronic states do not appear as discrete peaks but rather as broad features. For example, absorption can occur for energies below the vibrationally relaxed ground to excited state transition (E_{0-0}) and emission for energies above the same E_{0-0} transition. Assuming the low frequency transitions are harmonic oscillators, the absorption and emission curves follow Gaussian lineshapes according to:

$$A(E) \sim E \exp \left(-\frac{(E - E_{0-0} - \lambda_L)^2}{4\lambda_L k_B T} \right) \quad (7.1)$$

$$N(E) \sim E^3 \exp \left(-\frac{(E - E_{0-0} + \lambda_L)^2}{4\lambda_L k_B T} \right) \quad (7.2)$$

where E is the energy of the photon being absorbed or emitted, k_B the Boltzmann constant, T the temperature, and λ_L the low frequency relaxation energy, which is equal to half the Stokes shift for mirror image spectra. To compare the spectra, they must first be reduced: $A(E)$ must be divided by E , and $N(E)$ by E^3 . The intersection of the normalised reduced spectra is equal to the E_{0-0} energy, which is the bandgap of the material.

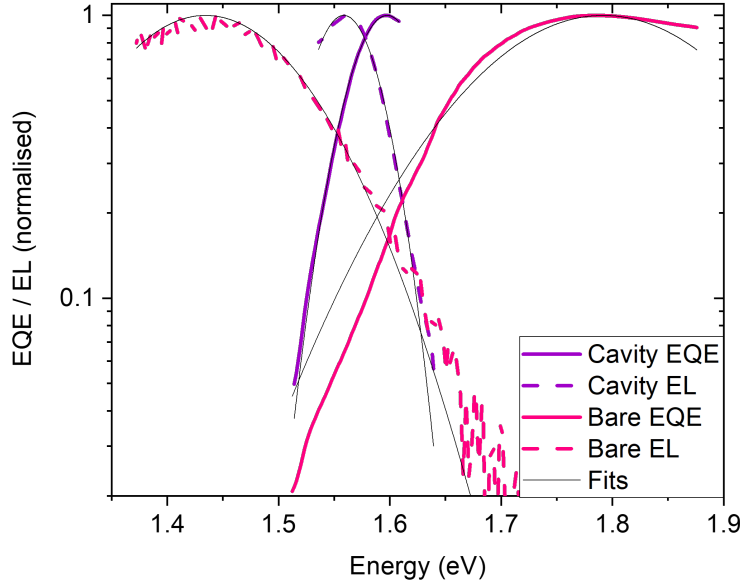


Figure 7.8: Reduced and normalised EQE and EL (2 V applied bias) for the bare and cavity devices. The S_1 or LP energy for the bare and cavity device respectively is given by the point of intersection between the fit to the EQE and EL spectra.

In devices, absorption is demonstrated through EQE measurements, and emission through EL measurements. The reduced and normalised lowest energy peak of the EQE from Figure 7.3 a) is plotted against the reduced and normalised EL measured at 2 V applied bias for the bare and cavity device in Figure 7.8. Notably, the cavity device demonstrates significant line narrowing for both the EQE and EL peaks. The selected sections of the EQE and EL shown in Figure 7.8 were then fit to Equations 7.1 and 7.2. In the bare device, the intersection of these two curves gives a measurement of the bandgap of the PTB7-Th component of the blend, due to it having a lower bandgap than TPDI. In the cavity device, this provides an electrically detected value of the LP peak. A slight red shift of ~ 11 meV was found in the intersection of the reduced and normalised EQE and EL for the cavity device compared to the bare device.

7.3 Impact of positive and negative detuning

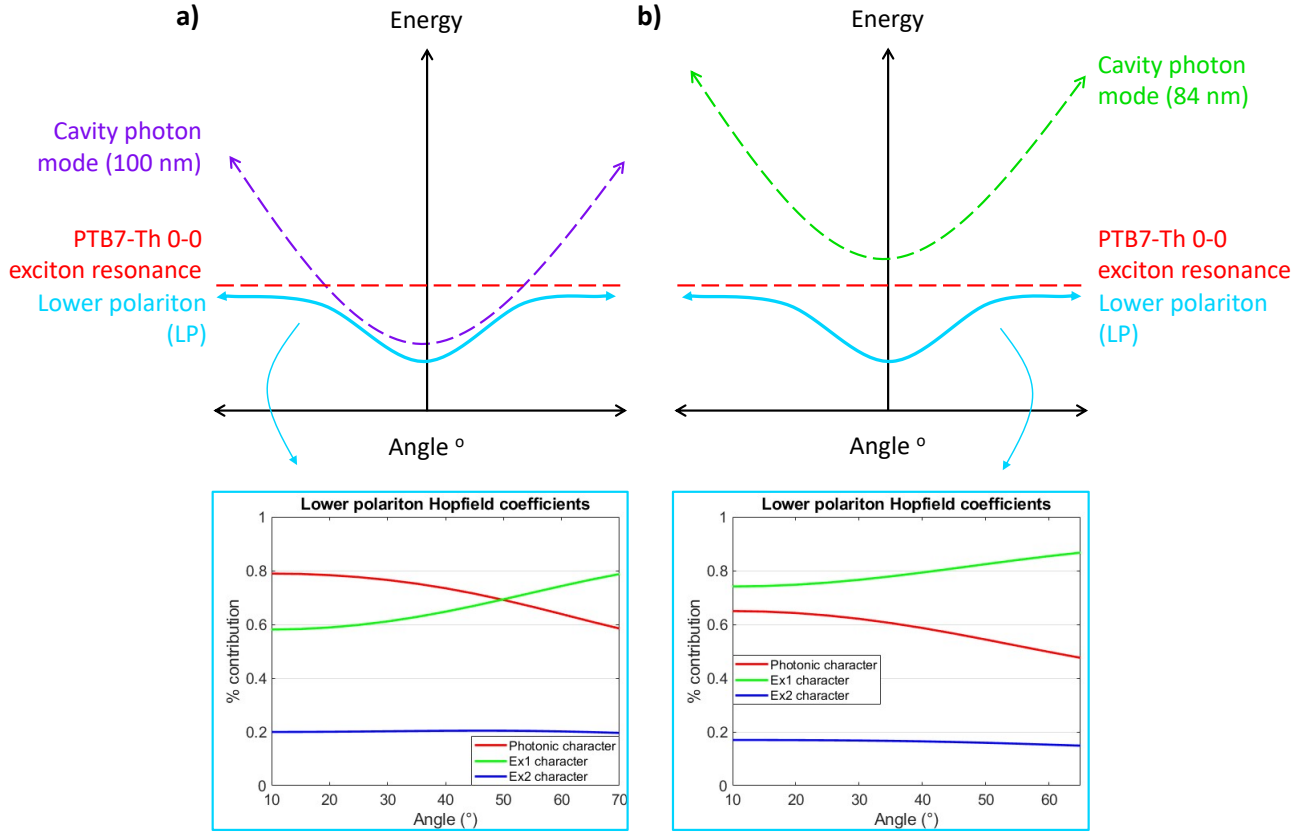


Figure 7.9: Detuning schematic for a) the negatively detuned device discussed in Section 7.2 and b) the positively detuned device discussed in Section 7.3. Hopfield coefficients for the lower polariton are shown for each sample, obtained from coupled oscillator model fits to angular reflectometry data.

The cavity device discussed in Section 7.2 is negatively detuned, since the cavity photon mode sits below the energy of the lowest PTB7-Th exciton resonance at 0° incidence as shown in Figure 7.3 b) and in the schematic in Figure 7.9 a). This gives the lower polariton mostly photonic character at low angles of incidence. In contrast, a positively detuned sample with respect to the lowest energy PTB7-Th results in a lower polariton with mostly excitonic character, as shown in the schematic in Figure 7.9 b). This implies that any effects of the polariton formation and partial photonic character of the lower polariton are lessened for this device, however it still makes for an interesting study to continue to understand the effects of polariton formation.

The EQE of this positively detuned device is shown in Figure 7.10 a). Peak splitting is again visible around the PTB7-Th wavelengths with a highly prominent LP feature appearing

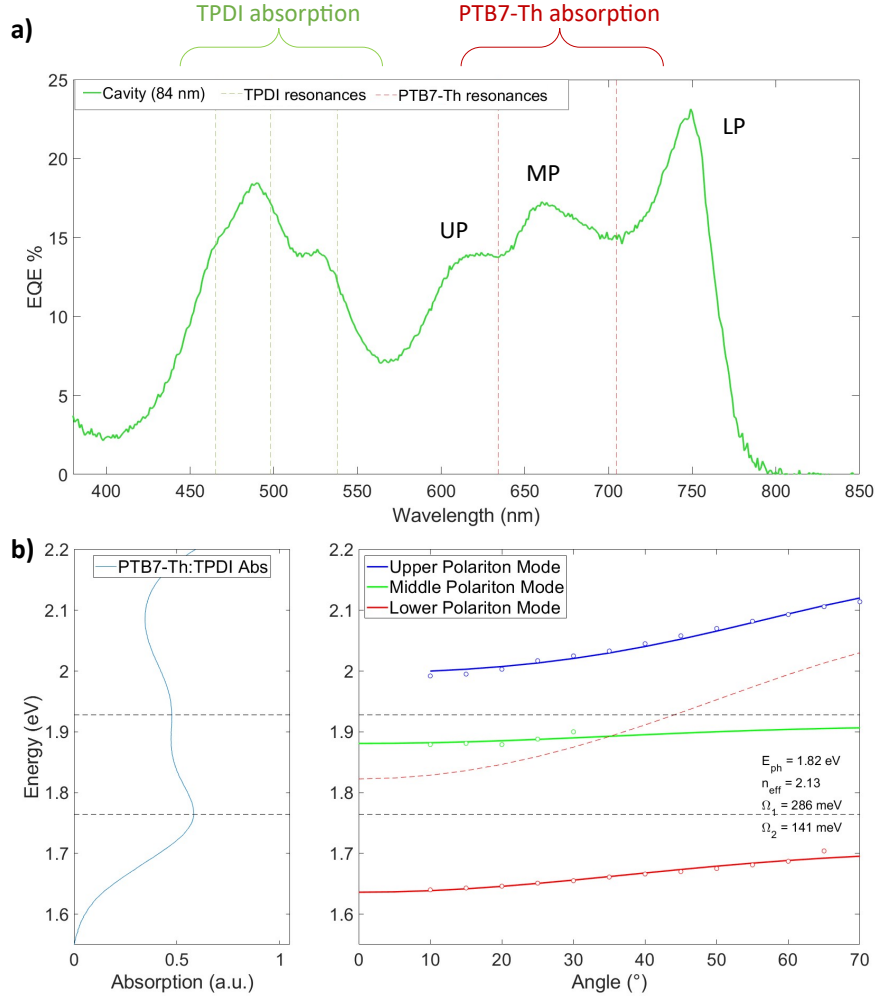


Figure 7.10: a) EQE measurement of a positively detuned cavity device, again demonstrating electrical detection of energy level splitting around the wavelengths of PTB7-Th absorption and the creation of polariton branches. b) Angular reflectometry Rabi splitting graph demonstrating optical detection of energy level splitting around the PTB7-Th absorption wavelengths. Coupled oscillator model fits are shown. The sample is positively detuned (59 meV) with respect to the lowest vibrational resonance of PTB7-Th.

at 750 nm, blue-shifted from the LP of the negatively detuned device EQE shown in Figure 7.3 a). Peak splitting is also demonstrated optically through angular reflectometry as shown in Figure 7.10 b). The LP-MP Rabi splitting is calculated as 286 meV, which exceeds the PTB7-Th linewidth of 217 meV, placing this sample in the strong coupling regime. Coupled oscillator fits suggest the cavity mode is positively detuned by 59 meV with respect to the lowest energy PTB7-Th resonance. The Hopfield coefficients for the lower polariton branch shown in Figure 7.9 b) demonstrate that the lower polariton is excitonic in character for all wavelengths studied, which may be related to the increased LP signal in the EQE compared to the negatively detuned sample. Full Rabi splitting and Hopfield coefficient data is given for this sample in Figure C.5 in the Appendix.

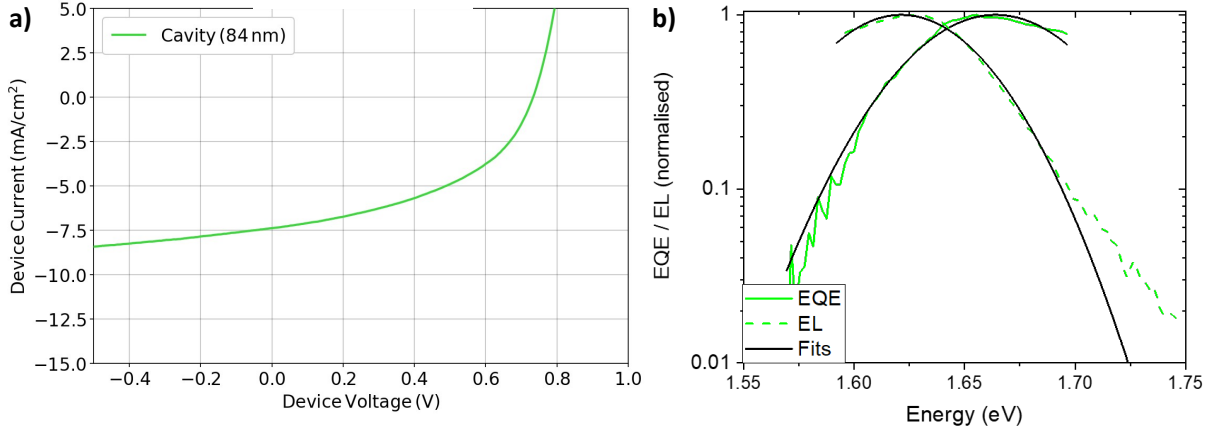


Figure 7.11: a) JV curve and b) normalised and reduced EQE and EL for a positively detuned cavity device (84 nm).

Figure 7.11 a) shows the JV curve for this sample, and Figure 7.11 b) shows the reduced and normalised EQE and EL. The intersection of the curves gives the energy of the LP as 1.64 eV, which is above the energy of the bare device (1.59 eV) due to the increased positive detuning.

7.4 Impact of coupling to TPDI resonance

The cavity devices discussed so far in Section 7.2 and 7.3 are detuned with respect to the PTB7-Th resonance, since the cavity photon mode crosses one or both of the PTB7-Th resonances. This causes the lowest three polariton features to be the most dispersive, hence we have considered them as the lower, middle and upper polariton branches. If we continue to push the detuning higher (more positive) by fabricating samples with a thinner active layer, the cavity photon mode will be pushed to higher energies such that the crossing point of the cavity photon mode with the PTB7-Th exciton resonances will occur outside the range of angles measured. In this case, it makes sense to instead define the detuning of the sample with respect to the TPDI resonances, where the crossing of the cavity photon mode with the TPDI exciton resonances can occur within the range of angles measured. Additionally, the upper three polariton features are now more dispersive than the lower three as demonstrated by Figure C.6 in the Appendix, indicating a greater interaction of the photon with the TPDI exciton resonances.

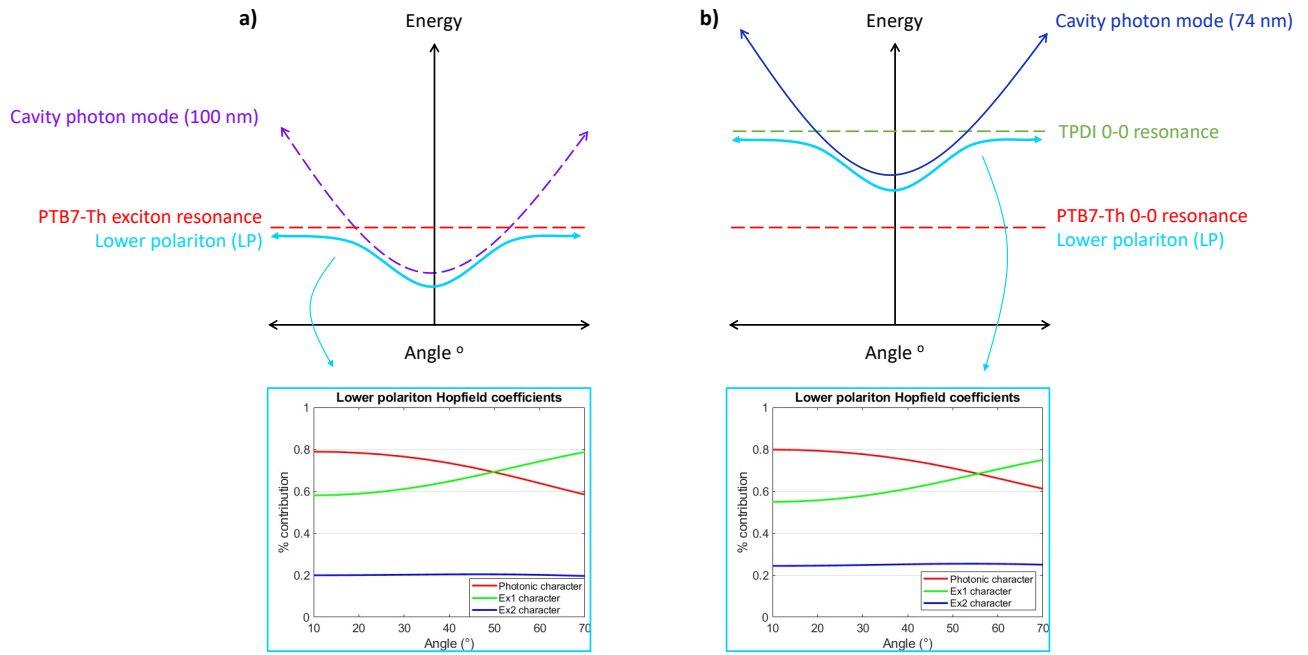


Figure 7.12: Detuning schematic for a) the device negatively detuned with respect to PTB7-Th resonance discussed in Section 7.2 and b) the device negatively detuned with respect to the TPDI resonance discussed in Section 7.4. Hopfield coefficients for the lower polariton are also shown for each sample.

The EQE and Rabi splitting graph of a device of this type is shown in Figure 7.13. The EQE in Figure 7.13 a) still shows peak splitting around the PTB7-Th wavelengths, but now due to the increased energy of the cavity photon mode, the peaks in the low wavelength region of the EQE are also significantly offset from the film absorption values. In Figure 7.13 b) we consider the Rabi splitting with respect to these TPDI resonances which now intersect with the cavity photon mode. The LP-MP Rabi splitting is calculated to be 320 meV, well in excess of the TPDI linewidth for the lowest vibronic peak of 262 meV. Coupled oscillator model fitting suggests the cavity is negatively detuned by 86 meV with respect to the lowest energy TPDI vibronic peak. The Hopfield coefficients for the lower polariton closely match those of the cavity device discussed in Section 7.2 which is negatively detuned with respect to the PTB7-Th resonance, except here the polariton takes excitonic character from TPDI instead of PTB7-Th. Full Rabi splitting and Hopfield coefficient data is given for this sample in Figure C.6 in the Appendix.

Figure 7.14 a) shows the JV curve for this sample, whilst Figure 7.14 b) shows the reduced and normalised EQE and EL. The energy of the LP as determined by the intersection of these curves is 1.67 eV.

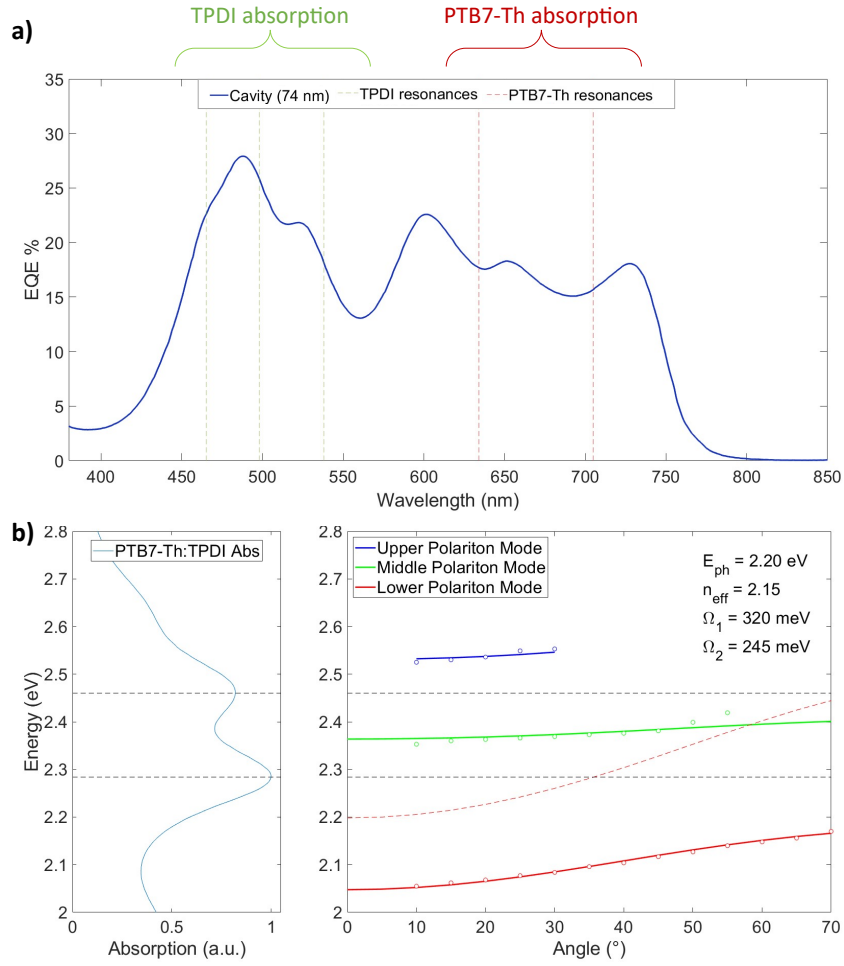


Figure 7.13: a) EQE measurement of a negatively detuned device with respect to the TPDI resonances, demonstrating electrical detection of energy level splitting around the wavelengths of TPDI absorption. b) Angular reflectometry Rabi splitting graph demonstrating optical detection of energy level splitting around the TPDI absorption wavelengths. The sample is negatively detuned (86 meV) with respect to the lowest vibrational resonance of TPDI.

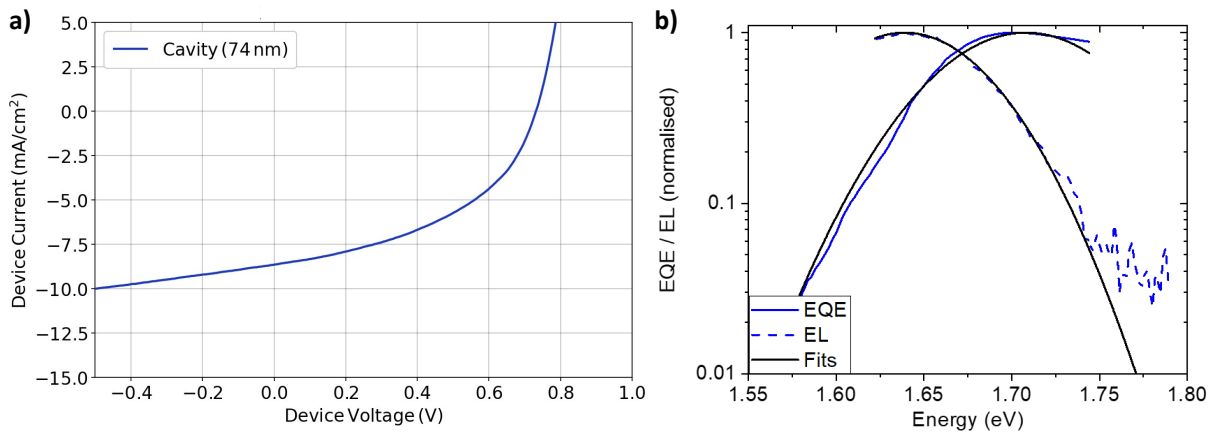


Figure 7.14: a) JV curve and b) normalised and reduced EQE and EL for a negatively detuned cavity device with respect to the TPDI resonances (74 nm).

7.5 Comparison of devices

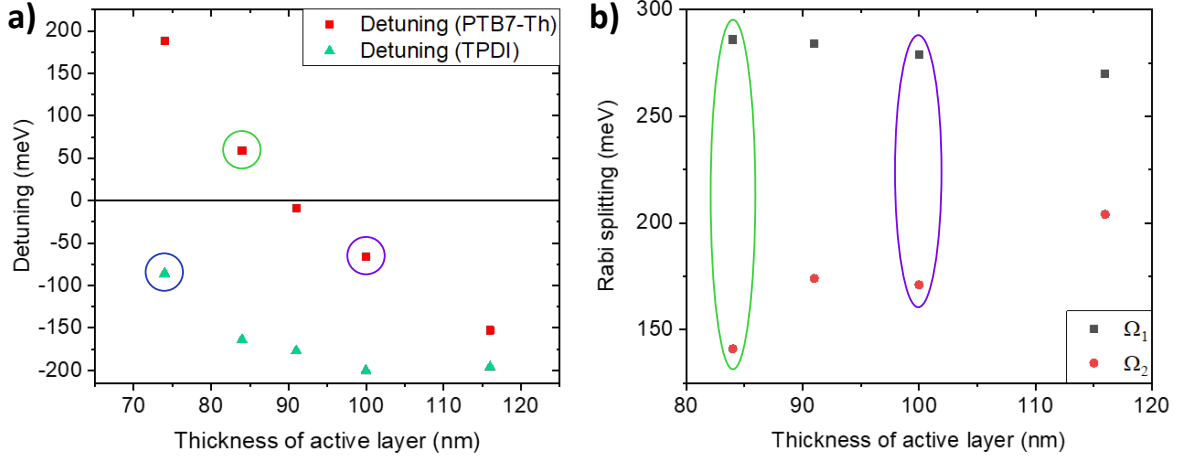


Figure 7.15: a) Detuning of five cavity devices as a function of active layer thickness, as determined by coupled oscillator model fits detailed in Figures C.2-C.6 in the Appendix. Devices discussed in this chapter and the detuning with which they are considered are circled. b) Rabi splitting as a function of active layer thickness for four of the five devices, with the devices discussed in this chapter circled.

In this section, the devices studied thus far are compared. Firstly, the detuning with respect to both the PTB7-Th and the TPDI lowest exciton resonance are shown as a function of active layer thickness for five cavity OPV samples including the three discussed in Sections 7.2-7.4 in Figure 7.15 a). The detunings of the devices with respect to the lowest PTB7-Th resonance range from ~ 150 meV negatively detuned to ~ 200 meV positively detuned. The detunings with respect to the TPDI resonance are also plotted on the same graph. Since the PTB7-Th resonance is the lowest in energy, we expect it to be closest in energy to the charge transfer state and thus the most likely to influence charge generation. Therefore for the most part we consider the detuning of the samples with respect to PTB7-Th, with the exception of the thinnest sample for which we consider the detuning with respect to TPDI, since the higher-energy features are more dispersive than the lower features due to the intersection of the cavity photon mode with the lowest TPDI resonance.

Figure 7.15 b) shows the Rabi splittings between the LP-MP and MP-UP branches for the thickest four devices as a function of active layer thickness. Again, the devices discussed above are circled for clarity. The thinnest device is not included here as it is more coupled to the TPDI resonance and thus does not follow the trend of the previous four devices. For the

devices shown, the first Rabi splitting Ω_1 decreases with increasing thickness/more negative detuning, whereas the second Rabi splitting Ω_2 increases. This can be explained by the shifting of the middle polariton branch to higher energies as the detuning becomes more positive in line with the shifting of the cavity mode.

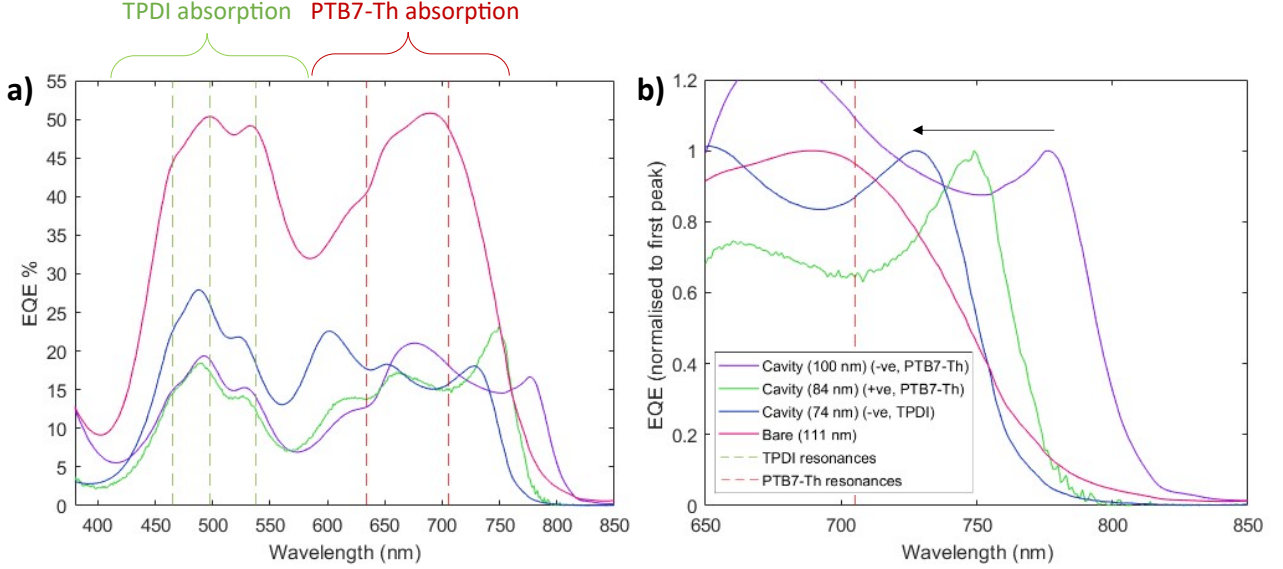


Figure 7.16: Comparison of a) raw and b) normalised (to the LP peak) EQE. Peak splitting is visible around the PTB7-Th resonances and especially around the TPDI resonances for the highest detuned device, demonstrating the emergence of polariton branches in contrast to the bare device and peak shifting to higher energies with increasing detuning. (Common legend)

A comparison of the EQE curves for the three cavity devices and the bare device discussed above in Sections 7.2-7.4 is shown in Figure 7.16. As the detuning of the devices is increased, the locations of the EQE peaks blue shift, since the resonant photonic mode exists at higher energies. All three cavity devices show clear peak splitting in the region of PTB7-Th absorption. As the device detuning increases, the peak offset in the region of TPDI absorption increases as these exciton resonances increase in their interaction with the cavity mode photon as discussed above in Section 7.4. Figure 7.16 b) shows a close-up image of the EQE normalised to the lowest energy peak for the four devices demonstrating the shifting of the LP peak to higher energies as the detuning is increased.

We now consider a comparison of the device JV curves presented in Figure 7.17. Apart from the effect of the additional Ag layer between the cavity and bare devices, there appears to be a trend of increasing J_{SC} with increased positive detuning (decreasing thickness). This is the opposite trend to what is expected of bare devices, since it is expected for bare devices in this

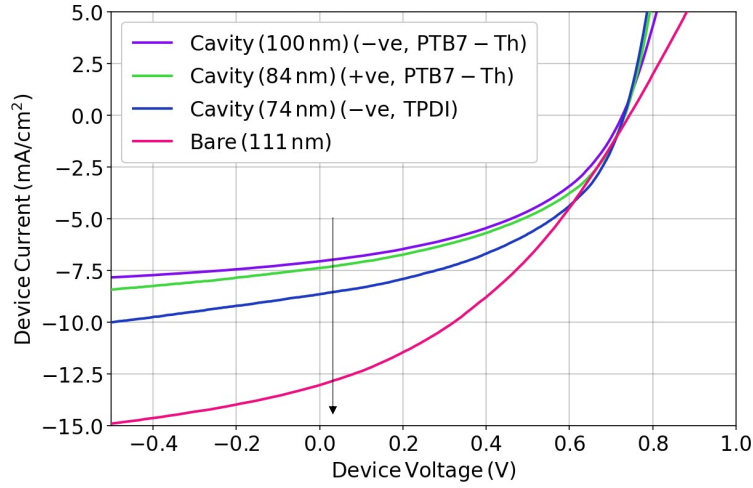


Figure 7.17: Comparison of JV curves for the cavity and bare devices discussed in Sections 7.2-7.4.

thickness range to have an increased J_{SC} with increasing layer thickness. Devices thinner than the ideal thickness are not able to absorb as many incident photons, however thicker devices may also experience losses due to insufficient charge transport leading to charges recombining before they can be extracted at the electrodes, as has been shown previously for PTB7-Th devices.³⁰⁴ Modelling detailed in Chapter 8 suggests that the ideal thickness for cavity devices is significantly thinner than for bare devices (65 nm compared to 105 nm), placing these three cavity devices in the thickness range where device performance worsens as the thickness is increased. The expected value of the J_{SC} for a cavity device of thickness 100 nm is calculated to be $\sim 80\%$ of that of a 74 nm thick device, which is the same as the result measured here.

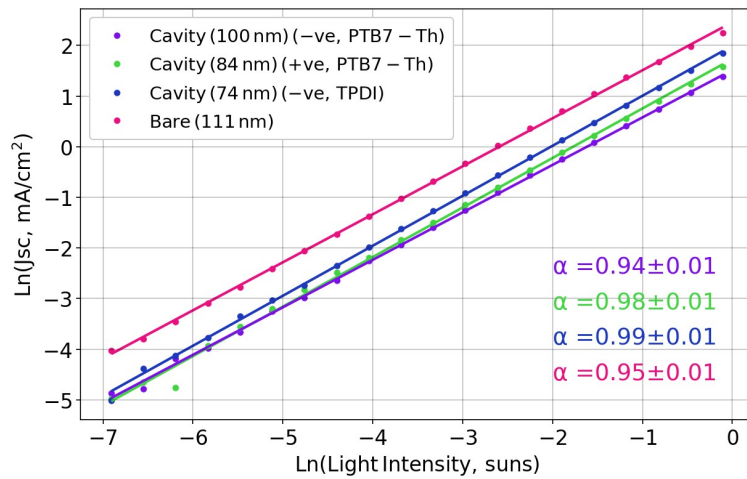


Figure 7.18: Intensity-dependent J_{SC} for the four devices studied in Sections 7.2-7.4. The data is fit according to Equation 3.7 to yield the alpha values written on the graph.

Figure 7.18 shows the intensity-dependent J_{SC} and the corresponding alpha values fit according to Equation 3.7. As the detuning is increased, the alpha values approach unity, demonstrating a reduction in bimolecular recombination. It is possible that the polariton could cause reduced bimolecular recombination due to delocalisation of charge in the device for more positively detuned devices with increased mixing between the PTB7-Th and TPDI excitons. This is discussed more in Chapter 8 in the context of the Langevin reduction factor.

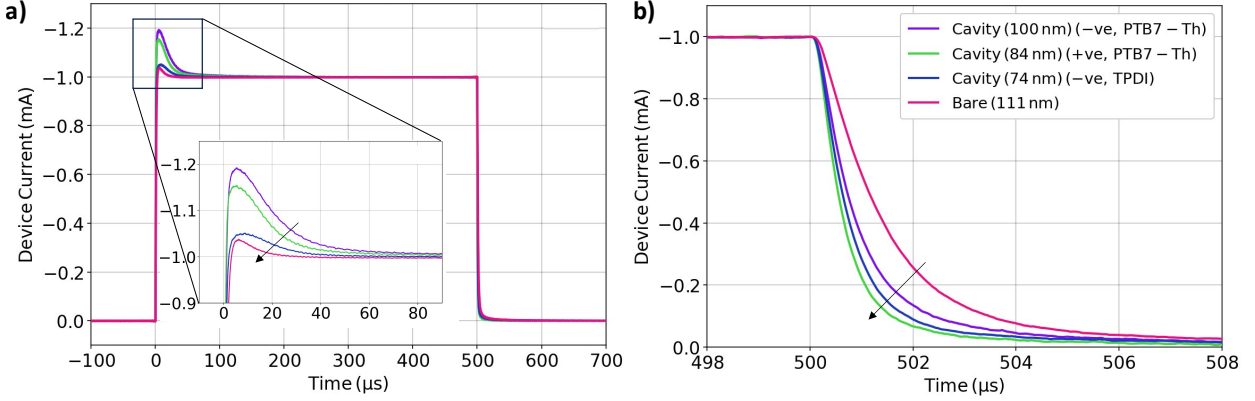


Figure 7.19: a) TPC response for the bare and three cavity devices discussed in Sections 7.2-7.4 measured at short circuit and 90% light intensity, normalised to the value of the plateau. All devices exhibit an overshoot. b) A close-up of the photocurrent response showing the fall times of the devices. (Common legend)

TPC measurements are shown for the four devices in Figure 7.19. The full set of TPC measurements for various bias and intensity parameters are shown in Appendix section C.3. All four devices exhibit an overshoot which we ascribe to charge trapping or extraction issues as discussed in Section 7.2. We see that the more positively detuned the device, the lower the current overshoot with respect to the plateau value, and the less the device appears to suffer from these issues. This also agrees with the increased charge extraction as determined by the J_{SC} values found in Figure 7.17. It may be the case that more positively detuned cavities with higher LP energies as discussed below are able to bypass shallow (low-lying) trap states. It may alternatively be the case that increased optical mixing between the two domains for more positively detuned devices reduces the effect of trap states and leads to a reduced current overshoot. However, the question of the origin of the trap states in the cavity devices as compared to the bare device remains, and we cannot disentangle the effect of poor extraction since this also leads to the appearance of trap states.

Figure 7.19 b) shows a closer look at the fall time of the TPC response. Just as for

Figure 7.6 b), if extraction issues in cavity devices were to be completely responsible for the current transients, we would expect the charges to be extracted more slowly; yet here it is the bare device which has the slowest extraction of charge.

We turn next to a discussion of the charge carrier lifetimes as a function of carrier density shown in Figure 7.20. The more positively detuned the device, the longer the charges live inside the device. Again, this demonstrates more favourable device performance for more positively detuned devices, and again, we propose that this may be due to increased excitonic mixing between the two material domains and the formation of a delocalised polariton state leading to reduced bimolecular and trap-assisted recombination.

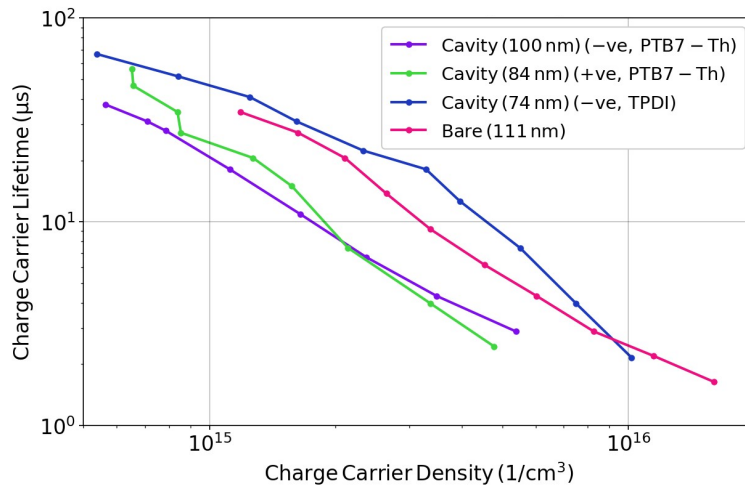


Figure 7.20: Charge carrier lifetimes as a function of carrier density for the four devices, extracted from TPC and TPV measurements.

Finally, we compare the impact of strong coupling on the bandgap energy by fitting reduced and normalised EQE and EL spectra to Equations 7.1 and 7.2. For cavity devices this refers to the energy of the LP. As discussed in Section 7.2, this method is a way of determining the LP energy by electrical measurement and is complimentary to the optical measurement of angular reflectometry. The higher the detuning of the device with respect to the PTB7-Th resonance, the higher the first Rabi splitting Ω_1 , and as shown in Figure 7.21, the higher the LP energy. This follows from the blue-shifting of the EQE and EL with increasing positive detuning of the devices.

It is important to consider the effect of photon filtering and ensure that the difference between shifted EL and changed outcoupling of light due to changed cavity dimensions is well understood. Photons in resonance with the cavity dimension will be sustained by constructive interference, whereas all other energies experience destructive interference and cannot be

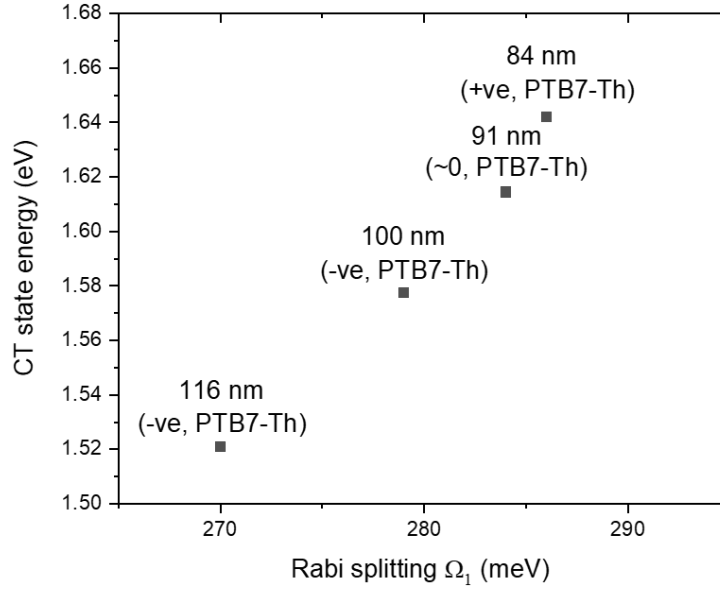


Figure 7.21: LP energy of four cavity devices as a function of Ω_1 (LP-MP) Rabi splitting.

sustained in the cavity. This effect is the cause for the dips in reflectance (or peaks in 1-reflectance) seen during angular reflectance measurements such as that in Figure 6.2 and 6.3 in Chapter 6. Therefore, it is important to consider whether the shifted EL peaks are simply due to the interaction between the cavity mode and the underlying emission spectrum such that only certain wavelengths can be outcoupled and measured.

To investigate photon filtering, the electroluminescence from the bare device was multiplied by the transmission of three polystyrene Fabry-Pérot cavities and compared to the EL of the cavity devices as detailed in Appendix section C.4. A similar procedure is performed for the EQE spectra. The effect of photon filtering is unable to reproduce the observed EQE and EL, just as the effect of the cavity mode is unable to reproduce the EQE peak splitting as detailed in 6.3. Rather, these effects must be due to coupling.

The system of measured energy levels is summarised in Figure 7.22 for the three cavity devices studied in Sections 7.2-7.4. The PTB7-Th S_1 energy levels are determined by the absorption maxima of a thin film. The S_1 state couples to the E_0 cavity mode to produce the LP, MP and UP branches with energies determined by fits to the angular reflectance (AR) data. The LP energies as determined electrically from the intersection of the reduced and normalised EQE and EL are also shown (EQE/EL). Dashed lines indicate peak splitting of the S_1 state due to strong light-matter coupling, and the V_{OC} is also shown.

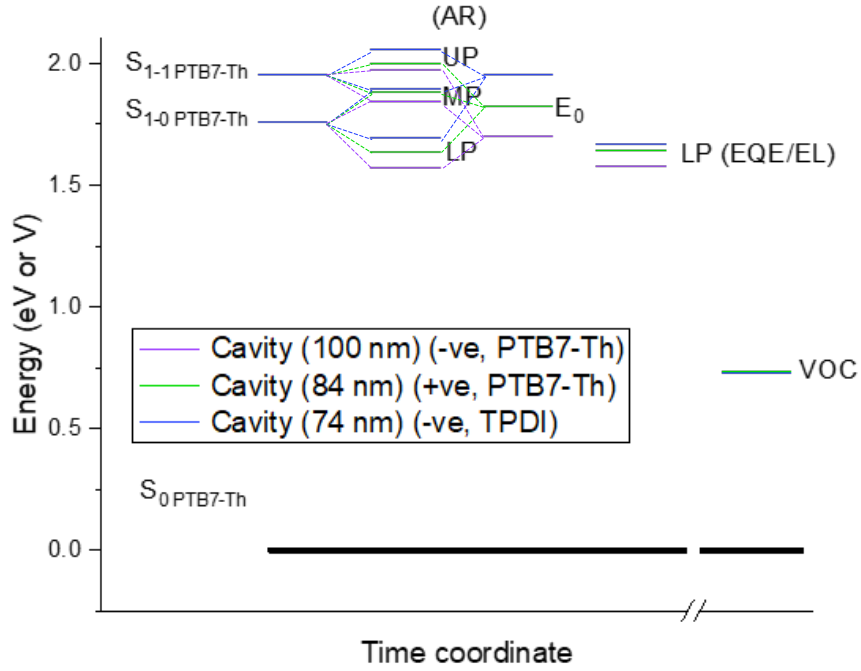


Figure 7.22: Energy levels for cavity devices studied in Sections 7.2-7.4. The PTB7-Th S_1 levels are determined by film absorption maxima, the E_0 levels by the cavity photon at 0° incidence, and the LP, MP and UP levels by fits to the angular reflectance (AR) data as well as by the intersection of reduced and normalised EQE and EL spectra for the LP.

Since the creation (EQE) or annihilation (EL) of charge also involves the creation or annihilation of CT states, it may be the case that the act of strongly coupling the materials in the devices causes the accessibility of certain CT states to change, such that a different state is accessed during strong coupling than would otherwise be the case for a bare device. CT states often exist not at a singular energy but rather as part of a manifold of states spread over a potential energy surface, caused by disorder inherent to organic materials. Strong coupling has been proposed to enable polaritons to select a subset of excitonic states within a broadened ensemble of states,³⁰⁵ contrary to earlier suggestions that splitting is independent of the homogeneous or inhomogeneous nature of electronic states.³⁰⁶ Since the LP energy detected through electrical measurements shifts as a function of detuning, it is possible that strong coupling can alter which CT state is accessible for a particular material. A similar effect was observed by Nikolis et al.²⁰¹ who also found that the measured CT state energy was affected by strong coupling for SubNc/C₆₀ strongly coupled OPV devices.

In contrast to the LP energy, the V_{OC} remains unaffected by coupling for this experiment, as was also seen by Nikolis et al. This implies that whilst the properties of the material can be changed by strong coupling, the V_{OC} is unable to be manipulated in the same way. Put another

way, any changes to the recombination in the device as a result of the strong coupling, such as that suggested by the differing FF in Figure 7.2 b), are not sufficient enough to effect a change in the V_{OC} . Previous work in our group has suggested that devices with poor charge mobilities are required in order to see a reduction in recombination losses in strongly coupled devices.³⁰² It may be that the mobilities of the system studied here are sufficiently high as to prohibit the observation of strong-coupling induced enhancements.

The difference in energy between the optical bandgap and the CT state energy is commonly referred to as the driving force for charge separation. Non-fullerene acceptors are known for their ability to achieve charge separation with little driving force, in contrast to fullerene acceptors which require a driving force of ~ 0.3 eV.^{21,307} If the detuning of the cavity devices can be used to select a certain CT state energy, then this can also be used to influence the driving force for charge separation in the material. This forms an interesting angle for a variety of future investigations, since the effect of driving force on the device performance can now be studied without the need to change materials and add associated complexity. Unpacking the reasons behind the lack of requirement for a driving force in non-fullerene acceptors is a topical area of debate, and thus is also an exciting avenue for which to pursue further work.

The energy difference between the CT state and the V_{OC} determines the total loss after CT state formation in the device, and is comprised of both the radiative V_r and non-radiative V_{nr} voltage losses.³⁰³ Again, if the detuning of the cavity devices can be used to select a certain CT state energy, then this can also be used to influence the radiative and non-radiative losses in the device. This is also an intriguing avenue of future work as discussed in Section 9.2.5.

7.6 Conclusions

In conclusion, coupled OPV devices were successfully fabricated and peak splitting was demonstrated both optically through angular reflectometry and electrically through EQE measurements for a range of device detunings.

In Section 7.2, a negatively detuned cavity device was compared to a bare device fabricated with the same processing conditions. The cavity device was found to have a higher J_{SC} than predicted, taking into account the effect of the semi-transparent additional Ag layer. There was also an appreciable difference in the fill factor between the two devices, with the cavity device again outperforming the bare device, suggesting reduced recombination for cavity devices.

Complementary EQE and Rabi splitting techniques demonstrated electrical and optical detection of peak splitting. Intensity-dependent J_{SC} and V_{OC} measurements indicated low bimolecular recombination but significant trap-assisted recombination in the devices. TPC measurements also revealed a peak overshoot characteristic of charge trapping or extraction issues, which are more significant in the cavity device. The cavity device also surprisingly appears to have a shorter charge carrier lifetime for a particular charge carrier density measured through TPC and TPV compared to the bare device. Finally, the LP energy is found electrically by the intersection of the reduced and normalised EQE and EL spectra in addition to fitting of the optical angular reflectometry data, and is found to be slightly red-shifted for the cavity device by ~ 11 meV.

In Section 7.3, a device having positive detuning with respect to the lowest PTB7-Th resonance is studied. This causes the lower polariton peak to take on more excitonic character than photonic character. Peak splitting is demonstrated optically and electrically, and the JV curve and LP energy determination are shown.

Similarly, in Section 7.4, a device having negative detuning now considered with respect to the lowest TPDI resonance is studied. This produces more dispersive polariton features around the TPDI resonances, as opposed to the PTB7-Th resonances. Again, peak splitting is demonstrated optically and electrically, and the JV curve and LP energy determination are shown.

Comparisons are drawn between cavity devices of different detunings in Section 7.5. The detuning and Rabi splitting are studied as a function of active layer thickness. The LP-MP splitting is seen to increase as a function of active layer thickness, whilst the MP-UP is seen to decrease. This can be interpreted as a shift of the MP to higher energies with increasingly positive detuning. EQE peaks are seen to shift to higher energies for more positively detuned devices, and the peaks around the TPDI resonance become more offset as the cavity photon mode interacts more with the TPDI exciton resonances.

For the electrical performance of the devices, the JV curves show an increased J_{SC} with increasingly positive detuning. However, this is likely due to thickness effects only as will be discussed in Chapter 8. Intensity-dependent J_{SC} measurements demonstrate reduced bimolecular recombination for more positively detuned devices. TPC measurements show an overshoot especially for cavity devices demonstrating the presence of charge trapping or extraction issues, which are reduced for more positively detuned devices. Finally, the electrically determined

LP energy for each device is seen to be affected by strong coupling according to the detuning. Namely, the LP is higher in energy for thinner devices due to their positive detuning.

In summary, we see that we are able to change the properties and performance of OPV materials through strong light-matter coupling without changing the material itself. In order to gain a deeper understanding of the performance of the bare and cavity devices studied experimentally, we turn to simulations in Chapter 8. We explore the effect of device thickness as distinct from cavity detuning and the effect of the additional Ag layer, reproduce the TPC current transient and fit the JV curves reported here.

Chapter 8

Drift-diffusion simulations on TPDI-based OPV devices

8.1 Introduction

In Chapter 7, we have studied coupled TPDI-based devices as a function of detuning. This material system is chosen due to its higher performance than the PDI-based system as shown in Chapters 4 and 5 and ability to achieve strong coupling as shown in Chapter 6.

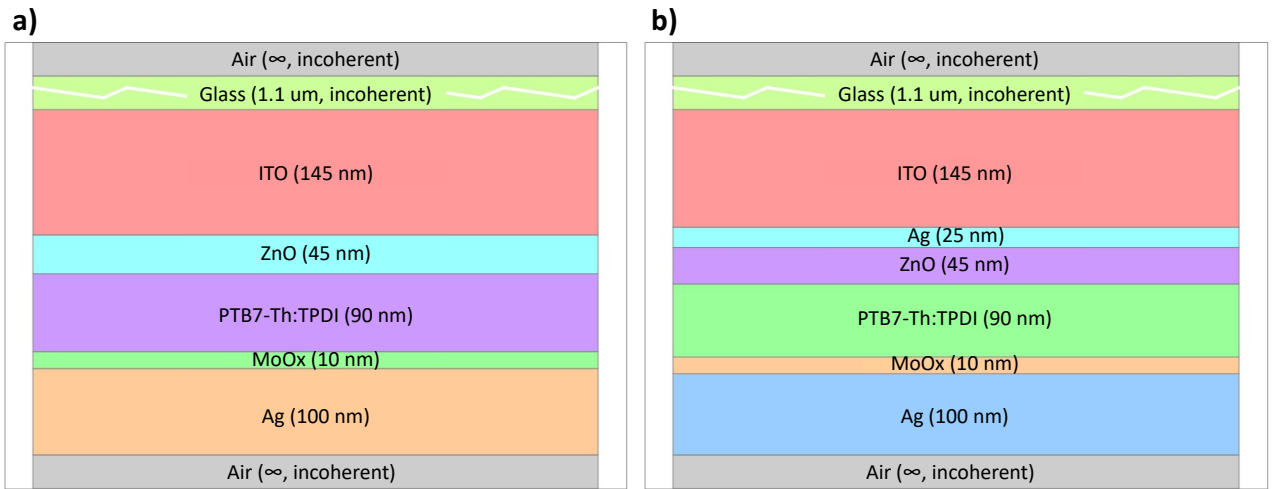


Figure 8.1: Device layer structure for a) bare devices and b) cavity devices simulated in Setfos.

In this chapter, simulations are performed for PTB7-Th:TPDI OPVs using the Fluxim modelling suite Setfos to compare the performance of bare and cavity devices in the absence of strong coupling. Despite being an advanced computational package for the simulation of OPV devices, this package does not include the effects of strong coupling. As a result, these simulations provide further information on device performance separate to the effects of strong

coupling, enabling the distinction between polaritonic effects and thickness-induced effects. Traps are also included in order to mimic the TPC overshoot seen in Chapter 7. Finally, experimental curves are fit to determine constants such as the series and shunt resistance, density of charged sites and langevin recombination factor in bare and cavity devices in order to reveal information about the effects of strong light-matter coupling on device performance. More details including the parameters used in the simulations and their justification are provided in Chapter 2.

Devices are built in the Setfos program as shown in Figure 8.1 for bare and cavity devices. As was the case for experiments, the only difference between the two configurations is the addition of a partially transmissive Ag layer in between the ITO and the ZnO layers. Illumination occurs on the top (glass) side of the device.

8.2 Bare and cavity device compared

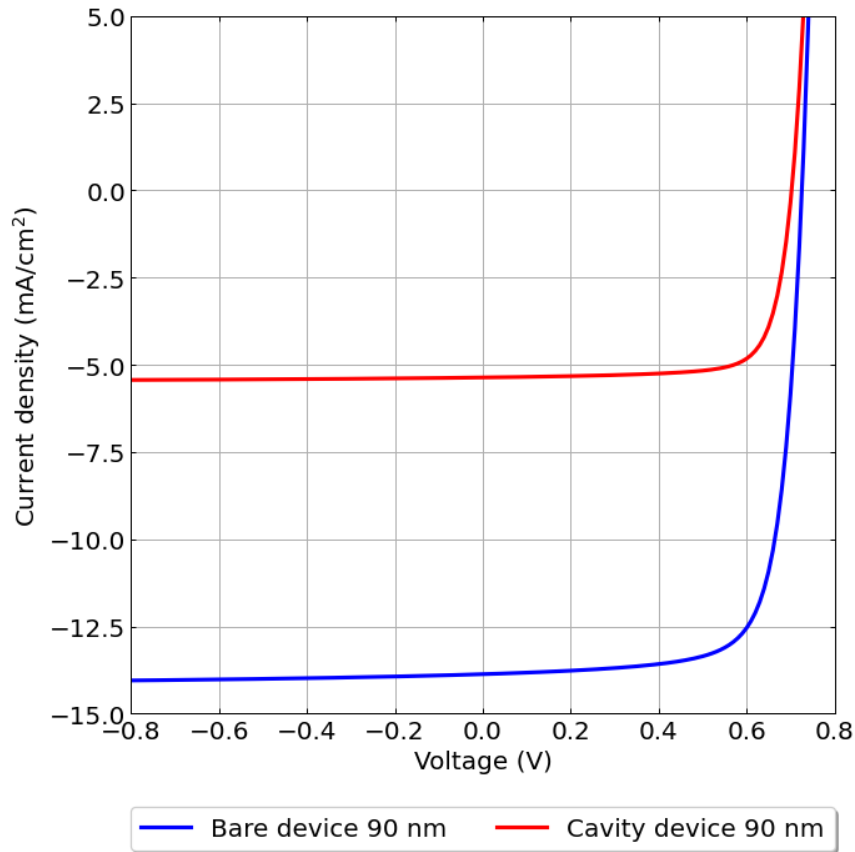


Figure 8.2: Simulation results for a bare and a cavity device differing only by the presence or absence of the partially transparent Ag layer. The active layer was set at 90 nm thick.

JV curves for the simulated bare and cavity devices are shown in Figure 8.2. The active layer was set at 90 nm thick and no recombination mechanisms were included. As is expected, the partially transmissive nature of the additional Ag layer restricts the number of photons that reach the active layer in the cavity device, causing a larger than two-fold reduction in the J_{SC} . The V_{OC} is also reduced by ~ 25 meV, likely due to the reduced built-in field inside the device due to the lower concentration of charges.

The wavelength-resolved EQE of the two simulated samples is also shown in Figure 8.3. As expected, we see a dramatic decrease in EQE for the cavity device due to the reduced light reaching the active layer.

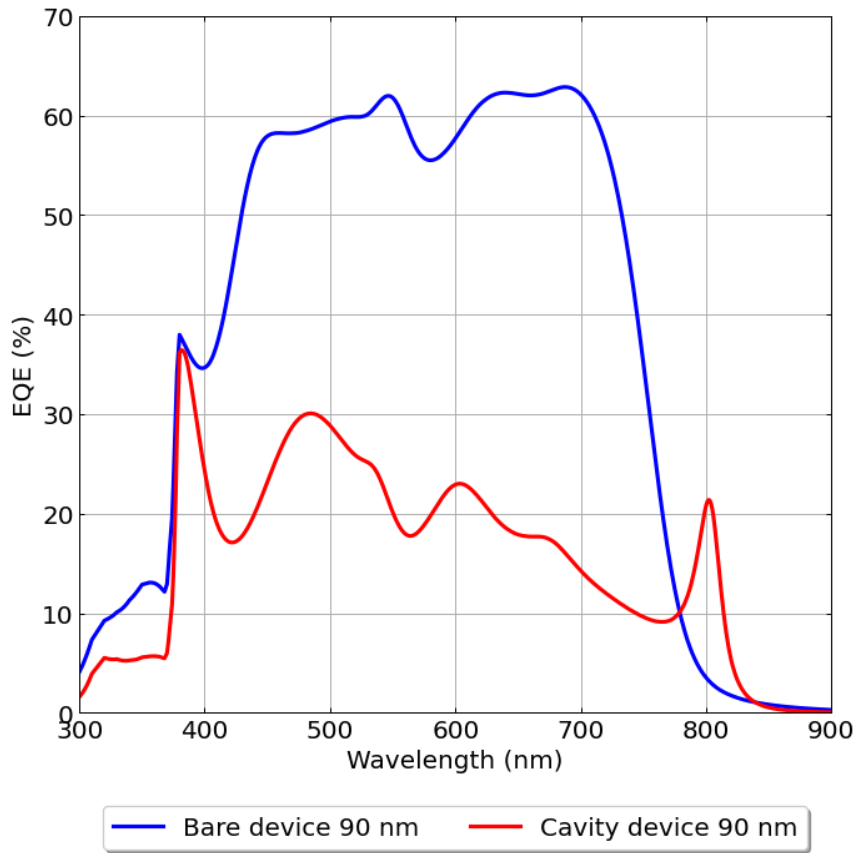


Figure 8.3: Simulated EQE for bare and cavity devices with active layer thicknesses of 90 nm.

Care must be taken in the interpretation of the EQE of the cavity device presented in Figure 8.3. It is deceiving to compare the similarities of this result to that of Figure C.12 where the effect of coupling and peak splitting is distinguished from photon filtering since one might be tempted to conclude that coupling is present in the simulation in Figure 8.3. The Setfos modelling package is advanced in its treatment of OPV devices, however it does not have the

capability to simulate coupling. Therefore, whilst the peak at 800 nm appears comparable to the lower polariton features in Figure C.12, in this case it arises simply due to the increased absorption caused by the presence of the photonic mode at this wavelength. Albeit small, there is still some absorption by the blend film at this wavelength, as shown by the non-zero EQE of the bare device at 800 nm. In addition to the feature at 800 nm which corresponds to the first photonic mode, there is also a feature at approximately half the wavelength at ~ 380 nm, which corresponds to the second photonic mode. Hence we see that great care must be taken in interpreting these spectra so that the presence of the photonic mode and its effect on film absorption is not confused for strong coupling.

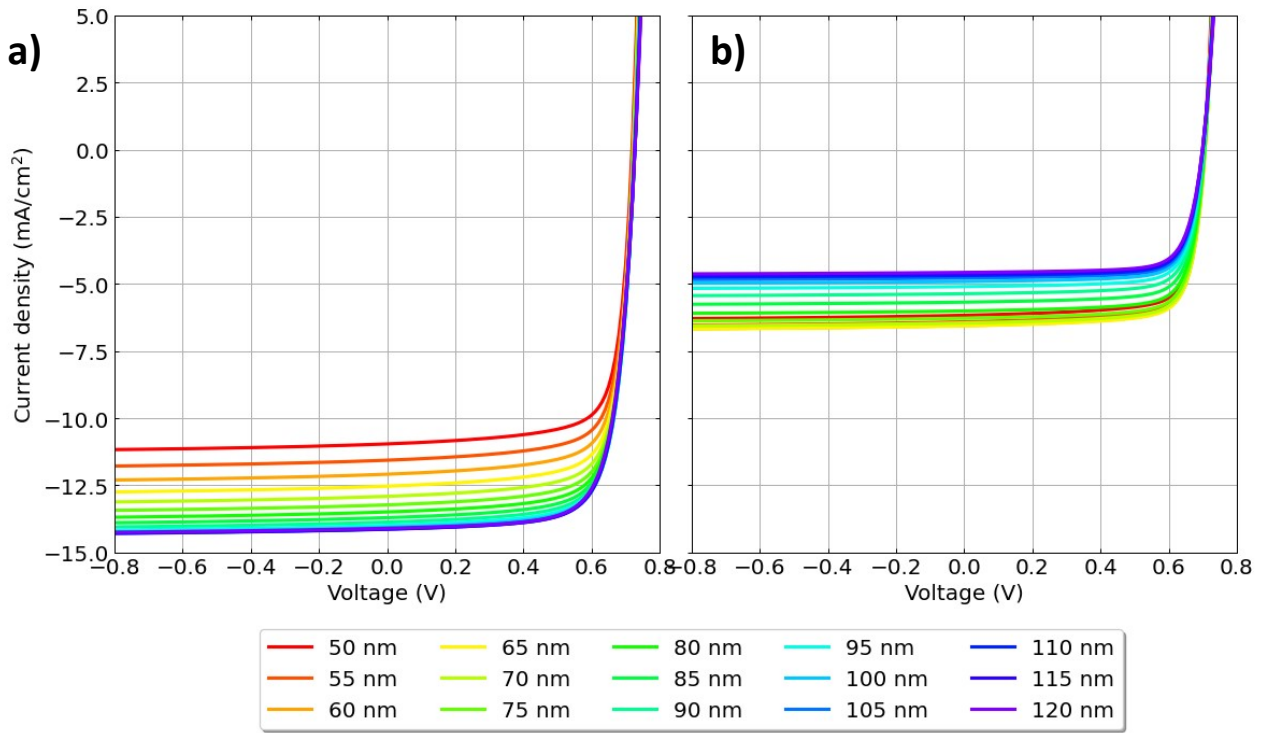


Figure 8.4: JV curves for a) bare and b) cavity devices with varying thicknesses.

We performed simulations as a function of thickness to demonstrate the effect of changing the active layer thickness on the current generation and the EQE of the device. Figure 8.4 demonstrates an increase in the current generation for the bare device with increasing thickness, whereas the current produced in the cavity device peaks around 65 nm and then decreases with increasing thickness. This is also clear to see in Figure 8.5 a) where the J_{SC} is plotted as a function of thickness. Figure 8.5 b) then displays the overall device PCE as a function of thickness, reflecting maximum performance at the point of maximum current generation.

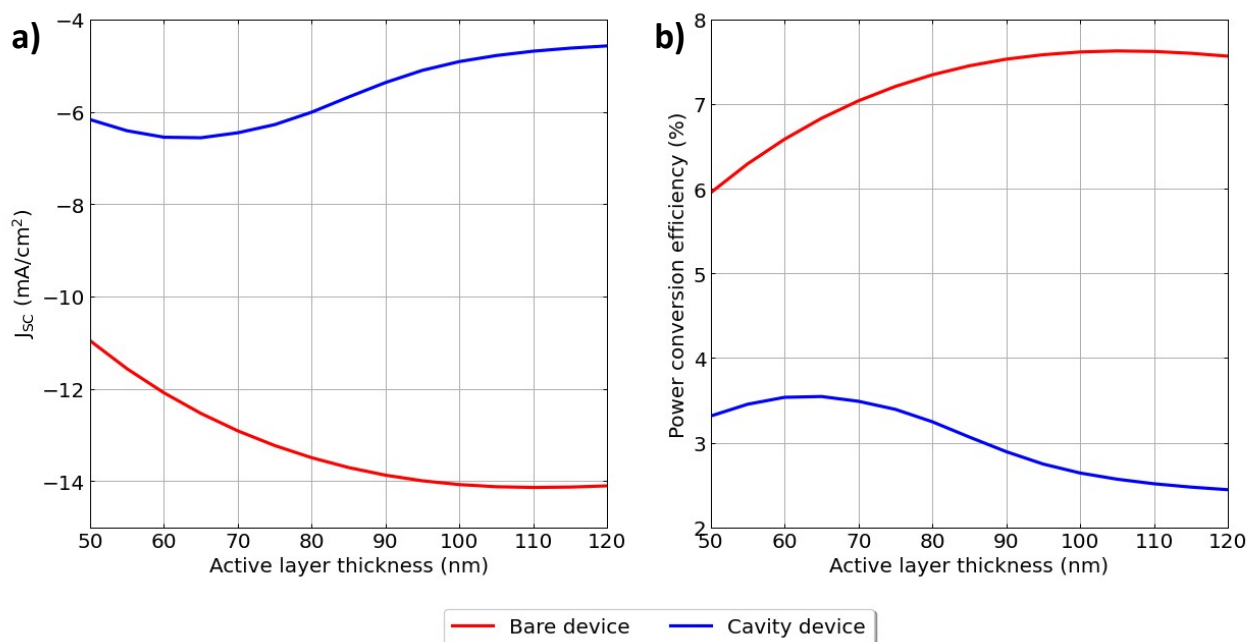


Figure 8.5: a) J_{SC} and b) PCE for bare and cavity devices of varying thicknesses.

This is in line with what would be expected for the addition of a partially reflective layer at the cathode. In the bare device, increasing the active layer thickness allows for increased chance of absorption of the photon. In the presence of recombination, increasing the thickness of the device will also increase the number of recombination events that each charge carrier experiences as it traverses through the cell on its way to the electrode. This results in a trade-off where thicker active layers can result in a higher amount of photon absorption but also higher recombination losses, leading to a peak in performance where both factors are balanced. Here, in the absence of recombination, the bare device performance simply improves with increasing thickness until a point where only marginal improvement in charge generation is made, at which point the built-in field becomes weaker with increasing distance between the electrodes, leading to a slight decrease in overall performance.

In contrast, the cavity device current peaks at ~ 65 nm. This is likely due to the fact that the additional Ag mirror allows more of the photons in the cell to be absorbed for a particular thickness compared to the bare device, as the additional reflective surface allows the photon to experience more passes through the active layer and thus have more chance for absorption. Even without considering any recombination loss mechanisms, the device current decreases with increasing thickness for > 65 nm, which is the range studied experimentally in Figure 7.17

in Chapter 7. Thus the experimentally observed relationship between the current production and the thickness of these devices is a pure question of device geometry rather than one of polaritonic effects, since it is likely that the cavity devices studied were simply thicker than the ideal active layer thickness for achieving maximum charge generation. The magnitude of the J_{SC} change between the cavity devices observed through experiments in Figure 7.17 and through simulation in Figure 8.5 is also similar, with both methods suggesting $\sim 80\%$ of the J_{SC} value of a 74 nm thick cavity device remains for a 100 nm thick cavity device.

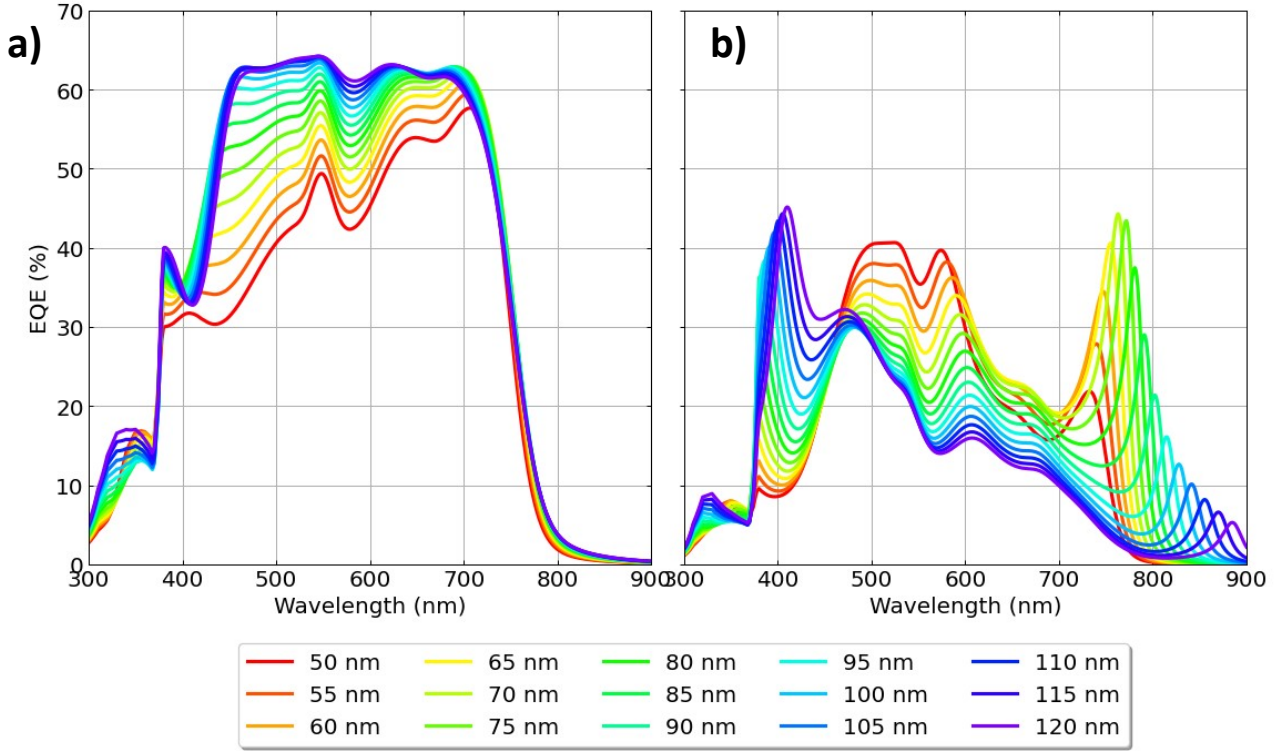


Figure 8.6: Thickness dependent EQE simulated measurements for a) bare and b) cavity devices.

Next, we present thickness dependent EQE simulations for bare and cavity devices in Figure 8.6 a) and b). For the bare devices, the increased absorption in thicker devices has the effect of levelling out the EQE. In other words, the wavelengths of lower absorption are the most affected by increasing device active layer thickness, causing the EQE to appear flat. In contrast, the EQE of the cavity device is heavily affected by the location of the photonic mode, which shifts to lower energies with increasing active layer thickness.

It is no surprise that the EQE of the devices, in particular the bare device, bears great similarity to the absorbance of the thin film. The absorption, reflectance and transmission of

bare and cavity devices are shown in Appendix section D.1. Again, it is possible to see the flattening or ‘levelling out’ of the absorption profile of the bare devices with increasing thickness, whereas the absorption of the cavity devices is dictated heavily by the photonic mode sustained by the cavity.

Whilst the shifting photonic mode may appear similar to the shifting LP peak in experimentally observed EQE of strongly coupled devices, it is important to make the distinction clear between them. We refer again to Appendix section C.4 where a discussion of the subtle differences between EQE peak splitting due to coupling and photon filtering such as that shown in these simulation results is discussed.

8.3 Time-dependent modelling

Next, we use simulations to investigate the time-resolved current response of the devices measured through TPC.

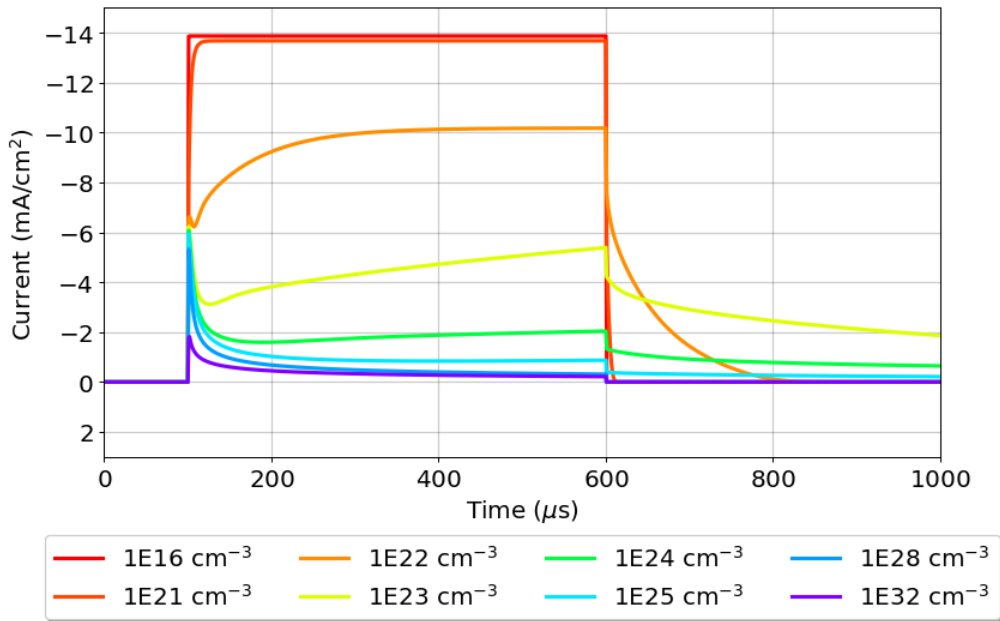


Figure 8.7: Simulated TPC curves for a bare PTB7-Th:TPDI device with varying electron trap densities at short circuit. The hole trap density is fixed to $1 \times 10^{17} \text{ cm}^{-3}$.

We introduce charge trapping to the simulations discussed in Section 8.2 for a bare PTB7-Th:TPDI device in order to mimic the transient behaviour of bare and cavity devices observed in Chapter 7. The hole trap density is set to $1 \times 10^{17} \text{ cm}^{-3}$, whereas the electron trap density is varied from 1×10^{16} to $1 \times 10^{32} \text{ cm}^{-3}$. At 0 V offset, i.e. short circuit conditions,

the TPC overshoot characteristic of charge trapping appears for electron trap densities above $1 \times 10^{23} \text{ cm}^{-3}$ as shown in Figure 8.7. The same information for forward and reverse bias (0.5 and -0.5 V respectively) is shown in Figure D.3 in the Appendix. An electron trap density of $1 \times 10^{25} \text{ cm}^{-3}$ is chosen for further simulations as this is the lowest trap density that produces an overshoot and plateau feature as seen in experimental measurements of the devices in Figure 7.19 and in Appendix section C.3.

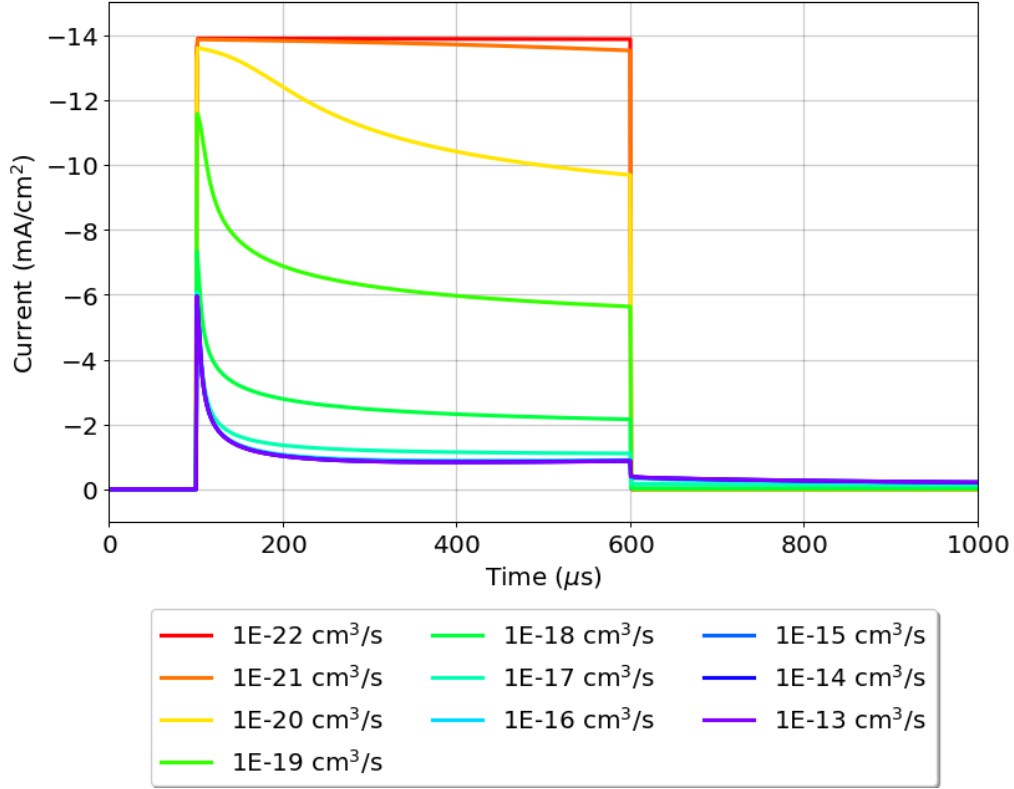


Figure 8.8: Simulated TPC curves for varying electron capture rates. The electron trap density is fixed to $1 \times 10^{25} \text{ cm}^{-3}$ and the hole trap density to $1 \times 10^{17} \text{ cm}^{-3}$.

To investigate the dynamics of charge trapping, the capture and decapture rates of the electron traps were varied. First, the capture rate was varied from $1 \times 10^{-22} \text{ cm}^3/\text{s}$ to $1 \times 10^{-13} \text{ cm}^3/\text{s}$. The results for short circuit are shown in Figure 8.8 and for forward and reverse bias in Figure D.4 in the Appendix. As the electron capture rate increases, both the value of the plateau and the timescale of the disappearance of the overshoot peak decrease, consistent with greater trapping effects.

The effect of changing the illumination level on the appearance of the transient overshoot is investigated in Figure 8.9, and the same information is shown for forward and reverse bias in Figure D.5 in the Appendix. Although increasing light intensity results in higher current

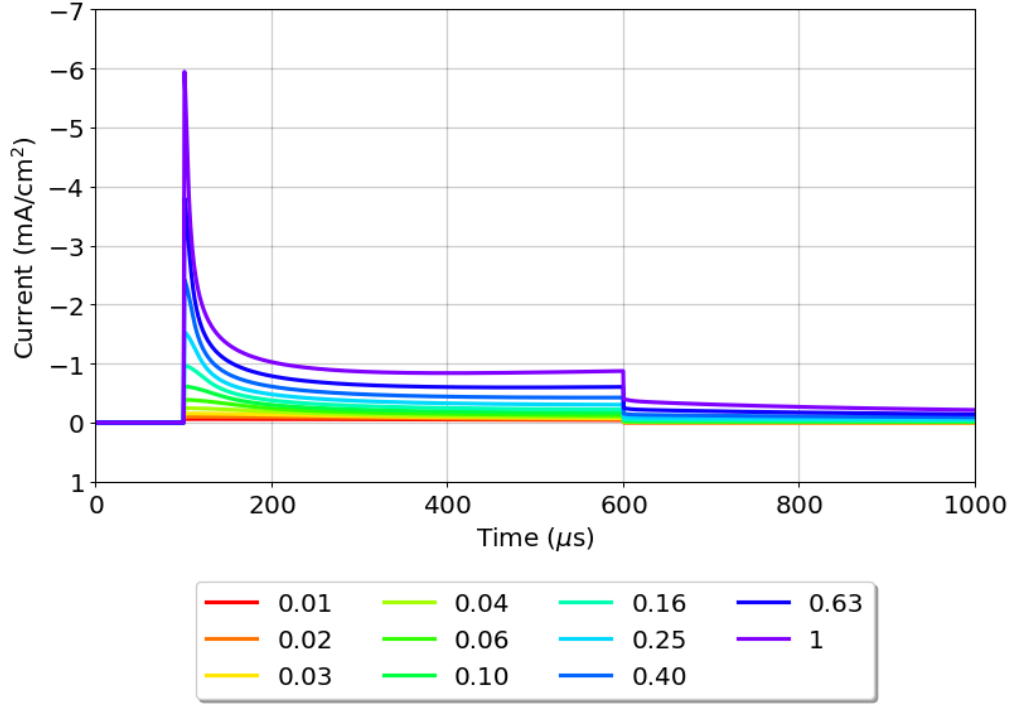


Figure 8.9: Simulated TPC curves for varying illumination levels at short circuit. The electron trap density is fixed to $1 \times 10^{25} \text{ cm}^{-3}$ and the hole trap density to $1 \times 10^{17} \text{ cm}^{-3}$.

production, the value of the plateau with respect to the magnitude of the peak decreases with increasing light intensity due to the annihilation of charge inside the device. This suggests that the role of trapping is increasingly important for higher illumination intensities. This effect matches well with what is seen in the experimentally measured TPC curves.

Since we can qualitatively reproduce the current overshoot seen experimentally by varying the electron trap density, electron capture rate, illumination intensity and applied bias, we see that charge trapping is a viable explanation for the TPC overshoot observed in Figure 7.19. However, extraction issues would also produce the same result, and must also be considered as a possible cause of the TPC overshoot.

In order to move from a qualitative to a quantitative description of device behaviour, the experimentally measured JV curves from the devices presented in Chapter 7 are fit to a device model in the section below. Note that only JV curves can be fit in this way; we are not aware of the functionality to fit transient data in the same way.

8.4 Fitting experimental JV curves

In this section, we introduce additional variables to the simulation parameter space and perform simulations which are integrated with the device measurement system Paios. Specifically, we aim to match the JV curves produced from simulations to those measured experimentally and reported in Chapter 7. We fit for the Langevin recombination factor to give an understanding of recombination effects, the density of chargeable sites to give an understanding of trap densities, and the series resistance to give an understanding of device extraction processes.

In order to achieve a good fit to the experimentally measured JV curves, we introduce the parameters in Table 8.1 at their starting value and let the fitting algorithm run until convergence is reached.

Table 8.1: Parameters used in Setfos simulations

Parameter	Start value
Density of chargeable sites ($1/\text{m}^3$)	1×10^{24}
Optical Charge generation efficiency	0.55
Langevin recombination efficiency	0.8
Series resistance (Ω)	300
Parallel resistance ($\text{M}\Omega$)	200

The results of the fit for a bare and cavity device with the same geometry as those discussed in Section 7.2 are shown in Figure 8.10 a) and b), whilst the results of the devices discussed in Sections 7.3 and 7.4 are shown in Figure 8.10 c) and d). The bare cavity is fit across a large portion of the voltage range (-0.5 to 1.0 V), whereas the cavity devices are fit to a restricted range (-0.2 to 1.0 V) so as to place less emphasis on the reverse bias measurement where some current leakage takes place.

The resulting fit parameters at the point of convergence are reported in full in Table 8.2. The fits suggest minimal changes to the charge generation efficiency, demonstrating that the differences in device performance are caused by processes taking place after the charges have been generated.

As the extent of positive detuning is increased (reading down the table) for cavity devices, the Langevin recombination factor is significantly reduced. This is a promising step towards understanding the ability of polariton formation to improve recombination processes occurring within the device. This result agrees with the trend seen in Figure 7.18 where increasing alpha values suggest reduced bimolecular recombination for more positively detuned devices. It also

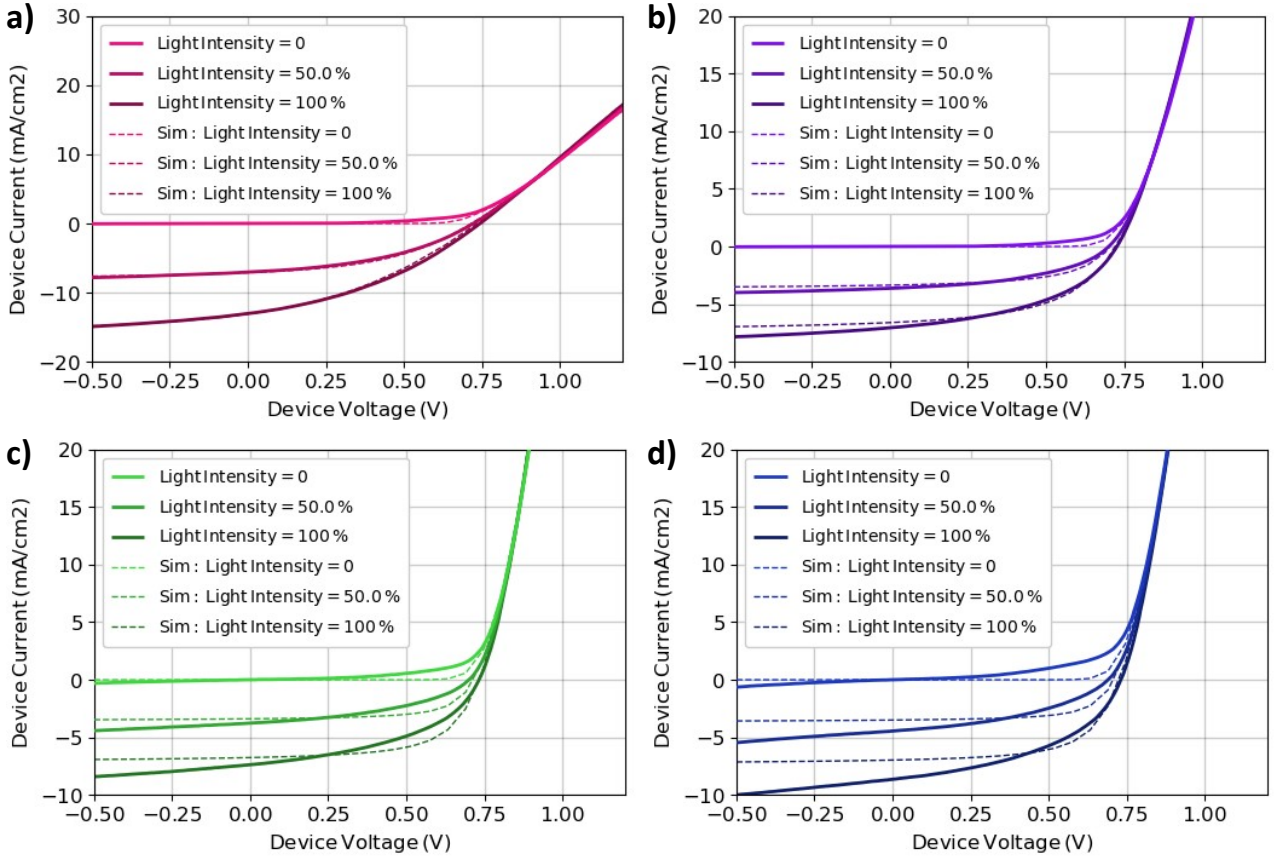


Figure 8.10: Comparison of experimentally measured and simulated JV curves for a) the bare device and b) the negatively detuned cavity device, both discussed in Section 7.2, c) the positively detuned cavity device discussed in Section 7.3 and d) the negatively detuned device with respect to TPDI resonances discussed in Section 7.4.

agrees with the observation that charges live longer (accounting for their densities) as shown in Figure 7.20. Finally, it also agrees with the trend of a higher J_{SC} seen for devices of increasingly positive detuning in Figure 7.17, although as mentioned before care must be taken to disentangle the possible effect of improved J_{SC} from polaritonic effects from the known effect of simple decreases to device thickness as demonstrated in Figure 8.5.

The density of chargeable sites is increased as the extent of positive detuning increases. This is the opposite trend from what is expected from the size of the TPC overshoot in Figure 7.19, since an increased density of chargeable sites should lead to an increase in the peak overshoot for more positively detuned devices, or rather a decrease in the plateau value, which is the opposite of what is seen. Reconciling this observation with the results of Chapter 7 makes for a critical piece of future work.

In order to further understand charge extraction in the devices, the fitted series resistance

Table 8.2: Outputs of Setfos-Paios integrated simulations

Sample type	Thick- ness used in sim. (nm)	Density of chargeable sites ($\times 10^{25}$ $1/\text{m}^{-3}$)	Gener- ation efficiency	Langevin Recomb- ination	Series resist- ance (Ω)	Parallel resist- ance ($\text{M}\Omega$)
Bare (Section 7.2)	90	1.06	0.56	0.78	312.42	199.45
Cavity: -ve (PTB7) (Section 7.2)	90	0.86	0.70	0.87	27.34	100.03
Cavity: +ve (PTB7) (Section 7.3)	76	1.35	0.68	0.20	10	100.06
Cavity: -ve (TPDI) (Section 7.4)	59	1.68	0.70	0.18	12.57	162.74

is studied as a function of cavity detuning. The series resistance is far improved for the cavity devices compared to the bare device, with an average of $50\ \Omega$ for the cavity devices compared to $> 300\ \text{M}\Omega$ for the bare device. This shows in the JV curves as the tangent to the curve at V_{OC} . Silver is known to have the highest conductivity of all metals and has a resistance two orders of magnitude less than that of the ITO layer on the substrates used here.³⁰¹ Therefore the additional Ag layer improves charge conductivity through the electrode for the cavity devices, since charges can travel laterally in either the ITO layer or the Ag layer, whereas in bare devices this must occur in the ITO layer. Charge extraction issues such as blockages at the electrode should also result in increased series resistance, however this is just one cause among many for series resistance of a device to be affected. Therefore, whilst this result provides insight into the conductivity of the Ag layer, it cannot confirm whether the TPC overshoot seen in Chapter 7 is due to trapping or charge extraction issues.

Finally, the parallel (or shunt) resistance betrays the existence of some leakage current especially for the cavity devices as seen from the non-flat reverse bias photocurrent shape in Figure 8.10. This is present only for cavity devices, suggesting that the presence of the additional Ag layer may lessen the selectivity of the electron transport layer. The addition of polymer PEIE to ZnO cathodes as is done here for bare and cavity devices has been shown to reduce the work function, suppress trap-assisted recombination and improve the stability of devices in air.^{308,309} By suppressing the oxidation of the ZnO film, PEIE has also been shown to slow aging effects such as the increasing Fermi level and increasing field required for charge

extraction that is seen in non-passivated devices.³¹⁰ The improvement of PEIE-treated ZnO ETLs has been attributed to the formation of a dipole moment due to PEIE deposition.^{311,312} PEIE has even been used as the complete electron collecting layer, i.e. without the presence of ZnO or another interlayer material.³¹³ However, in this system it appears that there are variables as yet unaccounted for that may be responsible for the worsened charge selectivity of the PEIE/ZnO interface in the presence of Ag. Further work should be done to focus on understanding the interfacial effects of the Ag at the PEIE/ZnO cathode, as is suggested in Section 9.2.1.

8.5 Conclusions

In conclusion, we have demonstrated a model system for the simulation of bare and cavity PTB7-Th:TPDI OPV device performance. We first understand the impact of increasing device thickness on the performance metrics, so as to disentangle the effect of coupling from the effect of changing the device thickness in Figure 7.17. We also study the EQE of cavity and bare devices and separate out the effect of the photonic mode from that of strong light-matter coupling.

We introduce charge trapping to the simulation model and see that the time-dependent TPC transients produce a qualitatively similar peak overshoot to that seen in experimental measurements in Chapter 7. The peak overshoot is seen to be affected by the trap density, capture rate, intensity of illumination, and applied bias voltage. Since the simulation can reproduce the features experimentally observed, we see that charge trapping is a viable explanation of the TPC overshoot peaks studied in Chapter 7, however charge extraction issues must also be considered as they lead to the same result.

Finally, we aim to quantitatively understand the devices presented in Chapter 7. We introduce additional variables to the simulation and fit the experimental JV curves to obtain an estimate for the charge generation efficiency, Langevin recombination factor, density of chargeable sites, series and parallel resistances. Minimal change is seen for the generation efficiency between the devices. In contrast, a significant reduction in the Langevin recombination factor is seen for more positively detuned devices. The suggestion of reduced bimolecular recombination agrees with experimental observations from Chapter 7 where larger α values and longer lifetimes are seen for more positively detuned devices.

The density of chargeable sites was surprisingly seen to increase with increasing positive detuning, which is the opposite trend to what would have been expected to correlate with the decreasing magnitude of the TPC peak overshoot. The series resistance fit results suggest that the electrodes of the cavity devices have a higher conductivity than that of the bare device due to the ability of charges to move laterally in the Ag layer. However, it is unable to distinguish between whether the TPC overshoot arises from charge trapping or extraction issues in the electron and hole blocking layers or at the interfaces. The shunt resistance betrays that some leakage current is present, particularly for the cavity devices. Future work should be done to understand the contribution of the electrode to the current extraction. This could involve the use of alternate electrode materials, or the encapsulation of devices to prohibit oxygen-induced trap formation at the ZnO interface.

Chapter 9

Conclusions and future work

9.1 Conclusions

The aims of this thesis were to:

1. Examine the role of dual-direction energy harvesting in OPV devices, and quantify the contribution of the donor and acceptor to charge generation
2. Investigate the impact of strong light-matter coupling on device physics, particularly charge generation and transport

Specifically, the thesis aimed to explore the effects of molecular structure on blend film and device photophysics through the comparison of the PDI monomer and the TPDI dimer paired sequentially with the polymer donor PTB7-Th, and through a subsequent investigation of strong coupling in these materials in and outside of OPV devices.

In Chapter 3, we first establish a reliable routine for the fabrication and measurement of OPV devices. We report benchmarking work undertaken to ensure the trustworthiness of future measurements and demonstrate satisfactory performance of devices, including for a single component Y6 device.

In Chapter 4, we compare the device performance of PTB7-Th:PDI and PTB7-Th:TPDI devices, and demonstrate dual-direction energy harvesting in both material combinations. We find that the TPDI-based device has a superior performance due to the minimisation of unfavourable morphology in the active layer. Specifically, TPDI-based devices show an improved J_{SC} and fill factor, leading to a three-fold improvement in PCE. They exhibit approximately twice the EQE of PDI-based devices and reduced bimolecular recombination. Morphology studies suggest that PDI suffers from aggregation on a scale visible by AFM whereas TPDI

does not, due to the twist in the plane of the two linked chromophores which minimises the $\pi - \pi$ stacking plaguing PDI films. We demonstrate the crucial link between active layer morphology and device performance, and show that simple structural changes can have far reaching implications for device photophysics.

Chapter 5 continues the investigation of the effects of morphology on the photophysics of charge production using TA spectroscopy on blend films. We provide a direct visualisation of both electron and hole transfer processes, and also show that the latter is indistinguishable from energy transfer plus back electron transfer. We also quantify the contribution of each of these processes to the overall charge production through modelling and fitting of the TA data. This reveals that electron transfer in PDI-based devices is responsible for two-thirds of the charge production in these devices, whereas in TPDI-based devices there is a near-even contribution to charge generation from electron and hole transfer type processes. We again demonstrate the crucial influence of film morphology on charge production in blend films and reiterate its importance in device design. As far as we are aware, this is the first report of quantification of the charge generating capability of donor and acceptor domains, and we suggest that this quantification of dual-direction energy harvesting is a useful technique which can be applied to many other systems in the future. The comprehensive analysis of charge generation from both thin films and devices based on perylene monomers and dimers provides an in-depth understanding of the role of the donor and acceptor in charge generation, thus answering the first section of the overarching aim.

Chapter 6 is dedicated to the study of thin films in Fabry-Pérot cavities comprised of the same (T)PDI and PTB7-Th materials. We first study the photon mode in order to understand the properties of optical cavities and the effect of changing the cavity thickness, mode, angle of incidence and Q-factor. We demonstrate the tendency of (T)PDI to form excimers even when dispersed in a PS matrix which outcompete the exchange interaction between the exciton and the photon. In contrast, PTB7-Th is able to demonstrate strong coupling when dispersed in a PS matrix such that the domains of neat PTB7-Th are sufficiently broken up. We also demonstrate that the mixing of these two materials in blend films gives satisfactory morphology such that coupling can be achieved when the cavity is detuned where the cavity mode is resonant with the (T)PDI or the PTB7-Th exciton resonances. Strong coupling is achieved in particular in the TPDI-based blend film when coupled to the (T)PDI resonance. We thus demonstrate that strong coupling is experimentally feasible in OPV-like blend films, ahead of fabricating

coupled OPVs.

In Chapter 7, we demonstrate the fabrication and characterisation of coupled PTB7-Th:TPDI OPV devices. Peak splitting is observed via both optical detection using angular reflectometry as well as electrical detection using EQE. Cavity devices demonstrate a higher effective J_{SC} compared to bare devices and an improved fill factor, suggesting lower recombination losses. However, cavity devices appear to suffer from charge trapping or extraction issues as demonstrated by high light intensity ideality factors and an overshoot peak in TPC measurements. Charges are seen to live longer in bare devices from combined TPC and TPV measurements. More positively detuned devices show decreased bimolecular recombination in intensity-dependent J_{SC} measurements and longer charge lifetimes as measured by TPC and TPV. Lastly, we show that EQE and EL can be used to electrically detect the LP energy, with more positively detuned devices demonstrating higher energy LP states. Overall, we demonstrate the ability to tune the device properties without changing the material itself using strong coupling.

Finally, in Chapter 8 we present simulations providing insight into the coupled device behaviour measured in Chapter 7. We reproduce experimentally obtained JV curves via simulation and consider the effect of device detuning on the Langevin recombination factor and the density of chargeable sites. We also show that the overshoot peak in the TPC trace is reproducible by the inclusion of trapping, which may arise from traps or extraction issues in the devices.

To summarise, we reveal here the intricate role that morphology plays in blend film and device photophysics, as well as the ability to tune device properties without changing the material through strong light-matter coupling. As a result of this work, a number of exciting and intriguing questions are raised which require further work to investigate. These avenues of possible further investigation are discussed below.

9.2 Future work

As is often the case in research, the more one uncovers, the more one realises there is left to uncover; in other words, the more you know, the more that there is to know. This sentiment is said to have originated in the era of ancient Greek philosophy and is often attributed to Aristotle, but regardless of its origins, it remains highly relevant today. There are several avenues for future work stemming from this project, the most intriguing of which are listed below.

9.2.1 Origin of charge trapping

The observation of a greater TPC overshoot in cavity devices as compared to bare devices raises the question of why cavity devices might suffer from trap-assisted recombination or extraction issues. Strong coupling is known to result in the formation of delocalised polaritons which would be reasonably expected to cause a reduction in trapping effects. Work has already begun towards investigating the origin of this overshoot. Three bare and three cavity TPDI-based OPV devices were fabricated and encapsulated with epoxy resin in the glovebox before testing, and the normalised TPC is shown in Figure 9.1. All six devices showed a near complete reduction of the TPC overshoot compared to that reported in Chapter 7. This indicates that the TPC

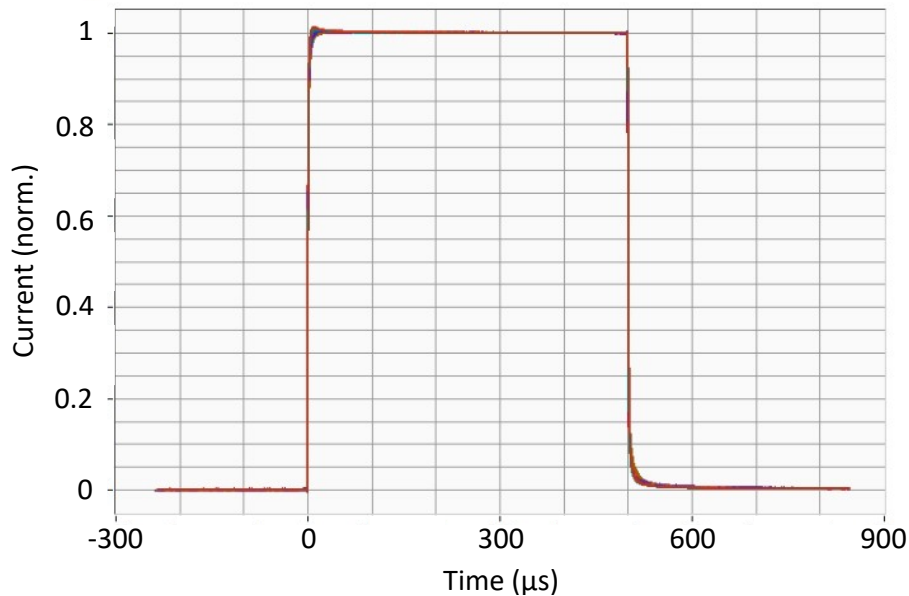


Figure 9.1: Six encapsulated TPDI-based devices (3x bare devices and 3x cavity devices) demonstrating reproducible and near complete suppression of the TPC overshoot.

overshoot only appears in the presence of oxygen. ZnO is known to be susceptible to oxidation, with oxygen atoms adsorbed onto the film causing trapping of electrons at the interface between the ZnO and the active layer.^{314–316} The polymer PEIE suppresses this as discussed in Chapter 8, but since the overshoot was still seen in Chapter 7 we concluded that there were either traps present in the device or extraction issues due to this not being complete suppression. Since the encapsulated devices show near complete suppression of the overshoot peak, we can confirm that this is due to charge extraction issues related to the exposure of the devices to oxygen-containing atmosphere. Future work should be performed to fully characterise these samples without the TPC overshoot and search for new insights into device behaviour that may have been obscured by the TPC overshoot. Any conclusions relating to the better effective performance of the cavity devices should only be made stronger by controlling the extraction issue, since the extraction issue is shown to be worse for cavity non-encapsulated devices compared to the bare device. Future work could also be performed to investigate the role of the additional Ag layer in cavity devices and why this leads to a larger TPC overshoot peak in the non-encapsulated devices presented in Chapter 7.

9.2.2 Cavity transient absorption spectroscopy

In Chapter 5, we report a thorough investigation into the photophysics of the blend films, in particular the timescales of and relative contribution of each domain to charge production. Performing the same analysis on cavity-based films would allow for an investigation into the effect of polariton formation on these processes already characterised in neat films. Where TA can be performed at the resonant coupling condition, we expect that charges will have a longer lifetime in the cavity due to decreased recombination. However, performing TA on cavity devices is intrinsically more difficult due to overlapping spectral features between the molecular and polaritonic states,³¹⁷ the existence of multiple methods for determining polaritonic excited state lifetimes,³¹⁸ and the complex contribution of elusive dark states to the overall cavity photophysics.¹⁶⁴ Perhaps most significantly, artefacts may also arise in the TA data due to changes in cavity properties upon excitation,³¹⁹ as is discussed in more detail below.

Work has also already begun in this area and a number of measurements have been performed. Figure 9.2 reports the TA spectra of a thin film of TPDI dispersed in PS at 120 mM in between two 28 nm Ag mirrors. Figure 9.2 a) is taken in transmission mode, the same as all other TA spectra presented in Chapter 5, whereas Figure 9.2 b) is taken in reflection

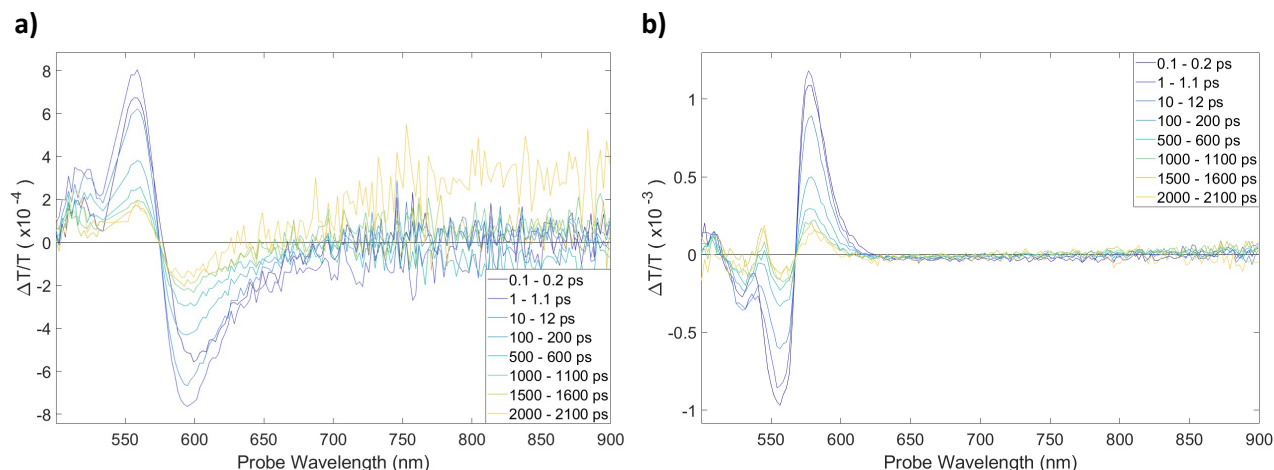


Figure 9.2: a) Transmission and b) reflection TA measurements of a thin film of TPDI dispersed in a PS matrix at 120 mM concentration and excited at 540 nm. Derivative-like features are seen centred around ~ 570 nm.

mode. A sharp derivative-like or sinusoidal-appearing feature is seen centred at ~ 570 nm, and the positive and negative lobes are reversed in sign between the two measurements. The true transient absorption can be calculated by taking the difference between the two measurements using $\Delta A = -(\Delta T + \Delta R)$ since the sum of the reflection, absorption and transmission signal for otherwise identical measurements should add to unity.³²⁰

Similar derivative-like features are often attributed to polariton excited state absorption, but may also be due to a host of other non-polaritonic effects. For example, similar features are produced by polariton contraction, whereby the formation of the polariton excited state leaves the ground state of the molecule unpopulated, changing the strength of the Rabi splitting; thermal expansion of the film, and associated dynamic changes in the cavity dimension; and refractive index changes in the polymer matrix and the mirror material due to heating.^{164,319} Transfer matrix modelling has shown that all four of these effects produce derivative-like features of a similar magnitude to that of typical TA measurements. Modelling has also shown that a linear sum of these effects can explain TA spectra in their entirety or in combination with true polaritonic effects. It is particularly important to consider these effects where signatures are long-lived, such as the measurements presented in 9.2, since polariton lifetimes are typically much smaller than the lifetimes represented here where the same signatures are still present at 2 ns. The short lifetime of polaritons is due to the combination of the exciton with the short-lived cavity photon, the lifetime of which depends on the Q-factor of the cavity. Since these experiments involve low Q-factor Ag cavities, it is likely that that lifetime of the polaritons

is less than the instrument response function.³¹⁹ It is important therefore to critically analyse and disentangle the contribution of any polaritonic effects from those of polariton contraction and non-specific heating effects through the use of a faster pump pulse, higher quality cavities and/or detailed modelling.

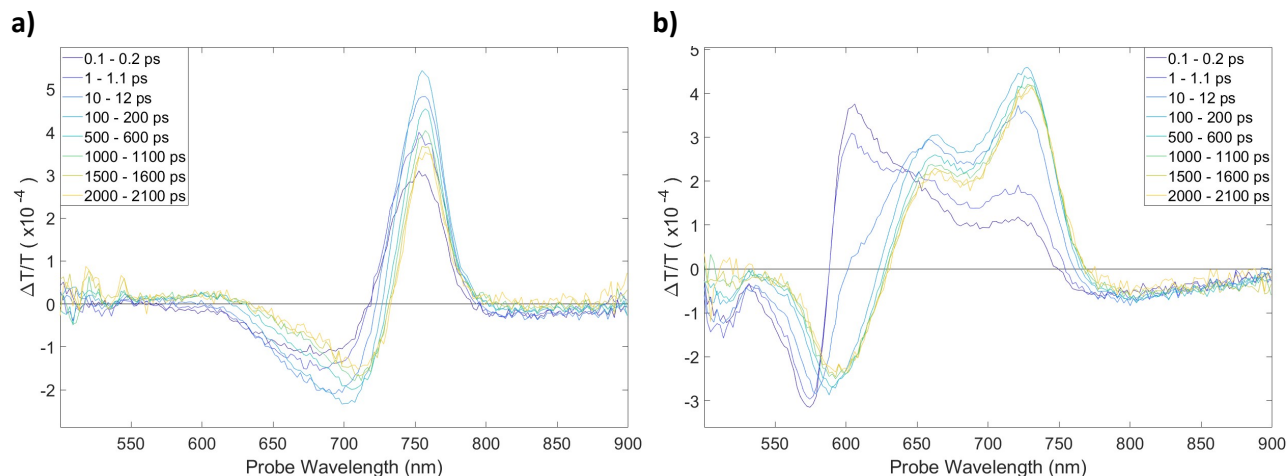


Figure 9.3: Transient absorption measurements of coupled films performed in reflection mode for a) PTB7-Th:PDI blend film coupled to the PTB7-Th resonance (sample K5) and b) PTB7-Th:TPDI blend film coupled to the TPDI resonance (sample L8). Spectral shift, rise/decay and evolution are exciting observations but must be carefully analysed in order to disentangle any effects due to measurement artefacts as described above.

Figure 9.3 a) and b) provide additional examples of reflection cavity TA measurements, performed on blend films coupled to the PTB7-Th and TPDI resonance respectively. The features for the former appear to rise before decaying, which may be due to the growth and decay of an excited state species such as the charge transfer state as was seen for the blend films presented in Chapter 5. The latter demonstrates significant spectral evolution between early and late time measurements, suggesting fast evolution between a TPDI-like spectrum (akin to that in Figure 9.2 b)) to a blend film-like spectrum (akin to those presented in Chapter 5) with GSB features similar to those corresponding to PTB7-Th. These are exciting preliminary observations, but further work must be done in order to properly assign the features and ensure that they represent a true spectral signature of the material and are not simply artefacts as discussed above and in Renken et al.³¹⁹ due to the difficulty of performing measurements on cavity samples.

9.2.3 Detuning coupled OPV devices with respect to the acceptor

In Chapter 6, we saw that it was possible to couple blend films to the (T)PDI resonance as well as the PTB7-Th resonance. Future work on devices with varying degrees of detuning with respect to the acceptor may reveal more information about the role of strong coupling specifically involving the acceptor in the OPVs. Since PTB7-Th is a more disordered material than (T)PDI, coupling instead to (T)PDI could reduce the effect of the improvement of strong coupling since there is less disorder to be overcome. This may lead to results where the effect of the cavity is not as pronounced as it is for PTB7-Th. On the other hand, increasing the detuning so that the photon couples to the excitons in the acceptor would increase the extent of optical mixing. A study could be performed where the optical mixing of the PTB7-Th and TPDI excitons is increased then decreased with increasingly positive detuning. In Chapter 7, the most positively detuned cavity device with respect to the PTB7-Th resonance was still negatively detuned with respect to the (T)PDI resonance. This film was very thin, approaching the limit of what is feasibly possible for a working OPV device without introducing additional complications such as the effect of pinholes in the ITO electrode. In order to increase the detuning and achieve positive detuning with respect to the (T)PDI resonance, thin films may instead need to be deposited by thermal evaporation. Alternatively, the thickness of the cells can be increased such that the (T)PDI exciton is resonant with the second-order cavity photon, although thicker active layers are likely to introduce further loss mechanisms and reduce the device performance as seen in Figure 8.5 b). Instead of altering the thickness of the active layer, it may be possible instead to alter the thickness of the interlayers, namely ZnO and MoO₃. This may affect current extraction, which may in turn either help or hinder device performance. If the devices can be successfully fabricated, studying the effect of detuning to the acceptor should reveal whether this has a positive or negative effect on device performance according to the increased optical mixing or decreased disorder in the films as mentioned above.

9.2.4 Coupled PDI-based OPVs

We have focused on TPDI-based devices for the investigations into strongly coupled OPV devices presented here. In the future, it would be insightful to study PDI-based strongly coupled devices as well and compare the effects of strong coupling of both the donor and acceptor domains between the two material systems. We chose TPDI-based blends to focus on as they

exhibited stronger coupling as described in Chapter 4, but it is also possible to couple PDI-based blends. Specifically, it would be interesting to see if strong coupling could be used to achieve extended delocalisation of the exciton and reduce geminate recombination in PDI-based OPVs. We have proposed that the nanoscale morphology in blend films is characterised by large PDI domains which preclude some excitons from reaching the interface and forming a CT state there. Strong coupling has the potential to overcome geminate recombination, since the partial photonic character assumed by the exciton during coupling allows for efficient long-range energy transport.^{192–196} The bimolecular recombination losses prevalent in the PDI-based blend may also be overcome by strong coupling as it can also enable efficient charge transport even through disordered materials.^{154,187} Thus, it is possible that the PDI-based devices could show a more stark performance improvement through strong coupling compared to the TPDI-based devices.

9.2.5 Identifying radiative and non-radiative losses

The energy lost in OPVs between photon absorption and charge collection at the electrode can be quantified as the difference in energy between the bandgap and the voltage of the cell, i.e. $E_{\text{opt}}/e - V_{\text{OC}}$.³⁰³ This picture does not consider losses arising from the absorption of photons with energy greater than the optical bandgap - these are lost due to thermalisation and require processes such as photon downconversion (singlet fission) to avoid these losses.³²¹ CT state losses, known by the term driving energy in the context of OPVs, are separate again and are often small for non-fullerene acceptor OPVs as discussed in Section 1.1.3. The difference in energy between the CT state and the V_{OC} of a device (specifically, the charge of an electron multiplied by the V_{OC} , i.e. eV_{OC}) is known as the recombination loss and arises from a combination of radiative and non-radiative losses.

It would be insightful to study these recombination losses in more detail, in particular to see the role that radiative and non-radiative losses play and their contribution to the total recombination losses. It is possible to calculate the radiative limit of the V_{OC} , i.e. the V_{OC} when only radiative recombination occurs.³⁰³ The radiative recombination losses can then be calculated by taking the difference between the radiative limit of V_{OC} and the CT state energy. Finally, the non-radiative losses can be calculated by taking the difference of the measured V_{OC} and the V_{OC} in the radiative limit. Since the detuning of the cavity affects the photonic/excitonic character of the polaritons formed, it is likely that a relationship can be drawn between the detuning of the device and the voltage losses. In particular, we hypothesise that increased

photonic character of the lower polariton branch through negative detuning should lead to delocalisation of the excitons and charges present in the device, and lower non-radiative losses as a result.

9.2.6 Bilayer devices

The ultimate level of morphological control in OPV devices is achieved through the use of bilayers, which form a planar heterojunction (PHJ) structure as pictured in Figure 1.4 a). Whilst bulk heterojunctions (BHJs) are commonly used and currently outperform PHJs, this may change if the key issues of PHJs can be overcome. PHJs have the benefit of eliminating the effects of domain mixing which complicate device physics in BHJs. Additionally, PHJs have only one interface between donor and acceptor domains rather than many, making it much easier to accurately characterise the interface. The main setback for PHJs is that the donor and acceptor layers must be made to be thick enough to warrant sufficient absorption of incident light, whilst needing to be thin enough to allow for excitons generated in each domain to travel to the interface to form a CT state before they decay. Charge transport through the relevant layers is also a concern but this is common to both PHJs and BHJs, and many high-performing materials can achieve efficient charge transport particularly with the use of additives which mitigates this issue.^{322–324}

Since strong coupling is able to achieve efficient energy transport across large distances - for example up to several microns and at speeds up to two-thirds the speed of light - this has enormous potential to overcome the issue of exciton transport in bilayer devices. Using strong coupling, it is feasible that devices can be made even thicker to ensure maximum absorption of visible light, although we have seen in Chapter 8 that the optimum active layer dimension is smaller for cavity compared to bare devices. In any case, as long as the charge transport is not negatively affected by thicker donor and acceptor layers, it follows that strong coupling could greatly assist the functioning of bilayer devices to the point of making them a viable and competitive device architecture. Some work has been done on this topic already, for example by Wang et al.,²⁰² however these devices had low efficiency, measuring an EQE of $< 0.05\%$. Nikolis et al. also made use of bilayer devices to demonstrate increased steepness of the absorption edge in strongly coupled devices through measurements of the Urbach energy,²⁰¹ which would also be interesting to perform for the devices measured here. Overall, the fabrication of bilayer devices constitutes an area of enormous potential for the improvement of OPV devices and is

an exciting avenue of future research to explore.

Ideally, the goal for the future of coupled OPVs is for the performance of the cavity-based devices to improve such that the hinderance of the partially transmissive silver is overcome. Other exotic architectures may also be used, or perhaps no cavity architecture at all, since strong coupling and polariton formation has even been observed in cavity-free films.¹⁵⁹ Ultimately, bilayer devices with careful optical management is most likely to be the future of coupled OPVs.

9.3 Closing remarks

In summary, the photophysics of perylene monomers and dimers has been thoroughly investigated from thin films through to OPV devices both with and without strong light-matter coupling. Many interesting questions remain, but in time these will hopefully find answers through sustained and ongoing research efforts. We conclude with the hope that this thesis inspires readers through the information contained herein, but more importantly that it encourages them to keep pursuing learning opportunities and inspiring others to do the same, for the greater benefit of humanity.

List of publications

Goldingay, A.; Stuart, A. N.; Ghosh, P.; Yadav, S.; Gangadharappa, C.; Patil, S.; Rao, A.; Lakhwani, G. Quantifying dual-direction energy harvesting in twisted perylene non-fullerene acceptor organic photovoltaics. *Journal of Physical Chemistry C*, **2023**. DOI: doi/10.1021/acs.jpcc.3c05050

Price, M. B.; Hume, P. A.; Ilina, A.; Wagner, I.; Tamming, R. R.; Thorn, K. E.; Jiao, W.; Goldingay, A.; Conaghan, P. J.; Lakhwani, G.; Davis, N. J. L. K.; Wang, Y.; Xue, P.; Lu, H.; Chen, K.; Zhan, X.; Hodgkiss, J. Free charge photogeneration in a single component high photovoltaic efficiency organic semiconductor. *Nature Communications*, **2022**, *13*, 2827. DOI: doi.org/10.1038/s41467-022-30127-8

A. Sharma, Campbell, A., Leoni, J., Cheng, Y.T., Müllner, M., Lakhwani, G. Circular Intensity Differential Scattering Reveals the Internal Structure of Polymer Fibrils, *Journal of Physical Chemistry Letters*, **2019**, *10* 24, 7547-7553. DOI: <https://doi.org/10.1021/acs.jpcllett.9b02993>

Appendix A

Appendix to Chapter 5: Time-resolved studies of PDI- and TPDI-based blend films

A.1 Deconvolution

The following information details the procedure for the deconvolution of TA spectra using blend films of (T)PDI and PTB7-Th. An example of the deconvolution process is also provided in Chapter 5 for neat PTB7-Th.

A.1.1 PTB7-Th:PDI blend film excited at 700 nm

To deconvolute the PTB7-Th:PDI film excited at 700 nm 0.2 uJ/cm², the PTB7-Th S₁ basis spectrum was taken from the neat PTB7-Th TA spectra (700 nm, 0.04 uJ/cm² excitation) at 1 ps. The PDI S₁ basis spectrum was taken from the neat PDI TA spectra (540 nm, 2.2 uJ/cm² excitation) at 1 ps. The CT basis spectrum was taken from PTB7-Th:PDI 700 nm excitation TA at 100 ps. 100 ps was chosen to avoid artefacts in the TA spectra that appear at late times around 500–600 nm. Extracting the CT spectrum from 100 ps forces the S₁ contributions to be zero at that time, which may not be accurate. However, when we instead extracted the CT spectra from 2000 ps (i.e. at a time where TCSPC confirms the absence of S₁ states) the fit to the TA data was substantially poorer at times before 1000 ps, and the kinetics of the resulting concentrations were largely unchanged. Notably the S₁ population still fit to zero after 10 ps, supporting our assumption S₁ can be ignored at 100 ps.

The basis spectra chosen are shown in Figure A.1, and the fit to the experimental data in Figures A.2 and A.3. The basis spectra are able to reproduce the experimental data extremely well until about 1000 ps. After this time, the quality of the fit is reduced around 600 nm, likely because of artefacts that arise at late times due to the alignment of the probe.

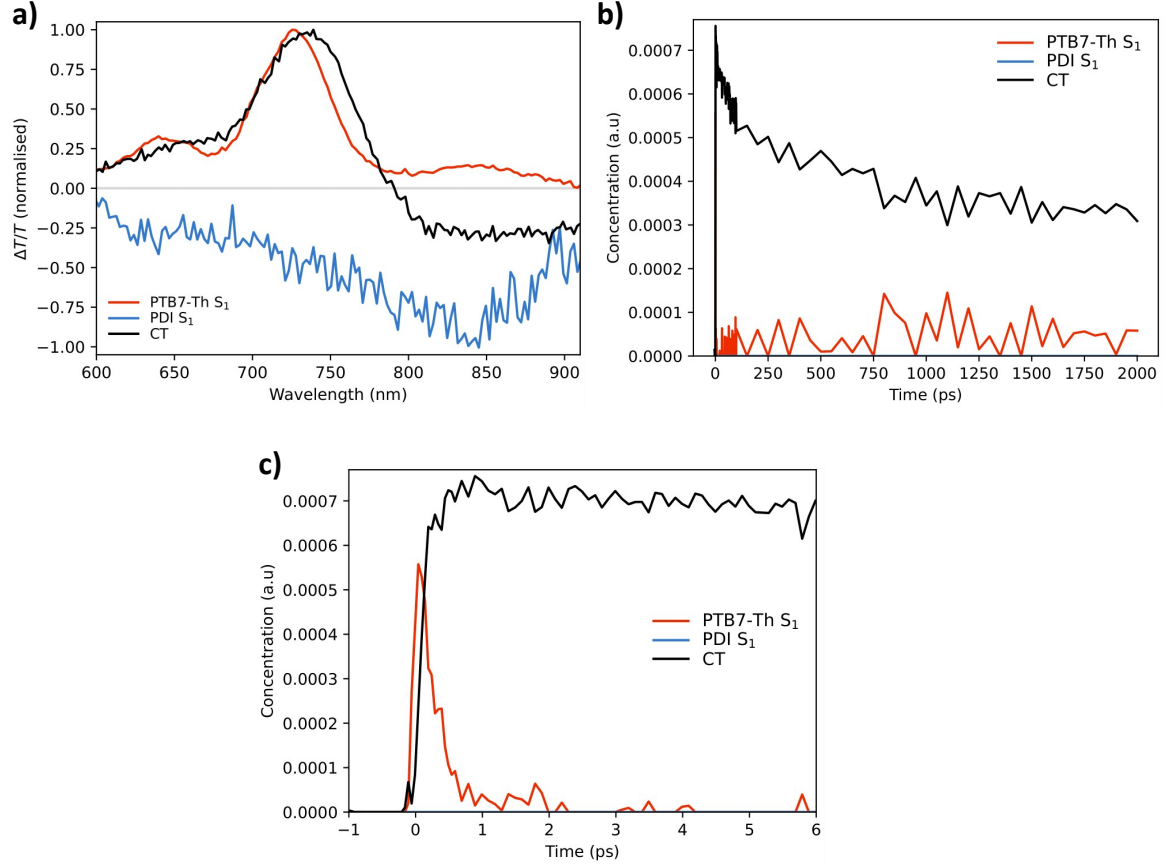


Figure A.1: a) TA basis spectra of the PTB7-Th:PDI film excited at 700 nm and 0.2 uJ/cm². b) Deconvoluted concentrations of PTB7-Th S_1 , PDI S_1 states, and CT states over 2 ns. c) S_1 and CT concentrations over 6 ps.

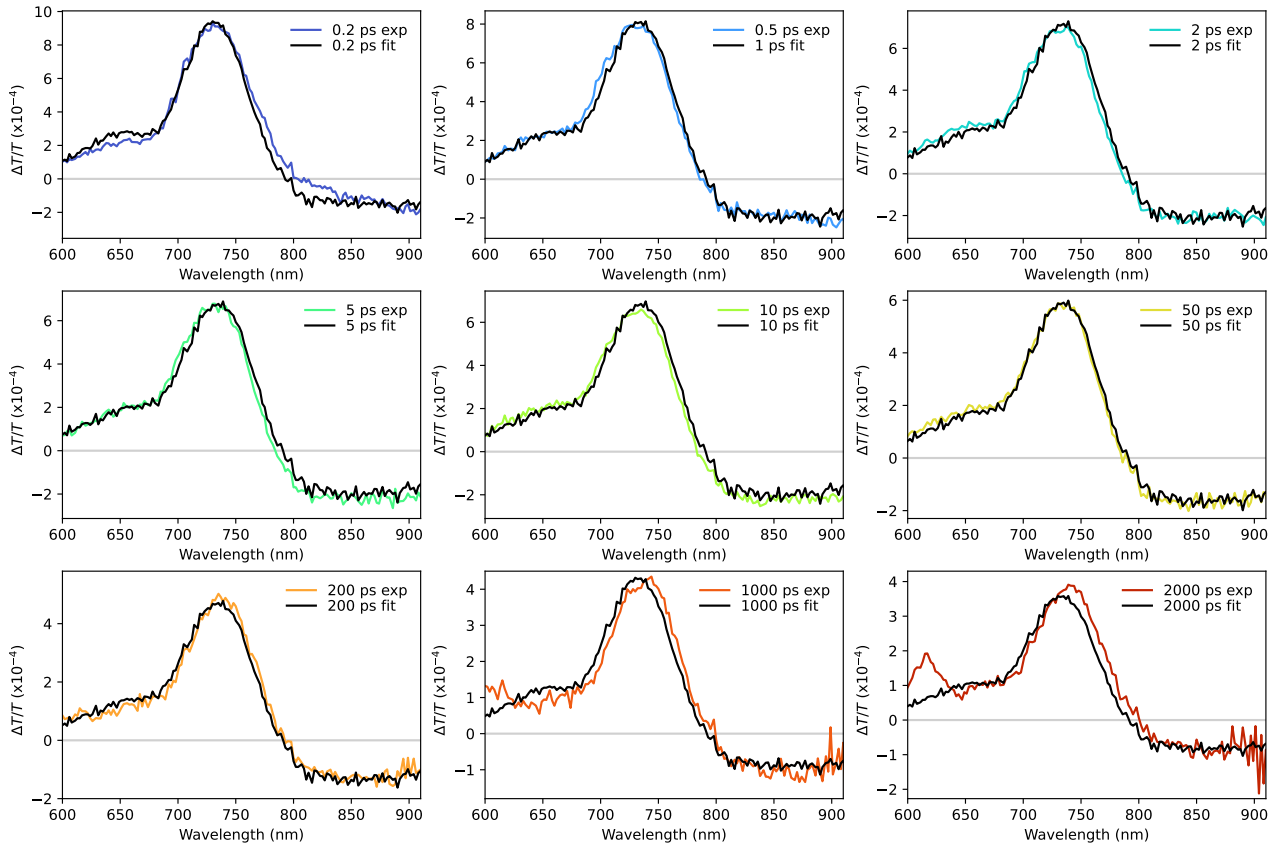


Figure A.2: Deconvolution fit of the PTB7-Th:PDI film excited at 700 nm and 0.2 uJ/cm^2 at different delay times. Corresponding basis spectra and concentrations are in Figure A.1.

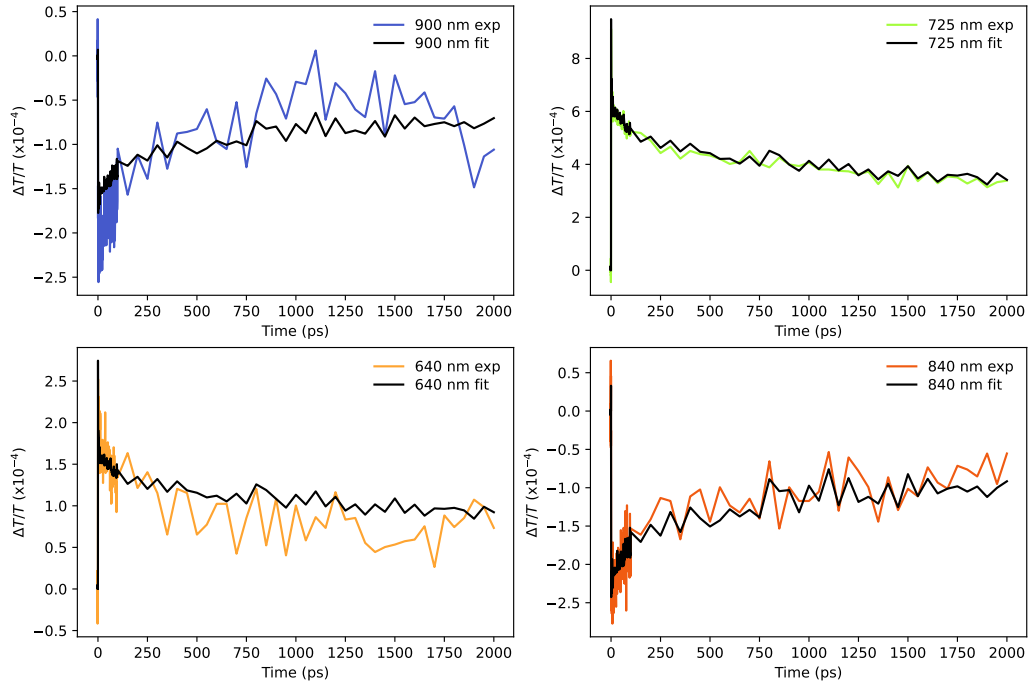


Figure A.3: Deconvolution fit of the PTB7-Th:PDI film excited at 700 nm and 0.2 uJ/cm^2 at different wavelengths. Corresponding basis spectra and concentrations are in Figure A.1.

A.1.2 PTB7-Th:TPDI blend film excited at 700 nm

To deconvolute the PTB7-Th:TPDI film excited at 700 nm (0.2 uJ/cm^2), the PTB7-Th S_1 basis spectrum was taken from the neat PTB7-Th TA spectra (700 nm, 0.04 uJ/cm^2 excitation) at 1 ps. The TPDI S_1 basis spectrum was taken from the neat TPDI TA spectra (540 nm, 2.2 uJ/cm^2 excitation) at 1 ps. The CT basis spectrum was taken from PTB7-Th:TPDI 700 nm excitation TA at 500 ps.

The basis spectra chosen are shown in Figure A.4, and the fit to the experimental data in Figures A.5 and A.6. The basis spectra are able to reproduce the experimental data very well. There are some minor discrepancies at early times arising from PTB7-Th S_1 spectra. This is likely due to different morphologies of PTB7-Th in the neat and blend films causing the GSB in the neat PTB7-Th spectra (which is used to extract the PTB7-Th S_1 basis spectra) to be different to the PTB7-Th GSB in the blend. This can also be observed in the steady-state absorption spectra.

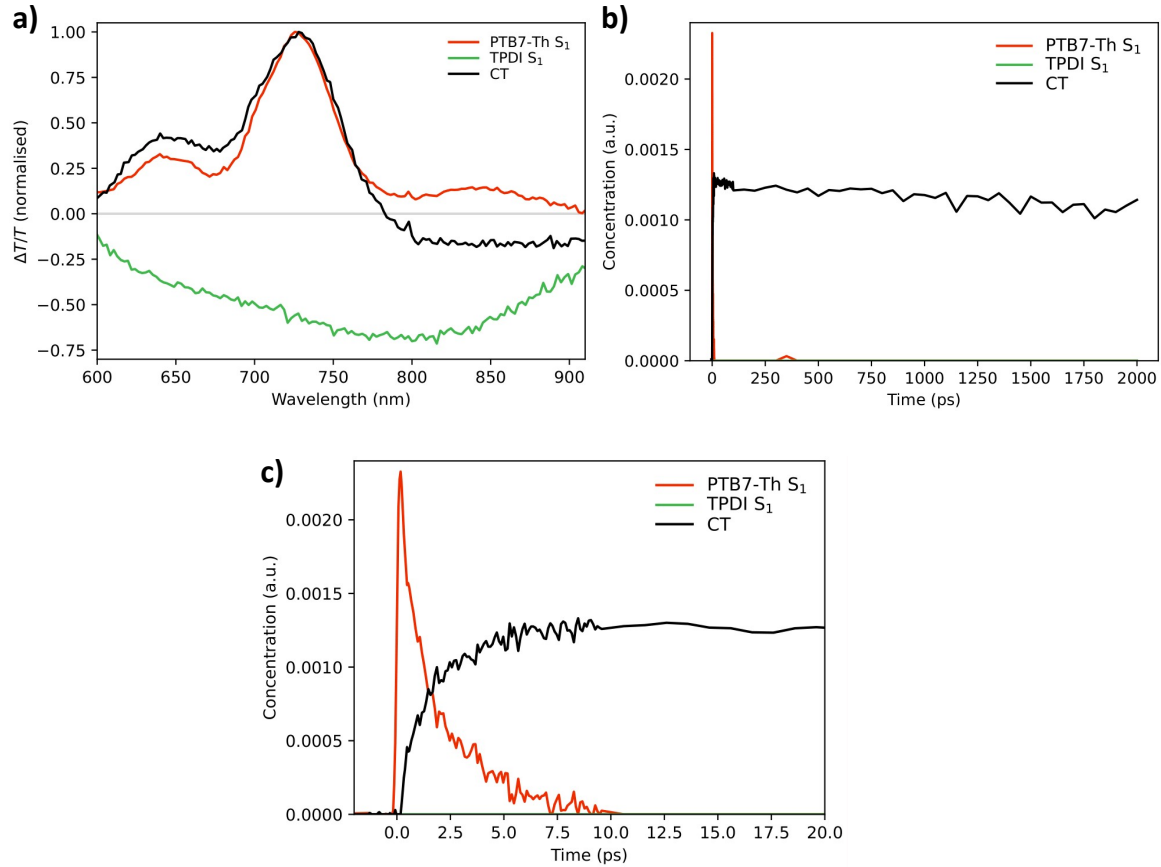


Figure A.4: a) TA basis spectra of the PTB7-Th:TPDI film excited at 700 nm and 0.2 uJ/cm^2 . b) Deconvoluted concentrations of PTB7-Th S_1 , TPDI S_1 states and CT states over 2 ns. c) S_1 and CT concentrations over 40 ps.

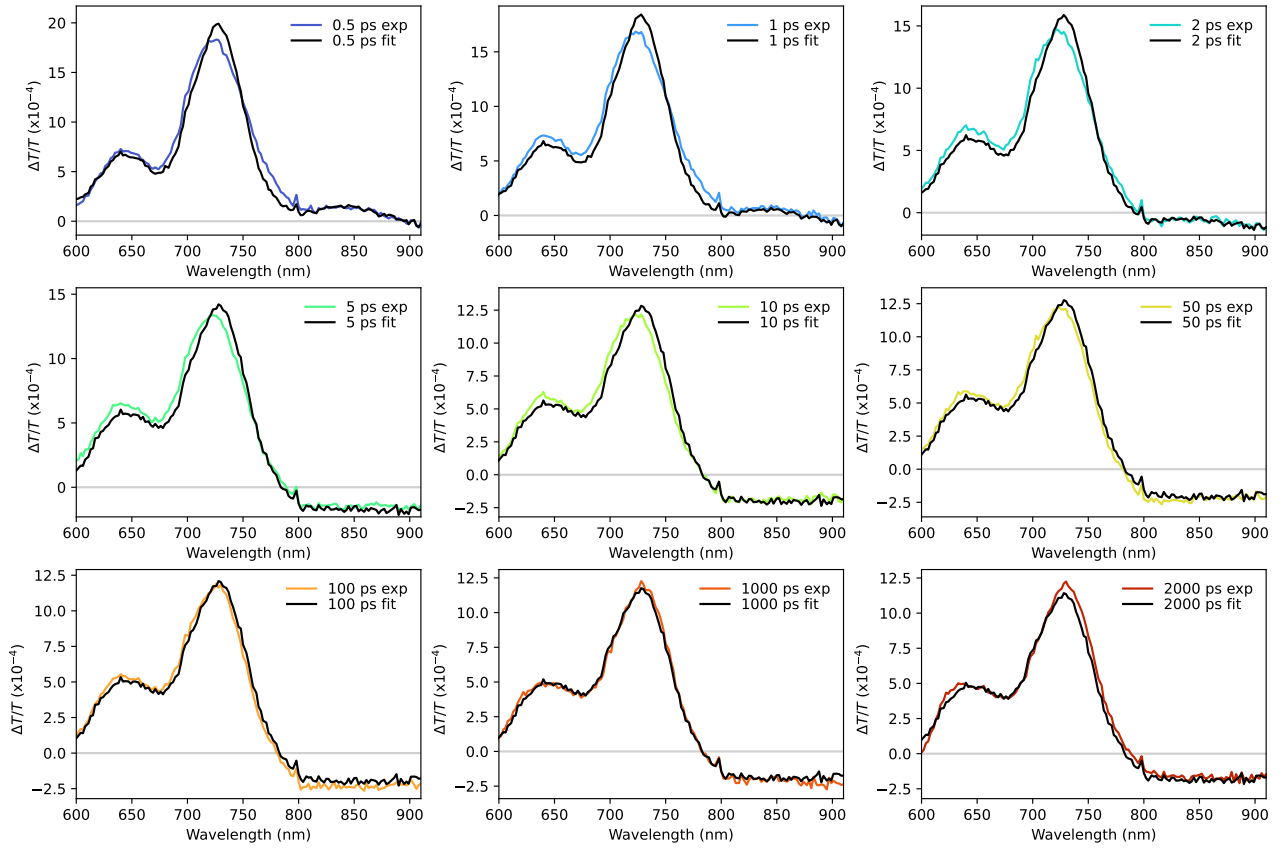


Figure A.5: Deconvolution fit of the PTB7-Th:TPDI film excited at 700 nm and 0.2 uJ/cm^2 at different delay times. Corresponding basis spectra and concentrations are in Figure A.4.

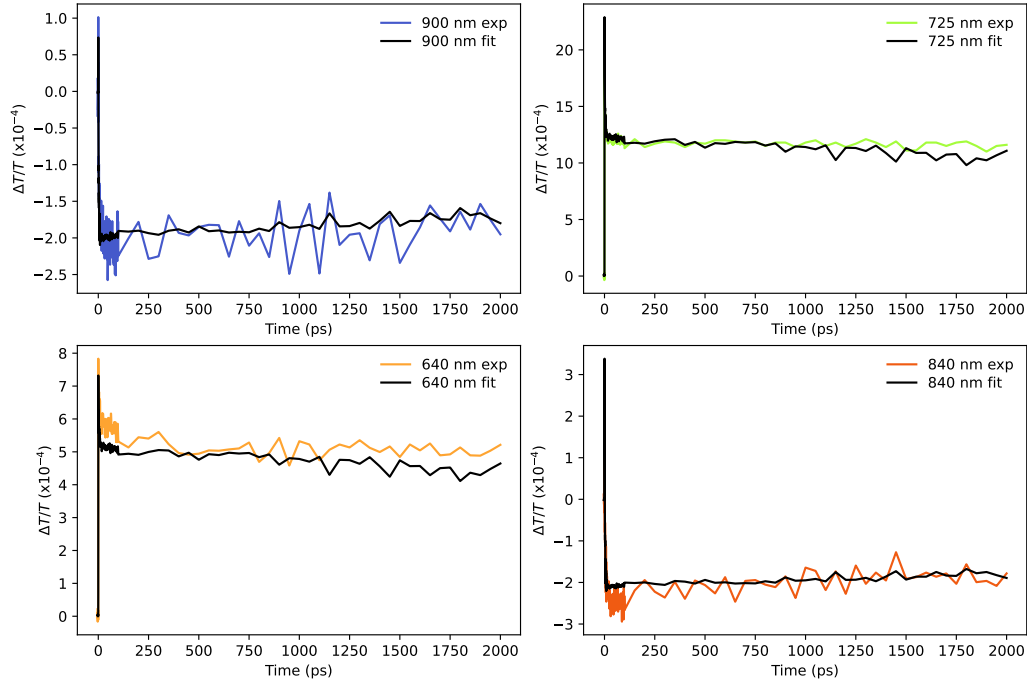


Figure A.6: Deconvolution fit of the PTB7-Th:TPDI film excited at 700 nm and 0.2 uJ/cm^2 at different wavelengths. Corresponding basis spectra and concentrations are in Figure A.4.

A.1.3 PTB7-Th:PDI blend film excited at 540 nm

To deconvolute the PTB7-Th:PDI film excited at 540 nm (3.5 uJ/cm^2), the PTB7-Th S_1 basis spectrum was taken from the neat PTB7-Th TA spectra (700 nm, 0.04 uJ/cm^2 excitation) at 1 ps. The PDI S_1 basis spectrum was taken from the neat PDI TA spectra (540 nm, 2.2 uJ/cm^2 excitation) at 1 ps. The CT basis spectrum was taken from the 540 nm excited PTB7-Th:PDI TA at 2 ns.

The basis spectra chosen are shown in Figure A.7, and the fit to the experimental data in Figures A.2 and A.9. The basis spectra are able to reproduce the experimental data extremely well from 700–900 nm. However at early times the fits around 600–700 nm are poor. The discrepancies cannot be explained by PDI or PTB7-Th S_1 spectra, so are likely either due to artefacts from changes in the probe continuum across the delay stage, or due to a shape change in the CT state over time (i.e. due to delocalisation or separation). Since the fits are still able to reproduce the change in shape from 700–900 nm well, in particular the evolution of the ESA from PDI S_1 to the flatter CT ESA, we consider the concentrations resulting from this fit to be good representations of the true kinetics. We do note that the PDI S_1 population is somewhat long-lived, agreeing with the long-lived fluorescence observed in the TCSPC. However as a result of this, the TA signal at 2 ns used to extract the CT state spectra may not be a pure CT signal. This would result in an underestimate of the S_1 state at late times, and an overestimate amount of CT states at late times, but will not affect the rate of formation of the CT state at early times.

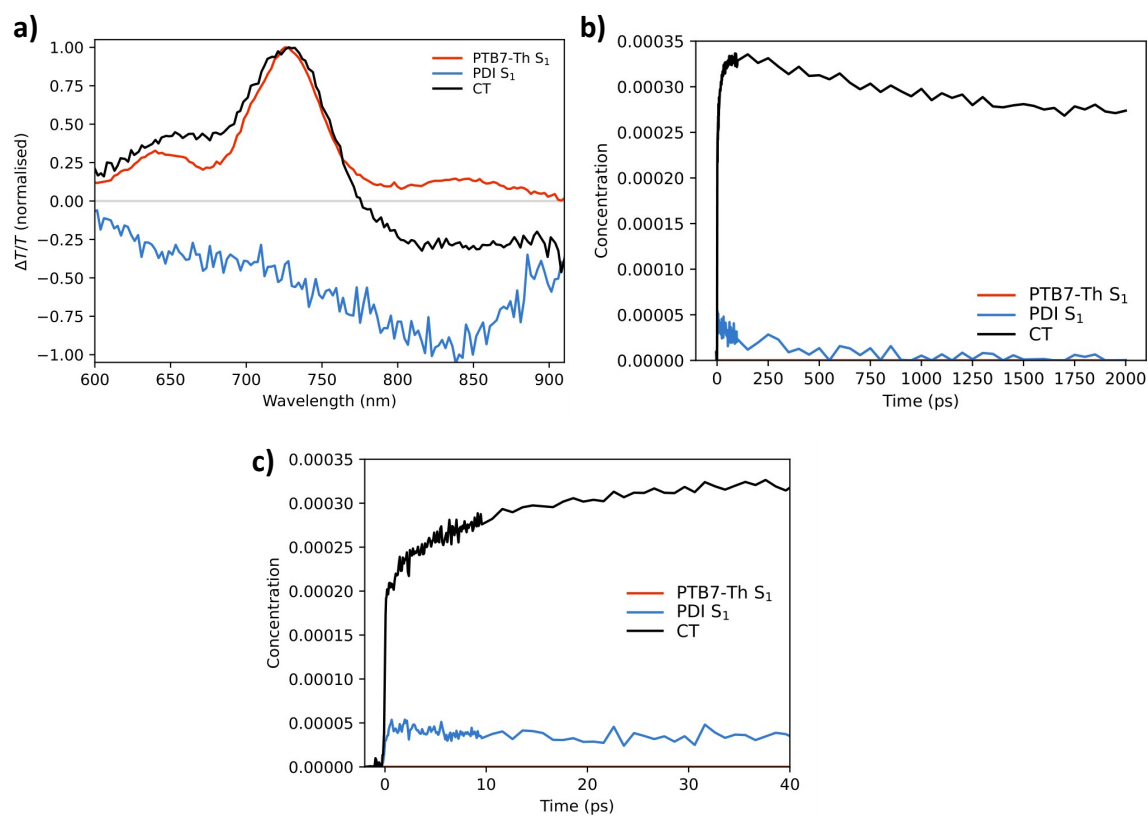


Figure A.7: a) TA basis spectra of the PTB7-Th:PDI film excited at 540 nm and 3.5 uJ/cm². b) Deconvoluted concentrations of PTB7-Th S₁, PDI S₁ states and CT states over 2 ns. c) S₁ and CT concentrations over 40 ps.

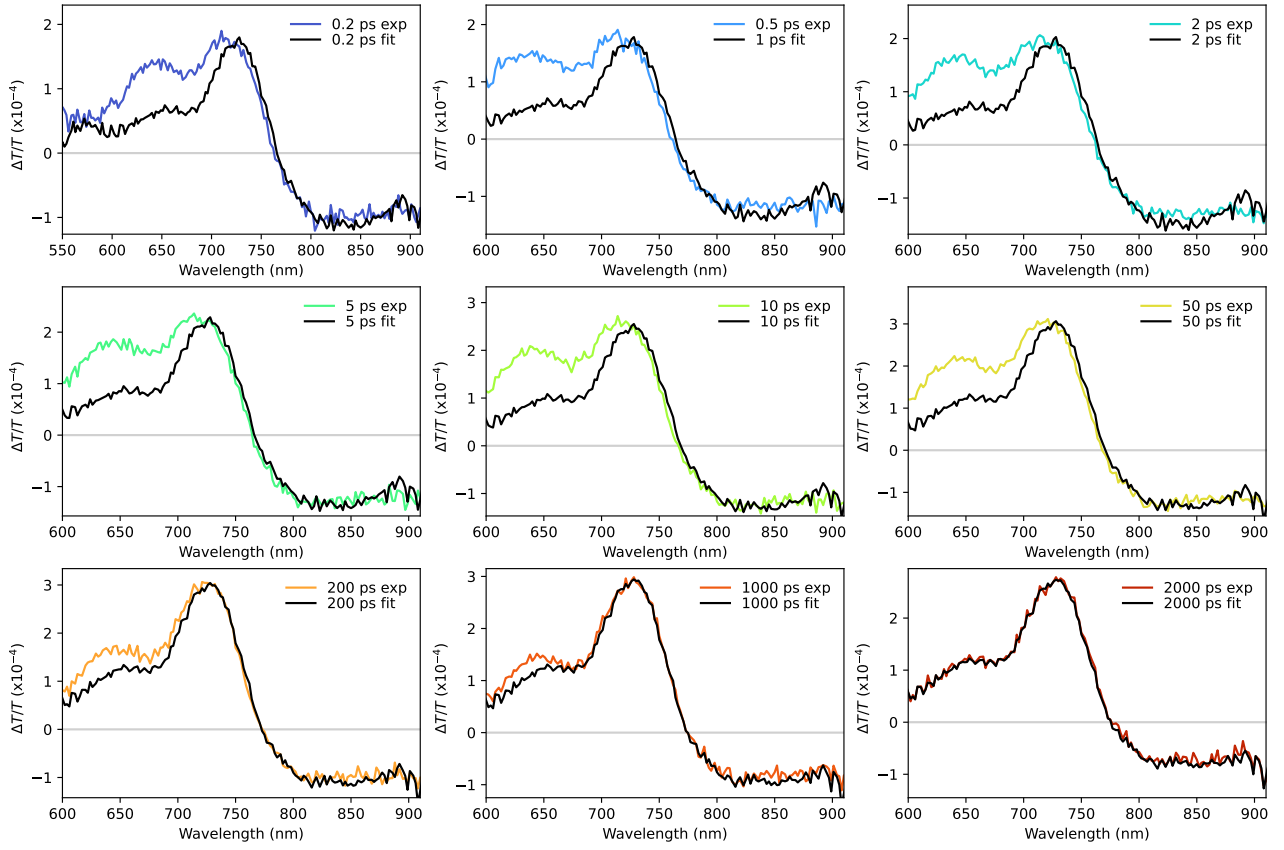


Figure A.8: Deconvolution fit of the PTB7-Th:PDI film excited at 540 nm and 3.5 uJ/cm^2 at different delay times. Corresponding basis spectra and concentrations are in Figure A.7.

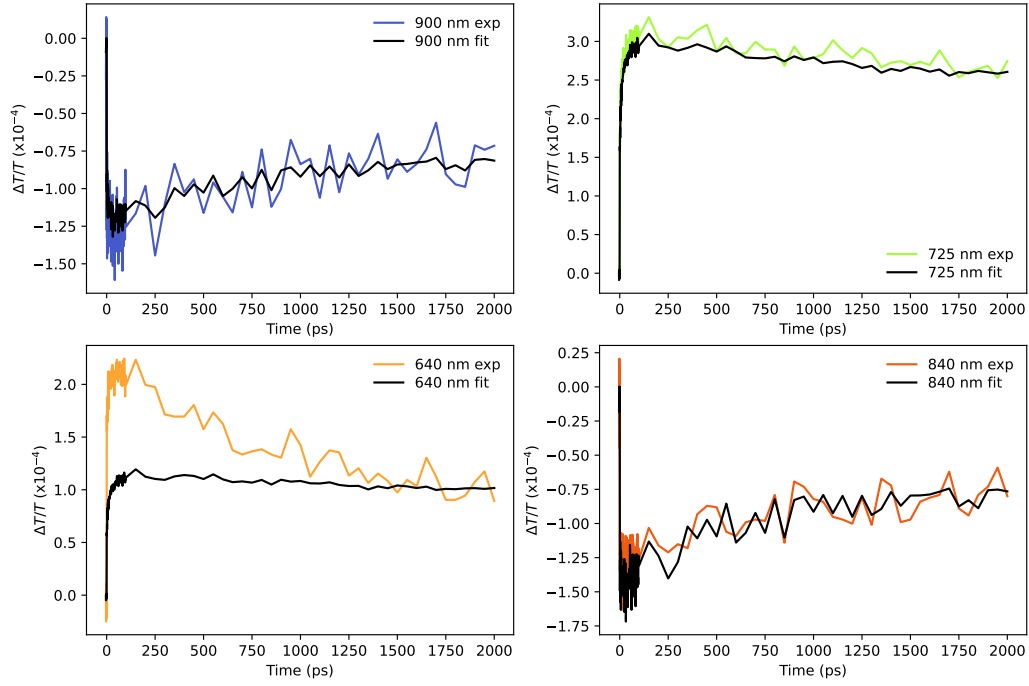


Figure A.9: Deconvolution fit of the PTB7-Th:PDI film excited at 540 nm and 3.5 uJ/cm^2 at different wavelengths. Corresponding basis spectra and concentrations are in Figure A.7.

A.1.4 PTB7-Th:TPDI blend film excited at 540 nm

To deconvolute the PTB7-Th:TPDI film excited at 540 nm (3.5 uJ/cm^2), the PTB7-Th S_1 basis spectrum was taken from the neat PTB7-Th TA spectra (700 nm, 0.04 uJ/cm^2 excitation) at 1 ps. The TPDI S_1 basis spectrum was taken from the neat TPDI TA spectra (540 nm, 2.2 uJ/cm^2 excitation) at 1 ps. The CT basis spectrum was taken from the 540 nm excited PTB7-Th:TPDI TA at 2 ns.

The basis spectra chosen are shown in Figure A.10, and the fit to the experimental data in Figures A.5 and A.12. The fit is slightly poorer at early times, mostly due to a shift in the GSB wavelengths, potentially due to delocalisation of separation of the CT state over time. As with the PTB7-Th:PDI 540 nm fits, we note that the ESA from 800–900 nm is fit very well, and therefore consider the CT and TPDI S_1 kinetics to be described accurately. Also similarly to the PTB7-Th:PDI 540 nm fits, there is a long-lived component of TPDI S_1 (agreeing with the TCSPC). As such, the time the CT spectra was extracted from may not be purely CT, and the TPDI S_1 population may be underestimated at late times, and the CT population overestimated at late times. However, we again note that this will not affect the formation kinetics of the CT state.

A.2 Modelling

The following section details the modelling performed to blend PTB7-Th:(T)PDI films with excitation at 540 nm and 700 nm following the general procedure outlined in Chapter 5 for neat PTB7-Th films.

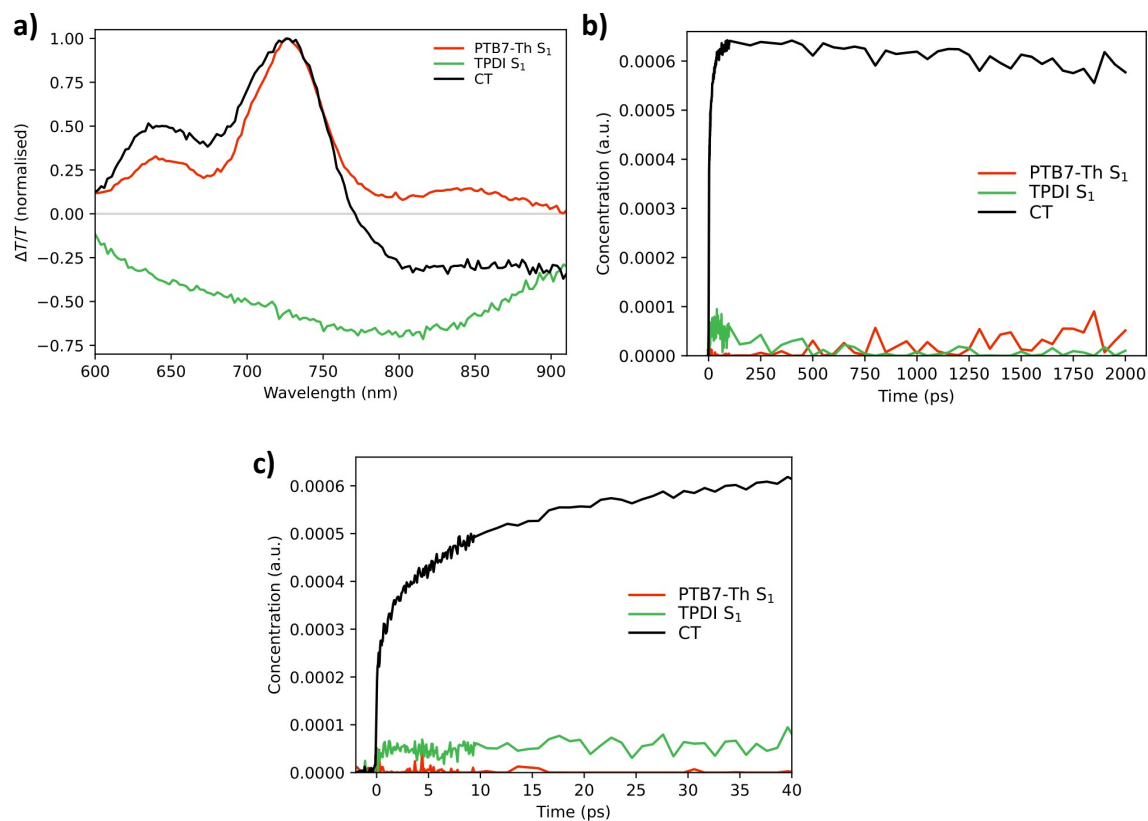


Figure A.10: a) TA basis spectra of the PTB7-Th:TPDI film excited at 540 nm and 3.5 uJ/cm². b) Deconvoluted concentrations of PTB7-Th S_1 , TPDI S_1 states and CT states over 2 ns. c) S_1 and CT concentrations over 40 ps.

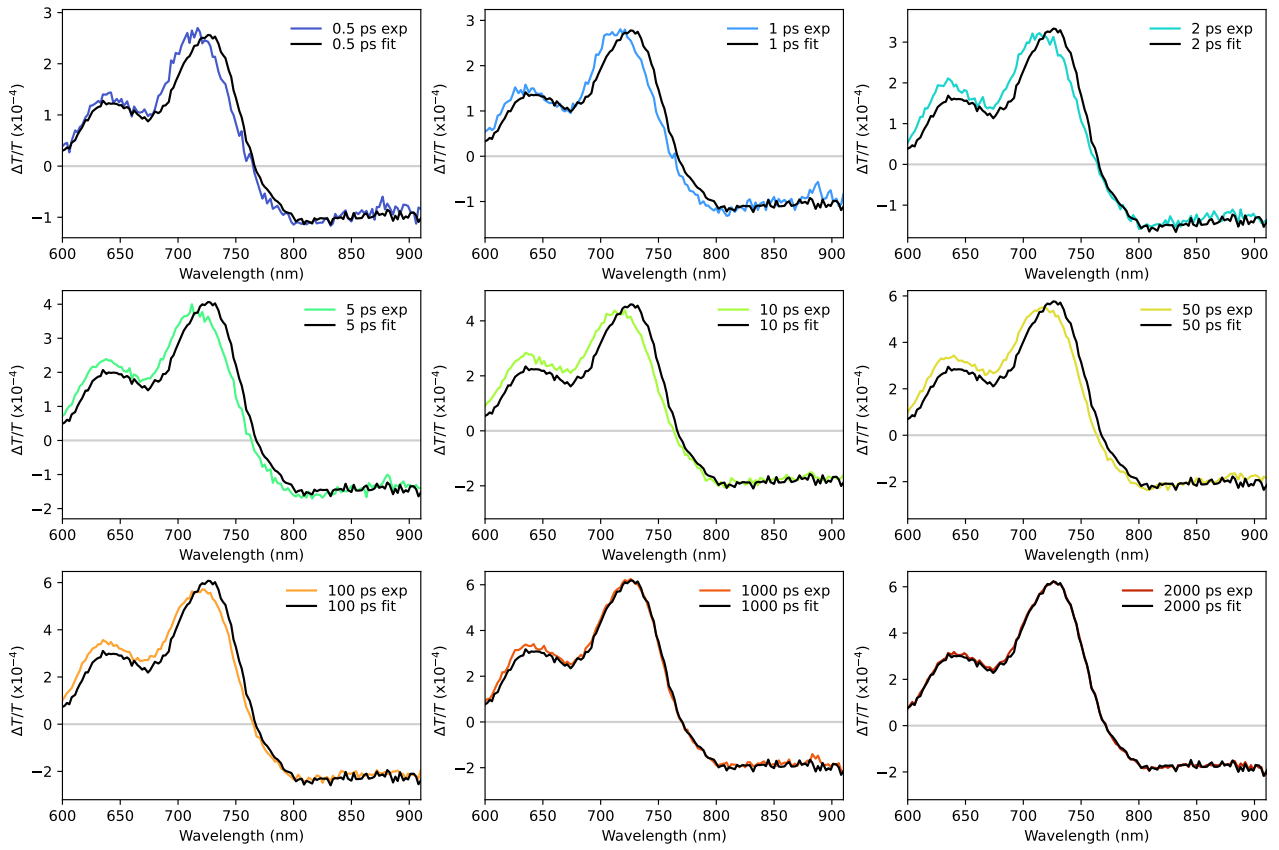


Figure A.11: Deconvolution fit of the PTB7-Th:TPDI film excited at 540 nm and 3.5 uJ/cm^2 at different delay times. Corresponding basis spectra and concentrations are in Figure A.10.

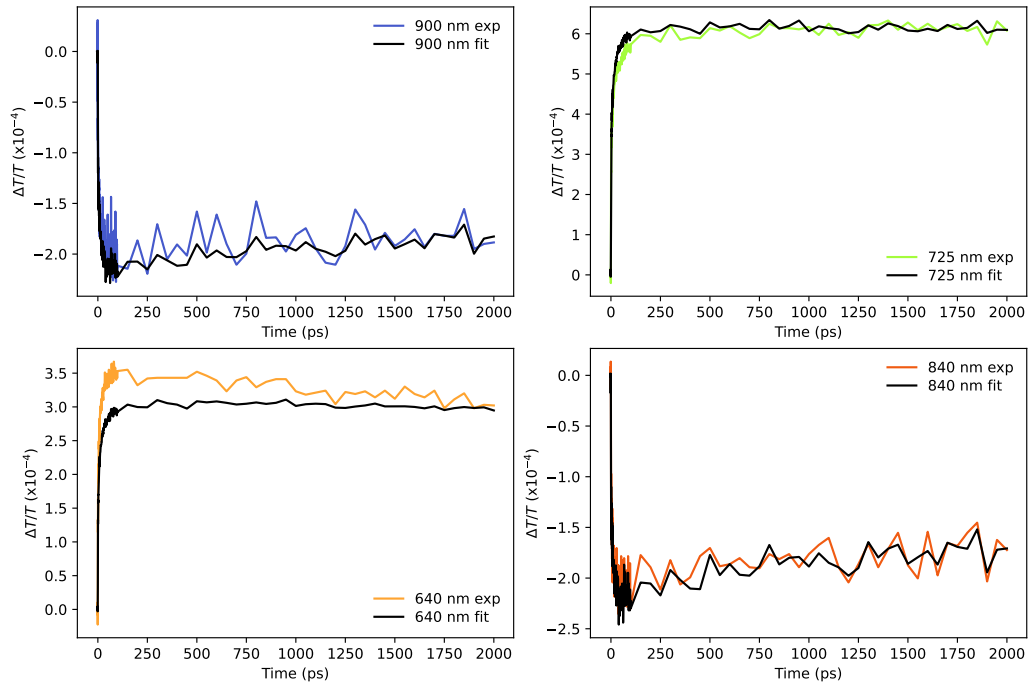


Figure A.12: Deconvolution fit of the PTB7-Th:TPDI film excited at 540 nm and 3.5 uJ/cm^2 at different wavelengths. Corresponding basis spectra and concentrations are in Figure A.10.

A.2.1 PTB7-Th:PDI blend film excited at 700 nm

The deconvoluted kinetics of the blend PTB7-Th:PDI film excited at 700 nm (selective excitation of PTB7-Th) and 0.2 uJ/cm² were fit to the following set of coupled differential equations:

$$\begin{aligned}
\frac{d[\text{PTB7-Th } S_1]}{dt} &= -k_{\text{PTB7-Th } S_1}[\text{PTB7-Th } S_1] - k_{\text{HET}}[\text{PTB7-Th } S_1] - k_{\text{ET}}[\text{PTB7-Th } S_1] \\
\frac{d[\text{PTB7-Th } S_1 - \text{trap}]}{dt} &= -k_{\text{PTB7-Th } S_1}[\text{PTB7-Th } S_1 - \text{trap}] \\
\frac{d[\text{CT}]}{dt} &= k_{\text{ET}}[\text{PTB7-Th } S_1] + k_{\text{HET}}[\text{PTB7-Th } S_1] - k_{\text{CT}}[\text{CT}]
\end{aligned}
\tag{A.1}$$

where $[\text{PTB7-Th } S_1]$ and $k_{\text{PTB7-Th } S_1}$ are the concentration and decay rate of the PTB7-Th singlet exciton basis spectrum and $[\text{PTB7-Th } S_1 - \text{trap}]$ the concentration of the PTB7-Th morphologically trapped exciton population. Note PDI is not directly excited at this wavelength and therefore no PDI S_1 population is present. The decay rate for PTB7-Th is fixed to 1/128 ps⁻¹ from the fit to neat PTB7-Th, though we note that this pathway is insignificant compared to competing pathways and therefore the model is not sensitive to this rate. We also fix the rate of homoelectron transfer within the PTB7-Th domains k_{HET} to 1/3.88 ps⁻¹, again from the neat PTB7-Th fit. We now include electron transfer as an additional decay mechanism occurring with a rate of k_{ET} , which leads to the formation of a CT state at the interface with concentration $[\text{CT}]$ and decay rate of k_{CT} . Note that in this model we treat the ICT and CT states as spectrally identical, but in reality they are likely to be slightly different. Figure A.13 provides a summary flowchart representing the coupled differential equations including the treatment of the grouped together CT and ICT states.

The decay curves and the fit to the CT state and the PTB7-Th S_1 state are shown in Figure A.14. The time constants for electron transfer and the CT state lifetime are shown in Table A.1. The population of morphologically trapped PTB7-Th excitons is less than 2% of the PTB7-Th population so we deem it unnecessary to include this in future blend modelling. Electron transfer is seen to occur over 0.09 ps, which is faster than the width of the probe pulse (0.15 ps), thus we are only able to reliably conclude that electron transfer occurs with a rate <0.15 ps.

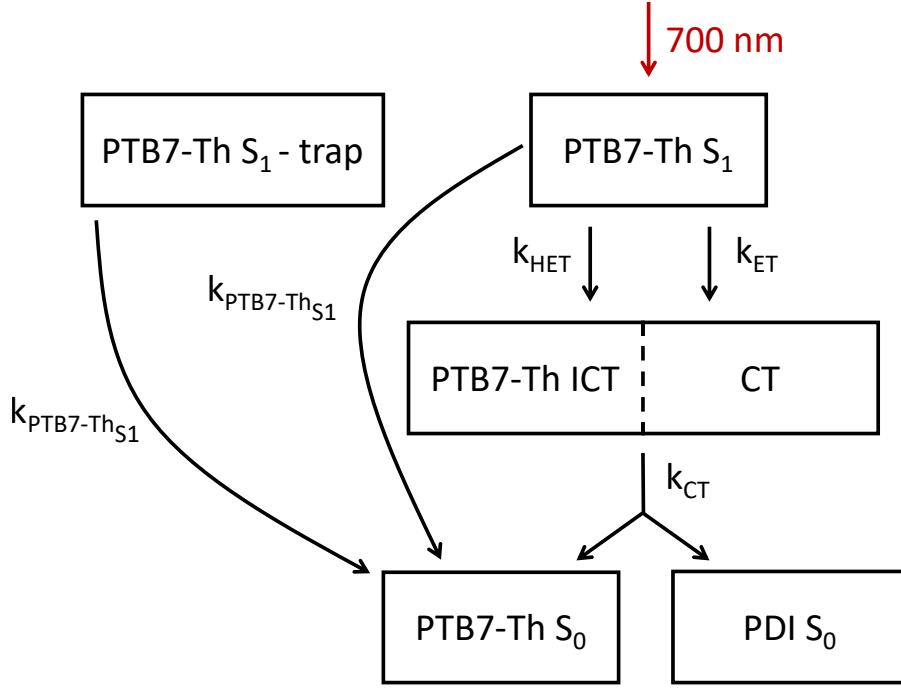


Figure A.13: Flow diagram representing the coupled differential Equations A.1 used to model the PTB7-Th:PDI blend with 700 nm excitation.

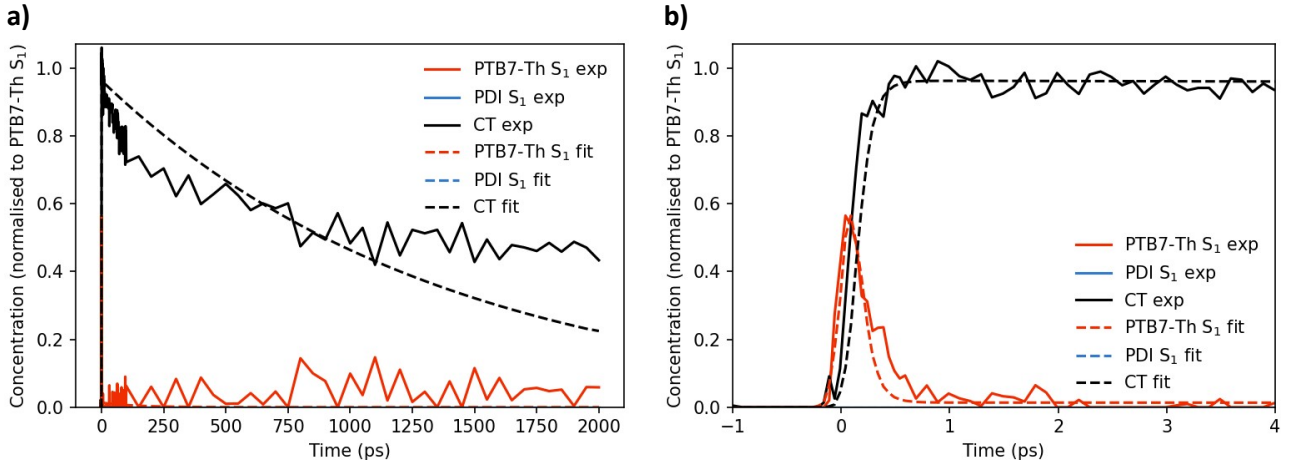


Figure A.14: a) Decay curve of the PTB7-Th S_1 and CT basis spectra in the PTB7-Th:PDI film excited at 700 nm and 0.2 uJ/cm². The data is normalised to PTB7-Th and fit to both the PTB7-Th S_1 and the CT state. b) PTB7-Th S_1 decay and CT rise and decay over 4 ps.

Table A.1: Time constants for PTB7-Th:PDI blend film (excitation at 700 nm)

Electron transfer: $1/k_{ET}$ (ps)	0.09 ± 0.01
CT state decay: $1/k_{CT}$ (ps)	1400 ± 100

A.2.2 PTB7-Th:PDI blend film excited at 540 nm

Blend films excited at 540 nm were modelled separately with two different charge generation mechanisms: hole transfer from (T)PDI to PTB7-Th (channel II charge generation) and FRET from (T)PDI to PTB7-Th followed by back electron transfer (channel I charge generation).

Hole transfer:

The deconvoluted kinetics of the blend PTB7-Th:PDI blend film excited at 540 nm and 3.5 uJ/cm² were fit to the following set of coupled differential equations:

$$\begin{aligned}
\frac{d[\text{PDI } S_1]}{dt} &= -k_{\text{PDI } S_1}[\text{PDI } S_1] - k_{\text{HT}}[\text{PDI } S_1] \\
\frac{d[\text{PDI } S_1 - \text{trap}]}{dt} &= -k_{\text{PDI } S_1}[\text{PDI } S_1 - \text{trap}] \\
\frac{d[\text{PTB7-Th } S_1]}{dt} &= -k_{\text{PTB7-Th } S_1}[\text{PTB7-Th } S_1] - k_{\text{HET}}[\text{PTB7-Th } S_1] - k_{\text{ET}}[\text{PTB7-Th } S_1] \\
\frac{d[\text{CT}]}{dt} &= k_{\text{ET}}[\text{PTB7-Th } S_1] + k_{\text{HT}}[\text{PDI } S_1] + k_{\text{HET}}[\text{PTB7-Th } S_1] - k_{\text{CT}}[\text{CT}]
\end{aligned} \tag{A.2}$$

where the concentrations of the different species and their decays are the same as described above, but now with the addition of hole transfer from PDI to PTB7-Th with a rate of k_{HT} . Note that both PDI and PTB7-Th are excited in this case. To fit the data it was necessary to also include a population of isolated or ‘trapped’ PDI excitons that are unable to diffuse to the interface and can only decay with rate $k_{\text{PDI } S_1 - \text{trap}}$. The proportion of this population was fit to the data. It was not necessary to include a trapped or isolated population of PTB7-Th. Figure A.15 provides a visual summary of the decay mechanisms considered.

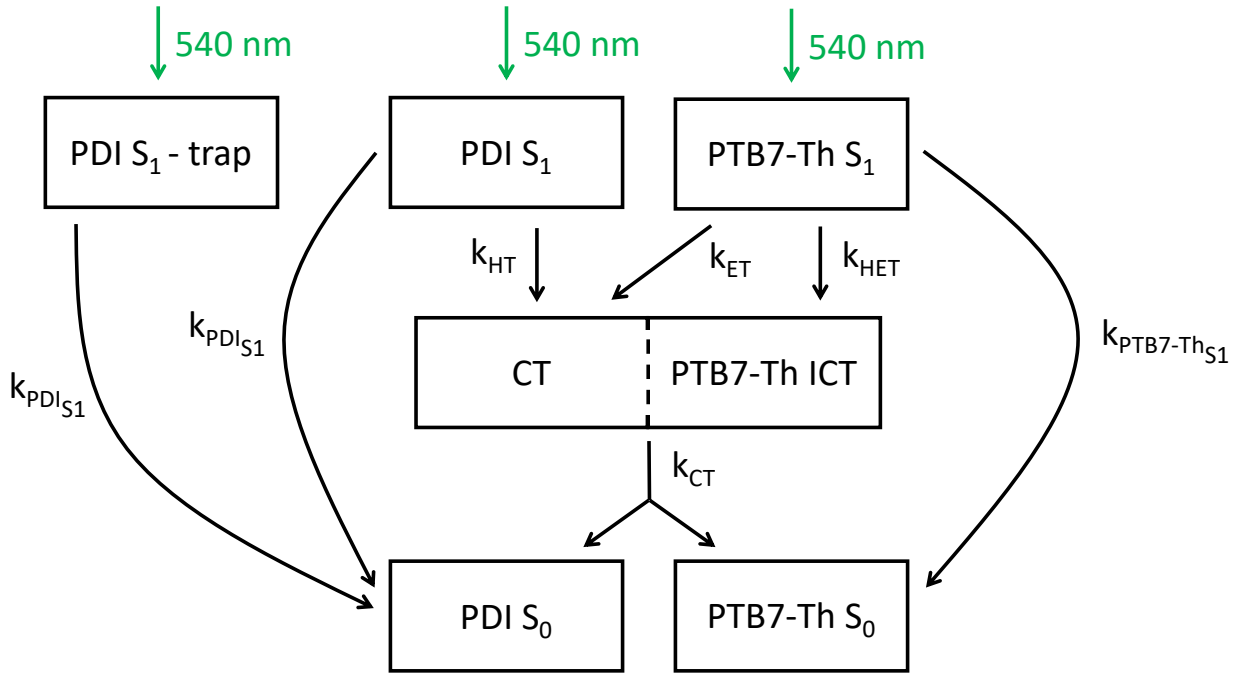


Figure A.15: Flow diagram representing the coupled differential Equations A.2 used to model the PTB7-Th:PDI blend with 540 nm excitation and hole transfer.

The decay of the PDI S_1 state is set as a variable due to fluence dependent decay in PDI. The decay rate of the PTB7-Th S_1 basis spectrum and the time constant for homoelectron transfer remain fixed to that determined from fits to neat PTB7-Th, though we again note the model is insensitive to $k_{\text{PTB7-Th } S_1}$. The decay of the PDI S_1 state and the rise and decay of the CT basis spectrum are shown in Figure A.16 along with the fit generated from both kinetics. The time constant for hole transfer, electron transfer and the percentage of trapped excitons in PDI domains is given in Table A.2. The lifetime of the CT state is much longer than the timescale of the experiment (2000 ps) so this should be regarded as only an approximation.

Table A.2: Time constants for PTB7-Th:PDI blend film (excitation at 540 nm, modelled using hole transfer)

CT state decay: $1/k_{\text{CT}}$ (ps)	14000 ± 4000
Hole transfer: $1/k_{\text{HT}}$ (ps)	7.1 ± 0.9
Electron transfer: $1/k_{\text{ET}}$ (ps)	0.02 ± 0.02
PDI S_1 decay: $1/k_{\text{PDI } S_1}$ (ps)	450 ± 70
% trapped PDI	68 ± 2

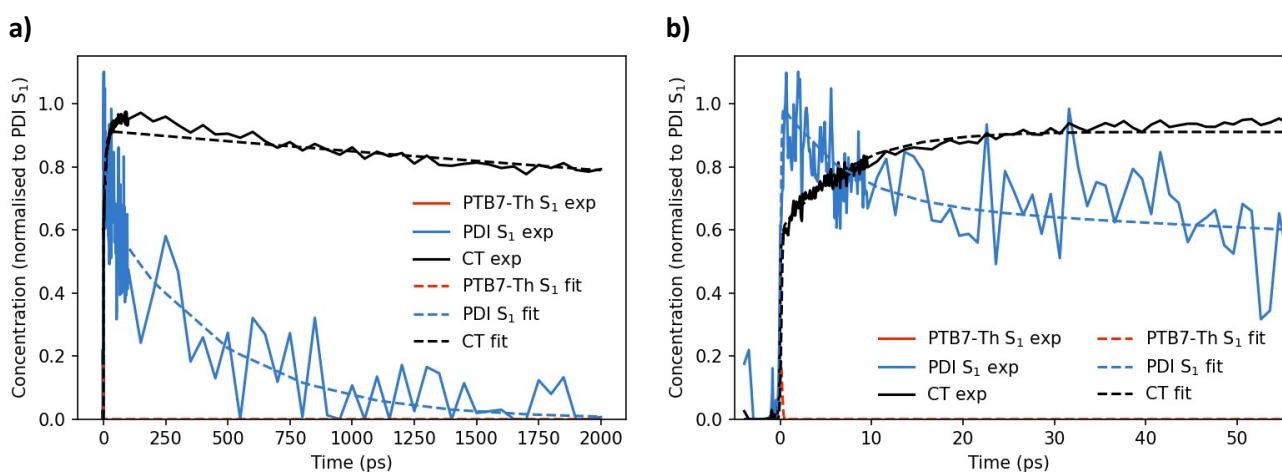


Figure A.16: a) Decay curve of the PDI S₁ and CT basis spectra in the PTB7-Th:PDI film excited at 540 nm and 3.5 uJ/cm². The data is normalised to PTB7-Th and fit to both the PDI S₁ and the CT state using a hole transfer model. b) PDI S₁ decay and CT rise and fits over 50 ps.

Energy transfer plus back electron transfer

The same decay of the PTB7-Th:PDI blend film excited at 540 nm and 3.5 uJ/cm² was fit to the following set of coupled differential equations:

$$\begin{aligned}
 \frac{d[\text{PDI } S_1]}{dt} &= -k_{\text{PDI } S_1}[\text{PDI } S_1] - k_{\text{EnT}}[\text{PDI } S_1] \\
 \frac{d[\text{PDI } S_1 - \text{trap}]}{dt} &= -k_{\text{PDI } S_1}[\text{PDI } S_1 - \text{trap}] \\
 \frac{d[\text{PTB7-Th } S_1]}{dt} &= k_{\text{EnT}}[\text{PDI } S_1] - k_{\text{PTB7-Th } S_1}[\text{PTB7-Th } S_1] - k_{\text{HET}}[\text{PTB7-Th } S_1] - k_{\text{ET}}[\text{PTB7-Th } S_1] \\
 \frac{d[\text{CT}]}{dt} &= k_{\text{ET}}[\text{PTB7-Th } S_1] + k_{\text{HET}}[\text{PTB7-Th } S_1] - k_{\text{CT}}[\text{CT}]
 \end{aligned}
 \tag{A.3}$$

where the concentrations of the different species and their decays are the same as described above, but now with FRET from PDI to PTB7-Th plus back electron transfer being responsible for charge generation instead of hole transfer. FRET energy transfer is modelled with a rate of k_{EnT} and electron transfer with k_{ET} as before. The population of excitons trapped in PDI is represented with $[\text{PDI } S_1 - \text{trap}]$ as before. A visual summary of the coupled equations is presented in Figure A.17.

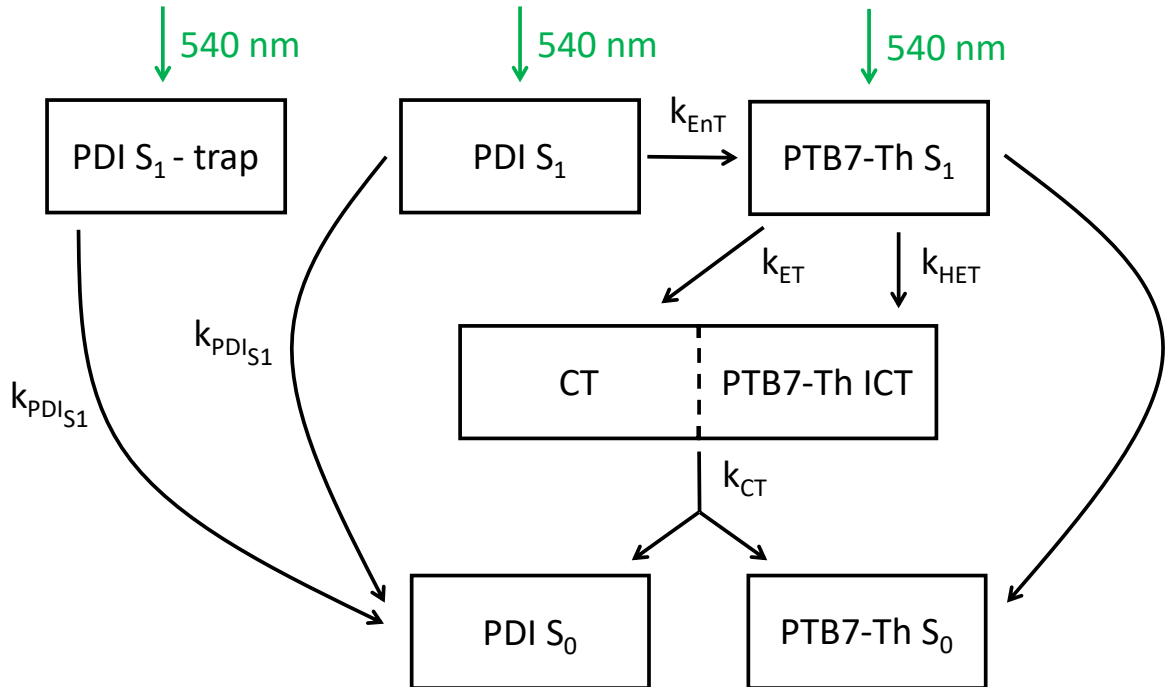


Figure A.17: Flow diagram representing the coupled differential Equations A.3 used to model the PTB7-Th:PDI blend with 540 nm excitation and FRET plus back electron transfer.

The decay of the PDI S_1 state is left as a variable but the decay rate of the PTB7-Th S_1 basis spectrum and the time constant for homoelectron transfer remain fixed as before. The decay of the PDI S_1 state and the rise of the CT basis spectrum are shown in Figure A.18 along with the fit generated from both kinetics. The time constant for energy transfer, electron transfer and the percentage of trapped excitons in PDI domains is given in Table A.3. Again, the lifetime of the CT state is much longer than the timescale of the experiment (2000 ps) so this should be regarded as only an approximation.

Table A.3: Time constants for PTB7-Th:PDI blend film (excitation at 540 nm, modelled using energy transfer)

CT state decay: $1/k_{CT}$ (ps)	14000 ± 4000
Energy transfer: $1/k_{EnT}$ (ps)	7.1 ± 0.9
Electron transfer: $1/k_{ET}$ (ps)	0.02 ± 0.01
PDI S_1 decay: $1/k_{PDI S_1}$ (ps)	450 ± 60
% trapped PDI	68 ± 2

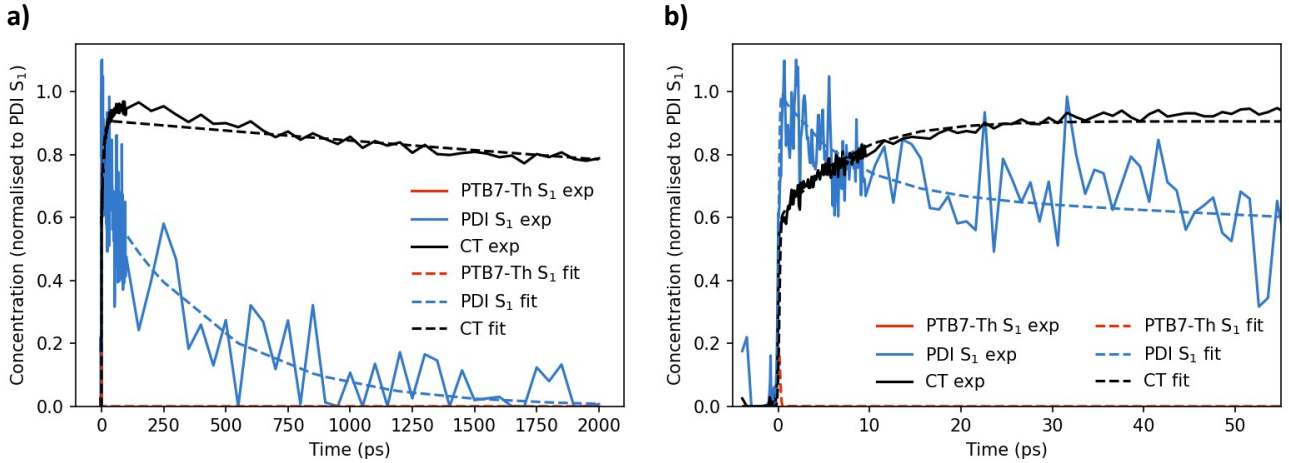


Figure A.18: a) Decay curve of the PDI S_1 and CT basis spectra in the PTB7-Th:PDI film excited at 540 nm and 3.5 uJ/cm^2 . The data is normalised to PTB7-Th and fit to both the PDI S_1 and the CT state using an energy transfer and back electron transfer model. b) PDI S_1 decay and CT rise and fits over 50 ps.

A.2.3 PTB7-Th:TPDI blend film excited at 700 nm

The deconvoluted kinetics of the blend PTB7-Th:TPDI film excited at 700 nm (selective excitation of PTB7-Th) and 0.2 uJ/cm² were fit to the following set of coupled differential equations:

$$\begin{aligned}\frac{d[\text{PTB7-Th } S_1]}{dt} &= -k_{\text{PTB7-Th } S_1}[\text{PTB7-Th } S_1] - k_{\text{HET}}[\text{PTB7-Th } S_1] - k_{\text{ET}}[\text{PTB7-Th } S_1] \\ \frac{d[\text{CT}]}{dt} &= k_{\text{ET}}[\text{PTB7-Th } S_1] + k_{\text{HET}}[\text{PTB7-Th } S_1] - k_{\text{CT}}[\text{CT}]\end{aligned}\tag{A.4}$$

which are constructed the same as for the PTB7-Th:PDI blend film with 700 nm excitation. A visual representation of the coupled equations in A.4 is shown in Figure A.19.

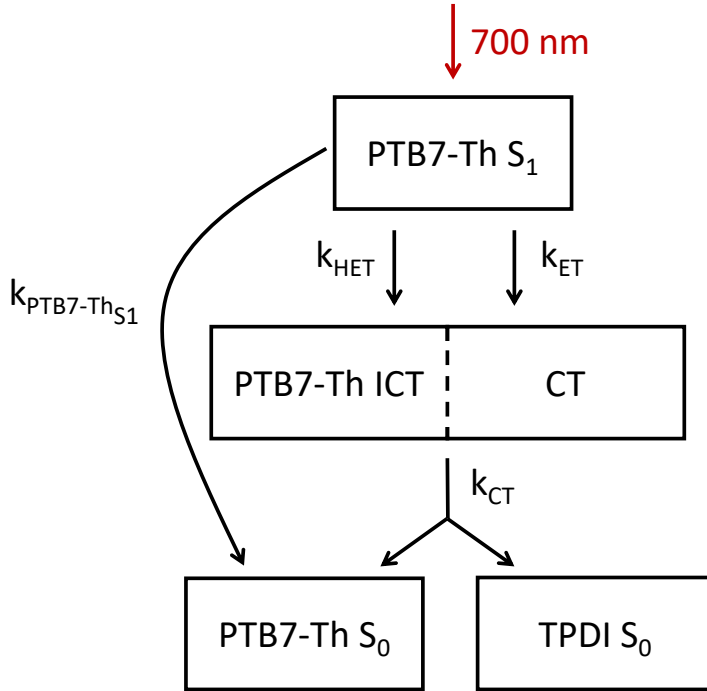


Figure A.19: Flow diagram representing the coupled differential Equations A.4 used to model the PTB7-Th:TPDI blend with 700 nm excitation and one electron transfer lifetime.

The decay of the PTB7-Th CT and S₁ basis spectra are shown alongside the fit to these states in Figure A.20. The time constant for electron transfer and the CT state lifetime are shown in Table A.4. Electron transfer is seen to occur over 2.34 ps, more than two times slower than that of the PDI blend film. This is similar to the rate found by Shivanna et al. of 1.6 ps for the same molecule.²⁵⁷ Again, the lifetime of the CT state is much longer than the timescale

of the experiment (2000 ps) so this should be regarded as only an approximation.

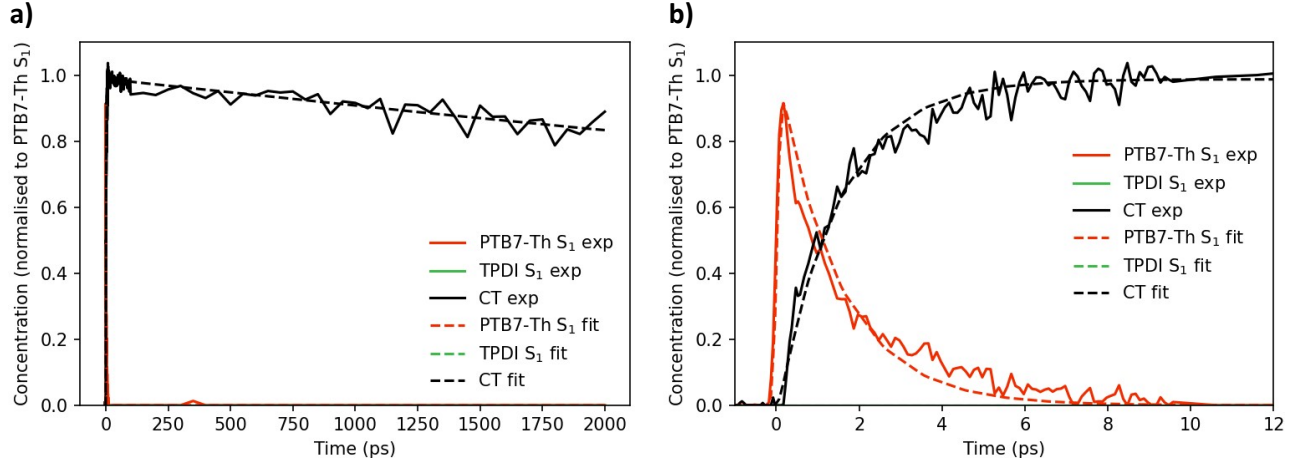


Figure A.20: a) Decay curve of the PTB7-Th S_1 and CT basis spectra in the PTB7-Th:TPDI film excited at 700 nm and 0.2 uJ/cm². The data is normalised to PTB7-Th and fit to both the PTB7-Th S_1 and the CT state. b) PTB7-Th S_1 decay and CT rise and decay over 12 ps.

Table A.4: Time constants for PTB7-Th:TPDI blend film (excitation at 700 nm)

Electron transfer: $1/k_{ET}$ (ps)	2.34 ± 0.08
CT state decay: $1/k_{CT}$ (ps)	12000 ± 1000

The fit is performed again with two components for electron transfer from PTB7-Th to TPDI, consisting of a fast and a slow electron transfer rate. This is done due to the electron transfer rate from the TPDI film excited at 540 nm being fit to a significantly faster rate compared to that found in 700 nm excitation (see below).

The following system of coupled differential equations is used to fit the decay with two lifetimes for electron transfer:

$$\begin{aligned}
\frac{d[\text{PTB7-Th } S_1]}{dt} &= -k_{\text{PTB7-Th } S_1}[\text{PTB7-Th } S_1] - k_{\text{HET}}[\text{PTB7-Th } S_1] - k_{\text{ET}}[\text{PTB7-Th } S_1] \\
\frac{d[\text{PTB7-Th } S_{12}]}{dt} &= -k_{\text{PTB7-Th } S_1}[\text{PTB7-Th } S_{12}] - 1/0.12[\text{PTB7-Th } S_{12}] - k_{\text{HET}}[\text{PTB7-Th } S_{12}] \\
\frac{d[\text{CT}]}{dt} &= k_{\text{ET}}[\text{PTB7-Th } S_1] + k_{\text{HET}}[\text{PTB7-Th } S_1] - k_{\text{CT}}[\text{CT}]
\end{aligned}
\tag{A.5}$$

where $d[\text{PTB7-Th } S_{12}]$ represents the population of PTB7-Th excitons which undergo electron transfer with a fast lifetime of 0.12 ps as fit below in the section describing excitation at 540 nm. This could alternatively be described with a diffusion-limited electron transfer model, but we consider this level of detail to be beyond the scope of this work. A flow diagram to represent the two different populations of PTB7-Th excitations having different electron transfer rates is summarised in Figure A.21.

The resulting fit is shown alongside the decay of the PTB7-Th S_1 and CT basis spectra in Figure A.22. The time constants for the variable electron transfer and the CT state lifetime are shown in Table A.5 along with the percentage of the population of PTB7-Th which undergoes fast electron transfer.

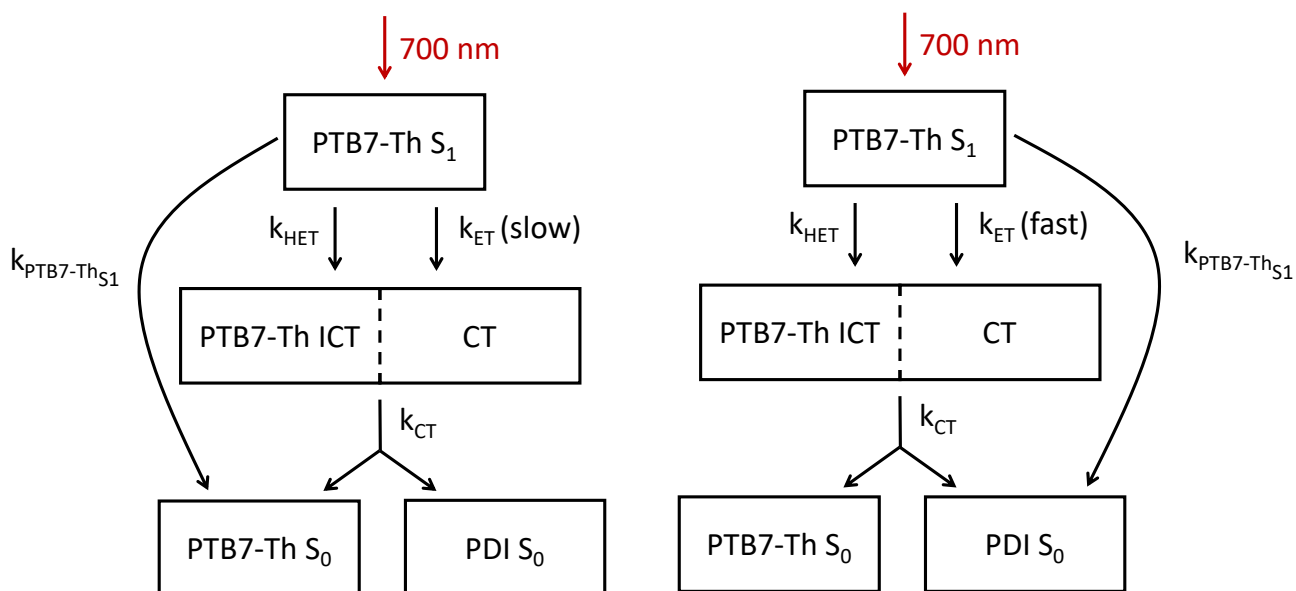


Figure A.21: Flow diagram representing the coupled differential Equations A.5 used to model the PTB7-Th:TPDI blend with 700 nm excitation and two electron transfer lifetimes.

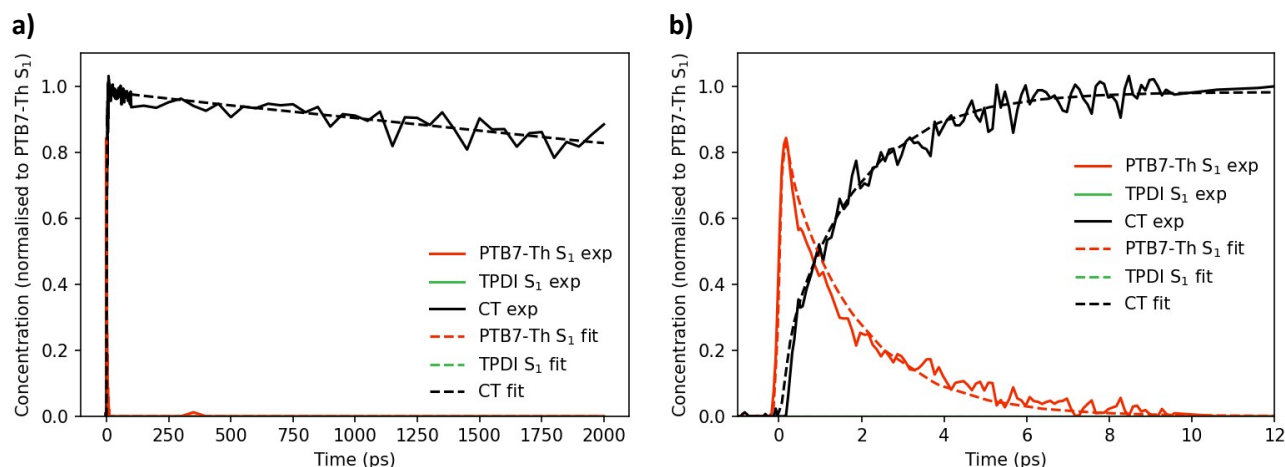


Figure A.22: a) Decay curve of the PTB7-Th S_1 and CT basis spectra in the PTB7-Th:TPDI film excited at 700 nm and 0.2 uJ/cm^2 and fit with two components for electron transfer. The data is normalised to PTB7-Th and fit to both the PTB7-Th S_1 and the CT state. b) PTB7-Th S_1 decay and CT rise and decay over 12 ps.

We conclude it is reasonable to include the fast electron transfer component from the fit with excitation at 540 nm in the fit with 700 nm excitation, and it produces a better fit. Physically, the presence of a fast and slow electron transfer mechanism represents that some excitons in PTB7-Th domains are able to reach the interface quickly and generate CT states while other excitons may need to travel further through slower, diffusion-limited transport. Alternatively, energetic and morphological disorder in the TPDI blend film could lead to sites

Table A.5: Time constants for PTB7-Th:TPDI blend film (excitation at 700nm, two lifetimes for electron transfer)

Slow electron transfer: $1/k_{\text{ET}}$ (ps)	3.3 ± 0.1
CT state decay: $1/k_{\text{CT}}$ (ps)	11600 ± 600
Fast electron transfer (%)	$18\% \pm 1$

with slower electron transfer rates than others. The fit suggests that only 18% of the PTB7-Th population undergoes rapid electron transfer with a time constant of <0.15 ps, and the rest of the population undergoes slow electron transfer with a time constant of 3.3 ps.

A.2.4 PTB7-Th:TPDI blend film excited at 540 nm

As for PTB7-Th:PDI, blend films excited at 540 nm were modelled separately using hole transfer and FRET plus back electron transfer.

Hole transfer

The deconvoluted kinetics of the blend PTB7-Th:TPDI film excited at 540 nm and 2.2 uJ/cm² were fit to the following set of coupled differential equations:

$$\begin{aligned}
 \frac{d[\text{TPDI } S_1]}{dt} &= -k_{\text{TPDI } S_1}[\text{TPDI } S_1] - k_{\text{HT}}[\text{TPDI } S_1] \\
 \frac{d[\text{TPDI } S_1 - \text{trap}]}{dt} &= -k_{\text{TPDI } S_1}[\text{TPDI } S_1 - \text{trap}] \\
 \frac{d[\text{PTB7-Th } S_1]}{dt} &= -k_{\text{PTB7-Th } S_1}[\text{PTB7-Th } S_1] - k_{\text{HET}}[\text{PTB7-Th } S_1] - k_{\text{ET}}[\text{PTB7-Th } S_1] \\
 \frac{d[\text{CT}]}{dt} &= k_{\text{ET}}[\text{PTB7-Th } S_1] + k_{\text{HT}}[\text{TPDI } S_1] + k_{\text{HET}}[\text{PTB7-Th } S_1] - k_{\text{CT}}[\text{CT}]
 \end{aligned}
 \tag{A.6}$$

where the concentrations of the different species and their decays are the same as described previously. The decay rate of the PTB7-Th S_1 basis spectrum and the homoelectron transfer rate are set to the same values as above (1/128 and 1/3.88 ps⁻¹). A sufficient fit is achievable without the inclusion of any trapped populations in PTB7-Th, however the fit requires a population of trapped TPDI S_1 excitons described by [TPDI S_1 - trap]. A summary of the coupled differential equations in A.6 is shown in Figure A.23.

The decay of the TPDI S_1 state and the rise and decay of the CT basis spectrum are shown in Figure A.24 along with the fit generated from both kinetics. The very early time (<10 ps) fit to TPDI S_1 overestimates the decay, however there is a large amount of uncertainty in the deconvoluted TPDI S_1 component, so we do not consider this unreasonable.

The time constant for hole transfer, electron transfer and the percentage of trapped excitons in TPDI domains is given in Table A.6. The time constant for electron transfer is faster than that initially fit using the 700 nm excitation of the TPDI blend film, hence the 700 nm excitation is refit using a fast and slow electron transfer component using the fast component generated with 540 nm excitation as described previously. We see therefore that the fast rate of electron transfer here is not unfeasible. Again, the lifetime of the CT state is much longer than the timescale of the experiment (2000 ps) so this should be regarded as only an approximation.

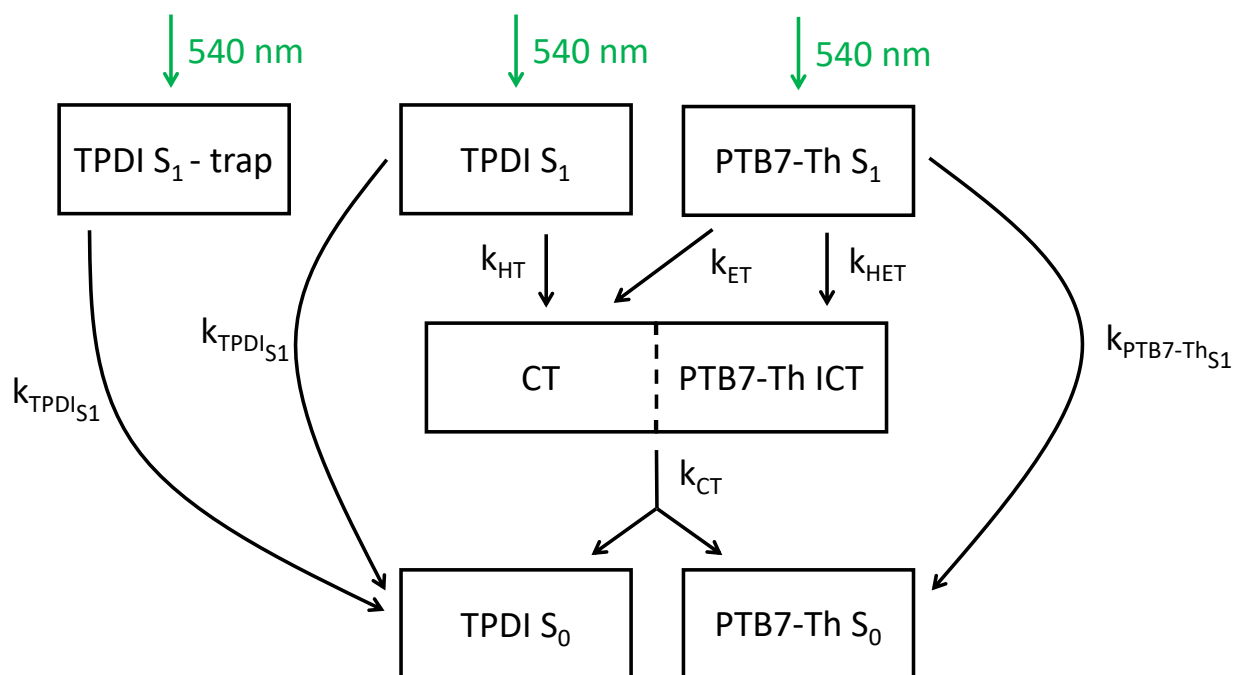


Figure A.23: Flow diagram representing the coupled differential Equations A.6 used to model the PTB7-Th:TPDI blend with 540 nm excitation and hole transfer.

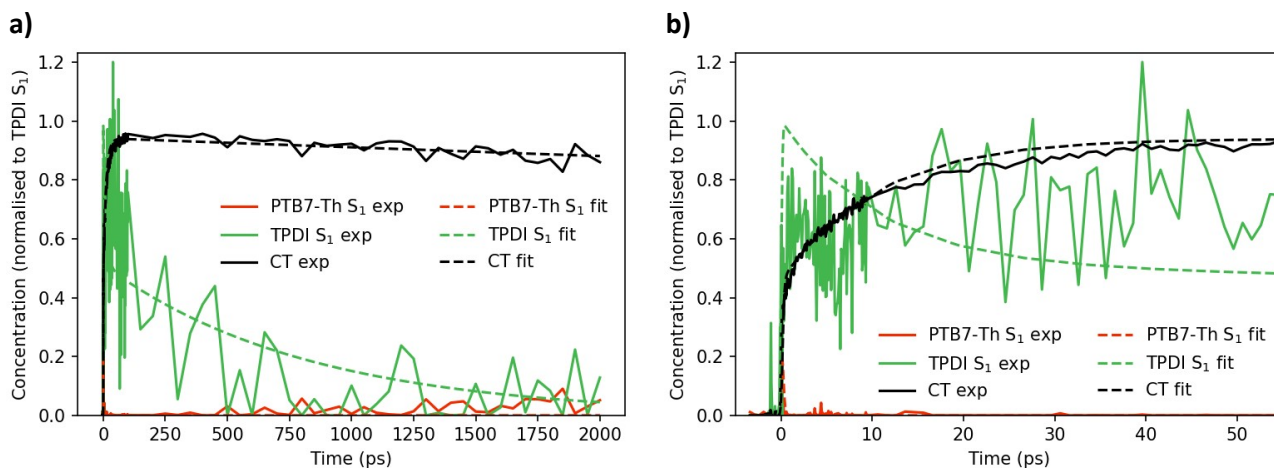


Figure A.24: a) Decay curve of the TPDI S_1 and CT basis spectra in the PTB7-Th:TPDI film excited at 540 nm and 2.2 uJ/cm^2 . The data is normalised to PTB7-Th and fit to both the TPDI S_1 and the CT state using a hole transfer model. b) TPDI S_1 decay and CT rise and fits over 50 ps.

Table A.6: Time constants for PTB7-Th:TPDI blend film (excitation at 540 nm, modelled using hole transfer)

CT state decay: $1/k_{CT}$ (ps)	30000 ± 11000
Hole transfer: $1/k_{HT}$ (ps)	10.6 ± 0.6
Electron transfer: $1/k_{ET}$ (ps)	0.12 ± 0.03
TPDI S_1 decay: $1/k_{PDI S_1}$ (ps)	800 ± 260
% trapped TPDI	51 ± 2

Energy transfer plus back electron transfer

The same decay of the PTB7-Th:TPDI blend film excited at 540 nm and 2.2 uJ/cm² was fit to the following set of coupled differential equations:

$$\begin{aligned}
 \frac{d[\text{TPDI } S_1]}{dt} &= -k_{\text{TPDI } S_1}[\text{TPDI } S_1] - k_{\text{EnT}}[\text{TPDI } S_1] \\
 \frac{d[\text{TPDI } S_1 - \text{trap}]}{dt} &= -k_{\text{TPDI } S_1}[\text{TPDI } S_1 - \text{trap}] \\
 \frac{d[\text{PTB7-Th } S_1]}{dt} &= k_{\text{EnT}}[\text{TPDI } S_1] - k_{\text{PTB7-Th } S_1}[\text{PTB7-Th } S_1] - k_{\text{HET}}[\text{PTB7-Th } S_1] - k_{\text{ET}}[\text{PTB7-Th } S_1] \\
 \frac{d[\text{CT}]}{dt} &= k_{\text{ET}}[\text{PTB7-Th } S_1] + k_{\text{HET}}[\text{PTB7-Th } S_1] - k_{\text{CT}}[\text{CT}]
 \end{aligned}
 \tag{A.7}$$

where the concentrations of the different species and their decays are the same as described above, but now with FRET from TPDI to PTB7-Th plus back electron transfer being responsible for charge generation instead of hole transfer. Again, excitons trapped in the TPDI domain are represented with [TPDI S_1 - trap]. These decay processes described by Equation A.7 are summarised in Figure A.25.

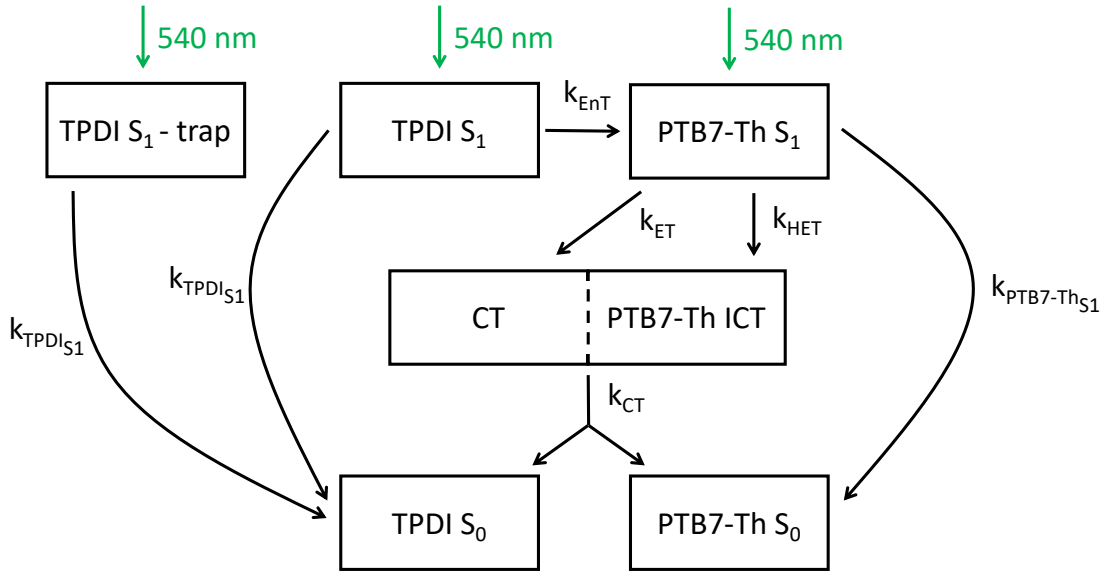


Figure A.25: Flow diagram representing the coupled differential Equations A.7 used to model the PTB7-Th:TPDI blend with 540 nm excitation and FRET plus back electron transfer.

The decay of the TPDI S_1 state and the rise of the CT basis spectrum are shown in Figure A.26 along with the fit generated using both kinetics. The time constants for energy transfer, electron transfer and the percentage of trapped excitons in TPDI domains is given in Table A.7.

Again, the lifetime of the CT state is much longer than the timescale of the experiment (2000 ps) so this should be regarded as only an approximation.

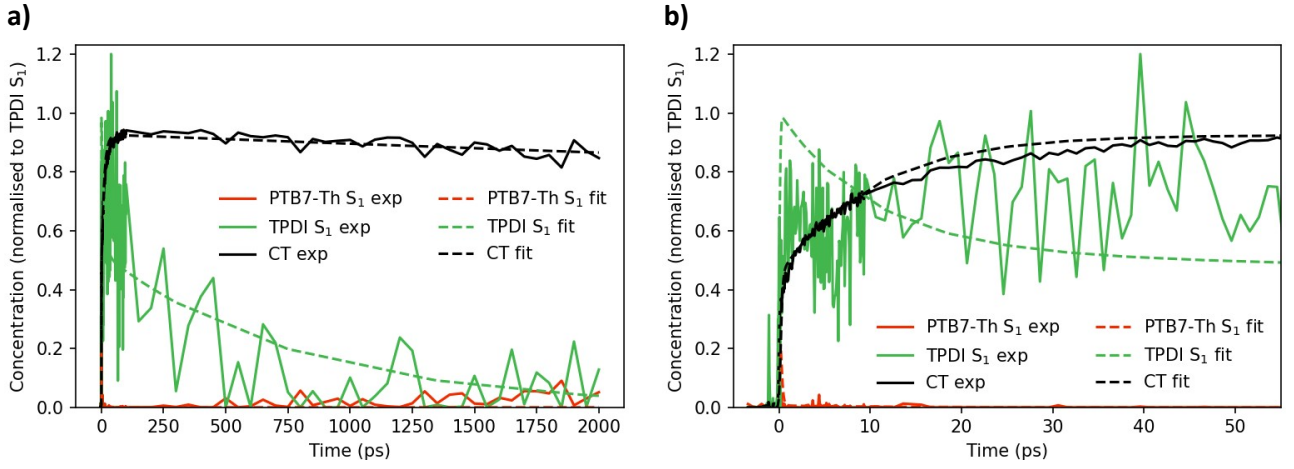


Figure A.26: a) Decay curve of the TPDI S_1 and CT basis spectra in the PTB7-Th:TPDI film excited at 540 nm and 2.2 uJ/cm². The data is normalised to PTB7-Th and fit to both the TPDI S_1 and the CT state using an energy transfer and back electron transfer model. b) TPDI S_1 decay and CT rise and fits over 50 ps.

Table A.7: Time constants for PTB7-Th:TPDI blend film (excitation at 540 nm, modelled using energy transfer)

CT state decay: $1/k_{CT}$ (ps)	29000 ± 13000
Energy transfer: $1/k_{ENT}$ (ps)	10.3 ± 0.6
Electron transfer: $1/k_{ET}$ (ps)	0.14 ± 0.03
TPDI S_1 decay: $1/k_{PDI S_1}$ (ps)	770 ± 240
% trapped TPDI	53 ± 2

Appendix B

Appendix to Chapter 6: Strong exciton-photon coupling in (T)PDI and PTB7-Th Fabry-Pérot thin films

B.1 PS cavities (exp S)

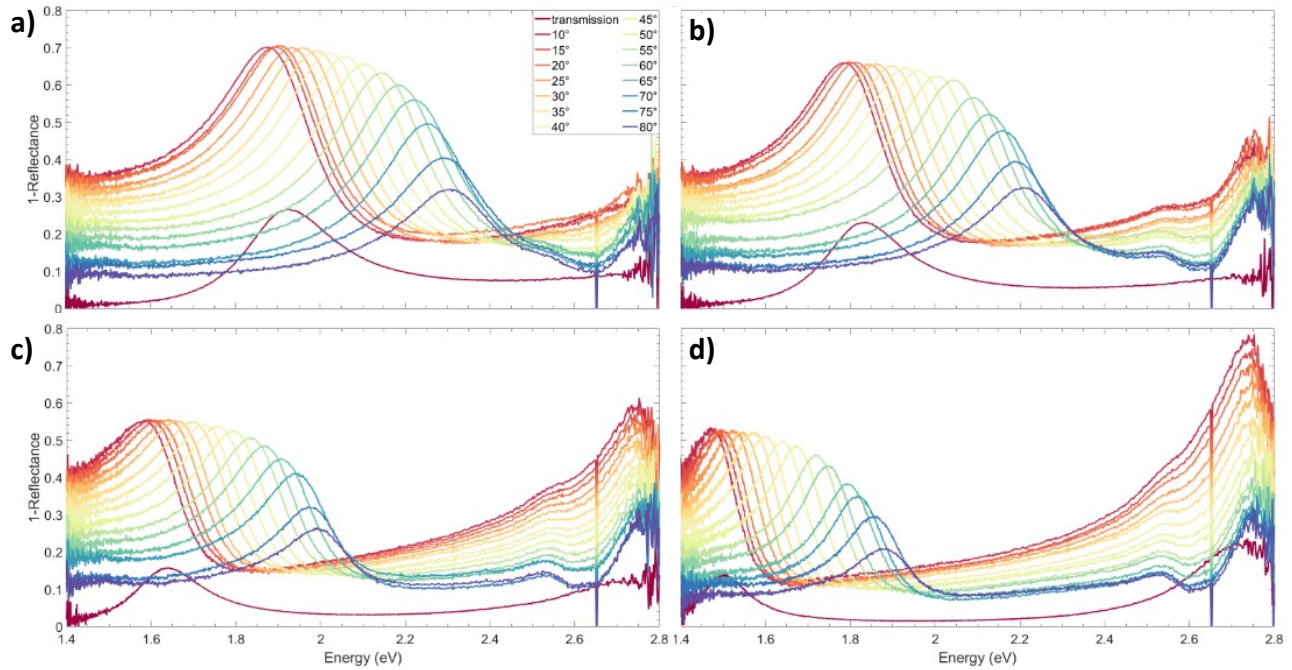


Figure B.1: Angular reflectance of PS FP cavity samples of varying thicknesses: a) S1 (147 nm), b) S2 (158 nm), c) S3 (184 nm) and d) S4 (214 nm). (Common legend.)

B.2 PTB7-Th

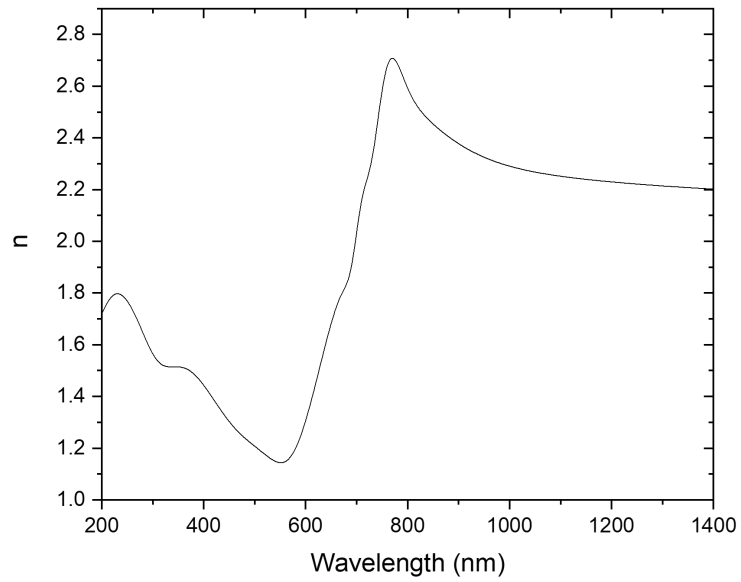


Figure B.2: Real part of the refractive index of PTB7-Th, measured using ellipsometry.

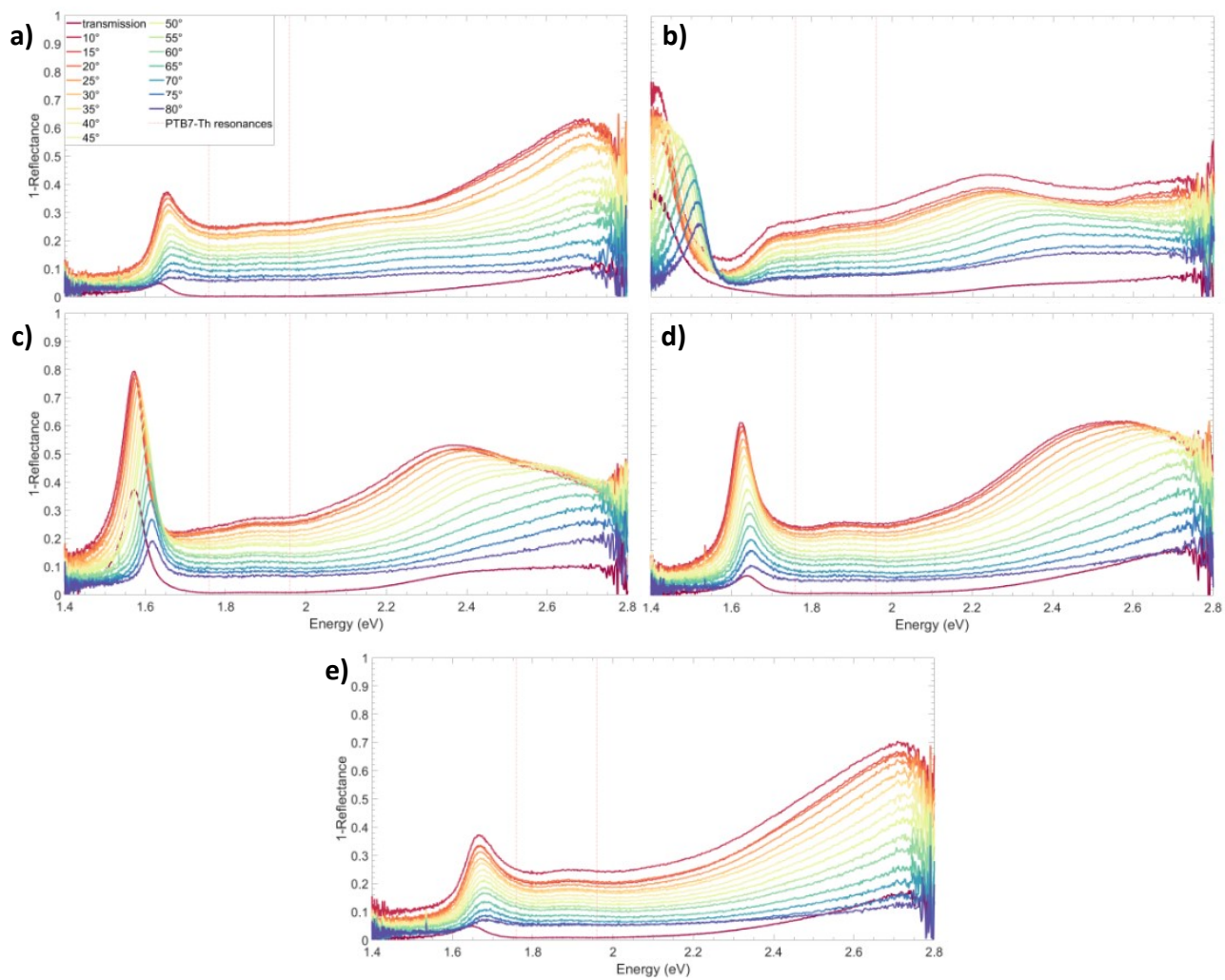


Figure B.3: Angular reflectance of neat PTB7-Th films of varying thicknesses: a) N1 (243 nm), b) N2 (148 nm), c) N4 (112 nm), d) N5 (100 nm) and e) N9 (79 nm). (Common legend.)

B.3 TCSPC

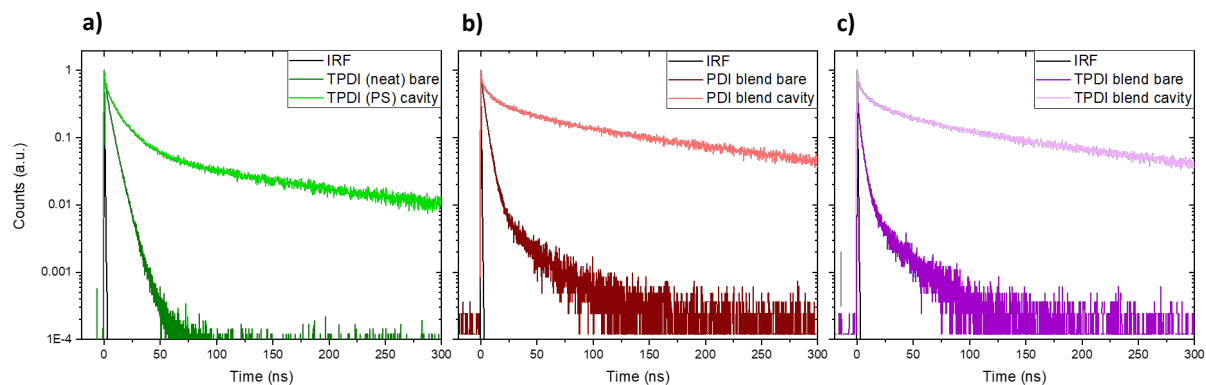


Figure B.4: TCSPC data demonstrating the elongation of the lifetime of samples in a cavity compared to bare films, and thus the lack of the Purcell effect, for uncoupled cavities. a) TPDI neat bare film compared to dispersed in PS in a cavity, b) PTB7-Th:PDI bare blend film compared to the same in a cavity and c) PTB7-Th:TPDI bare blend film compared to the same in a cavity.

Appendix C

Appendix to Chapter 7: PTB7-Th:TPDI OPV devices in Fabry-Pérot optical cavities

C.1 Reproducibility of cavity devices

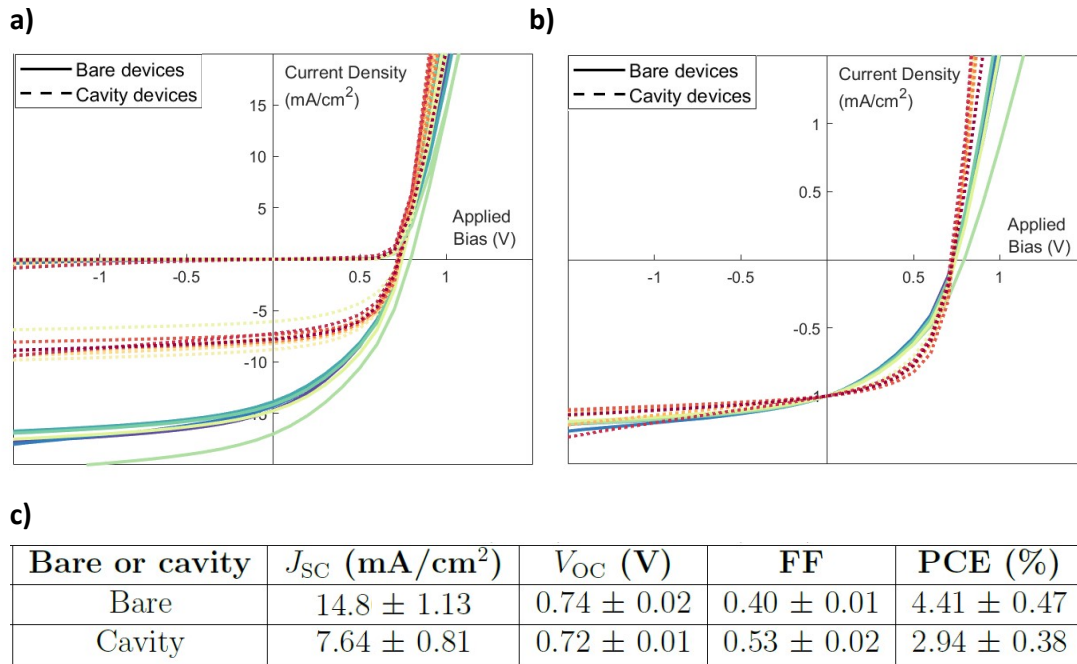


Figure C.1: a) JV curves comparing a number of bare and cavity devices to demonstrate measurement reproducibility. b) JV curves normalised to the J_{SC} demonstrating improved FF for cavity devices. c) Performance metrics for the bare (n=6) and cavity (n=8) devices shown in a) and b).

C.2 Rabi splitting of cavity devices

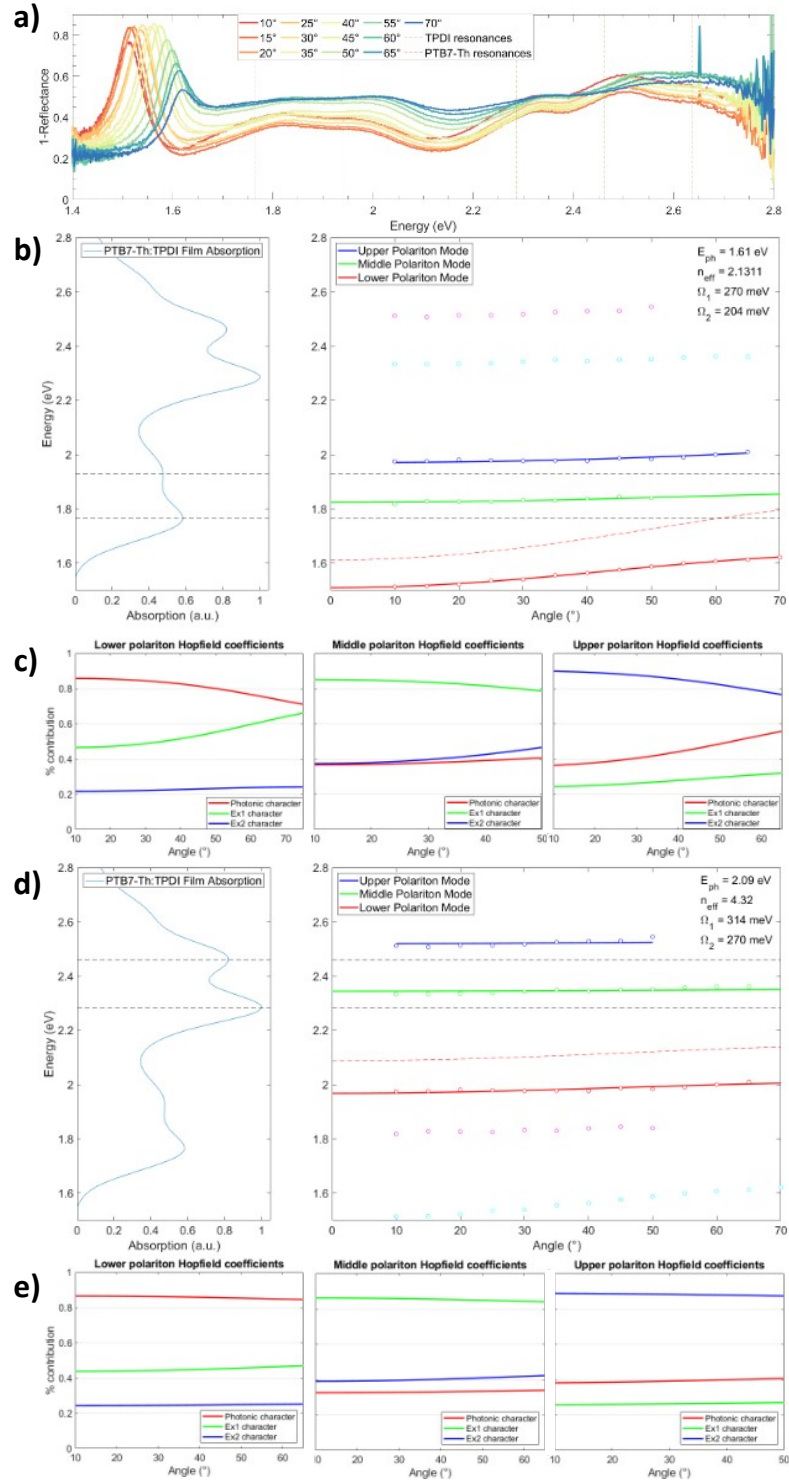


Figure C.2: a) Angular reflectance of a 116 nm thick coupled PTB7-Th:TPDI device. b) Rabi splitting of the lower three polariton branches. c) Hopfield coefficients for these branches. d) Rabi splitting of the upper three polariton branches. e) Hopfield coefficients for the same.

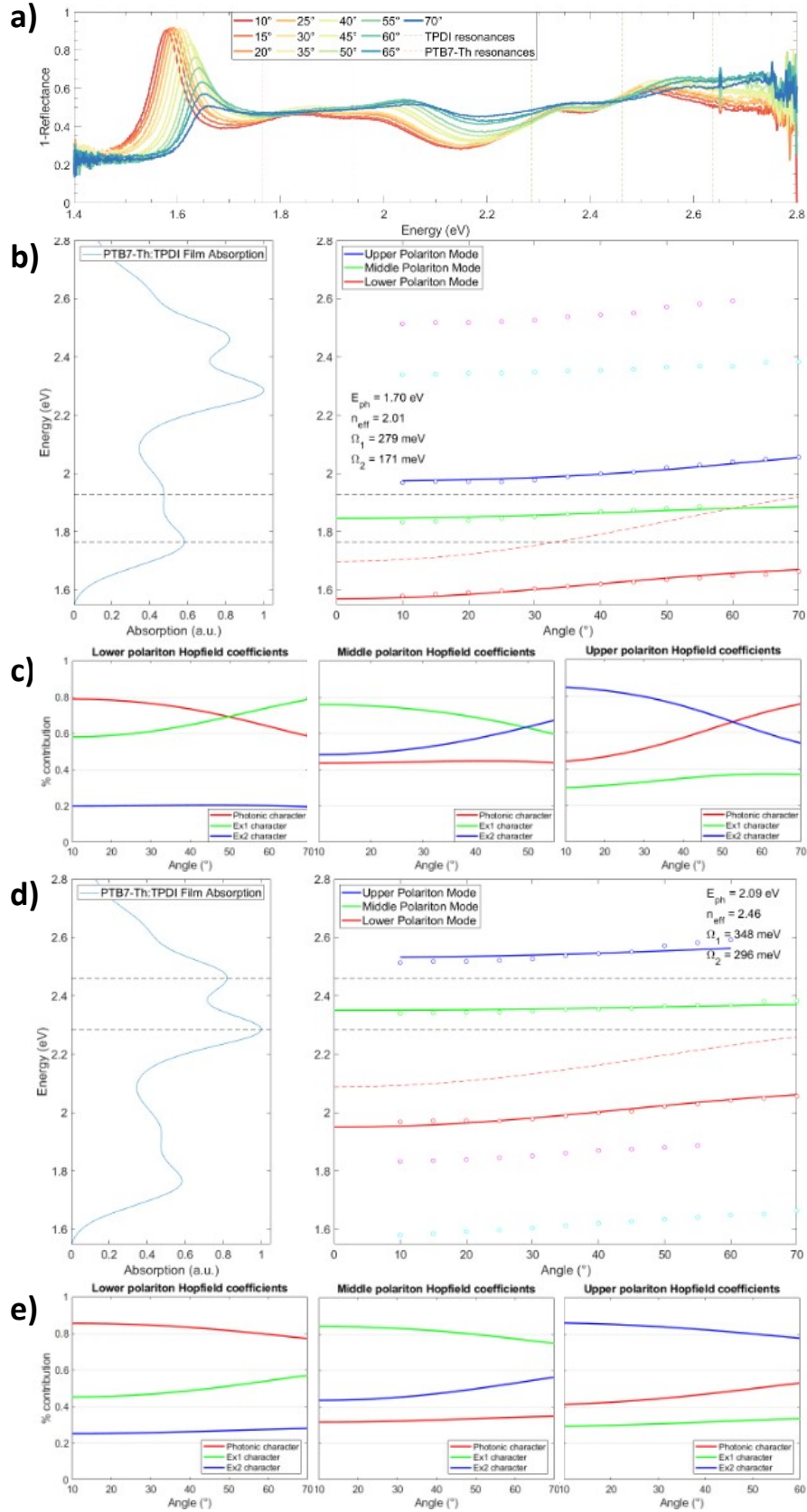


Figure C.3: a) Angular reflectance of a 100 nm thick coupled PTB7-Th:TPDI device. b) Rabi splitting of the lower three polariton branches. c) Hopfield coefficients for these branches. d) Rabi splitting of the upper three polariton branches. e) Hopfield coefficients for the same.

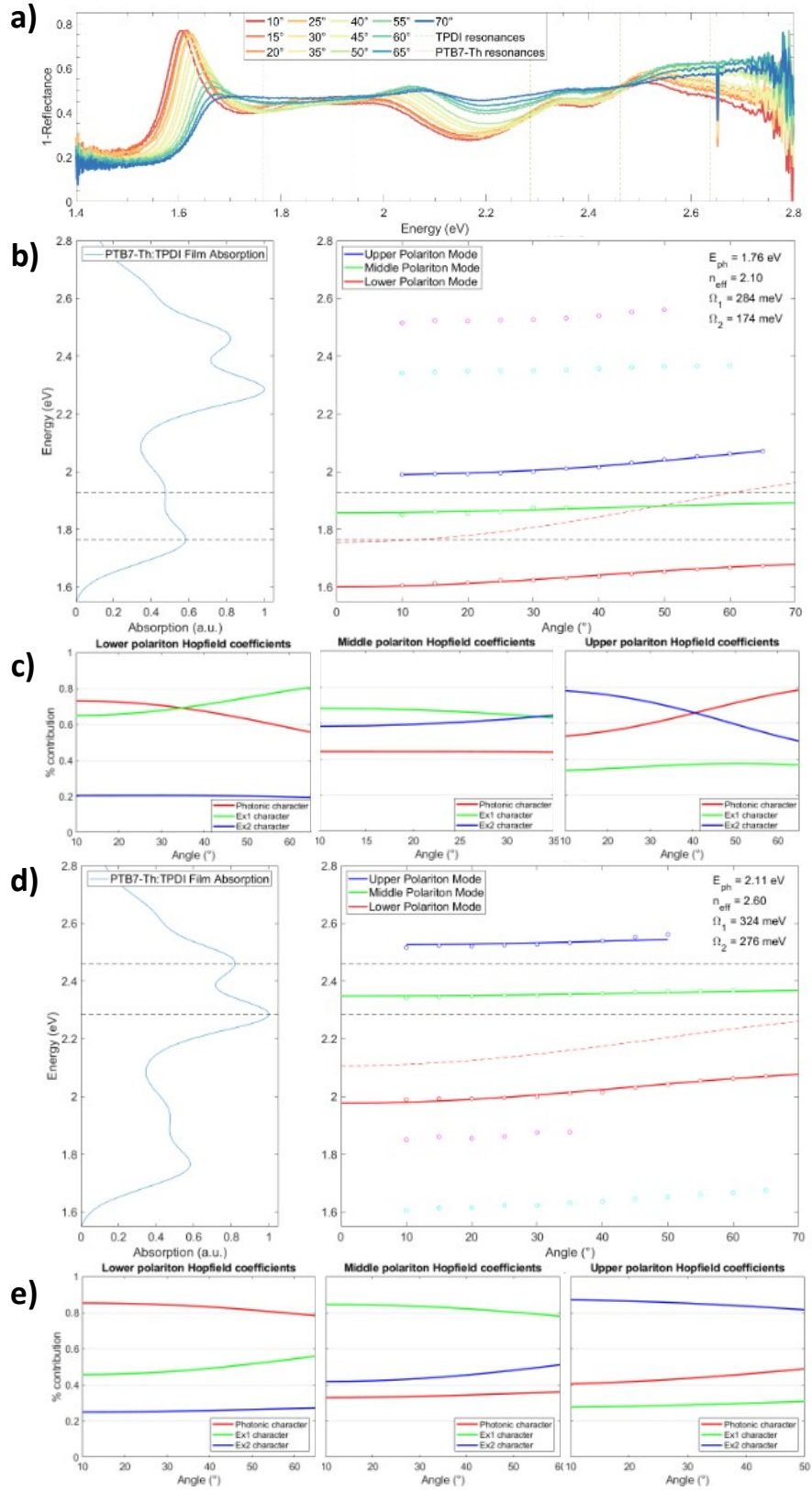


Figure C.4: a) Angular reflectance of a 91 nm thick coupled PTB7-Th:TPDI device. b) Rabi splitting of the lower three polariton branches. c) Hopfield coefficients for these branches. d) Rabi splitting of the upper three polariton branches. e) Hopfield coefficients for the same.

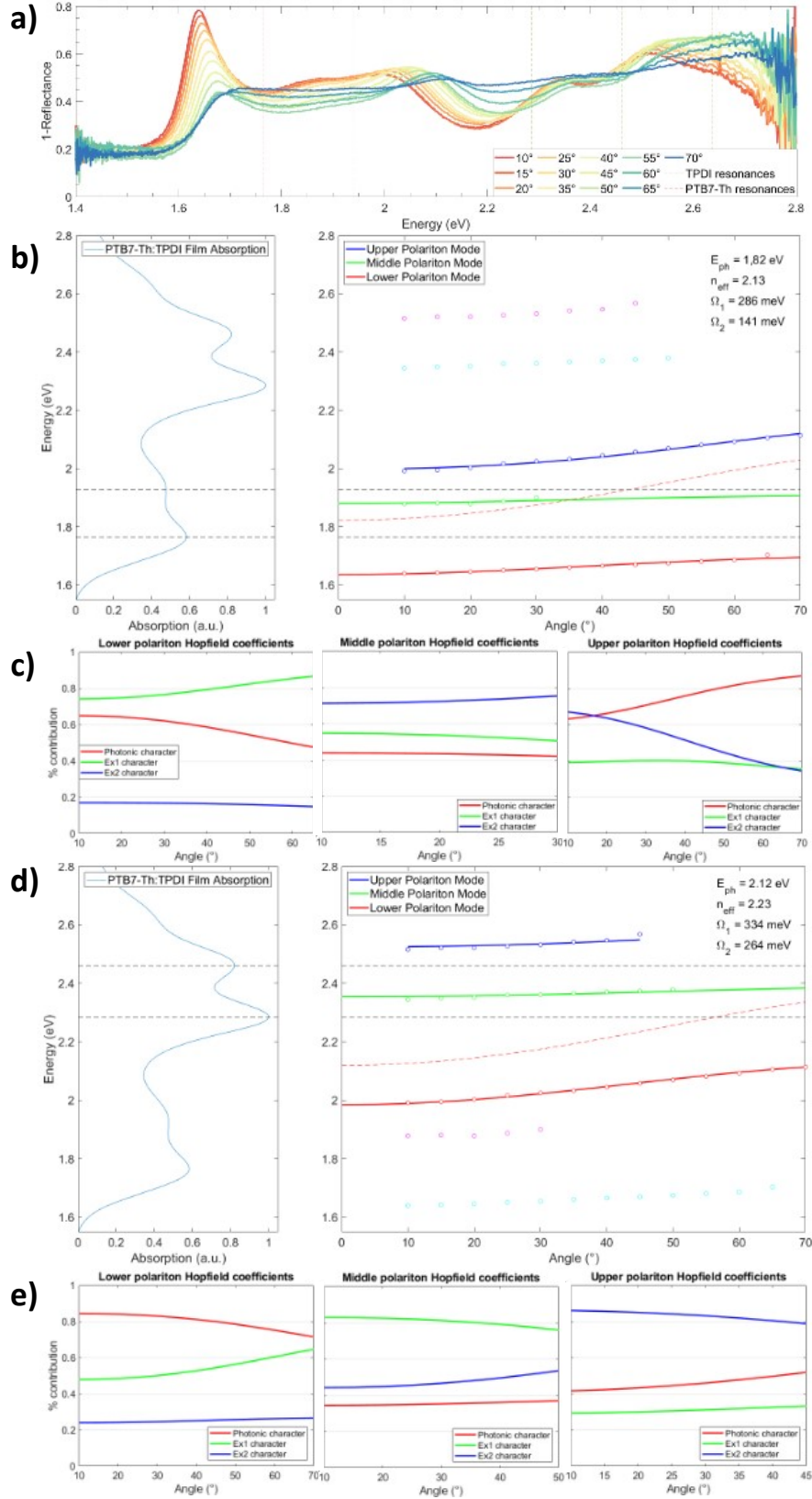


Figure C.5: a) Angular reflectance of a 84 nm thick coupled PTB7-Th:TPDI device. b) Rabi splitting of the lower three polariton branches. c) Hopfield coefficients for these branches. d) Rabi splitting of the upper three polariton branches. e) Hopfield coefficients for the same.

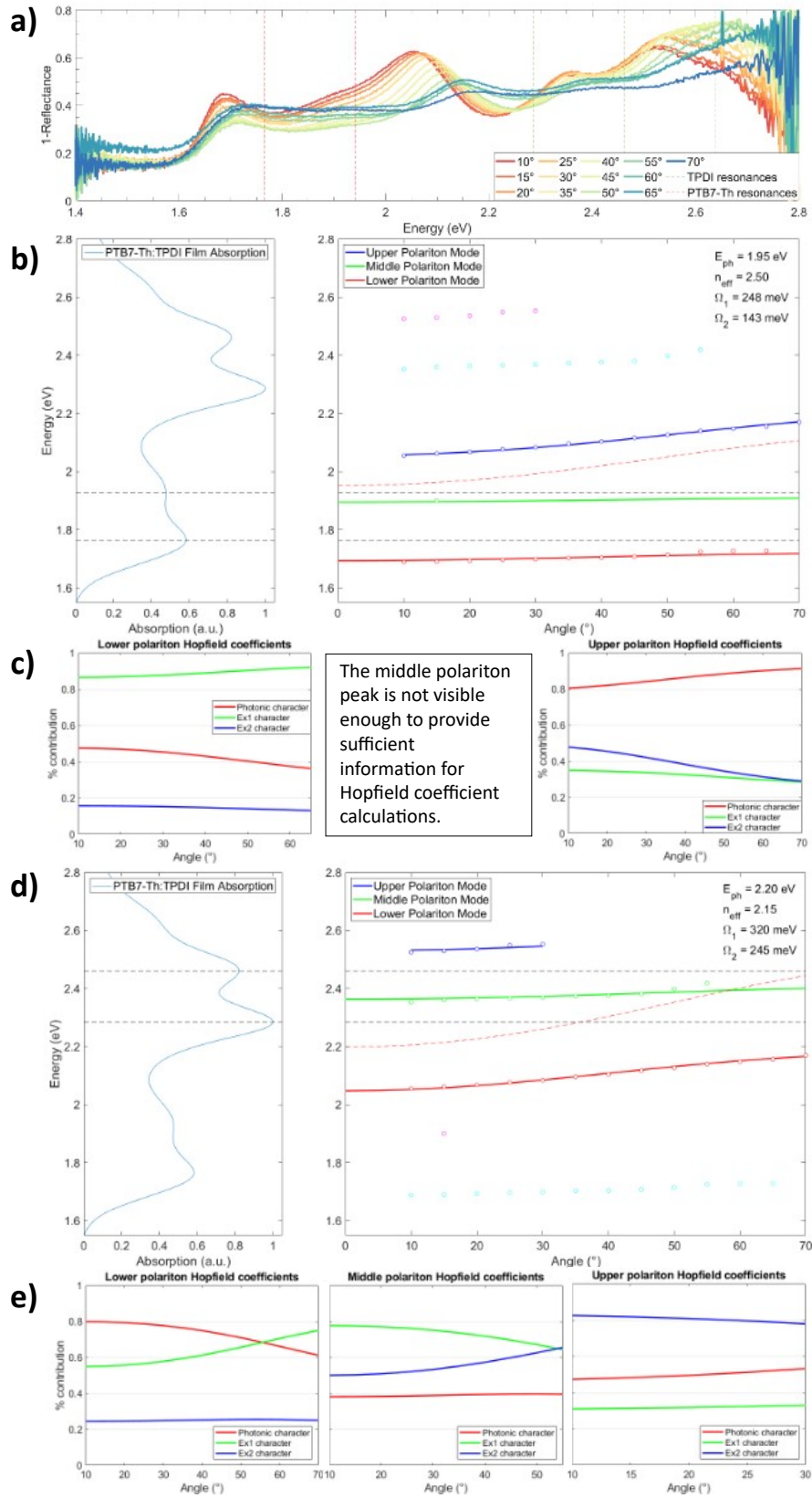


Figure C.6: a) Angular reflectance of a 74 nm thick coupled PTB7-Th:TPDI. b) Rabi splitting of the lower three polariton branches. c) Hopfield coefficients for these branches. d) Rabi splitting of the upper three polariton branches. e) Hopfield coefficients for the same.

C.3 Transient photocurrent at forward and reverse bias

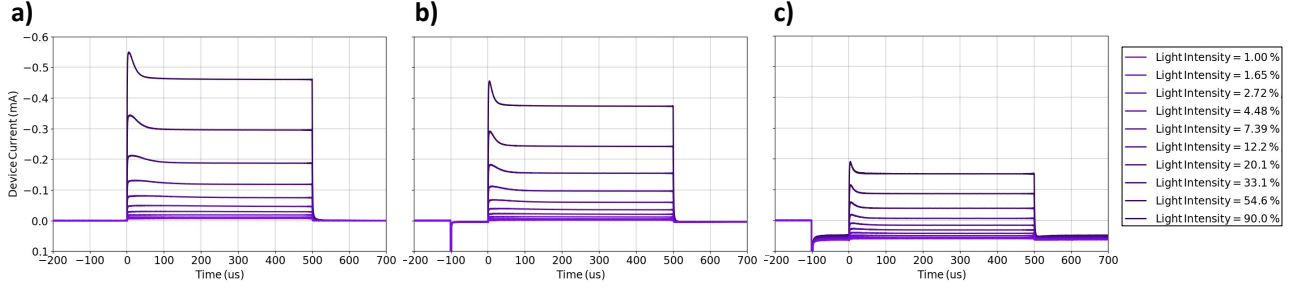


Figure C.7: Transient photocurrent for a 100 nm coupled PTB7-Th:TPDI device measured at a) 0 V, b) 320 mV and c) 640 mV applied bias.

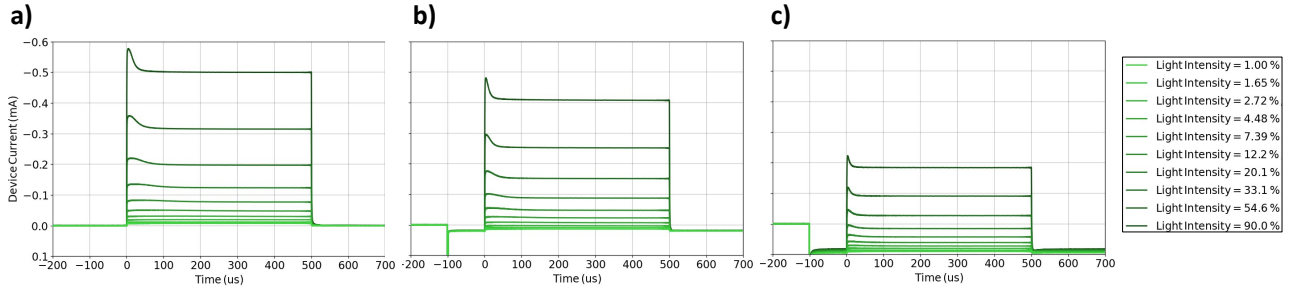


Figure C.8: Transient photocurrent for an 84 nm coupled PTB7-Th:TPDI device measured at a) 0 V, b) 320 mV and c) 640 mV applied bias.

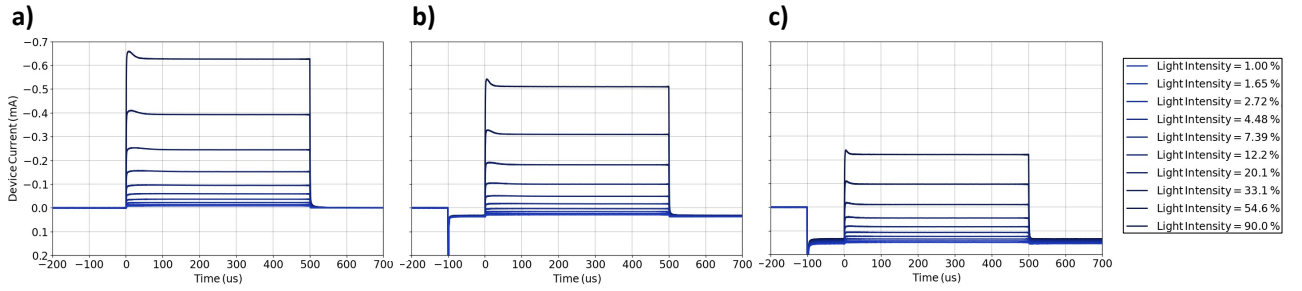


Figure C.9: Transient photocurrent for a 74 nm coupled PTB7-Th:TPDI device measured at a) 0 V, b) 320 mV and c) 640 mV applied bias.

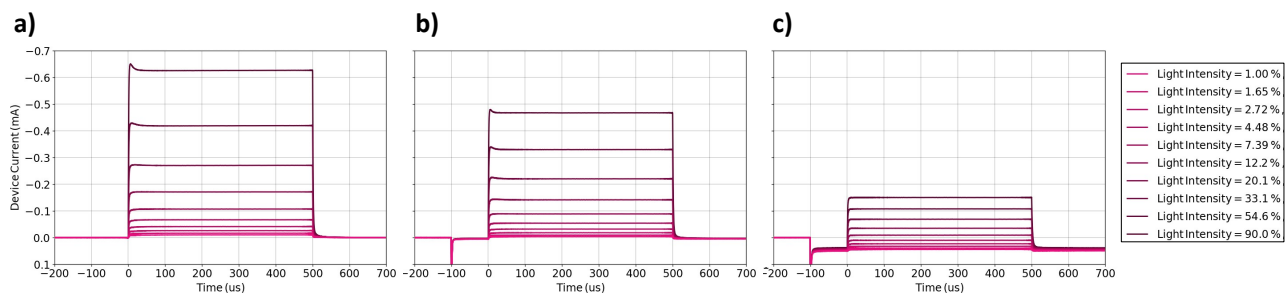


Figure C.10: Transient photocurrent for a 111 nm bare PTB7-Th:TPDI device measured at a) 0 V, b) 320 mV and c) 640 mV applied bias.

C.4 Photon filtering calculations for EL and EQE measurements

Figure C.11 plots the electroluminescence from a bare device, the transmission of three polystyrene Fabry-Pérot cavities and the result of the product of the two to provide an estimation of the expected result of photon filtering from the cavity. The peaks of the photon filtering curves become lower in magnitude as the cavity photon mode energy shifts further away from that of the EL of the bare device, and the curves widen in shape. Even the photon filtering for the thinnest cavity of the highest energy (S2) is unable to produce a peak energy near to that of the thinnest cavity device.

The same control procedure for the calculation of photonic effects is performed for EQE measurements as shown in Figure C.12 to distinguish the effect of strong coupling from the effect of the cavity mode described in detail in Section 6.2. Thus it is clear that the extent of both EL peak shifting and EQE peak splitting and shifting cannot be explained solely by the effect of the photonic mode, rather both the EL and EQE spectrum can only be produced via coupling.

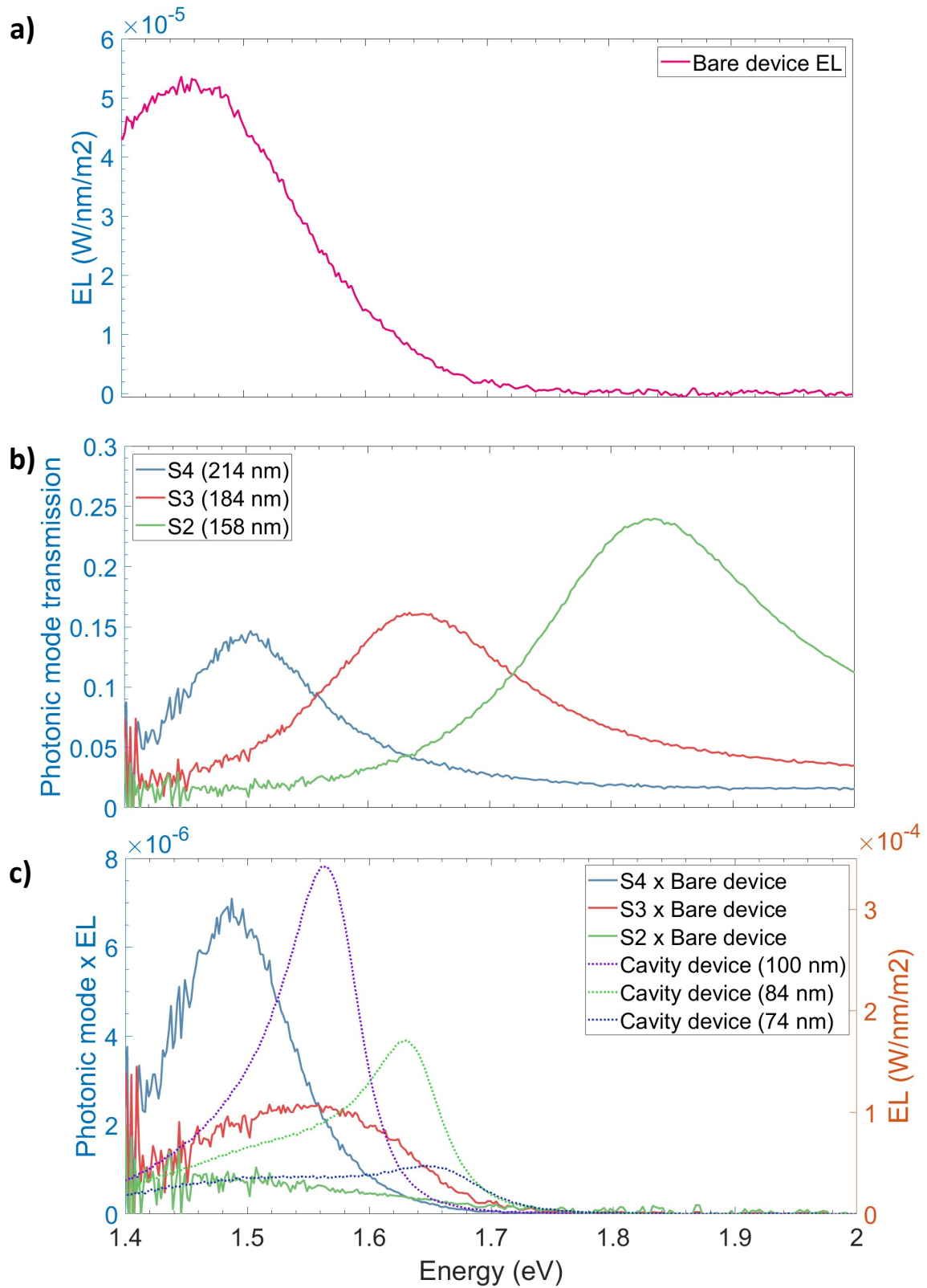


Figure C.11: a) Electroluminescence of a bare device at 3 V applied bias. b) Transmission spectra of polystyrene Fabry-Pérot devices demonstrating cavity modes for varying cavity thicknesses. c) Bare device EL spectrum from a) multiplied by the photonic modes from b) compared with EL spectra of the cavity devices.

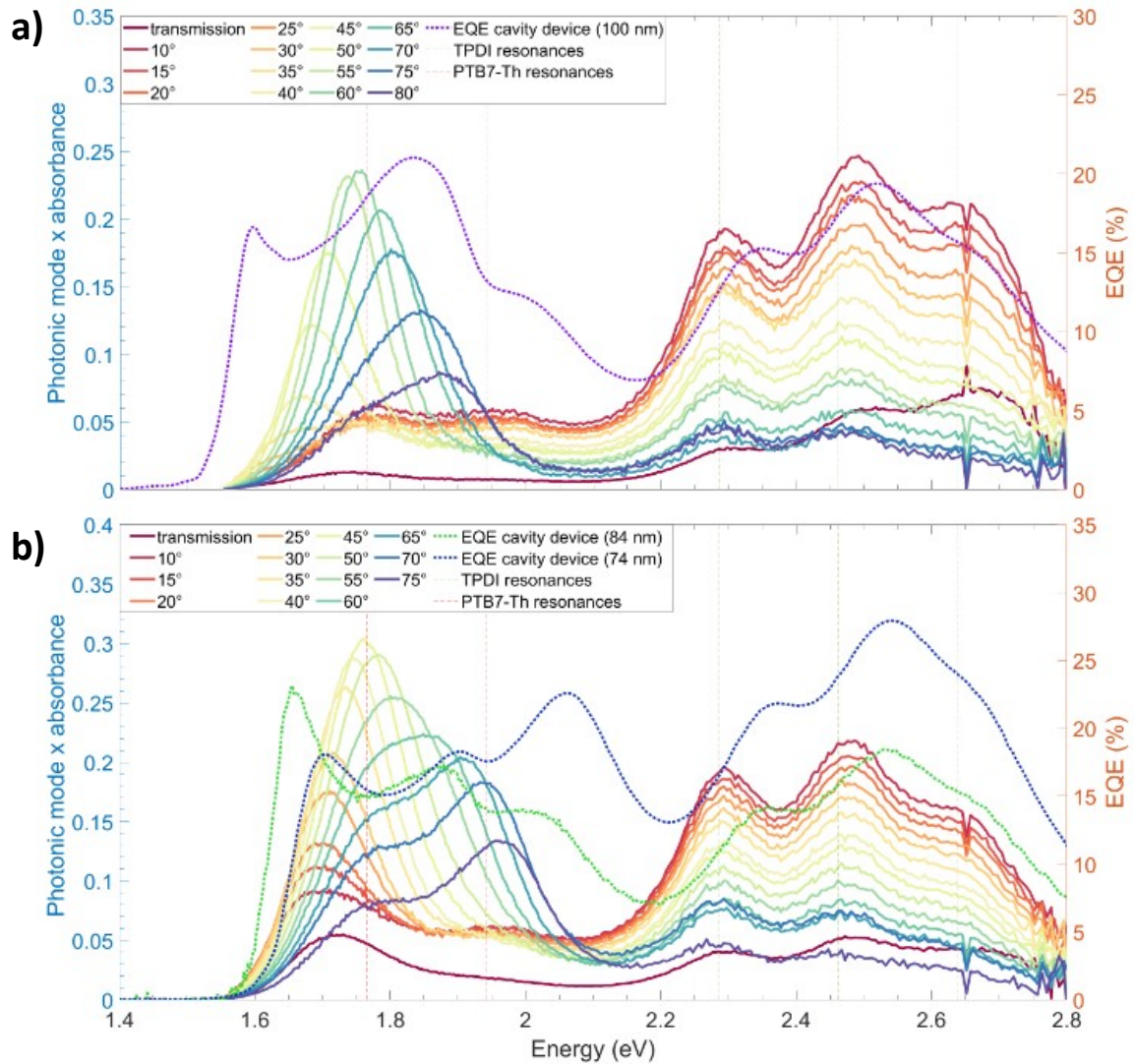


Figure C.12: a) Coupled cavity device (100 nm) EQE spectra compared with the spectra expected from photon filtering, calculated by multiplying the blend film absorption data by the photon mode of a polystyrene cavity with similar cavity mode energy (S4). The defining feature of strong coupling in EQE measurements is not simply the shifting of peak energies but the presence of peak splitting, as also seen in Figure 6.5. b) Similar comparison for two other cavity devices (84 and 74 nm thick) which are compared to the multiplication product of the blend film absorption and a thinner polystyrene cavity (S3).

Appendix D

Appendix to Chapter 8: Simulations of PTB7-Th:TPDI devices

D.1 Steady state optical effects

Steady state absorption, reflectance and transmission for bare and cavity devices of varying active layer thicknesses are shown on the following page.

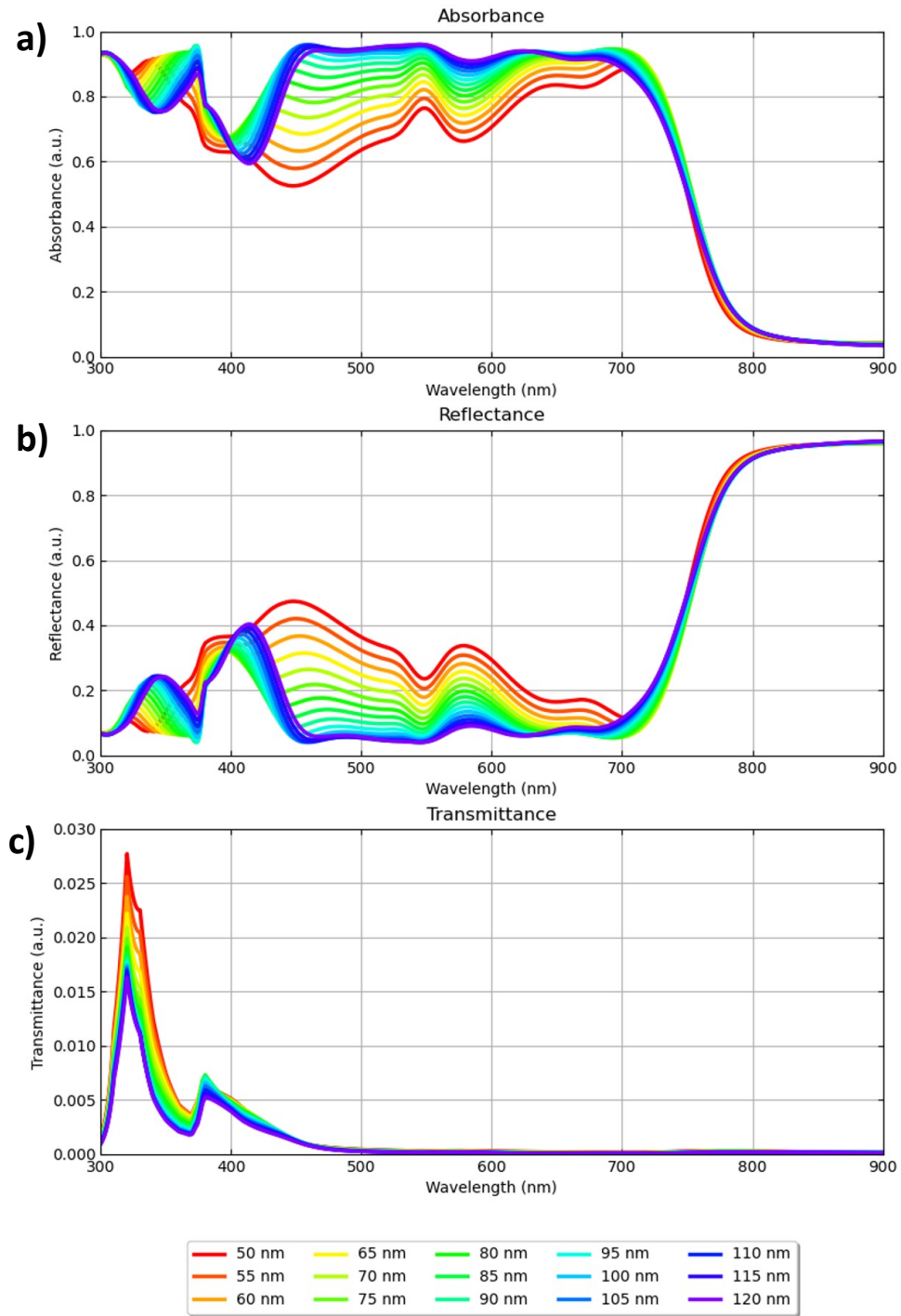


Figure D.1: a) Absorbance, b) reflectance and c) transmission for bare devices of varying thicknesses.

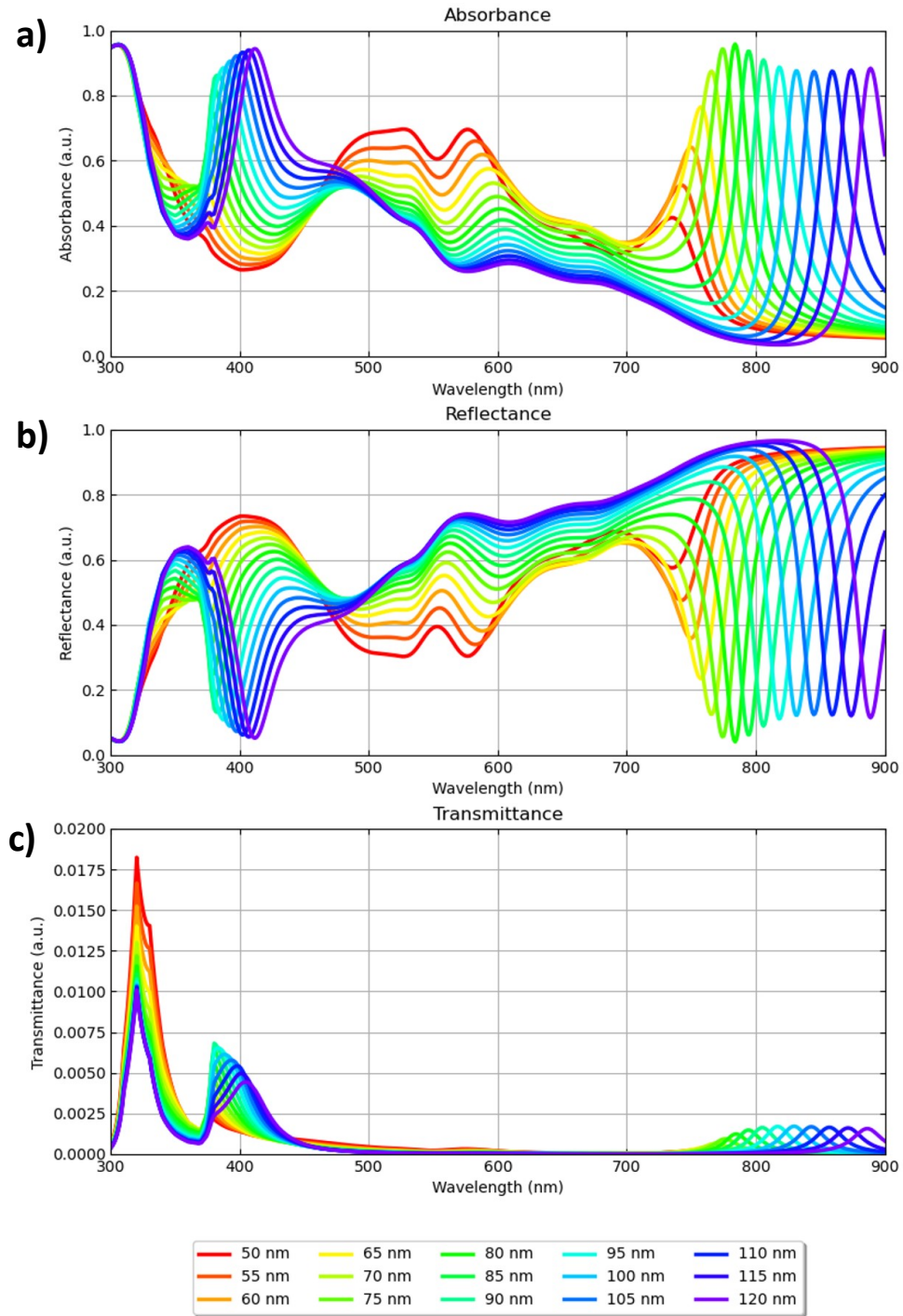


Figure D.2: a) Absorbance, b) reflectance and c) transmission for cavity devices of varying thicknesses.

D.2 Transient photocurrent modelling

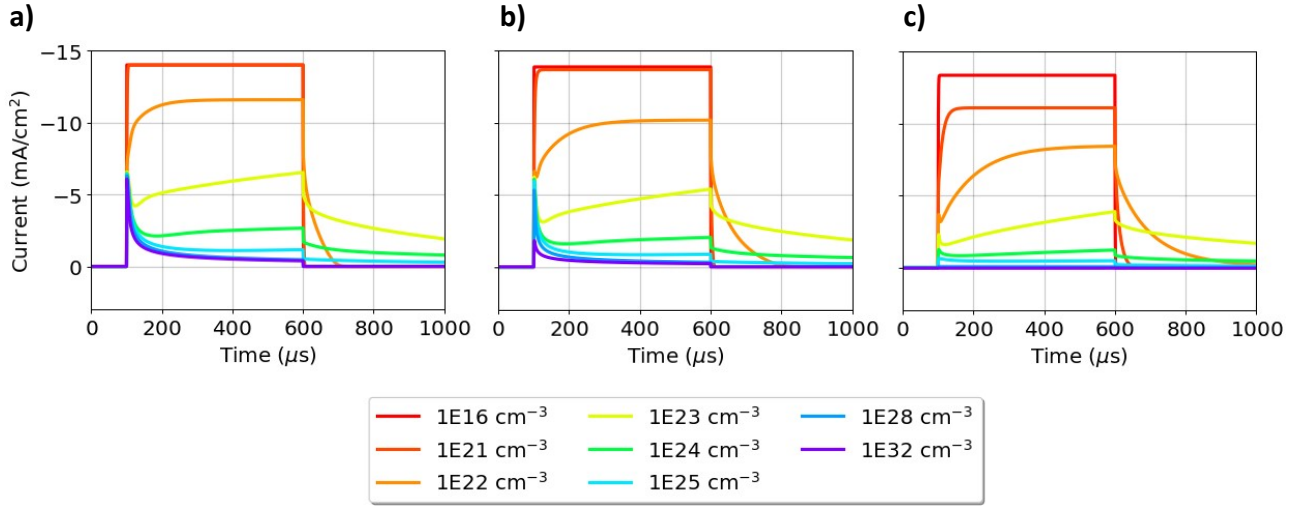


Figure D.3: Simulated TPC curves for a PTB7-Th:TPDI bare device with varying electron trap densities at a) -0.5 V offset bias, b) 0 V offset bias (short circuit) and c) 0.5 V offset bias. The hole trap density is fixed to $1 \times 10^{17} \text{ cm}^{-3}$.

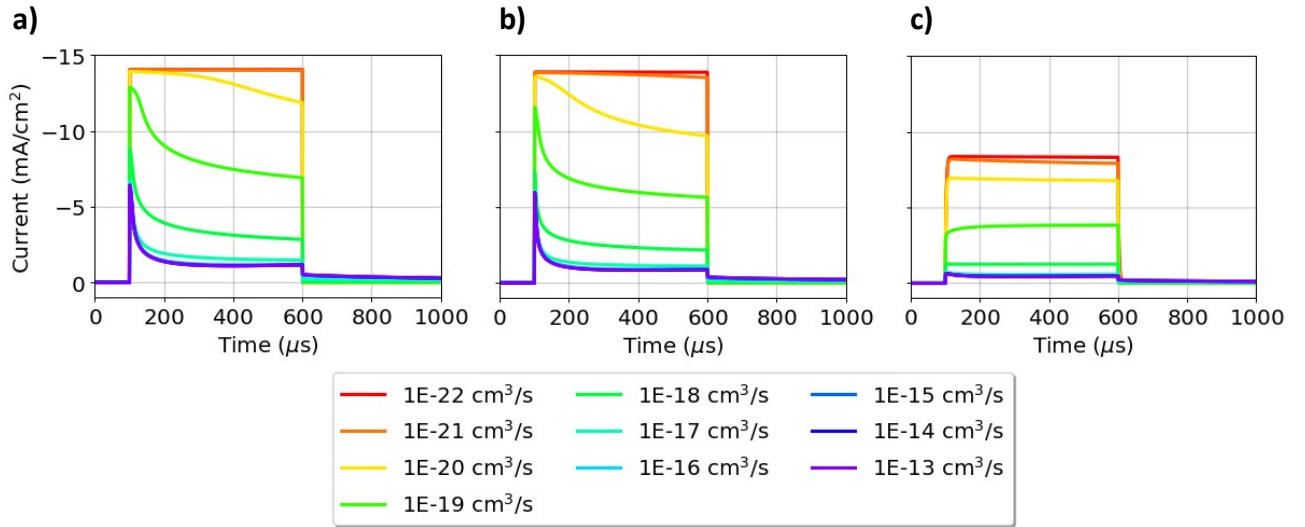


Figure D.4: Simulated TPC curves for varying electron capture rates measured at a) -0.5 V offset bias, b) 0 V offset bias and c) 0.5 V offset bias. The electron trap density is fixed to $1 \times 10^{25} \text{ cm}^{-3}$ and the hole trap density to $1 \times 10^{17} \text{ cm}^{-3}$.

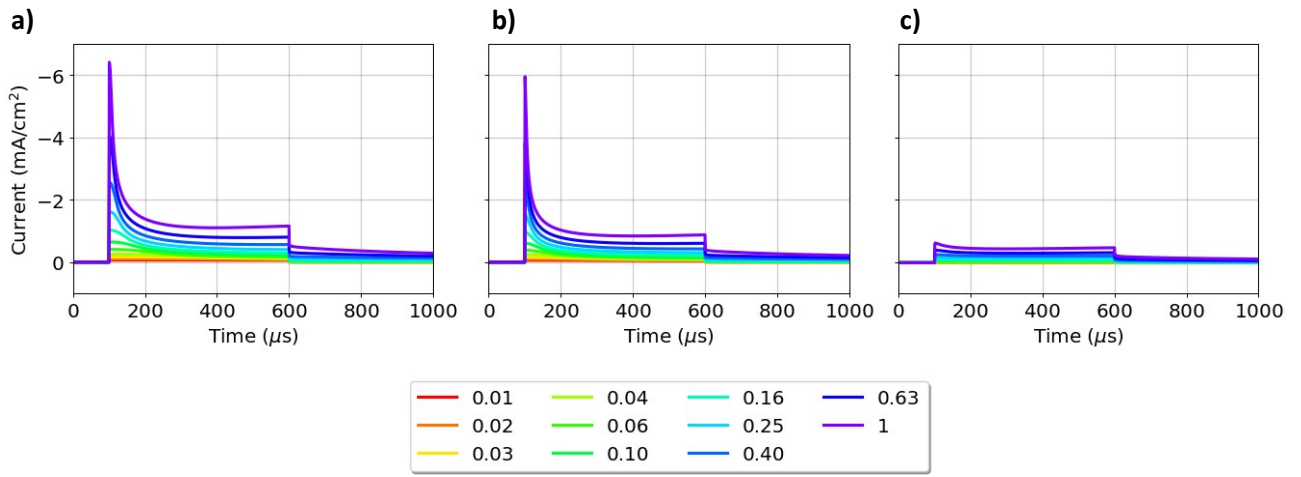


Figure D.5: Simulated TPC curves for varying illumination levels measured at a) -0.5 V offset bias, b) 0 V offset bias (short circuit) and c) 0.5 V offset bias. The electron trap density is fixed to $1 \times 10^{25} \text{ cm}^{-3}$ and the hole trap density to $1 \times 10^{17} \text{ cm}^{-3}$.

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